

PROCEEDINGS WITH PROGRAMME



IBA 2022 CONFERENCE

ORGANISED BY:



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WELCOME ADDRESS



On behalf of the Organizing Committee, we are pleased and delighted to welcome you to the International Battery Association (IBA2022) Meeting at Bled, Slovenia, from October 2nd to 7th, 2022. After the postponed and virtual meetings organized in 2020, we can finally say: "THE THIRD TIME IS THE CHARM". The hybrid IBA2022 edition is the result of an organizing committee that never gives up, just like we never give up on improving the quality of our everyday life with improved battery technologies.

The series of IBA Meetings has a great tradition and a unique style of blending fundamental research with practical applications in the field of advanced battery materials, characterisation techniques, technologies,

and applications. Recent progress and achievements in the field of battery research and development presented in 79 lectures (11 plenary, 18 keynote, and 50 invited) and 151 posters will provide a unique opportunity for discussion with leading experts from different parts of the world. Your participation in IBA2022 will make the event very exciting and hopefully fruitful.

We are grateful to all our sponsors and partners who have greatly helped in making IBA2022 even more successful and memorable.

On the occasion of the IBA2022 meeting, we will honour the winners of this year's IBA awards: Wolfgang Zeier for the Early Career Award, Peter Lamp and Hong Li for the Technology Award, Jun Lu and Hikari Sakaebe for the Research Award, Esther Takeuchi for the Yeager Award and Emanuel Peled for the Medal of Excellence.

Finally, we sincerely thank you for attending the IBA2022 meeting. It is our deep hope that you engage in fruitful discussions and exchange of ideas with colleagues at the meeting, resulting in many new collaborations that will add small but important pieces into the mosaic of the development of batteries - one of the key components for the smooth transition into a carbon-free society. In concluding, I would like to invite you to explore one of the most beautiful Alpine resorts, the city of Bled, and enjoy a relaxing walk around the lake.

Robert Dominko IBA 2022 Conference Chair

Danto



COMMITTEES

IBA 2022 Conference Chair

Robert Dominko

IBA Advisory Committee

Dominique Guyomard Minoru Inaba Boryann Liaw Michael M. Thackeray Christian Masquelier Zempachi Ogumi Rosa Palacín Christopher S. Johnson Ying Shirley Meng Venkat Srinivasan Martin Winter Xiao-Qing Yang Yong Yang Won-Sub Yoon

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Venue Rikli Balance Hotel Cankarjeva cesta 4 4260 Bled



ACKNOWLEDGEMENTS

The Advisory Committee is deeply appreciative of the sponsorship generously provided by the following companies:

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Sponsors







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SCIENTIFIC PROGRAMME

2 October 2022 18:00 - 18:30

OPENING ADRESS

Arnold Hall

3 October 2022 08:30 - 10:25

Session I Monday Chair: Rosa Palacin

> Pushing the Limits of Layered Oxide Cathodes Arumugam Manthiram

Kinetics, Rate Limitations and Aging of Interfaces in Solid State Batteries

Jürgen Janek

Halide-based Solid-State Batteries: Electrolyte, Stability, Interface and Electrode

Andy (Xueliang) Sun

Structural Features for Affecting Electrochemical Performance in Co-free Li-Rich Materials

Byoungwoo Kang

Advanced & Beyond Lithium Ion Technologies: What's Around the Corner? **Patrick Bernard**

10:25 - 10:50 **Coffee break**

10:50 - 12:20

Session II Monday Chair: Mathieu Morcrette

Artificial Intelligence-Based Optimization of Battery Manufacturing Processes **Alejandro Franco**

Millisecond Ion-Transport in Mixed Polyanion Battery Materials **Pieremanuele Canepa**



Electrochemical Impedance Spectroscopy and Quality Indicators

Jeremy Appell

Ni-Rich Cathodes in All-Solid-State Batteries: Electrochemical Behavior and Stabilization Approaches

Aleksandr Kondrakov

12:20 - 14:00

Lunch break

14:00 - 15:50

Session III Monday Chair: Yair Ein-Eli

Increasing the Cycle Life of Lithium Batteries

Emanuel Peled

How Transition Metals in Lib Electrolytes Influence the Cycling of Positive Electrodes

Ulf Breddemann, Petr Novák

Towards Mechanistic Understanding of Electrode/Electrolyte Interphases With Operando Characterization

Erik Berg

Advancing Quantitative Understanding of Functionality in the Lithium Sei Betar Gallant

Impedance Spectroscopy of Battery Cell's Impedance: Theory vs. Experiments Miran Gaberscek, Sara Drvaric Talian, Joze Moskon, Robert Dominko

15:50 - 16:20 **Coffee break**



16:20 - 18:00

Session IV Monday Chair: Robert Kostecki

From Interfaces to Interphases in Different Battery Chemistries* Yair Ein-Eli

Tailored Polymer Electrolytes for High-Energy Lithium-Metal Batteries Hai-Peng Liang, Zhen Chen, Xu Dong, Alexander Mayer, Medina Jasarevic, Stefano Passerini, **Dominic Bresser**

Operando Terahertz Spectroscopy of Solid Electrolyte Interphase Evolution on Silicon Anodes

Diana Golodnitsky, Daniel Krotkov, Dan Schneier, Svetlana Menkin, Yonatan Horowitz, Emanuel Peled, Sharly Fleischer

17:30-18:00 INTRODUCTION INTO THE RECEPTION BY MARTIN WINTER

18:00 - 20:00 WELCOME RECEPTION IN HONOR OF EMANUEL PELED'S BIRTHDAY



4 October 2022 08:30 - 10:25

Session I Tuesday Chair: Clare P. Grey

High Safety Batteries With High Energy Density by In Situ Solidification Strategy

Hong Li

Balancing the Inharmony Between Electrons and Alkali Ions in Layered Cathode Materials

Yong-Mook Kang

Recent Achievement of the RS2E Prototyping Platform: From Li-Ion to Na-Ion Technology

Mathieu Morcrette, François Rabuel

Sodium-Ion Batteries: From Material Properties to Upscaled Cell Prototypes **Ivana Hasa**, Katerina Gonos, Faduma Maddar, Jacob Compton, Mark Copley

Oxygen Redox Chemistry in Dynamically Changing Layered Transition Metal Oxide Structure

Kisuk Kang

10:25 - 10:50

Coffee break

10:50 - 12:20

Session II Tuesday Chair: Sandrine Lyonnard

Understanding Metals' Roles in Layered Structure Oxides for High-Energy Lithium-Ion Batteries

Jun Lu

Probing Battery Interfaces Using Operando Ambient Pressure Photoelectron Spectroscopy

<u>Maria Hahlin</u>, Ida Källquist, Fredrik Lindgren, Tove Ericson, Heyin Chen, Robert Temperton, Andrey Shavorskiy, Julia Maibach, Håkan Rensmo, Kristina Edström



Polyanionic Sulfate Based Cathode Materials: Few Case Studies

Shashwat Singh, Pubali Barman, Shubham Lochab, Valerie Pralong, <u>Prabeer</u> <u>Barpanda</u>

Strategy to Optimize Nmc Materials for All-Solid State Batteries **Shinichi Kumakura**, JiHoon Kang, TaeHyeon Yang

12:20 - 14:00

Lunch

14:00 - 15:50

Session III Tuesday Chair: Betar Gallant

Ionic Transport and Structure in Electrolytes, Electrodes and Interfaces: NMR, Xrd and Optical Microscopy Studies

Clare P. Grey

Polymorphism, Disorder, and Conduction in Halide-Type Solid Electrolytes Elias Sebti, **Raphaele Clement**

Physicochemical and Electrochemical Properties of Novel Electrolytes for Sodium and Lithium Metal Batteries

Faezeh Makhlooghiazad, Jennifer Pringle, Maria Forsyth, Luke O'Dell

Ionic Liquid Electrolytes Enter Into Market

Rongying Lin, Anaïs Falgayrat, Pauline Rullière, Emma Bremmond, Tom Douzou, Sébastien Fantini, François Malbosc

Understanding Self-Discharge in LFP and NMC811/Graphite Cells

Sebastian Buechele, Thomas Boulanger, Tom Boetticher, Anu Adamson, Ahmed Eldesoky, Eric Logan, **Michael Metzger**

15:50 - 16:20 **Coffee break**



16:20 - 17:50 Session IV Tuesday Chair: Brett Lucht

Characterizing Interphase Architecture in Li Metal Batteries Lauren Marbella

Infrared Nanospectroscopy of the Local Processes at Electrode/Electrolyte Interfaces in Batteries

Robert Kostecki, Xin He, Jonathan Larson, Hans Bechtel

Understanding Reactant Decay and Capacity Fade in Organic Redox-Flow Batteries Using Statistical Inference Techniques and Zero-Dimensional Modeling

David Kwabi

A Unified Perspective and Analytical Approach of Layered Cathode Active Materials

Boryann Liaw, Meng Li

18:00 - 19:00

Poster Session I

Poster area



5 October 2022 08:30 - 10:25

Session I Wednesday Chair: Christian Masquelier

Battery Technologies for Automotive Applications - Trends and Challenges **Peter Lamp**

High-Voltage Multi-Electron Reactions in Metal-Ion Batteries Using Vanadium Phosphate Positive Electrode Materials

Laurence Croguennec, Sunkyu Park, Romain Wernert, Long H.B. Nguyen, Emmanuel Petit, Antonella Iadecola, Laure Monconduit, Jacob Olchowka, Jean-Noël Chotard, Dany Carlier, Christian Masquelier

Solid State NMR Characterization of Na3V2(PO4)2F3-yOy Positive Electrode Materials for Na-Ion Batteries

Long Nguyen, Chloé Pablos, Emmanuel Petit, Paula Sanz Camacho, Jacob Olchowka, Christian Masquelier, Laurence Croguennec, **Dany Carlier**

Time for a New Classification for Battery Materials?

Wouter ljzermans

Development of a Polyanionic Cathode Material and a Liquid Electrolyte Formulation for High Power Na-Ion Cells

Laure Bertry, Marc-David Braida, Florent Leclercq, Marion Dufour, Xavier Kouoi, Chloé Pablos, Quentin Loiseleux, Corentin Querne, John Abou-Rjeily, Valerie Buissette

10:25 - 10:50

Coffee break

10:50 - 12:20

Session II Wednesday Chair: Laurence Croguennec

> Interfaces and Scaling Relations in Solid-State Batteries Wolfgang Zeier

Crystal Chemistry of Li3PS4 and Na3PS4, Solid Electrolytes for Batteries

<u>Christian Masquelier</u>, Theodosios Famprikis, Ulas Omer Kudu, Jean-Noël Chotard, François Fauth, Elodie Salager, Saïful Islam, Pieremanuele Canepa, Marc-David Braida, Thierry Le Mercier, Houssny Bouyanfif



Towards High-Voltage Solid-State Lithium-Metal Batteries

Corsin Battaglia

Towards an Autonomous Materials Development Platform to Accelerate the Development of New Battery Materials

Icíar Monterrubio, Maha Ismail, Javier García, Evaristo Castillo, Joseba Orive, Maria Angeles Cabañero, Agnieszka Wizner, Nebil A. Katcho, Montse Casas-Cabanas, Javier Carrasco, **Marine Reynaud**

12:20 - 14:00 **Lunch break**

14:00 - 15:50

Session III Wednesday Chair: Shirley Meng

> Perspectives on Lithium Batteries for Biomedical Applications **Esther Takeuchi**, Kenneth Takeuchi, Amy Marschilok

Negating the Interfacial Resistance Between Solid and Liquid Electrolytes for Next Generation Lithium Batteries

Nuria Garcia-Araez, J. Padmanabhan Vivek, Nina Meddings

Electrochemistry Based and Coupled Characterization of Energy Storage Materials and Systems

Amy Marschilok

Synergistic Role of Functional Electrolyte Additives to Address Interfacial Chemistry and Phenomena in Lithium-Based Batteries

Isidora Cekic-Laskovic

Mastering Equilibrium at the Solid/Liquid Interface to Design Novel Intercalation Compounds

Alexis Grimaud

15:50 - 16:20 **Coffee break**



16:20 - 18:20 Session IV Wednesday Chair: Alejandro Franco

Recent Advances in Theoretical Methodology to Battery Interfaces Marie-liesse Doublet

A Big-Map Approach to AI-Accelerated Discovery of Next-Generation Battery Materials and Interfaces

Tejs Vegge

Techno-Economic and Environmental Analysis of Aluminium Batteries <u>Patrik Johansson</u>, Niklas Lindahl

Ionic Liquid Electrolytes for Next Generation Sodium Batteries

<u>Maria Forsyth</u>, P. C. Howlett, J. Sun, K. Biernacka, N. Byrne, J. Pringle, H. Sarma, L. O'Dell

17:50 - 18:20

IBA Awards Ceremony

Chair: Rosa Palacin

18:25 - 19:20

Virtual Posters Session

onAIR Hybrid platform

20:00 - 23:00

CONFERENCE DINNER

Grand hotel Toplice



6 October 2022 08:30 - 10:25

Session I Thursday Chair: Christopher Johnson

Fluoride Shuttle Batteries: Current Status and Prospects Takeshi Abe

The Cathode Interfacial Evolution in Sulfide-Based Solid State Li Batteries Yong Yang

Asymmetric Delithiation and Lithiation of Li Layered Oxides under High Current Density Driven by SOC-dependent Charge Transfer Kinetics **Jihyun Hong**

Liquid Madelung Potential as a Descriptor for Better Electrode Reactions Atsuo Yamada

Emerging Energy Chemistry at Li Metal Anode and Electrolyte Interfaces **Qiang Zhang**

10:25 - 10:50 **Coffee break**

10:50 - 12:20

Session II Thursday Chair: Miran Gaberšček

> Resolving Complex Mechanistic Questions Related to Aqueous Batteries Using Analysis by EQCM-D <u>**Doron Aurbach**</u>, Netanel Shpigel

A Rechargeable Calcium Battery With High Cyclic Stability Maximilian Fichtner, Zhirong Zhao-Karger, Zhenyou Li

Electrolyte, Cation Solvation Shell and Interphase for the Emerging Ca Metal Anode Battery

Alexandre Ponrouch

Engineering Graphite Interface for Enhancing Safety of Li-Ion Batteries Nae-lih Nick Wu



14:00 - 15:50

Session III Thursday Chair: Isidora Cekic-Laskovic

Design of Next-Gen Cathode Materials With Both Cation and Anion Redox Shirley Meng

BlueSolutions Achievements on the Way to GEN4 Batteries

Margaud Lécuyer

Unveiling the Redox Mechanisms of KVPO4F1-xOx As Positive Electrode for K-ion Batteries

<u>Antonella Iadecola</u>, Romain Wernert, Laurence Croguennec, Lorenzo Stievano, Laure Monconduit, Dany Carlier-Larregaray

Multi-Modal Multi-Scale Characterization of Heterogeneities in Li-Ion Batteries by Neutron & Synchrotron Techniques

Sandrine Lyonnard

Understanding the Correlation Between Structure – Morphology and Performance of All Solid-State Batteries

Oskar Thompson, Patrice Perrenot, Ove Korjus, Lucas Trassart, Adrien Fauchier-Magnan, Emmannuelle Suard, François Fauth, Fannie Alloin, <u>Claire</u> <u>Villevieille</u>

15:50 - 16:20

Coffee break

16:20 - 17:50

Session IV Thursday Chair: Petr Novák

Electrolyte Oxidation and the Role of Acidic Fluorophosphates in Capacity Loss for Lithium Ion Batteries

Brett Lucht

Imperfect Battery Materials: Impact of Structural Disorder in Cell Performance Jon Serrano-Sevillano, Marine Reynaud, Damien Saurel, <u>Montse Casas-</u> <u>Cabanas</u>



Synthesis by Design: A Framework to Manipulate Cathode Composition and Morphology

<u>Venkat Srinivasan</u>, Pallab Barai, Hakim Iddir, Juan Garcia, Mark Wolfman, Xiaoping Wang, Deepti Tewari

Anion Redox Mechanisms in Alkali-Rich Sulfides

<u>**Kimberly See**</u>, Joshua J. Zak, Seong Shik Kim, Andrew J. Martinolich, Eshaan Patheria

18:00 - 19:00

Poster Session II Poster area



7 October 2022 08:30 - 10:25

Session I Friday Chair: Alexandre Ponrouch

Development of High Energy Battery Materials Without Natural Resource Constraints

Hikari Sakaebe

Speeding Up Electrochemical Reactions in Batteries Using Light Mediated Energy

Christopher Johnson

Electrolyte Enabled Structural Evolutions of Na3V2(PO4)2F3 Electrode Upon Repeated Cycling and Their Influence on Degradation Mechanism of Na-Ion Cells.

Sathiya Mariyappan, Parth Desai, Jean-Marie Tarascon

Influence of Pristine NMC811 Secondary and Primary Particle Surfaces on the Materials Reactivity

<u>Philippe Moreau</u>, Angelica Laurita, Liang Zhu, Pierre-Etienne Cabelgen, Jérémie Auvergniot, Dominique Guyomard, Nicolas Dupré

Advanced Anode Materials for Li-Ion and Na-Ion Batteries

Alexey Koposov

10:25 - 10:50

Coffee break

10:50 - 11:50

Session II Friday Chair: Robert Dominko

Recent Advancements in the Development of Magnesium Metal Negative Electrodes – Metallurgical Approaches

Toshihiko Mandai, Hidetoshi Somekawa

Design of Lithium Metal Battery Electrolytes Based on Lithium-Ion Chemical Potential

Yuki Yamada

The Science and Engineering of Structural Batteries – But Are They a Practical Solution?

Adam S. Best, J. Galos, I. L. Kyratzis, P. Attar, K. Pattarakunnan, A. P. Mouritz

11:50 - 12:00 IBA 2023 PRESENTATION AND CONFERENCE CLOSING



POSTER SESSION I TUESDAY 4 OCTOBER, 18:00 – 19:00

PS1-01	3D Digital-Twin Based Anode Structure Modeling Considering Electrolyte Swelling for Lithium-Ion Batteries
	Kyung-Geun Kim , Jaejin Lim, Jihun Song, Giyong Kim, Hyobin Lee, Suhwan Kim, Sung Yeol Kim, Yong Min Lee
PS1-02	3D Micro Structure Resolved Electro-Mechanical Simulations of a Full Battery Cell: A New Modelling Method and Its Verification With Time Resolved X-ray Tomography. <u>Nils Wenzler</u> , Stefan Rief, Sven Linden, Fabian Biebl, Ilona Glatt, Anja Streit, Raphael Zahn, Mathias Fingerle, Vanessa Wood
PS1-03	A Comprehensive Study on the Effect of Washing on Nickel-Rich NCMs: Part I. Methodology for the Quantification of the Proton Content and the Li ⁺ /H ⁺ - Exchange Kinetics <u>Stefan Oswald</u> , Rebecca Wilhelm, Hubert A. Gasteiger
PS1-04	A Comprehensive Study on the Effect of Washing on Nickel-Rich NCMs:Part II. Impact of the Li+/H+-Exchange on the Electrochemical Performance <u>Rebecca Wilhelm</u> , Stefan Oswald, Hubert Gasteiger
PS1-05	A Multi-Layer Phase Field Model to Study Lithium Intercalation in Graphite: Focusing on the Coupling With Graphene Stacking Sequence <u>Marion Chandesris</u> , Matthieu Rykner, Antoine Cordoba, Mathis Plapp
PS1-06	A Nanoporous Polymeric Coating on Thin Metallic Lithium to Enhance Li-S Cell Cycle Life via Improved Deposition Behaviour <u>Declan Mcnamara</u> , Matthew Hill, Mahdokht Shaibani, Mainak Majumder
PS1-07	A Systematic Study on Structure, Ionic Conductivity, and Air Stability of Li4SnS4– Li3PS4 Electrolytes for All-Solid-State Batteries <u>Misae Otoyama</u> , Kentaro Kuratani, Hironori Kobayashi
PS1-08	A Trade-off-Free Fluorosulfate-Based Electrolyte Additive Developed for Lithium- Ion Batteries Using Ni-Rich Cathode Materials Jimin Oh, Kwang Man Kim, Sung You Hong
PS1-09	Accelerated Degradation of SiO/Ncm Cell Quick Rechargeability Due to Li Dendrite Formation Caused by State-of-Charge Dependent Failure of SiO Electrode During Normal Cycle History <u>Hyun-seung Kim</u> , Tae Hyeon Kim, Sung Su Park, Min Su Kang, Ye Rin Kim, Goojin Jeong
PS1-10	Accessing Degradation Mechanisms of Ni-Rich Lnca in State-of-the-Art Cells for Electromobility <u>Anastasiia Mikheenkova</u> , Niladri Roy Chowdhury, Kristian Bartholdsson Frenander, Yonas Tesfamhret, Erik J. Berg, Torbjörn Thiringer, Maria Hahlin, Matthew Lacey
PS1-11	Accurate Gas Chromatography-Mass Spectroscopy Analysis of Li-Ion Battery Electrolyte <u>Lana Regent</u> , Jože Moškon, Robert Dominko, Ana Kroflič, Martin Šala



PS1-12	Accurately Measuring Cathode Solid State Diffusivity Using Amidr, a Replacement for Gitt <u>Mitchell Ball</u>
PS1-13	Addressing Key Challenges in the Development "Beyond Li-Ion" Chemistries Giuseppe Antonio Elia, Claudio Gerbaldi
PS1-14	Analysis and Modeling of Side Reaction Mechanisms Inside a Lithium-Ion Battery During Thermal Runaway Through the Design of Experiment With Combination of Battery Components <u>Minuk Kim</u> , Jaeyoung Jeon, Jongsup Hong
PS1-15	Anion-Polarisation–Induced Short-Range-Order in the Heterocationic Lithium-Ion Cathode Material Li2FeSO <u>Samuel Coles</u> , Viktoria Falkowski, Harold Geddes, Gabriel Perez, Alexander Squires, Samuel Booth, Andrew Goodwin, Conn O'Rourke, Kit McColl, Serena Cussen, Simon Clarke, Saiful Islam, Benjamin Morgan
PS1-16	Atomic-Scale Investigation of Doping Effects in the Anti-perovskite Na3OCI Sodium-Ion Battery Material <u>Benedek Goldmann</u> , Matt Clarke, James Dawson, Saiful Islam
PS1-17	Atomistic Insights Into New Hydroxy Sulfate Polyanionic Insertion Materials for Li- Ion Batteries <u>Arup Chakraborty</u> , Shaswat Singh, Prabeer Barpanda, M Saiful Islam
PS1-18	Ceramic-Coated Separator With Competitive Electrochemical Properties for Lithium-Ion Batteries <u>Meisam Hasanpoor</u> , Maria Forsyth, Patrick C. Howlett
PS1-19	Complementary Operando Detection of Metallic Lithium Deposition in Lithium-Ion Batteries With High Sensitivity <u>Michael Danzer</u> , Felix Katzer, Leonard Jahn
PS1-20	Comprehensive Study of the Impact of MoS2 Structure / Reactivity Relationship on the Polysulfide Conversion in Lithium Sulfur Batteries <u>Célestine Desoeurbrun</u> , Renaud Bouchet, Didier Devaux, Denis Uzio, Julien Bernard
PS1-21	Correlation Between Morphology, Surface Properties and Electrochemical Performance of Ni-Rich Cathode Active Material in Lithium Ion Batteries <u>Kilian Vettori</u> , Raffael Ruess, Anja Henss, Jürgen Janek
PS1-22	Cycling Performance and Safety Characteristics of NMC811/G-si Battery Cells With Optimised Electrolyte Formulations <u>Marzi Barghamadi</u> , Thomas Ruether, Christian Lechtenfeld, Adam S. Best
PS1-23	Data-Driven Tools for Accelerating Battery Innovation Across Spatio-Temporal Scales <u>Arghya Bhowmik</u>
PS1-24	Depth-Profiling the Li Intercalation in Graphite Electrodes for Li-Ion Batteries: Model and Experiment <u>Samuel Tardif</u> , Jean-Francois Colin, Marion Chandesris, Sandrine Lyonnard



PS1-25	Double Layer Chemical Structure Analysis via Advanced Electrogravimetry on Model LixMoO3 Electrode
	Ezzoubair Bendadesse , Anatolii Morozov, Artem Abakumov, Hubert Perrot, Jean-
	Marie Tarascon, Ozlem Sel
PS1-26	Drawing the Landscape for Li+ Diffusion in Solid-State Electrolytes <u>Amber Mace</u>
PS1-27	Dynamically Disproportionating Structure, and High-Valence Doping of Prototype Model Cathode LiNiO2
	Andrey Poletayev, Jonathon Cottom, Benjamin Morgan, Saiful Islam
PS1-28	Electrochemical Characteristics and Degradation Analysis of NCM523 With All Solid State Three Electrode Cells
	<u>Goro Fukunishi</u> , Mayu Tabuchi, Atsunori Ikezawa, Takeyoshi Okajima, Fusao Kitamura, Kota Suzuki, Masaaki Hirayama, Ryoji Kanno, Hajime Arai
PS1-29	Elucidating the Morphology of Partially Lithiated Silicon Microparticles Using Transmission Electron Microscopy
	Philip Rapp, Helen Valencia, Maximilian Graf, Joachim Mayer, Hubert Gasteiger
PS1-30	Elucidation of Failure Mechanism and the Importance of Stack Pressure in the Li Metal Solid State Battery
	Jian Duan , Till Fuchs, Anja Henss, Juergen Janek
PS1-31	Evaluation and Improvement of the Stability of Poly(ethylene Oxide) Based Solid- State Batteries With High Voltage Cathodes
	Anja Henss, <u>Yuriy Yusim</u> , Enrico Trevisanello, Raffael Ruess, Jurgen Janek
PS1-32	Evolution of Spinel LiMn2O4 Single Crystal Morphology by Tuning Oxygen Partial Pressure
	Animesh Dutta , Arthur Van Der Est, Michel Johnson, Chongyin Yang, Jeff Dahn
PS1-33	Extending of Cycle Life of Nmc Cathode by Bn Surface Coating
	Tayfun Koçak , Semih Engün, Ahmet Uygar Simsek, Ezgi Yilmaz, Nuran Ay, Servet Turan, Zhang Xiogang
PS1-34	High-Energy and High-Flux X-rays to Investigate the Lithium Metal Electrode Inside the Cell
	Valentin Vinci , Philippe Dumaz, Isaac Martens, Marta Mirolo, Florian Russelo, Jakub Drnec
PS1-35	Influence of Anion Structure on Electrochemical Performance of Fluorinated Alkoxyborate Electrolytes for Mg Rechargeable Batteries
	<u>Tjaša Pavčnik</u> , Jan Bitenc, Robert Dominko
PS1-36	Influence of Protons on the Redox Chemistry of Verdazyl Radicals for the
1 51 50	Application in Redox Flow Batteries
	Emmel, Felix Kerner, Doreen Mollenhauer, Hermann Wegner, Daniel Schröder
PS1-37	Interfaces Analysis in Lithium Solid-State Batteries Using Operando Auger, Xps and ToF-Sims.
	Julien Morey, Jean-Bernard Ledeuil, Hervé Martinez, Lénaïc Madec



PS1-38	Interfacial Engineering for Stable Interphase to Realize High-Voltage Ni-Rich
	Haidong Liu, Gaole Qian, Kristina Edström
PS1-39	Investigation of Charge Compensation Mechanism in Co-free Materials for Na-Ion Batteries <u>Łukasz Kondracki</u> , Samuel Steiner, Julian Stropp, Dominik Wierzbicki, Anna Wach,
	Sigita Trabesinger
PS1-40	Kinetic Study of Organic Cathodes in Multivalent Batteries Enabled by Quasi- symmetric Cells Olivera Luzanin Joze Moskon Jan Bitenc, Pobert Dominko
	Li, Transnert Dhenemene in a Compositedalid State Electrolyte
PS1-41	Melania Kozdra, Daniel Brandell, Carlos Moyses Araujo, Amber Mace
PS1-42	Lithiation Heterogeneities at High Cycling Rates in LiNiO2/Graphite Full Cells Monitored by Multimodal Operando Characterizations: Combining Neutron Imaging and Micro-Xrd. Ouentin Jacquet, Lukas Helfen, Marta Mirolo, Samuel Tardif, Jakub Drnec, Claire
	Villevieille, Sandrine Lyonnard
PS1-43	Local Disorder Hindering Fast Ionic Transport: Case Study on Nanocrystalline and Amorphous Li10GeP2S12 – Poster Presentation
	Martin H. M. R. Wilkening
PS1-44	Mass and Charge Transport in Li1- δ CoO2 Thin Films – A Defect Chemical
	Perspective <u>Andreas Bumberger</u> , Claudia Steinbach, Joseph Ring, Jürgen Fleig
DS1-45	Mediated Lithium-Air Batteries: What Can We Learn From Cyclic Voltammetry?
	<u>Gabriela Horwitz</u> , Clare P. Grey,
PS1-46	Metal-Organic Framework Based Solid Electrolyte With High Magnesium-Ion Conductivity for Solid-State Magnesium Batteries
	Zhixuan Wei , Ruben Maile, Luise Riegger, Marcus Rohnke, Klaus Müller-Buschbaum, Jürgen Janek
PS1-47	Modelling Oxygen-Redox and Structural Rearrangements in a Lithium-Rich Layered Cathode Kit McColl Dozhman Zarabadi Door Samuel Colos, Bonjamin Morgan, Saiful Islam
	<u>And Maching Anglanding and Lines Differing in Deal Daned</u>
PS1-48	Molecular Understanding of Li-Ion Diffusion in Dual Doped Ga^{3+}/Sc^{3+} Li_{7}La_{3}Zr_{2}O_{12}
	Henry Andres Cortes Paez , Mauricio Rincón Bonilla, Pinku Pinku Nath, Elena Akhmatskaya
PS1-49	Multi-Scale Modelling of Li-Ion Batteries – Demonstration of Advanced Features on the Lfp Material
	Klemen Zelič, Igor Mele, Tomaž Katrašnik
PS1-50	NMR Spectroscopic Investigations of the Performance Limiting Mechanisms of Lithium-Sulfur Batteries
	Jana Beatrice Fritzke, Sunita Dey, Christopher O´Keefe, Clare Grey



PS1-51	Novel Organic Cathode Material for Rechargeable Aqueous Zinc-Ion Batteries <u>Svit Menart</u> , Klemen Pirnat, Robert Dominko
PS1-52	On the Relative Importance of Li Bulk Diffusivity and Interface Morphology in Determining the Stripped Capacity of Metallic Anodes in Solid-State Batteries <u>Marco Siniscalchi</u> , Junliang Liu, Joshua Gibson, Stephen Turrell, Susannah Speller, Chris Grovenor
PS1-53	One-Pot Solvent-Assisted Synthesis of All-Solid-State Composite Cathodes Using Li3PS4 and LiFePO4 Christoph Mandl, Katharina Hogrefe, Martin Wilkening, <u>Bernhard Gadermaier</u>
PS1-54	Operando Atr-IR Spectroscopy: An Appropriate Tool to Characterize Metal-Organic Batteries <u>Alen Vizintin</u> , Jan Bitenc, Niklas Lindahl, Anja Kopač Lautar, Klemen Pirnat, Jože Grdadolnik, Anna Randon-Vitanova, Patrik Johansson, Robert Dominko
PS1-55	Operando Haxpes Probing Solid Electrolyte Interphase Growth Through Ultra-Thin Film Electrodes Joshua Gibson, Marco Siniscalchi, Susie Speller, Chris Grovenor, Tien-Lin Lee, Robert Weatherup
PS1-56	Operando Study of Phase Transitions and Defect Imaging of Single Crystal Cathode Particles With Scanning X-ray Nanodiffraction Microscopy <u>Nikita Vostrov</u> , Isaac Martens, Marta Mirolo, Steven Leake, Xiaobo Zhu, Lianzhu Wang, Jakub Drnec, Marie-Ingrid Richard, Tobias Schulli
PS1-57	Operando Swelling Measurement of Si-C/G Based Anode in Pouch Cell: Effect of External Pressure and Impact of Cathode Material Delphine Vidal, Benoit Mathieu, Sylvie Géniès, Eric De Vito, Michal Tulodziecki, <u>Willy</u> <u>Porcher</u>
PS1-58	Operando Synchrotron-Based Fourier Transform Infrared (Sr-FTIR) Microspectroscopy for Battery Materials <u>Ashley Balck</u> , Ibraheem Yousef, Damien Monti, Nagaraj Patillbraheem, Nicolas Goujon, David Mecerreyes, Rebeca Marcilla, Alexandre Ponrouch
PS1-59	Organic Cathode Materials for Multivalent Rechargeable Batteries Jan Bitenc , Tjaša Pavčnik, Klemen Pirnat, Alen Vizintin, Anna Randon-Vitanova, Niklas Lindahl, Patrik Johansson, Robert Dominko
PS1-60	Pre-lithiation of Silicon-Based Anodes Using an Electrochemical Bath Lukas Haneke , Felix Pfeiffer, Fabian Kux, Peer Bärmann, Jens Wrogemann, Christoph Peschel, Jonas Neumann, Sascha Nowak, Martin Winter, Tobias Placke
PS1-61	Probing the Interface of Thin Film Battery Materials Using XAS and XPS <u>Michael Fraser</u> , Erik Björklund, Jack Swallow, Jodie Charlton, Robert Weatherup
PS1-62	Probing the Operation of Non-graphitizable Carbons in Na-Ion Batteries by Nuclear Magnetic Resonance (NMR) <u>Matej Gabrijelčič</u> , Blaž Tratnik, Robert Dominko, Alen Vizintin, Gregor Mali
PS1-63	Probing the Phase Evolution Between High Voltage Spinel Cathode and Coatings <u>Farheen Sayed</u>, Steffen Emge, Erik Bjorklund, Adam Lovett, Sundeep Vema, Rob Weatherup, Judith Driscoll, Sian Dutton, Clare Grey



PS1-64	Quantifying Dissolved Transition Metals and Understanding the Metal Solvation Shell With Magnetic Resonance Spectroscopy
	Jennifer Allen , Conrad Szczuka, Christopher O'Keefe, Rüdiger-A. Eichel, Josef Granwehr, Clare Grey
PS1-65	Real Time Observation of Structure Changes in LiNiO2/Graphite Cell During Fast Cycling <u>Xinyu Li</u>, Kristoffer Graae, Daniel Sørensen, Mads Jørgensen, Poul Norby
PS1-66	Sensitivity Analysis of Sei-Based Capacity Fade Model for Lithium-Ion Batteries <u>Williams Agyei Appiah</u> , Jonas Busk, Tejs Vegge, Arghya Bhowmik
PS1-67	Synergies and Differences at the Alkali Metal/Electrolyte Interface Leonie Wildersinn, Freya Müller, Fabian Jeschull, Andreas Hofmann, Julia Maibach
PS1-68	Tem Lamella Preparation and Subsequent Atomic Resolution Imaging From a Pure Li Metal Using Inert Gas Transfer Workflow From DualBeam to Tem Brandon Van Leer, <u>Letian Li</u> , Lin Jiang
PS1-69	The Atlung Method for Intercalant Diffusion (Amid) – A Reinvented Diffusion Measurement <u>Eniko Zsoldos</u> , Marc Cormier, Nutthaphon Phattharasupakun, Jeff Dahn
DC1_70	The Role of Trapped O2 in O-redox Cathodes
P31-70	Robert House, Gregory Rees, Miguel Perez-Osorio, John-Joseph Marie, Peter Bruce
PS1-71	Time-Resolved Electrochemical Heat Flow Calorimetry for the Analysis of Highly Dynamic Processes in Lithium-Ion Batteries
	Alexander Kunz, Clara Berg, Franziska Friedrich, Hubert A. Gasteiger, Andreas Jossen
PS1-72	To Improve the Li/Solid Electrolyte Interphase of Halide Solid Electrolytes by Formation of In Situ LiF Sei Layer
	Priya Ganesan , Maximilian Fichtner,
PS1-73	Transition Metal Deposition, Electrochemical Activity and Cell Capacity Fade
	Zachary Ruff, Megan Pernod, Erik Bjorklund, Robert Weatherup, Clare Grey
PS1-74	Visualization of the Accelerated Sulfur Redox Processes on Atomic Zn-N2 Sites for Room-Temperature Na-S Batteries <u>Daliang Fang</u>
DC1 75	Worflows for Detecting Cross-Talking Mechanisms for Ni-Rich Coumpounds
P21-75	Valentin Meunier, Alexis Grimaud,



VIRTUAL POSTER SESSION WEDNESDAY 5 OCTOBER, 18:25 – 19:20

PSV-01	Conversion-type Metaphosphate Electrodes for Lithium/Sodium-ion Batteries:
	Working and Degradation Mechanisms
	Qingbo Xia , Maxim Avdeev, Siegbert Schmid, Hongwei Liu, Bernt Johannessen, Chris Ling
PSV-02	Cow Hair Based Biochar As Sulfur Host for Lithium-Sulfur Batteries
	<u>Victoria Bracamonte,</u> Guillermina Luque, Andrea Calderón, Melina Cozzarin, Leandro García Tsuruoka, Fabio Saccone, Ezequiel Leiva
PSV-03	Graphene-Based Activated Carbon Composite for High-Performance Lithium- Sulfur Batteries
	Julen Castillo
PSV-04	Maximizing the Triple Phase Boundary Area in Sodium-Oxygen Batteries
	<u>Marina Enterría</u> , Arantzazu Letona-Elizburu, Lidia Medinilla, María Echeverría, Nagore Ortiz-Vitoriano
DSV-05	Power Capabilities in Lithium-Ion Capacitors
	<u>Alexey Glushenkov</u> , Chiara Cementon, Thrinathreddy Ramireddy, Daniel Dewar, Michael Brennan
PSV-06	The Effect of Cu (II) Substitution on Material and Electrochemical Properties in Sodium Deficient Manganese-Based Oxides
	Eun Jeong Kim , Tomooki Hosaka, Kei Kubota, Ryoichi Tatara, Shinichi Kumakura, Shinichi Komaba
	Ultragonically Assisted Masted Cathoda Lanching Dragons
PSV-07	
	<u>Ella Colleoni</u> , Chiara Canciani, Paolo Guida, William Roberts



POSTER SESSION II THURSDAY 6 OCTOBER, 18:00 – 19:00

PS2-01	Advanced Rechargeable Aqueous Zinc Ion Batteries by Electrospun Ferroelectric Polymer With Hierarchically Porous Structures
	Bo Keun Park, Ki Jae Kim
PS2-02	Analysis of Lithium-Ion Batteries Seriously Degraded Under Floating-Charging Conditions
	Tetsuya Omiya , Atsunori Ikezawa, Hajime Arai
PS2-03	Anion Effect on the Transport Properties of Ternary Ion-Gel Electrolytes <u>Nicola Boaretto</u> , Leire Meabe, Xiaoen Wang, Haijin Zhu, Alexander Santiago, Oihane Zugazua, Maria Forsyth, Michel Armand, Heng Zhang, Maria Martinez-Ibañez
PS2-04	Architectural Aspects of Silicon Nanowires and Its Effects on the Performance of Li-Ion Batteries <u>Rashmi Tripathi</u> , Gandharapu Pranay, Vaishali Chauhan, Amartya Mukhopadhyay, Rajiv Dusane
PS2-05	Charge Rate Dependence of Delithiation Mechanism in High Nickel Content Layered Materials for Li-Ion Batteries <u>Thibaut Jousseaume</u> , Jean-François Colin, Marion Chandesris, Sandrine Lyonnard, Samuel Tardif
PS2-06	Chemical Fire Extinguishing Materials Embedded Microcapsules for the Safety Enhanced Lithium-Ion Batteries Jin Hyuk Yang, Ki Jae Kim,
PS2-07	Computational Design of High Voltage Li-Rich Sulphide Cathode Materials. Hollie Richards, Pezhman Zarabadi-Poor, Benjamin Morgan, M. Saiful Islam
PS2-08	Dendrite Growth in Lithium Metal Solid-State Batteries Dominic L. R. Melvin, Ziyang Ning, Guanchen Li, T. James Marrow, Charles W. Monroe, Peter G. Bruce
PS2-09	Designing Prussian Blue Analogues for High-Energy-Density and Long-Life K-ion Batteries <u>Tomooki Hosaka</u> , Shinichi Komaba,
PS2-10	Differential Electrochemical Mass-Spectrometry (Dems) for In-Situ Gas Evolution Studies on Solid-State and Sodium-Ion Batteries <u>Soeren Lukas Dreyer</u> , Jun Hao Teo, Aleksandr Kondrakov, Torsten Brezesinski, Jürgen Janek
PS2-11	Dry Battery Electrode Manufacturing Using a Twin-Screw Extruder for Continous Powder Granulation <u>Korbinian Huber</u> , Stefan Stojcevic, Charlotte Schriever
PS2-12	Effect of Anion Chaotropicity in the Expansion of Electrochemical Stability Window in "Water-in-Salt" Electrolytes Zahid Ali Zafar



PS2-13	Effect of Sintering Conditions on Ionic Conductivity of Na3Zr2(SiO4)2(PO4) <u>Mina Nishi</u> , Dai Kutsuzawa, Takeshi Kobayashi
PS2-14	Electrophoretic Deposition of Electrodes for Flexible Batteries David Stark
PS2-15	Electrospun Hierarchical Vanadium Oxide Nanostructures As Electrode Materials for Post-lithium Batteries <u>Rezwana Binte Ahmed</u> , Montaha Anjass,
PS2-16	Electrospun Nanofiber Mesh Cathodes for Ultrathin Flexible Batteries Edi Mados-Kantor, Diana Golodnitsky, Amit Sitt
PS2-17	Enabling Uniform Li Plating/Stripping for Long-Life Thin Li Metal Batteries via Li2O/LiOH-Rich Passivation Layer <u>Tian Liu</u> , Mohammed Srout, Carlos A. F. Vaz, Marco Carboni, José-Antonio Gonzalez, Sigita Trabesinger, Mario El Kazzi
PS2-18	Evaluating Charge Transport Bottlenecks in Composite Cathodes of All-Solid-State Batteries <u>Philip Minnmann</u> , Lars Quillmann, Johannes Schubert, Simon Burkhardt, Felix H. Richter, Jürgen Janek
PS2-19	Evaluation of γ-Butyrolactone-Based Electrolytes for Fast-Charging Polymer- Based Dual-Ion Batteries <u>Katharina Rudolf</u> , Simon Münch, Lars Frankenstein, Tobias Placke, Ulrich Schubert, Martin Winter
PS2-20	Fast Na Ion Dynamics in Nb5+ Bearing Na3+xZr2Si2+xP1-xO12 <u>Florian Stainer</u> , Alexander Kügerl, Lukas Ladenstein, Martin Wilkening
PS2-21	Flexible Biodegradable Electrolytes for Custom-Shaped Batteries <u>Gilat Ardel</u> , Tommer Kidar, Olga Guchok, Adi Vinograd, Moty Marcos Dorfman, Heftsi Ragones, Diana Golodnitsky
PS2-22	High-Throughput Experimental Automated Module for Battery Materials Exploration <u>Iciar Monterrubio</u> , E. Castillo, A. Saracibar, J. Carrasco, M. Casas-Cabanas, M. Reynaud
PS2-23	Hydrogen Bond Assisted Ultra-Stable and Fast Aqueous NH4+ Storage Xikun Zhang, Bao-Lian Su,
PS2-24	Impact of Structure and Interface Properties on Charge Distribution and Transport in Composite Solid Electrolytes <u>Markus Wied</u> , Anne Bonnin, Vanessa Wood
PS2-25	Increasing the Cycle Life of Anode-Free Li-Metal Batteries and Li-Metal Batteries by Addition of Ceramic Nanoparticles to the Electrolyte <u>Roy Marrache</u> , Tzach Mukra, Tamir Assa, Emanuel Peled
PS2-26	Increasing the Cycle Life of Silicon-Anode Lithium Ion Battery Lina Faktorovich, Niv Aloni, Gilat Ardel, Emanuel Peled
PS2-27	Inductive Heating as a Recycling Preatreatment for the Recycling of Li-Ion Electrodes <u>Michael Wagner</u> , Arno Kwade



DS2-28	Innovative Polymer-Based Electrolytes for Advanced Li Metal Batteries
F 52 20	<u>Gabriele Lingua</u> , Marisa Falco, Ying Zhang, Silvia Porporato, Elisa Maruccia, Alessandro
	Piovano, Giuseppe A. Elia, Giuseppina Meligrana, Claudio Gerbaldi
PS2-29	In-Operando Structural Stability and Electrical Performance of Spark-Plasma- Ablation Derived Porous Films Based on Cathode Nanomaterials for Li-Ion Batteries
	<u>VIIKO Mandic</u> , FIOTEN Radovanovic-Peric, Ivana Parizic, Mattia Gaboardi
PS2-30	Interlayer Expansion of Layered Transition Metal Oxides by Alkylamine Functionalization and Its Effects on Lithium Ion Intercalation <u>Mennatalla Elmanzalawy</u> , Simon Fleischmann
PS2-31	Investigating Thick Positive Electrodes for Li-Ion Batteries Produced by 3D-Printing Tú Nguyen, Sébastien Sallard, Mohammadhosein Safari, Jasper Lefevere
	Tu nguyen, Sebastien Salara, Monarminaanosein Salah, Sasper Leievere
PS2-32	Ionically Conducting Inorganic Binders: A Paradigm Shift in Electrochemical Energy Storage <u>Shivam Trivedi</u>
PS2-33	Low Voltage Operation and LiFSI Salt Enable Long Li-Ion Cell Lifetimes at 85°C <u>Tina Taskovic</u> , Connor Aiken, Jeff R Dahn
PS2-34	Mechanism of Action of the Tungsten Dopant in LiNiO2 Positive Electrode Materials
	Chenxi Geng , Divya Rathore, Dylan Heino, Ning Zhang, Ines Hamam, Nafiseh Zaker, Gianluigi Botton, Roee Omessi, Nutthaphon Phattharasupakun, Toby Bond, Chongyin Yang, Jeff Dahn,
PS2-35	Microscale-Silicon Anodes With High Silicon Content Fabricated by Water-Based Slurry Processing for Use in All-Solid-State Batteries Gioele Conforto, Hubert Gasteiger,
PS2-36	High Ni-Based Cathode in Li Ion Battery Jaeyoung Jeon, Minuk Kim, Jongsup Hong
	Madalling the Daday Chamistry of Lithium Diah Culmhida Cathada Mataviala
PS2-37	Pezhman Zarabadi-Poor, Benjamin J Morgan, Saiful Islam
PS2-38	New Experimental Binder for Si-Based Anode <u>Maurizio Biso</u> , Stefano Mauri, Riccardo Pieri
DC0 70	New Hybrid Solid Electrolytes Based on Metal Organic Frameworks
PS2-39	Roman Zettl, Sarah Lunghammer, Bernhard Gadermaier, Katharina Hogrefe, Athmane Boulaoued, Patrik Johansson, Martin Wilkening, Ilie Hanzu
PS2-40	Oligoethylene Oxide Functionalized Vinylphosphonic Esters As Solid Polymer Electrolytes With Intrinsic Flame Retardancy and Adjustable Flexibility Philipp Pfändner Thomas Pebl. Bernhard Rieger
PS2-41	Optimized Cathode Active Materials for Llzo Based All-Solid-State Lithium Batteries
	<u>Christoph Roitzheim</u> , Helen Valencia, Liang-Yin Kuo, Martin Finsterbusch, Payam Kaghazchi, Olivier Guillon, Dina Fattakhova-Rohlfing



PS2-42	Organic Batteries and Four Electron Reaction
-	Klemen Pirnat, Nerea Casado, Luca Porcarelli, David Mecerreyes, Robert Dominko
PS2-43	P3-Type Mn and Fe-Based Layered Oxide Positive Electrode Materials for Sodium- Ion Batteries
	Joel Jr Cabañero, Russell E. Morris, A. Robert Armstrong
PS2-44	Probing the "Adsorption-Intercalation-Pore Filling" Mechanism in Corncob Derived Non-graphitizable Carbons
	Matija Tomšič, Andrej Jamnik, Boštjan Genorio, Alen Vižintin, Robert Dominko
PS2-45	Quasi-simultaneous Operando Waxs and Saxs Investigation of the Charge Dynamics Between Graphite and SiOx Particles
	<u>Marta Mirolo</u> , Maxime Servajon, Willy Porcher, Isaac Martens, Jakub Drnec, Claire Villevieille, Sandrine Lyonnard
PS2-46	Safe, Flexible, and High-Performing Gel-Polymer Electrolyte for Rechargeable Lithium Metal Batteries
	Alexander Santiago , Julen Castillo, Xabier Judez, Iñigo Garbayo, José Antonio Coca- Clemente, María C. Morant-Miñana, Aitor Villaverde, Heng Zhang, Michel Armand, Chunmei Li
DS2-47	Si Nanowires Based Materials for Lithium-Ion Battery Anodes
F 52-47	Caroline Keller, Saravanan Karuppiah, Cédric Haon, Nathalie Herlin, Pascale Chenevier
PS2-48	Silicon Nanowires Grown on a Stainless Steel Fiber Cloth as a Flexible and Robust Anode for Lithium-Ion Batteries <u>Sumair Imtiaz</u> , Ibrahim Saana Amiinu, Tadhg Kennedy, Kevin M. Ryan
PS2-49	Single Crystal P2-Na0.67Mn0.67Ni0.33O2 Cathode Material With Improved Cycling Stability for Sodium Ion Batteries
	Venkateswarlu Pamidi , Carlos Naranjo, Stefan Fuchs, Helge Stein, Yueliang Li, Sabine Grözinger, Johannes Biskupek, Ute Kaiser, Sirshendu Dinda, Yang Hu, Maximilian Fichtner
PS2-50	Spherical Templating of CoSe2 Nanoparticle-Decorated MXenes for Lithium-Sulfur
	Wei Ying Lieu , Hui Ying Yang, Zhi Wei Seh
PS2-51	Study of Limiting Factors of Power Performance Within Li-Ion Batteries
	Mohamed Raghibi, Didier Devaux, Lauréline Lecarme, Renaud Bouchet
PS2-52	Sustainable & Safe Energy Storage; From Electrolyte to Electrode to Full Cell <u>Martin Karlsmo</u>
PS2-53	Synergistic Investigation of P2- and P3-Type Layered Transition Metal Oxide Cathodes for Potassium-Ion Batteries
	Pawan Kumar Jha , Sai Gautam Gopalakrishnan, Prabeer Barpanda
PS2-54	Temperature and Stack-Pressure Dependence of the Critical Current for Voiding in Lithium and Sodium Anode Solid-State Batteries
	Dominic Spencer Jolly, Ziyang Ning, Peter Bruce
PS2-55	The Challenge of Polyanion Redox in Oxalates <u>Alexis Manche</u>



DS2-56	The Hydrotropic Effect of Ionic Liquids in Water-in-Salt Electrolytes
F 52 50	Maximilian Becker, David Reber, Ruben-Simon Kühnel, Corsin Battaglia
PS2-57	Three-Dimensional Porous Flower-Like CoMoO4 As Cathode for Li-O2 Batteries Pengcheng Xing, Baolian Su
PS2-58	Tuning the Transition Metal (Tm) Layer Composition of 'Layered' Na-Tm-Oxide Cathode Materials for Na-Ion Batteries Towards Enabling Water-Stability, High Capacity and Cyclic Stability <u>Bachu Sravan Kumar</u> , Anagha Pradeep, Animesh Dutta, Amartya Mukhopadhyay
PS2-59	Understanding and Applications of Phosphate-Based Electrode Materials for Aqueous Na-Ion Batteries <u>Linas Vilčiauskas</u> , Jurga Juodkazytė, Jurgis Pilipavičius, Milda Petrulevičienė, Davit Tediashvili, Gustautas Snarskis
PS2-60	Understanding Molecular-Scale Dynamics Inside Composite Polymer Electrolyte <u>Guillaume Navallon</u> , Lionel Picard, Quentin Berrod, Jacques Ollivier, Markus Appel, Federico Monaco, Sandrine Schlutig, Sandrine Lyonnard
PS2-61	Understanding the Redox Behaviour of Na+/Li+ Exchanged T2/O2- Li0.67+xNi0.33Mn0.67O2 Cathode Materials for Lithium-Ion Batteries <u>Timo Boehler</u> , Matthias Kuenzel, Tobias Eisenmann, Jakob Asenbauer, Sylvio Indris, Maider Zarrabeitia, Stefano Passerini, Dominic Bresser
PS2-62	Unraveling Cation-Anion Redox Mediated Electrochemical Lithium (De)insertion on Novel Layered Manganese Oxychalcogenides <u>Sunita Dey</u> , Souvik Giri, Shunsuke Sasaki, Simon J Clarke, Clare P. Grey
PS2-63	Unveiling the De-/Lithiation Mechanism for Monoclinic Nb2O5 As High Performance Li-Ion Anode <u>Xilai Xue</u> , Jakob Asenbauer, Tobias Eisenmann, Thomas Diemant, Stefano Passerini, Dominic Bresser
PS2-64	Very High Rate-Capable, Electrochemically Stable and Safe Bi-phase Na-Titanate Based Composite Anode for Na-Ion Batteries <u>Anagha Pradeep</u> , Bachu Sravan Kumar, Velaga Srihari, Himanshu K Poswal, Amartya Mukhopadhyay
PS2-65	Which Contamination Do Cathodes for Lithium-Ion Batteries Tolerate? <u>Ulf Breddemann</u> , Petr Petr,
PS2-66	Y-TEC's Lithium R&D and Industrial Activities: From the Resource to the End Customer <u>Jorge Acosta</u> , Leandro García Tsurouka, Melina Cozzarin, Lucas Mardones, Sofía Gomez, Jorge Thomas, Fabio Saccone
PS2-67	Zirconium Substitution in Ni-Rich Nmc Layered Cathode Material for High-Energy Lithium-Ion Batteries <u>Mattia Colalongo</u> , Tanja Kallio, Basit Ali, Tobias Schulli, Jakub Drnec



INFORMATION FOR IN PERSON SPEAKERS AND POSTER PRESENTERS

Oral presentations

Speaker Ready Corner is located in Arnold Hall. All presenters must check into the Speaker Ready Corner at least 4 hours prior to their session. Conference staff will make sure that your presentation is downloaded on the lectern computer. At the end of the conference, all presentations will be deleted, so no copyright issues will arise. Please make sure that your computer presentation is fully operational before your talk. Only Power Point or PDF presentations on USB Memory cards will be accepted. The latest version of MS PowerPoint is recommended.

Whilst use of individual PC laptops is allowed, you still need to check into the Speakers Corner.

The Speakers Corner will have the same opening hours as the registration desk.

Poster presentations

Posters will be displayed in Sonce Hall at the Rikli Balance Hotel (IBA Conference venue) and on the onAIR digital conference portal.

Poster Session I authors Tuesday 4 October 18:00 - 19:00:

Mounting on 2 and 3 October. Removal before lunch break on 4 October.

Poster Session II authors Thursday 6 October 18:00 - 19:00:

Mounting on 4 October after lunch break. Removal on 7 October.

Digital/Hybrid poster session

All posters have been allocated to the digital session as well as on site poster session. During a poster session, the presenting authors are kindly requested to stay logged into the onAIR platform. Use of Google chrome or Edge is required for the onAIR portal.

Hybrid Poster Session, Wednesday 5 October 18:00-19:00 CEST - digital session is mandatory also for Poster Session I & II authors.



AWARDS

IBA AWARDS

Congratulations to all winners of IBA 2022 awards:

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IBA RESEARCH AWARD

Jun Lu Hikari Sakaebe

IBA TECHNOLOGY AWARD

Peter Lamp Hong Li

IBA EARLY CAREER AWARD

Wolfgang Zeier

IBA MEDAL OF EXCELLENCE

Emanuel Peled



GENERAL INFORMATION

Internet

Wireless internet connection is available in the foyer. No login or password is needed.W

Registration and Information Desk

The Registration Desk will be located opposite of hotel reception desk and will be clearly marked.

Opening times will be as follows:

Sunday	16.00 – 19.00
Monday	07.30 – 18.30
Tuesday	08.00 - 18.00
Wednesday	08.00 - 18.00
Thursday	08.00 - 18.00
Friday	08.00 - 12.00

Conference Identification Badge

A conference identification badge is included in the congress materials provided upon registration. There will be no admittance to the Scientific Sessions without the conference badge.

Coffee Breaks and Lunches

During coffee breaks and lunch, food will be served free of charge to participants wearing conference badges.

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Session I Monday

Pushing the Limits of Layered Oxide Cathodes <u>Arumugam Manthiram</u>

University Of Texas At Austin, Austin, United States

The widespread adoption of battery technologies for electric vehicles and grid electricity storage requires optimization of cost, energy density, power density, cycle life, safety, and environmental impact, all of which are directly linked to severe materials challenges. With respect to increasing the driving range, while also reducing the cost, layered oxide cathodes with high-nickel content and low or no cobalt are at the forefront. However, while the capacity increases with nickel content, the cycle life declines drastically, hampering their implementation in practical cells. It is critical to understand the factors that cause rapid degradation in order to overcome the cycle life limitations. This presentation will focus on developing an in-depth understanding of the degradation mechanisms by employing different electrolytes with high-nickel cathodes. With robust electrolytes, realization of capacities in excess of 220 mAh/g with LiNiO2 over 600 deep charge-discharge cycles will be presented. The underlying mechanisms that lead to long cycle life will be presented based on the analytical data collected with a suite of advanced characterization techniques after hundreds of cycles. The techniques include in-situ and ex-situ x-ray diffraction, scanning electron microscopy, aberration corrected transmission electron microscopy, x-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, etc.

Kinetics, Rate Limitations and Aging of Interfaces in Solid State Batteries Jürgen Janek

Justus Liebig University Giessen, Giessen, Germany

Interfaces are potential Achilles heels in solid-state batteries, as well as in liquid electrolyte-based batteries (e. g. LIB). Solid electrolytes (SEs) often show narrow electrochemical windows and are either easily reduced or oxidized at low or high potentials, respectively. In this lecture, the state of research on anode and cathode stability of the various solid electrolytes will be summarized, focussing to halides and thiophosphates. A comparison with theoretical calculations aims to compare thermodynamic and electrochemical stability.

In a next step, the kinetics of interface aging (degradation) will be discussed. Diffusion-controlled interface reactions, forming resistive interphases, have been identified at both anode and cathodes interfaces as rate-limiting for the aging processes. This calls either for the development of more stable solid electrolytes, like e.g. halide SEs for high potential operation, or for the development of protecting interlayers. The current understanding of interface degradation will be briefly summarized, highlighting the formation of SEI and CEI layers in sulphide SEs. Finally, the role of natural or artificially designed inter-layers on the rate capability of SE interfaces will be discussed.

Lithium Metal anode: The reversible and stable lithium metal anode is the ultimate target of SSB research. The state of research, focusing on ox-ide and sulphide SEs, will be summarized, and the current rate limitations will be identified. The lack of sufficient and reliable electronic conduc-tivity data is identified as one key issue in better understanding the failure at lithium metal anodes due to filamentory or dendrite growth.

Composite cathode: The proper operation of SSB cathodes requires the preparation of transportand storage optimized cathode composites. Electronic and ionic transport paths suffer from degradation of the SE; grain boundaries and porosity of the composite limit the rate capability. Results from recent theoretical modelling will be presented.

Halide-based Solid-State Batteries: Electrolyte, Stability, Interface and Electrode Andy (xueliang) Sun

University Of Western Ontario, London, Canada

All-state-state lithium batteries (ASSLBs) have gained worldwide attention because of intrinsic safety and increased energy density. Compared with other types of solid-state electrolytes including oxidebased, polymer-based and sulfide-based electrolytes, recently-developed halide-based solid-state electrolytes (SSEs) have garnered considerable attention for all-solid-state lithium batteries (ASSLBs) due to the high ionic conductivity, high oxidation voltage and good stability toward oxide cathode materials [1]. However, there are still many challenges in halide-based solid-state electrolytes for ASSLBs including controllable and mass-production synthesis, achieving high humidity tolerance and demonstrate high-performance of ASSLBs; in particular, increased understanding of mechanisms during synthesis and tuning their properties of the electrolytes as well as interface with electrode materials[1].

In this talk, (i) I will demonstrate synthesis strategy [2-4], in particular, new and salable watermediated synthesis method [2]. (ii) I will report a systematic study on the correlations among structural evolution, Li+ migration properties, and humidity stability resulting of the halide-based electrolytes, along with in-situ characterization for understanding of the mechanisms [5], (iii) Full cell battery performance will be optimized [6], and (iv) humidity ability [7]. In the end, perspectives of halide-based ASSLBs compared with other solid-state electrolytes in ASSLBs will be discussed [8,10].

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Structural Features for Affecting Electrochemical Performance in Co-free Li-Rich Materials

byoungwoo Rang

POSTECH, Pohang, South Korea

Rechargeable Li-ion batteries have become a key enabler for transformational changes in our society by powering advanced portable electronics and deploying electric vehicles and grid-scale applications. To realize this transformation, high energy density Li-ion batteries are needed. However, the conventional electrode materials such as Ni-rich materials and LiCoO2 has a theoretical limited capacity for achieving high energy density because they can use only transition metal redox reaction for providing available electrons. One of possible ways to overcome this limitation is the use of the oxygen redox reaction for additionally achieving capacity. Li-rich materials (Li1+xTM1-xO2, TM = Transition metals) have recently become one of the most attractive electrode materials because they can deliver much higher capacities (>250 mAh/g) than conventional layered materials (e.g. LiCoO2) via supplementary oxygen redox reaction in addition to the TM redox reaction. To exploit the potential of the oxygen redox reaction, several approaches have been suggested including applying surface coatings for reducing O loss, or replacing 3d-TMs with 4d or 5d-TMs. In this talk, I will discuss about the structural features that affect electrochemical activity and properties in Co-free Li-rich materials. Especially, I will focus on discussing how Li-TMs inter-diffusion between the phases in Li-rich materials can affect the oxygen redox activity and the intrinsic structure stability.

Advanced & Beyond Lithium Ion Technologies: What's Around the Corner? Patrick Bernard

Saft, Bordeaux, France

The increasing demand for more powerful, longer lasting and safer batteries is pushing the continuous improvement of the Li-ion battery technology while exploring new chemistries such as solid-state based one.

For the near term, besides NMC/Gr-Si based cells for high energy applications and LTO technology for heavy cycling applications, Saft is developing a new range of Li-ion products reflecting these current market needs : LFMP (Li(FexMn1-x)PO4 based technology, bridging the best of layered and phosphate worlds : high energy & power and excellent life & safety for all markets.

This new breakthrough in lithium-ion batteries has only been made possible by adopting new materials for cathode, anode and electrolyte, finely tune electrodes formulations and process which have a direct influence on electrodes structures which in turn impacts cell performances. Finally, cell design is also of great importance.

Process and Battery digital twins in link with advanced characterization techniques are instrumental to deep understanding and fast technology development.

Furthermore, for the mid/long term, Saft has launched a large program of research, development, and industrialization on solid-state technologies for high energy density lithium batteries with improved safety, lower cost and long-life.

Session II Monday

Artificial Intelligence-Based Optimization of Battery Manufacturing Processes <u>Alejandro Franco</u>

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The electrode microstructure determines the practical properties of Lithium Ion Battery (LIB) cells, such as their performance, durability and safety. Such microstructure is strongly influenced by the electrode manufacturing which is a complex process involving multiple steps and parameters. Optimizing this process based on a traditional trial-and-error approach is ineficient, time and ressources consuming and can lead to high scrap rates.

In this lecture I present a digital twin able to optimize in an efficient way the manufacturing process of Lithium Ion Batteries (LIBs). This digital twin, developed in the context of the ERC-funded ARTISTIC project,[1] allows to predict which manufacturing parameters to adopt in order to achieve LIB electrodes with optimal kinetics and transport properties.

This digital twin is supported on a hybrid approach encompassing an experimentally-validated physics-based multiscale modeling workflow and Machine Learning-based surrogate models.[2] It simulates the different steps along the LIB cells manufacturing process, such as the electrode slurry, coating, drying, calendering and electrolyte infiltration. The multiscale physical modeling workflow couples experimentally-validated Coarse Grained Molecular Dynamics, Discrete Element Method and Lattice Boltzmann simulations and it allows predicting the impact of the process parameters (e.g. formulation, coating speed, calendering pressure) on the final electrode mesostructure in three dimensions. The predicted electrode mesostructures are injected in a Finite Element Method-based performance simulator capturing the influence of the pore networks and spatial location of active material and carbon-binder within the electrodes on the electrochemical response upon discharge and charge. The Machine Learning models are used to accelerate the physical models' parameterization, to unravel manufacturing parameters interdependencies from the physical models' predictions and experimental data, and for inverse design.[3] The predictive and optimization capabilities of this digital twin are illustrated with results for different electrode chemistries (NMC, LFP, graphite, silicon/graphite blends). Furthermore, I also share results that demonstrate that this digital twin can be also used to optimize Sodium Ion and Solid State Batteries. Finally, I discuss the free online battery manufacturing simulation services offered by the project and our virtual and augmented reality tools for education of the next generation of scientists and technicians in the field of battery manufacturing.

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Millisecond Ion-Transport in Mixed Polyanion Battery Materials Pieremanuele Canepa

National University Of Singapore, Singapore, Singapore

Powering hundreds of millions of laptops, cameras, and phones worldwide, rechargeable Lithium(Li)ion batteries have performed admirably as the linchpin technology enabling today's mobile electronics industry. However, the energy density required for stationary energy storage devices and electric vehicles are quickly exceeding the limits of commercial Li-ion batteries. Finding alternatives to the Li-ion battery appears a crucial priority in the diversification and modernization of energy storage technologies. Indeed, when life-cycle analysis is examined in the design of batteries, sodium (Na) appears attractive because it can be "harvested" directly from seawater, making Na ~50 times lower in cost than Li.

An important class of phosphate electrodes and electrolytes discovered by Hong and Goodenough is the Natrium Super Ionic CONductors (NaSICONs) and chemical formula NaxMM' (XO4)3, where M and M' are transition metals and X = Si, P and/or S. NaSICON electrode materials and electrolytes typically display significant Na-ion mobility. In this talk I will show that computational materials science, in particular first-principles methodologies, can guide the design of better NaSICON electrode and electrolyte materials, with superior energy densities and improved ion transport. For example, our predictions indicate that suitably doped NASICON compositions, especially with high silicon content, can achieve high Na+ mobilities.

These findings are relevant for the optimization of mixed polyanion solid electrolytes and electrodes, including sulfide-based polyanion frameworks, which are known for their superior ionic conductivities.

Electrochemical Impedance Spectroscopy and Quality Indicators Jeremy Appell

BioLogic, Seyssinet-Pariset, France

There are two main types of techniques in electrochemistry: Direct Current (DC) and Alternative Current (AC). DC techniques mainly include potential or current steps, pulsed and sweep methods such as Chronopotentiometry, Chronoamperometry, Linear Scan Voltammetry or Cyclic Voltammetry. With DC techniques, the response of an electrochemical system is studied as a function of time.

With AC techniques, such as Electrochemical Impedance Spectroscopy (EIS), the response of the system to a potential or current sinusoidal perturbation is studied as a function of the frequency, which is swept over a few decades. The frequency sweep enables access to all processes taking place at the electrode such as charge transfer and mass transport. Any other electrical contribution and artefacts would also be visible with EIS.

To provide high quality data three conditions are required, the system must be linear, time invariant and with a good signal to noise ratio. Three indicators (THD, NSD and NSR) calculated by the EC-Lab software from BioLogic can be used to check that these conditions are met and that data can be trusted.

Total Harmonic Distortion (THD)

Most of the electrochemical systems are non-linear but by applying an input signal of small amplitude, non-linear systems can be considered as linear as the curve under study around the operating point can be approximated by its tangent.

THD indicates if the amplitude of the current or potential modulation applied to the system is small enough to consider that it behaves linearly. If a system behaves nonlinearly the output signal will contain some harmonics. The THD quantifies the nonlinearity by evaluating the amplitudes of the N harmonics.

THD is expressed as a percentage, it is generally considered that a THD below 5 % is acceptable. In EC-Lab, it is calculated on the potential and on the current and over 6 harmonics.

Non-Stationary Distorsion (NSD)

It is important that the system and its response do not change with time during an impedance measurement. We can distinguish two causes for the nonstationarity of a system, either the response of the system has not reached its permanent regime or either the parameters defining the system are changing with time. The response of a non-stationary system will contain, in addition to the fundamental frequency, some adjacent frequencies. We can then compute another indicator, the NSD.

Noise to signal ratio (NSR)

In an ideal measurement, all the signal energy is contained in the fundamental frequency, but because of various factors such as the accuracy and precision of the measuring device or external perturbations, there might be some energy in other frequencies than the fundamental one, which is called noise.

Besides reducing the sources for noise it is useful to increase the amplitude of the signal.

A third indicator can then be computed, the NSR which quantifies the extent of noise in the measurement. It represents all the signal not contained in the fundamental frequency, the 6 harmonics used to calculate THD or the signal at frequencies adjacent to the fundamental frequency used to calculate NSD.

Getting a linear system and the corresponding low THD requires decreasing the amplitude of the input signal but increasing the amplitude of the output signal helps to get a better NSR. We can therefore see that tuning the settings of an experiment requires compromises and likely several tries.

Ni-Rich Cathodes in All-Solid-State Batteries: Electrochemical Behavior and Stabilization Approaches <u>Aleksandr Kondrakov</u>

BASF SE, Ludwigshafen, Germany

All-solid-state batteries are a promising next-generation system for energy storage. To ensure proper scalability and satisfactory rate capabilities, mechanically soft inorganic solid electrolytes with high ionic conductivities and good slurry processibility, e.g., thiophosphates, are required to be used in the cathode composites. These solid electrolytes however have a voltage stability window, which is too narrow for the cathodes based on high energy density Ni-rich cathode materials. This instability results in resistance build up and rapid capacity fade during cycling. Understanding underlying interfacial reactions is crucial for rational development of Ni-rich cathode materials for ASSB applications. The presentation will summarize recent mechanistic studies on electrochemical behavior of Ni-rich cathodes in ASSB and will present stabilization approaches developed at the joint BASF-KIT lab BELLA (Battery and Electrochemistry Laboratory).

Session III Monday

Increasing the Cycle Life of Lithium Batteries

Tel Aviv University, Tel Aviv, Israel

Because of their higher energy density, compared to graphite-anode lithium-ion batteries (GLIB), rechargeable lithium-metal batteries (LMB) and silicon-anode lithium ion battery (SLIB) have been considered as the most attractive next-generation energy-storage systems (ESS). A promising approach to improving LMB performance, that has gained interest in recent years, is the use of anode-free lithium-metal batteries (AFLMB). Such battery configuration enables elimination of the problem of using excessive amounts of lithium in LMBs, hence increasing the specific energy of the battery. Furthermore, silicon is a low-cost and environmentally friendly material, and is the second most abundant element in the Earth's crust. Its theoretical capacity of 4200mAh g-1, is an order of magnitude greater than that of graphite. Nevertheless, the main and most important challenge with these systems is the short cycle life. This work explores the beneficial effects of integrating metal-oxide nanoparticles (MONPs) into the liquid electrolyte of these systems. It was recently found that the addition, to the electrolyte, of low concentrations (0.1 to 5%) of some MONPs significantly improve coulombic efficiency (CE), capacity retention (CR) and the SEI properties. Other MONPs have a smaller effect. In this presentation, the effect of many MONPs will be reviewed.

How Transition Metals in Lib Electrolytes Influence the Cycling of Positive Electrodes

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In the field of battery production, the key concept to achieve circular economy is the reuse of materials from spent cells. It is therefore of utmost importance to understand and specially to quantify the various effects of impurities which can be brought into the cell production via the recycling process. The majority of cells currently on the market is based on NMC or NCA active materials. During cell cycling both oxide types, NMC and NCA, gradually release transition metal ions into the electrolyte solution. The risk of transition metal dissolution will be higher when oxidic active materials from spent cells will be reused in a circular battery production loop. The first step in the project, as presented here, was therefore to quantify the influence of the transition metals on the cycling behavior of NMC811 and NCA based positive electrodes. To this point, standard carbonatebased battery electrolytes were intentionally contaminated with different concentrations of Ni, Mn, and Co acetates, sulfates, and carbonates. In order to separate the expected additional effects of recycled oxides and to avoid the known influence of the transition metals on the SEI layer at the graphite negative electrode, half-cells with pristine NMC811 and NCA electrodes coupled with oversized metallic lithium counter electrodes were used. Depending on their concentration, noticeable up to detrimental effects of the transition metals present in the solution on the cycling behavior of the oxide electrodes were identified. More specifically, both, the overpotentials and the fading rate increased. Roughly, the higher the concentration of the transition metals in the solution, the higher the overpotentials on the positive electrode and the worse the cycling performance. Supporting experiments confirmed that there was no significant decrease in the conductivity of the used "contaminated" electrolyte solutions, thus, there is no additional potential drop across the electrolyte when the contaminating metal ions are present. Further, cycling of symmetric Li/Li cells confirmed that the lithium counter electrode is not responsible for the observed increased overpotentials. Therefore, it was confirmed that the presence of the transition metals Ni, Mn, and Co in the electrolyte has significant effects on the cycling behavior of the oxide electrodes. In order to elucidate the mechanism of this influence, supporting analytical methods including GC/MS, NMR, and OEMS were applied.

Towards Mechanistic Understanding of Electrode/Electrolyte Interphases With Operando Characterization Erik Berg

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Electrode/electrolyte interphases are key components not only in modern Li-ion cells, but also in next-generation battery chemistries. The most prominent example thereof is the solid electrolyte interphase (SEI), which primarily is formed on the negative Li-ion electrode in the first few dis-/charge cycles and largely guarantees the function of the battery throughout its lifetime. Despite decades of research, no consensus on the underlying formation and operating mechanisms is established. Complex dynamics of the governing reactions of the SEI, its nm-sized dimensions, as well as the intermediacy and instability of many involved species are major challenges for any characterization approach. Operando analytical methods are therefore critical and the progress in the field has in recent years been rapid. In my talk, I will shortly introduce an experimental platform dedicated to the study of electrode/electrolyte interphases. Examples of how Online Electrochemical Mass Spectrometry (OEMS) coupled with Surface-Enhanced Raman Spectroscopy (SERS) and Electrochemical Quartz crystal Microbalance with Dissipation monitoring (EQCMD) is applied to analyze interphase will be presented. Focus is on how molecular structure-function relationships of interphase forming additives can be understood.

Advancing Quantitative Understanding of Functionality in the Lithium Sei Betar Gallant

MIT, Cambridge, United States

Li metal anodes offer significantly higher capacities than graphite and are therefore central to strategies to develop advanced rechargeable battery chemistries that meet range and performance targets for electric vehicles. Although closer than ever, lithium (Li) anodes still cannot meet the >99.9% Coulombic efficiency (CE) consistently needed for >1,000 cycle life. This shortfall arises from uncontrolled reactivity at the solid electrolyte interphase (SEI) and its resulting properties, leading to inhomogeneous plating and stripping, continuous electrolyte consumption and loss of active Li inventory. Despite much recent progress in electrolyte development, the lack of quantitative understanding of functionality from the perspective of the SEI itself still hinders attempts to rationally design an improved interface and bridge the remaining gap in CE.

To help inform such efforts, our work is developing techniques to gain insights into SEI phases and reveal interplays between their chemistry, structure and function. First, we developed approaches to isolate and synthesize SEI-relevant ionic and organic phases, including lithium oxide (Li2O), lithium fluoride (LiF), lithium carbonate (Li2CO3) and others, at representative nanometer-scale thicknesses directly on Li metal. These interfaces are interrogated via targeted electrochemical techniques to reveal their Li+ conductivity, providing a framework to assess which phases bolster, or hinder, transport in the SEI. These properties will be related to additional ongoing efforts to study the native SEI, where we are advancing titration-based techniques developed in the field to quantify the partitioning of phases in carbonate electrolytes, including isolated LiO, semicarbonates and Li2CO3, salt-derived phases, and Li2C2. Progress and challenges towards complete quantification, i.e. full accounting of all phases, will be described, as will the relationship between the proportions of key phases and CE. Collectively, these results are helping to test a long-standing hypothesis in the field that higher Li+ transport is a descriptor for an improved SEI.

Impedance Spectroscopy of Battery Cell's Impedance: Theory vs. Experiments

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Electrochemical impedance spectroscopy (EIS) is arguably the most accurate electrochemical technique. It often appears as the main or, more commonly, an additional technique in experimental investigation of advanced batteries. To a large extent, the popularity of impedance technique is probably due to fully automized, easy-to-use modern devices and, also, due to user-friendly softwares that facilitate the basic analysis of measured spectra in terms of equivalent circuit fitting. On the negative side, the final result of such a standard approach is a set of parameters (resistors, capacitors, inductors) which are difficult to interpret in terms of physical processes occurring in the measured cell. In the worst case, assignment of equivalent circuit parameters to physical processes is carried out arbitrarily which frequently leads to erroneous interpretation of cell's physics.

Interpretation of measured EIS spectra gets much more reliable if instead the equivalent circuit approach one relies on physical-chemical models that describe transport and reaction phenomena in given cell. The linearised physical-chemical models of electrochemical cells can be solved in three ways: (i) by finding an analytical solution, (ii) using conventional numerical procedures, (iii) using the transmission line approach derived from established physics based frameworks (Newman's model, Poisson-Nerst-Planck framework etc.).

In this presentation we will mainly (but not exclusively) demonstrate the power of physics-based transmission line (TLM) approach when used for interpretation of measured impedance features of advanced battery cells. After explaining the transmission line methodology on simple, well-known cases, we will demonstrate its use on a variety of different battery electrodes, from insertion cathodes (LiCoO2, NMC, LiFePO4) to metallic lithium anode or sulfur cathode. However, we will also show the limitations of the TLM approach in reaction-limited electrodes such as magnesium anode and other similar post-lithium systems where the conventional kinetic approach appears to be more suitable. In all cases we will compare the actual measured spectra with theoretical predictions of the corresponding model. On the other hand, we will also discuss the correspondence between physics-based approaches and the simple intuitive equivalent circuits frequently published in the literature.

Finally, we will clearly demonstrate (using a couple of systematic studies) that EIS can only give highquality information if coupled with complementary techniques such as various microscopies, spectroscopies, elemental analyses etc., which give information about the structure, morphology, composition etc. of the measurand, i.e. information that is not accessible by EIS.

From Interfaces to Interphases in Different Battery Chemistries* Yair Ein-Eli

Technion-israel Institute Of Technology, Haifa, Israel

Battery electrode's material identity is the most important factor in a battery scheme and engineering. While theoretical potentials and capacities (and hence, energy densities) are predetermined by the nature (thermodynamic parameters) and identity of the material, the actual and real life battery performances are controlled by the electrode's kinetics.

In this talk we will present and discuss how modifications made at the electrode-electrolytes interfaces of several battery chemistries were altered to produce interphases that control the electrode behavior and overall the batteries performances. Example for such modification in Li-ion graphite anodes and cathode electrodes, including the introduction of an artificial SEI (Peled's iconic Solid Electrolyte Interphase model) will be discussed in this talk. Other battery chemistries and modified electrodes surfaces to be discussed are the multi valent non-aqueous metal air battery systems, as well as the alkaline Zn anode based batteries.

*This keynote talk is in honor of Prof. Emanuel Peled's, the recipient of the IBA medal of excellence

Tailored Polymer Electrolytes for High-Energy Lithium-Metal Batteries

Hai-Peng Liang^{1,2}, Zhen Chen^{1,2}, Xu Dong^{1,2}, Alexander Mayer^{1,2}, Medina Jasarevic^{1,2}, Stefano Passerini^{1,2}, <u>Dominic Bresser^{1,2}</u>

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Polymer electrolytes based on poly(ethylene oxide) (PEO) have been successfully commercialized in lithium-metal batteries for electric vehicle applications. However, the rather low ionic conductivity at room temperature results in the need for a continuous heating of the battery cell to about 60-80 °C upon operation and also when charging the battery. This low ionic conductivity in combination with the rather limited electrochemical stability towards oxidation, restrict the choice of potential active materials for the positive electrode to those with a de-/lithiation potential well below 4 V. These two major challenges for the application of polymer electrolytes in a greater variety of applications are the direct result of the charge transport mechanism in PEO-type electrolytes, which is strongly coupled to the segmental relaxation of the polymer chains, and the chemical design of the polymer.

Herein, a comprehensive overview of our activities to overcome these challenges will be provided, including the (partial) decoupling of the charge transport from the polymer dynamics and the careful design of the polymer architecture in order to increase the electrochemical stability towards oxidation; while simultaneously maintaining suitable mechanical properties, high safety, and the compatibility with lithium metal at the negative electrode. The work is dedicated to the development of a fundamental understanding of the relevant impact factors that enable the realization of high-performance polymer-based electrolyte systems for high-energy lithium-metal batteries and beyond.

Operando Terahertz Spectroscopy of Solid Electrolyte Interphase Evolution on Silicon Anodes

Diana Golodnitsky¹, Daniel Krotkov¹, Dan Schneier¹, Svetlana Menkin², Yonatan Horowitz¹, Emanuel Peled¹, Sharly Fleischer¹

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The in-situ characterization of materials and interphases of battery electrodes is of crucial importance for the basic understanding of the complex, simultaneous processes that take place during the operation of secondary batteries. We present, for the first time, the use of a Terahertz (THz) time-domain-spectroscopy method for the operando characterization of the silicon/electrolyte interfacial phenomena and dynamics in a working lithium-ion battery. Our results show that THz-TDS is able to detect alterations of the SEI under cycling conditions and during rest periods. By on-line monitoring of the THz reflectivity from the electrode-electrolyte interface within a working electrochemical cell, we were able to identify the SEI formation on the surface of the Si electrode during the lithiation process, and its partial dissolution during prolonged delithiation. Our measurements show that certain parts of the SEI tend to dissolve during rest periods if not fully formed before, demonstrating the importance of efficient complete SEI formation in batteries. The presented technique lays the basis for utilizing terahertz spectroscopy as a uniquely desirable tool in the ever-growing field of operando characterization of electrochemical cells.

Session I Tuesday

High Safety Batteries With High Energy Density by In Situ Solidification Strategy

Institute Of Physics, CAS, Beijing, China Beijing WeLion New Energy Technology Co., Ltd, Beijing, China

Developing lithium batteries with high energy density, high power density and safety is an effective strategy for improving the driving range of electric vehicles and airplanes . It is also helpful to decrease cost and the frequency of battery charge . Conventional Li-ion batteries with liquid electrolyte could increase specific energy density further to 500Wh/kg but bring serious safety concern due to high thermal runaway probability. All-solid-state batteries (ASSB) are potentially safe. However, ASSB still face huge engineering challenges in material selection and interfacial optimization. It has been demonstrated that hybrid solid-liquid electrolyte batteries, especially based on in-situ solidification (ISS) technology are quite practically. We have purposed and confirmed that combining anode prelithiation, nanosized solid electrolyte coating on cathode particles and two sides of separator, low expansion nano-Si/C anode, the cell can operate at wide temperature range with reasonable rate performance, cycle life and improved safety. Specific energies of the 100Ah level pouch cells can approach to 360 Wh/kg and can support 1000km driving distance per charging. In this report, we will update related our progresses on ISS technology and scientific problems.

Balancing the Inharmony Between Electrons and Alkali Ions in Layered Cathode Materials Yong-Mook Kang

Korea University, Seoul, South Korea

Irreversible phase transformations of layered oxide cathodes during charging have been detrimental for most of them. Even if a lot of efforts have been made to relieve this highly irreversible phase transformation, there have been just a few successful results, which definitely limit the amount of extracted alkali ions and thereby the available capacities of the layered oxides. So, this presentation will suggest two strategies to get over the limitation of previous researches.

As an inverse conceptual strategy, we first observed the possibility to make this irreversible phase transformation extremely reversible by utilizing crystal water as a pillar. Although we found a few crystal structures working with this reversible phase transition, the works using Na-birnessite (NaxMnO2•yH2O; Na-bir) or Li-birnessite (Li-bir) as basic structural units will be highlighted here. The crystal water in the structure contributes to generating metastable spinel-like phase, which is the key factor for making this unusual reversibility happen. The reversible structural rearrangement between layered and spinel-like phases during electrochemical reaction could activate new cation sites and enhance ion diffusion with higher structure was maximized through modulating the steric coordination or amount of cyrstal water in the lattice resultantly optimizing the electrochemical performances of the birnessite layered oxides.

Pseudo Jahn-Teller effect (Pseudo JTE) will be also stressed out as a fundamental reason behind lattice distortion of layered oxide cathodes. Even though Jahn-Teller effect (JTE) has been regarded as one of the most important determinators of how much stress layered cathode materials undergo during charge and discharge, there have been many reports that traces of superstructure exist in pristine layered materials and irreversible phase transitions occur even after eliminating the JTE. A careful consideration of the energy of cationic distortion using a Taylor expansion indicated that second-order JTE (Pseudo JTE) is more widespread than the aforementioned JTE because of the various bonding states that occur between bonding and anti-bonding molecular orbitals in transition metal octahedra. As a model case, some of layered oxide cathodes including P2-type Mn-rich cathode (Na3/4MnO2) will be dealt with in this presentation

The two new insights provide deep insight into novel class of intercalating materials which can deal with highly reversible framework changes, and thus it can break up some typical prejudices which we have about the layered cathodes for Li or Na secondary batteries.

Recent Achievement of the RS2E Prototyping Platform: From Li-Ion to Na-Ion Technology

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One of the main goal of the French network on Electrochemical Energy Storage (RS2E) created in 2011 is to fasten the transition from interesting research results to a first advanced prototype in order to judge / evaluate their benefits in real conditions (Energy density, Power, Cyclability, and Temperature). That is why, at the Energy Hub in Amiens, we settled pre-transfert plateforms allowing the synthesis of active materials up to 1 kg and the reproducible manufacture of 18650 cells together with their testing. These pre-transfert platforms were designed to be at the interface with the industries.

Through several examples of materials (Li-ion and Na-ion) resulting from the research of the RS2E, we will show not only the different paths / pitfalls to avoid in order to achieve large-scale synthesis but also several new chemistries that may be interested according to the electrochemical properties of the cells obtained. We will assert that, although the materials are weakly mature compared to what we can find in the market today, the results obtained are very promising and can potentially be the new battery technologies once the materials are optimized. Specifically, we will highlight the recent of Tiamat (start-up coming from the RS2E network) on the Na-ion technology and together with the potential applications that are envisioned according to their fascinating properties.

Sodium-Ion Batteries: From Material Properties to Upscaled Cell Prototypes

Ivana Hasa¹, Katerina Gonos¹, Faduma Maddar¹, Jacob Compton¹, Mark Copley¹

¹University of Warwick (WMG), Coventry, United Kingdom

Recently, a great interest has emerged in rechargeable batteries based on abundant and non-critical raw materials. Sodium-ion batteries (SIBs) have the potential to become the next generation, sustainable, low cost and efficient energy storage technology. This has been recently confirmed by the growing interest in this technology of several battery producers and the many successful companies working toward SIB commercialization. Great achievements in terms of materials development have been reported in the recent years. However, further work is still needed to fully understand the structure-function correlation in several SIB active materials and to successfully validate lab scale results in industrially relevant scales.

This presentation gives an overview on the journey toward the development of 1Ah sodium-ion cell prototypes linking chemistry and electrochemistry of the employed materials. Challenges on the transition from lab to scaled-up processes and the development of industrially relevant cell prototypes are discussed.

Among the several proposed cathode materials for SIB application, Prussian Blue Analogue (PBA) have attracted much attention due to their open framework structure with large interstitial spaces allowing a range of different compositions and enabling fast Na+ insertion/extraction. However, a key factor affecting the electrochemical performance of PBAs is the crystal water in the structure arising from aqueous synthesis environments. So far, the water sensitivity of PBAs has hindered aqueous electrode processing as demonstrated by the several studies conducted on N-methyl pyrrolidone-based electrodes.

Herein, the electrochemical behavior of an aqueous-processed Fe-based Prussian white (PW) cathode material (Na2-xFe[Fe(CN)6]1-y·zH2O) is presented. The use of such material in combination with bio-mass derived hard carbon anodes processed in water, matches the requirements for low toxicity, low cost, and sustainability in large-scale applications. We demonstrate that, by carefully tuning the water content in the PW structure, the electrochemical performance can be significantly improved.

By combining electrochemical characterization with a comprehensive material characterization, the activity of the low spin/ high spin Fe2+/3+ redox reactions, the Na+ transport properties and the electrode's structural and morphological properties are elucidated.

1Ah sodium-ion multilayer pouch cells have been manufactured and their electrochemical performance as well as forensic analysis is discussed. Different testing conditions, including high and low temperature cycling as well as different discharge rates enabled the benchmarking of the developed cells satisfying some of the key performance indicators requested for stationary storage application.

The cell prototypes herein presented represent a step forward the achievement of high performance and sustainable sodium-ion cell moving from lab to pre-prototype scale. The research presented has been conducted within the European funded project SIMBA (Sodium-ion and sodium metal batteries).

Oxygen Redox Chemistry in Dynamically Changing Layered Transition Metal Oxide Structure Kisuk Kang

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Oxygen redox chemistry in dynamically changing layered transition metal oxide structure

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Abstract

For the past decades, extensive efforts have been placed in improving the performance of the layered compounds for cathodes such as by compositional tuning and structural modifications. One of the notable approaches in recent years is to adopt excess amounts of lithium-ions in the layered materials, which surprisingly revealed that the specific capacity can be boosted in the layered cathodes via the shift from the conventional cationic redox reaction relying on transition metals (Co, Ni and Mn) to the cumulative cationic and anionic (oxygen) redox reaction. In this journey to explore the 'lithium-excess layered cathodes', various new findings have been being disclosed. In this talk, I will present our recent understandings on these materials with respect to the lithium insertion mechanism that differs from what have been observed in conventional layered materials and the effect of the layered stacking sequences, and discuss on the outlook on the lithium-excess layered cathodes.

Understanding Metals' Roles in Layered Structure Oxides for High-Energy Lithium-Ion Batteries

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The ever-increasing requirements in the high-energy density of lithium-ion batteries (LIBs) and current bottlenecks in cobalt supply place restrictions on the development of the state-of-the-art cathode materials with fine-tuned chemical composition by substituting the cobalt with nickel and manganese. In the layered structure ternary systems (LiNi1-y-zMnyCozO2, NCM), three transitionmetal ions play a distinctive role that determines the physicochemical properties. A comprehensive understanding of the basic contribution of each transition metal is critical for further complete replacing expensive cobalt.[1] Here, we demonstrate cobalt and manganese behaviors by comparing various layered oxides with different chemical compositions to reveal their corresponding contributions.[2] Our results affirmed that cobalt plays an undeniable role in fast degradation, and found that cobalt is more destructive than Ni at high voltages. Even the possible instability induced by manganese (III) Jahn-Teller distortion [3], Mn(IV) substitution in the lattice can effectively alleviate this destructive and enables a high potential functionality. By further regulating the chemical composition with a concentration gradient strategy, Co-enriched surface and Mn-enriched core design in Ni-rich particles determines a robust structure, which can effectively suppress the owing to the low stiffness of the surface and stable structure in the core region. With these fundamental discoveries, we provide a guide for developing the promising Co-free cathodes to meet the increasing demand for high-energy density LIBs.

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Probing Battery Interfaces Using Operando Ambient Pressure Photoelectron Spectroscopy

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The development of operando ambient pressure photoelectron spectroscopy for use on battery materials is currently ongoing and it has come with some challenges. One main contributing factor to this is the surface sensitivity of APPES measurements combined with the requirements of a functional instrumental set up for batteries. This talk will give a summary of the lessons we have learned on the way during the past years experimental work performed at mainly the Swedish national synchrotron facility MAX IV, Lund. The talk will provide input on questions like: How can a operando set-up look like, what is practical?; What kind of spectroscopic phenomenon's can you expect to encounter?; How can we mitigate some effect in order to obtain reliable data?; What requirements do we need to have on the samples to be able to access information from the electrode/electrolyte interface?; How does the surface of the electrolyte behave? How does the applied potential affect the spectra?; How do we interpret these spectral changes on an atomic level?

Polyanionic Sulfate Based Cathode Materials: Few Case Studies

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The discovery of triphylite LiFePO4 cathode by Goodenough group unveiled the polyanionic materials to the forefront of explorations of high voltage battery cathodes. The polyanionic material offers rich crystal chemistry, robust framework, voltage tunability, and high redox potential based on the inductive effect due to the polyanionic unit [XO4, X = S, P, Si, W, Mo, etc.]. Among them, sulfate SO4-based polyanionic systems have the advantage of higher redox potential and ease of synthesis at lower temperatures. Following, various polyanionic sulfate compounds have been reported as promising candidates for alkali ion batteries.

We have investigated the polyanionic sulfate materials having bisulfate [A2-xM(SO4)2: A= Li, Na, K; x=0,1], hydroxy(fluoro)sulfate [AMSO4(OH-/F-): A = Li, Na, K], alluaudite sulfate and mixed sulfate frameworks. We will describe few such case studies.

(i) Spray drying route was used to discover a metastable monoclinic polymorph of Li2NiII(SO4)2 belonging to space group P21/c. As per first-principal calculations, it can work as 5.5 V (vs. Li+/Li) cathode for Li-ion battery. We further examined the crystal chemistry, phase stability landscape and the ground state magnetic structure. Following, eldfellite NaVIII(SO4)2 (C2/m) is demonstrated as a versatile cathode material for both Li-ion (2.57 V, 80 mAh/g) and Na-ion (2.28 V, 70 mAh/g) battery at current rate of C/20 and based on solid solution reaction mechanism.

(ii) The electrochemical performance of orthorhombic polymorphs of FeIIISO4OH, synthesized using hydrothermal route, as 3.2 V (110 mAh/g, C/20) Li-ion battery cathode working on the monophasic reaction is investigated. We further demonstrated the first reversible Na-ion (de)insertion in monoclinic FeIIISO4OH at ~2.9 V based on solid solution reaction mechanism with a discharge capacity of 85 mAh/g (C/100).

(iii) Sulfate class of alluaudite framework materials have been prepared and investigated for Na-ion batteries. The role of moisture on crystal structure and electrochemical properties will be described using thermochemistry, in-situ X-ray diffraction and theoretical calculations. The degree and effect of off-stoichiometry on final electrochemical performance will be demonstrated.
Strategy to Optimize Nmc Materials for All-Solid State Batteries <u>Shinichi Kumakura¹</u>, JiHoon Kang², TaeHyeon Yang²

¹Umicore Belgium, Olen, Belgium ²Umicore Korea Ltd., Cheonan, Korea

Solid state battery technology has attracted much attention in terms of energy density and safety. The energy density can be increased by solid electolyte enabling Li metal anode, high voltage operation, bipolar battery design and thick electrodes. Absence of flammable electrolyte improves safety of the battery. On the other hand, both for sulfide as well as polymer SSB, still a variety of challenges have to be overcome.

A major requirement for the cathode is the chemical stablity in contact with the electrolyte at high voltage. Therefore surface coating is applied to improve the interfacial stability. The literature discloses many kinds of surface modifications, however, there are only limited reports which discuss requirements for the core like morphology, particle size distribution and so on to be suitable for surface coating. In this presentation, we will discuss test result in SSB cells of customized cathodes for polymer and sulfide SSB with different NMC core and surface coating chemistries.

Session III Tuesday

Ionic Transport and Structure in Electrolytes, Electrodes and Interfaces: NMR, Xrd and Optical Microscopy Studies Clare P. Grey

University Of Cambridge, Cambridge, United Kingdom

This talk will describe how a combination of NMR to measure transport, X-ray diffraction to measure phase segregation within the bulk, optical measurements to explore processes at the particle level, and continuum modeling to tie transport with particle level observations, can be used to study electrode material function. First, NMR measurements provide hopping frequencies and diffusion coefficients. Second, operando diffraction measurements provide evidence for solid solution vs two phase behaviour as a function of cycling. New optical measurements allow phase transformation and phase fronts to be visualized directly. The processes that underpin the various phase fronts can then be explored via simulations.

Specifically, for NMCs, we observed heterogeneity within a particle at low SOCs, the extent varying with rate. Continuum modeling allows us to extract rates of Li diffusion as a function of SOC and compare with optical measurements performed under "GITT"-like conditions. The heterogeneity increases with cycling, most likely due to rock-salt formation. For high-rate niobium tungsten oxides we observe phase fronts under very high cycling rates. These can induce particle cracking – a process that we can visualize directly. Finally, we discuss the change in cycling behaviour in the context of electrode and electrolyte degradation. In the second part of the talk, I discuss Li mobility in new Li electrolytes and new methods to study Li metal – SEI interfaces.

Polymorphism, Disorder, and Conduction in Halide-Type Solid Electrolytes

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Rocksalt-type halide solid electrolytes have spurred significant research interest over the past few years due to their high ionic conductivities (on the order of mS/cm for Li systems) and good stability against high voltage cathodes. While their bulk conduction properties depend sensitively on synthesis conditions, these materials constitute a challenge for characterization due to their disordered nature. Here, I will show that a combination of synchrotron XRD, solid-state NMR techniques, and first principles and molecular dynamics simulations, allows us to determine the origin of high ion conduction even in highly disordered or multiphasic systems, providing key design principles for this family of solid electrolytes. For instance, our recent study of the Li₃YCl₆ system has revealed that the high conductivity of ball-milled Li₃YCl₆ (BM-LYC) stems from the presence of stacking faults and Li-rich planes in the rocksalt-type structure. First principles calculations and ⁶Li solid-state NMR on heat treated BM-LYC samples also indicated that these planar defects are highly metastable, consistent with the net decrease in conductivity at even moderate temperatures (60 °C). Hence, the development of more robust systems relies on the ability to stabilize these stacking faults, or to altogether eliminate the dependence of conduction on planar defects through compositional and structural tuning. Exploring the Na3-xY1-xZrxCl6 family of Na-ion solid electrolytes, we have once again found that cation disorder facilitates ionic diffusion in the mixed Y/Zr compositions, while it is affected by polymorphism in the Na₃YCl₆ and Na₂ZrCl₆ end-members. Overall, our work shows that solid electrolyte materials discovery requires a better understanding of the links between synthesis, processing and defect landscape, which can only be obtained through the use of complementary experimental and theoretical tools.

Physicochemical and Electrochemical Properties of Novel Electrolytes for Sodium and Lithium Metal Batteries

Faezeh Makhlooghiazad¹, Jennifer Pringle, Maria Forsyth, Luke O'Dell

¹Deakin University, Melbourne, Australia

Organic ionic plastic crystals (OIPCs) mixed with Li or Na salts have been used as electrolytes in electrochemical devices with lithium (Li) or sodium (Na) metals. OIPCs are structurally disordered solids that can possess a high concentration of vacancies within their structure that can encourage fast target ion conduction. However, the ions within the matrix of OIPC can compete with the target ion (Li+) migration under potential gradient, which may affect device performance. One approach to suppressing the migration of the matrix OIPC ions is tethering the cations and anions to produce zwitterions.

Zwitterions are a class of materials that contain covalently bonded positive and negative charges. They are non-volatile and can exhibit thermal and electrochemical stabilities comparable with ionic liquid (IIs) and OIPCs. They have previously been used as additives to enhance the degree of lithiumion dissociation within ILs and other electrolyte systems. However, their applications as a sole matrix electrolyte in electrochemical devices have yet to be explored. In this work, we have characterized the thermal, morphological and structural properties of three novel zwitterions using techniques including differential scanning calorimetry, scanning electron microscopy, solid-state nuclear magnetic resonance (NMR) and electrochemical impedance spectroscopy (EIS). We then use the most promising zwitterion to demonstrate their potential application as an electrolyte for Li- metal batteries. Three initial approaches have been used to demonstrate the breadth of scope of this material family: (1) plastic zwitterions can be used as the matrix material to provide a non-volatile, ionically conductive solid medium without competing ion transport; (2) the zwitterions can be used in composites with functional additives such as lithium-functionalized polymers to increase target ion transport and mechanical properties; and (3) for high-concentration electrolyte systems, the zwitterion can be combined with a high concentration of lithium salt to form a non-volatile liquid electrolyte with high lithium ion transport. Stable cycling of lithium metal cells has been achieved for the three demonstration systems.

Ionic Liquid Electrolytes Enter Into Market

<u>Rongying Lin</u>¹, Anaïs Falgayrat¹, Pauline Rullière¹, Emma Bremmond¹, Tom Douzou¹, Sébastien Fantini¹, François Malbosc¹

¹Solvionic, Toulouse, France

As the reliance on EES systems intensifies, consumers expectations push towards higher energy densities, faster charging, better safety and longer lasting storage devices. These improvements are expected with decreasing cost while increasing their performance. However, such improvements often come with a compromise in safety.

Solvionic's technology and expertise in ionic liquid electrolytes address not only the cost challenges, but also the access to high voltage storage systems (> 5V) and enhancement of safety. Moreover, being non-volatile, ionic liquid electrolytes enable improvements in manufacturing processes for both supercapacitors and batteries. They also allow solventless processes to be implemented which impacts overall cost and ease of manufacturing.

The reduction of environmental impact is also currently being tackled by changing Solvionic's production process from batch to intensive continuous flow process, and by studying the recyclability of used ionic liquids.

In this presentation, the advantages of solventless process and the electrochemical performances of ionic liquid electrolytes in various cathode/anode systems using this process will be discussed. Advancement on industrialisation of ionic liquids and production roadmap will also be presented.

Understanding Self-Discharge in LFP and NMC811/Graphite Cells

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The use of olivine LiFePO4 (LFP) in electric vehicle battery packs has generated renewed interest in olivine phosphate cathodes for lithium-ion batteries. Historically, LFP has been ascribed excellent capacity retention in charge/discharge cycling and storage at moderate temperatures. Advances in layered transition metal oxide cathodes, especially nickel-rich compositions with low cobalt content like LiNi0.8Mn0.1Co0.1O2 (NMC811), have motivated comparative studies of LFP/graphite and NMC/graphite batteries with state-of-the-art electrolytes. Despite the low operating voltage of LFP/graphite cells (2.5-3.65 V), NMC532/graphite cells (3.0-4.3 V) show better capacity retention in cycling tests at 40 and 55°C with identical artificial graphite (AG) anodes and similar electrolyte additives, e.g., vinylene carbonate (VC) and ethylene sulfate (DTD). Furthermore, LFP/graphite cells with standard alkyl carbonate electrolyte, e.g., 1.5 M lithium hexafluorophosphate (LiPF6) in a solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC), show complete self-discharge during ~500 h storage at 60°C (~1/3 irreversible, ~2/3 reversible capacity loss), unless effective electrolyte additives are used. Cells with NMC-type cathodes show significantly less self-discharge. These findings point to a mechanistic difference between LFP/graphite and NMC/graphite cells.

Redox shuttles can be used in LFP-based and NMC-based lithium-ion cells to prevent overcharge. Redox shuttles have also been identified as a possible cause of self-discharge in lithium-ion cells. The ability of lithium-ion cells to hold their charge over extended periods of time is especially important for electric vehicle applications. Hence, this study investigates the in-situ generation of a redox shuttle in LFP/graphite and NMC811/graphite pouch cells with common alkyl carbonate electrolyte. First, we quantify the reversible and irreversible self-discharge of LFP- and NMC811-based cells with three different types of artificial graphite. Subsequently, we focus on the influence of different formation temperatures on self-discharge. Visual inspection of the electrolyte extracted after formation at temperatures between 25 and 70°C reveals strong discoloration. Such extracted electrolytes with intense red and brown color show relatively large shuttling currents in Al/Li coin cells. Two weight percent of vinylene carbonate is effective at preventing the redox shuttle generation as indicated by the absence of electrolyte discoloration and shuttling current. Ultra-high precision coulometry demonstrates that the presence of a shuttle molecule during cycling of LFP/graphite and NMC811/graphite pouch cells leads to significant charge endpoint capacity slippage and coulombic inefficiency. A brief constant voltage hold at 4.2 V can eliminate the shuttle molecule. In this contribution we will also reveal the chemical structure of the redox shuttle molecule and its in-situ formation mechanism in lithium-ion cells.

Session IV Tuesday

Characterizing Interphase Architecture in Li Metal Batteries

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Although Li metal anodes offer the highest possible specific energy density for Li-based batteries, practical application is plagued by the growth of high surface area Li filaments. The presence of Li filaments is strongly correlated with the formation of dead (electrochemically inactive) Li that leads to low Coulombic efficiency (CE) and serious safety concerns due to short-circuiting. The morphology of Li deposits that form during Li stripping and plating is highly dependent on the composition and the structure of the solid electrolyte interphase (SEI) that forms upon exposure of Li metal to the electrolyte and continues to evolve during electrochemical cycling. In the first half of my talk, I will discuss our work on using a combination of nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopies (XPS) to show that fast Li transport and low solubility at the electrode/SEI interface are responsible for the formation of low surface area, bud-like deposits that form upon addition of LiNO3 to ether-based electrolytes for Li metal batteries. This improved performance in the presence of LiNO3 is observed despite the fact that there are higher quantities and more types of compounds in the SEI compared to a control electrolyte, suggesting that the arrangement of the electrolyte decomposition products into a multilayer pattern alters Li plating behavior. SEI design strategies that increase SEI stability and allow for more uniform Li flux to the electrode are thus expected to produce a more even current distribution. In the second half of my talk, I will examine failure modes of Li metal batteries when paired with solid electrolytes. Here, we combine MRI with operando acoustics measurements to simultaneously assess chemical and mechanical changes at the interface between Li metal and Li7La3Zr2O12 (LLZO) as a function of stack pressure during galvanostatic polarization. Insight from this work suggests that Li filament growth is correlated with the formation of electronically conductive compounds in the solid electrolyte regardless of stack pressure, motivating investigations on the origin of these species during battery operation.

Infrared Nanospectroscopy of the Local Processes at Electrode/Electrolyte Interfaces in Batteries

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Li-ion and Li-metal batteries still must overcome performance limitations associated with electrode/electrolyte interfaces, such as high interfacial impedance, electrochemical instability, and inhomogeneous, Li plating and stripping. Including and beyond these specific challenges, it is hard to overstate the central role that electrode/electrolyte interfaces hold. In fact, battery performance is largely determined by thermodynamic, kinetic, and mechanical properties of such electrochemical interfaces. Furthermore, in these electrochemical systems that operate far away from equilibrium, a thin passive film forms within the electrode/electrolyte interface. Situated at the surface of the electrode, and formed during battery assembly and/or operation, this so-called solid electrolyte interphase (SEI) layer is critical. It provides sufficient electronic resistivity and ionic conductivity to inhibit side reactions with the electrolyte while still allowing ion transport. Additionally, the SEI's inhomogeneous structure and chemistry influence localized current density distribution and the resulting Li nano/micro-morphology evolution during charge–discharge processes.

Our overall understanding of heterogeneous ionic interfaces and interphases is still very limited due to two main reasons. First, characterizing such interfaces and interphases in their native environment is extremely challenging, as they are buried between two dissimilar materials. Second, the interfaces and interphases have complex structure and chemistry, and can even evolve by chemical inter-diffusion, lattice strain, defects, and space charge effects which lead to a variety of chemical reactions across multiple spatial and temporal scales. Interface evolution is further propelled by the large amount of charge and mass transfer between electrodes in a battery over its lifetime (generally leading to degradation, performance loss, and eventual battery failure.

The importance of interfaces and interphases, in combination with our limited understanding brought about by the challenges outlined above, continues to motivate the need for the development and application of effective in situ and operando diagnostic approaches, especially those capable of characterizing interfacial structure, chemistry, and crystallinity over microscale regions with nanoscale spatial resolution that is, at the level of the film's individual building blocks and related functionalities. A variety of techniques have been used to characterize the SEI, however, no methodology has been demonstrated thus far that can characterize interface and SEI nondestructively, within their undisturbed native environment, and with nanoscale resolution.

In this work, we exploit the nanoscale spatial resolution, chemical selectivity, and surface sensitivity of near-field infrared nanospectroscopy to characterize electrode/liquid and solid electrolyte interfaces. We use single-layer graphene sheet that operates as both an infrared transparent window and a current collector for electrode active materials e.g., silicon or Li plating and stripping (similar in function to Li anode-free batteries). In general, nano-FTIR is realized by illuminating, with IR light, an oscillating metallic AFM probe tip and sample placed in one arm of an asymmetric Michelson interferometer. The back-scattered light is combined with a reference beam reflected off a moving mirror in the other arm of the interferometer. A small amount of the backscattered light (collected in the far-field) is attributable to scattering events resulting from near-(electric) field-induced excitations confined to nanoscopic regions below the probe tip end. The backscattered light from localized nanoscopic regions is isolated by a combination of lock-in demodulation (at the

second or higher harmonics of the tip-tapping frequency) and normalization (to a spectrally flat material such as silicon or gold) and in this way nondestructive, truly nanoscale IR spectroscopy (or imaging) can be conducted.

Near-field infrared measurements reveal that intrinsic molecular, structural, and chemical heterogeneities at the interface lead to the nonuniform current distribution and formation of a mosaic-like solid electrolyte interphase at the electrode/electrolyte interface on a similar length scale. This work provides a unique insight into the mechanisms of early-stage interphase formation at electrochemically active buried interfaces, and an experimental diagnostic means to aid in the development of methods to control local nanoscale variations in electrolyte chemistry, structure, and ionic conductivity at the surface of the electrode.

Acknowledgements

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Understanding Reactant Decay and Capacity Fade in Organic Redox-Flow Batteries Using Statistical Inference Techniques and Zero-Dimensional Modeling David Kwabi

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Aqueous-soluble organic and organometallic redox-active molecules have received a considerable amount of research attention as potential redox-flow battery (RFB) reactants because their costs at scale are projected to be low. Unfortunately, most aqueous organic RFB chemistries experience temporal rates of capacity fade higher than 0.1 %/day, owing in large part to rapid chemical decomposition of their organic active reactants. Such high fade rates render these chemistries unsuitable for practical deployment. In addition, for several candidate RFB reactants, competing or incompatible hypotheses about the relationship between reactant decay and capacity fade have been proposed.

We introduce the use of Bayesian inference and uncertainty quantification techniques to provide data-informed assessments of the probability of one or more given hypotheses of reactant decay, and to extract reactant decay parameters from experimental data with quantified uncertainty. As a case study, we use these techniques to extract rate constants describing the nucleophilic attack of quinone-based RFB reactants by water, as measured using in operando ultraviolet-visible spectrophotometry. We then introduce a zero-dimensional electrochemical flow cell model which can simulate capacity fade given a reactant decay mechanism and associated parameters, and the cycling protocol. This work has the potential to shed light on the relationship between capacity fade and reactant decay in various organic RFB chemistries, and to enable prediction of the lifetimes of commercial-scale RFBs.

A Unified Perspective and Analytical Approach of Layered Cathode Active Materials

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To understand the layered cathode active materials (CAMs) with a unified theoretical framework and perspective in order to understand their behaviors and performance characteristics remains elusive. Here, based on the theoretical specific capacity supported framework, we found a manner to align all charge discharge curves from the family of layered lithium (Li) transition metal oxides, commonly labeled as LixNiaMnbCocO2 or NMC compositions with a series of various stoichiometries. By aligning their Li content in the stoichiometry, we discovered the unison of such an alignment with the relationship of the equilibrium open circuit voltage (OCV or Veq) and Li content in the NMC stoichiometry, as defined by Gibbs free energy of formation of the NMC composition and their correspondence of theoretical specific capacity (QTh). Using this relationship, we were able to study the performance of the CAMs (or different NMCs) in a consistent manner. This presentation will provide the description of this theoretical framework and some interesting examples of how the analytic method based on this framework can provide in-depth understanding of the NMC performance and characteristic behavior in aging process. Session I Wednesday

Battery Technologies for Automotive Applications - Trends and Challenges Peter Lamp

BMW AG, München, Deutschland

BMW has set the course for the future at an early stage and consistently makes sustainability and efficient resource management central to its strategic direction, from the supply chain through production to the end of the use phase of all products.

BMW intends to have 10 million battery electric vehicles on the road within the next ten years and is continuously striving to improve battery performance and cost.

Over the last 10 years there was a substantial improvement of battery energy density by introducing new, higher capacity materials and optimizing electrode, battery cell and battery pack design. The increase of energy density imposes continuously increasing challenges on all integration level from materials to battery cells to battery packs. Recent trends in the vehicle architecture i.e. battery cell and pack integration as well as changes in regulations like directives on CO2 footprint or use of recyclates are new boundary conditions leading to changed requirements and hence different technical solutions.

There is still a clear demand for R&D and further optimisation of Li-Ion technology that will be the work horse of e-mobility for the next decade. Beyond the priority one key performance indicators energy density, safety and lifetime, this includes the further development of low cost materials as well as the optimisation of materials and electrodes to allow fast charge. Any upcoming technology like solid electrolyte based Li-metal battery cells have to deliver a substantial benefit compared to most advanced Li-Ion technology regarding performance, costr and quality.

This presentation will outline the battery technology of the present BMW vehicle generation (5th battery generation) and deduce the direction of the following 6th generation based on the changed boundary conditions and requirements. It will highlight some specific challenges and investigations and give an outlook to future development directions and long term visions.

High-Voltage Multi-Electron Reactions in Metal-Ion Batteries Using Vanadium Phosphate Positive Electrode Materials

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Vanadium phosphate positive electrode materials attract great interest in the field of Metal-ion (Li, Na and K-ion) batteries due to their ability to exchange several electrons per transition metal.[1-6] These multi-electron reactions (from V2+ to V5+) combined with the high voltage of corresponding redox couples (e.g., 4.0 V vs. Na+/Na for V3+/V4+ in Na3V2(PO4)2F3) allows the achievement of high energy density at the positive electrode level in Alkali-ion batteries.[7-10] However, a massive divergence in the voltage reported for the V3+/V4+ and V4+/V5+ redox couples as a function of crystal structure is noticed considering among Na3+x(V,M)2(PO4)3 (of NASICON-type),

Na3(V,M)2(PO4)2F3-yOy, LiVPO4F1-yOy (of Tavorite-type) and KVPO4F1-yOy (of KTP-type). Moreover, vanadium phosphates that operate at high voltages are usually unable to reversibly exchange several electrons in a narrow enough voltage range.

During this talk, through the review of redox mechanisms and structural evolutions occurring upon electrochemical operation of selected widely studied materials, we will identify the crystallographic origin of this trend: the distribution of PO4 groups around vanadium octahedra, that allows or prevents the formation of the vanadyl distortion (O---V4+=O or O---V5+=O). While the vanadyl entity often massively lowers the voltage of the V3+/V4+ and V4+/V5+ couples, it improves the reversibility of these redox reactions. Therefore, anionic substitutions, mainly O2- by F-, have been identified as a strategy allowing for combining the beneficial effect of the vanadyl distortion on the reversibility with the high voltage of vanadium redox couples in fluorine rich environments.

Acknowledgements

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Solid State NMR Characterization of Na3V2(PO4)2F3-yOy Positive Electrode Materials for Na-Ion Batteries

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For energy storage, nowadays, Li-ion and Na-ion batteries are major technologies for mobility applications and also for large-scale storage of energy and their integration in the grid. In the scope of finding new positive electrode materials with improved performances, the deep understanding of the link between their structure, electronic structure and electrochemical behavior is crucial. To that extent, Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) appeared to be a key tool, as for paramagnetic materials, it allows to probe both, the local structure and the local electronic structure thanks to the hyperfine interaction.

Using 23Na and 31P MAS-NMR we studied the Na3V2(PO4)2F3-yOy series, which are promising materials for positive electrode application Na-ion batteries. We showed that the end member Na3V2(PO4)2F3 exhibits some O-defects leading to the formation of V4+ ions locally as was also observed for LiVPO4F. NMR combined with DFT calculations, allows to characterize the very specific electronic configuration around V4+ ions forming a vanadyl-type bond with the O-defect, that affects the electrochemical cycling performances. 23Na and 31P MAS NMR was also used to probe the local structure and electronic structure other substituted Na3(V,M)2(PO4)2F3-yOy materials with M = Fe or Al.

Na+ ions deintercalation mechanism was also investigated by 23Na and 31P MAS NMR for two different systems: NaxV2(PO4)2F3 and NaxV2(PO4)2F2O. In NaxV2(PO4)2F3, the de-sodiation occurs through several bi-phasic and solid solution steps with the formation of Na+ orderings in the diffusion channels that results in the observation of different 23Na resonances, especially on the low voltage plateau. V3+/V4+ charge ordering was also observed for some specific compositions.

Finally we investigated the thermal stability of a series of NaxV3+2-yV4+y(PO4)2F3-yOy ($0 \le y \le 2$) materials in order to learn more about the influence of F- for O2- substitution and the state of charge. NMR studies were crucial to understand the degradation mechanisms.

Time for a New Classification for Battery Materials? Wouter IJzermans

BEPA, Brussels, Belgium

In different roadmaps for European battery development, a classification system has been used which defines different "generations" of battery chemistries in order to steer development efforts. While this classification has proven to be successful and has been adopted in many publications, some of its aspects may need to be reconsidered. The development of the new Strategic Research and Innovation Agenda by Batteries Europe and the Batt4EU Partnership might present an opportunity to do so.

While slightly different approaches have been used over the year, the main character of this classification is the definition of different battery "generations", based on developmental breakthroughs in the development of Li-ion battery chemistries[1], ranging from Generation 1 and 2, which encompass commercialised technologies, to advanced Gen 3 Li-ion batteries, Gen 4 solid-state batteries and Gen 5. "beyond Li-ion", technologies.

This classification, as some "Generation 5" technologies have reached a level of maturity beyond that of "Generation 4" technologies. Also, with the recent adoption of the REPowerEU communication by the European Commission[2], the need for batteries to become part of the European electricity grid, helping to integrate intermittent renewable energy sources. The original classification was made to create a roadmap for the further development traction batteries for mobile applications, however[3], and does not take into account chemistries developed for stationary applications, like redox-flow.

A new opportunity to re-evaluate this categorisation presents itself in the upcoming months. In the period until January 2023, Batteries Europe and the Batt4EU Partnership will develop a joint Strategic Research and Innovation Agenda (SRIA) on the research needs of the European battery industry. The collaborative effort between Batteries Europe and Batt4EU brings Europe's best and brightest battery experts together, and ensures continuity within the European battery research ecosystem. From the European Commission, to large industrial players, research organisations and innovative start-ups, the collaborative SRIA involves all levels, ensuring a coordinated effort towards a common goal.

Set to be published early 2023, the joint SRIA will replace the previous version adopted in 2021[4], and will build on the Roadmaps published by Batteries Europe in the same year[5]. It will cover the full battery value chain, in addition to transversal topics like safety and sustainability. Experts active in the European battery value chain are invited sign up for the 6 Working Groups that Batteries Europe and BEPA, on behalf of the Batt4EU Partnership, have set up[6].

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Development of a Polyanionic Cathode Material and a Liquid Electrolyte Formulation for High Power Na-Ion Cells

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Na-ion battery technology is currently seen as a very robust alternative to current and future Li-ion cells. Sharing similar architecture, they are compatible with existing cell assembly industrial assets, and benefit from a favorable sustainable positioning.

We are currently developing Na-ion battery cells that bring differentiating performances for power applications. The fast charge and discharge characteristics, associated with a reasonable energy density (~100 Wh/kg), make this technology interesting for multiple applications such as mild-hybridization, renewable energy storage or industry applications.

These unique power performances rely on a specific cell design, with optimized liquid electrolyte, positive and negative electrode materials. A polyanionic cathode active material was selected and specifically tailored by Solvay to meet the power application requirements. To manage cell aging under such fast charging and discharging conditions, an optimized salt formulation with specific additives and cyclic carbonate solvents was developed.

All these critical materials were first designed at lab scale and then scaled-up to build modules whose performances will be evaluated in real business cases.

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Session II Wednesday

Interfaces and Scaling Relations in Solid-State Batteries <u>Wolfgang Zeier</u>

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The advent of solid-state batteries has spawned a recent increase in interest in lithium conducting solid electrolytes. However, many open questions remain when trying to optimize electrolytes and understand solid state battery chemistries.

In this presentation, we will explore the current focus of halide-based ionic conductors in solid state batteries and discuss stability limitations in solid state battery cells at the anode as well as the cathode composites.

In a second part, we show the influence of Si type anode materials on the effective transport and behavior of solid-state batteries

Finally, we will discuss that it is not only important to find fast ionic conductors but that for an effective thermal battery management the thermal transport properties of solid ionic conductors need to be explored and understood. Here we will show the diffusive thermal transport nature of solid electrolytes and their different scaling relations that put in question the assumption of Bruggeman transport in solid state batteries.

Crystal Chemistry of Li3PS4 and Na3PS4, Solid Electrolytes for Batteries

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Solid electrolytes are crucial for next-generation solid-state batteries and immense activity is going on worldwide on many structural families of interest, including the ionic conductors Na3PS4 and Li3PS4.

Li3PS4 is an attractive solid-electrolyte material that possesses high RT ionic conductivity (10-4 S.cm–1) but the effects of specific synthesis parameters on the material's local structure and transport properties still demand clarifications. In particular, mecanochemistry induces the formation of a variety of PxSya– moieties that strongly influence the global transport properties of Li3PS4.

Na3PS4 is another very interesting material with complex crystal chemistry that w ewill present. The effects of mechanochemical synthesis that lead to increased ionic conductivity in an archetypical sodiumion conductor Na3PS4 were not fully understood and we undertook comprehensive analysis based on diffraction (Bragg and pair distribution function), spectroscopy (impedance, Raman, NMR and INS), and ab initio simulations.

Towards High-Voltage Solid-State Lithium-Metal Batteries Corsin Battaglia

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Integrating a lithium-metal anode and a high-voltage cathode into a solid-state battery remains a formidable challenge, especially when the battery is charged beyond 4 V. Most electrolytes genuinely do not possess such a wide electrochemical stability window, but have to rely on the formation of a passivating solid electrolyte interphase, require protective electrode coatings, or have to be combined with a secondary electrolyte to achieve stable dis-/charge cycling, adding complexity.

This is also the case for prototypical polyethylene oxide-based polymer electrolytes, which form a relatively stable interface to lithium metal [1], but start oxidizing already at 3.2 V vs Li/Li+ via deprotonation of the terminal O-H group, as we have recently shown combining electrochemical impedance spectroscopy, infrared spectroscopy, and differential electrochemical mass spectrometry [2].

We recently employed a polymer electrolyte based on a polymerized ionic liquid to demonstrate a 4 V class solid-state battery with a lithium metal anode and a LiNi0.8Mn0.1Co0.1 cathode operating at room temperature and delivering an initial capacity of 162 mAh/g and a capacity retention of 72% after 600 cycles to 4.4 V [3]. The polymer matrix consists of poly(diallyldimethylammonium) bis(fluorosulfonyl)imide (PDADMAFSI) and N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (PYR13FSI) is employed as plasticizer in combination with lithium bis(fluorosulfonyl)imide (LiFSI) as lithium salt. PDADMAFSI and PYR13FSI were selected because of their outstanding chemical stability and wide electrochemical stability window. Comparing to typical lithium-ion-coordinating polymer matrices, the positively charged PDADMA+ chains reduce lithium-ion coordination with the polymer promoting high lithium-ion mobility. LiFSI has low binding energy between Li+ and FSI- and the ability to form stable interphases in contact with lithium metal. To confirm the high oxidative stability of this electrolyte, we also assembled a solid-state lithium-metal cell with a high-voltage spinel LiMn1.5Ni0.5O4 cathode reaching an initial capacity of 132 mAh/g and a capacity retention of 76% after 300 cycles to an upper cut-off voltage of 5 V at room temperature.

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Towards an Autonomous Materials Development Platform to Accelerate the Development of New Battery Materials

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Battery innovation relies on developing new electroactive materials. To timely respond to the increasing demand for energy storage solutions, the European Battery 2030+ Initiative targets accelerating by 5-to-10 fold the current rate of battery materials discovery within the next 5-10 years. Taking up this challenge requires disruptive approaches that allow rethinking the traditional experimentation process (based on researcher's chemical intuition and trial-error scheme), which is inherently slow and economically expensive. Indeed, the crystal-chemical space offered by the periodic table for the search for new battery materials is huge and still far from being exhaustively explored.

To accelerate the exploration of broad chemical spaces, our group is developing an autonomous Materials Development Platform, capable of making effective modelling-based predictions, selfdriving inorganic synthesis and performing high-throughput characterization experiments. This requires a mind change in our approach to materials research, but also building new lab infrastructures and analytical tools, which include automated high-throughput synthesis modules, automated data analysis programs able to handle large amounts of data, as well as Al-aided experimental planners.

In this talk, we will discuss several strategies explored at CIC energiGUNE to speed up the different stages of the development of new materials: from (i) our approach to screen materials databases in search for new families of compounds that can be converted into electroactive materials, to (ii) solutions to automatize several types of inorganic syntheses as well as (iii) the presentation of the new FullProfAPP that enables automated Rietveld refinements of large series of data, in particular those generated from operando experiments.

Session III Wednesday

Perspectives on Lithium Batteries for Biomedical Applications

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The advent of battery-powered implantable devices ushered in an entirely new way to treat disease where the therapy is delivered by the device over long periods of time to treat a wide variety of medical conditions. Batteries power state-of-the-art implantable pulse generators to address cardiac arrhythmias and to serve as neurostimulators for numerous applications including deep brain stimulation treatments of disorders such as Parkinson's disease, tremor, chronic pain, and seizures. The implantable cardiac pacemaker, defibrillator, and resynchronization devices enabled by new battery technologies revolutionized cardiac health care for patients, providing a treatment for heart disease and sudden cardiac death due to ventricular fibrillation. The impact of battery powered implantable devices on human health is invaluable.

While the power demands, size, capacity, and configuration of the batteries vary based on the type of device and therapy, there are common requirements for the implantable batteries must provide. The batteries must operate over many years to minimize surgical frequency, be safe during installation and use, have predictable and reliable performance, low self-discharge, and high volumetric energy density for device miniaturization.

In 1972 an implantable pacemaker was placed in a patient powered by a lithium/iodine battery, thus 2022 marks the 50th anniversary of the first implant of a lithium anode battery in a human. In contrast to the small microampere currents demanded by pacemakers, batteries for implantable cardioverter defibrillators (ICDs) demand currents of 2-3 amperes to rapidly charge capacitors that apply high energy shocks to the heart to interrupt ventricular fibrillation. The battery must also be able to supply a lower current drain to power the heart monitoring circuitry, must be of suitable size for implantation, and have a voltage profile that enables state of charge indication for determining the state of charge of the battery. The lithium/silver vanadium oxide (Li/SVO) battery meets this set of requirements and powers many ICDs in the present day. The chemistry and electrochemistry of Li/SVO as well as potential next generation cathode materials will be discussed.

Negating the Interfacial Resistance Between Solid and Liquid Electrolytes for Next Generation Lithium Batteries

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Batteries with a hybrid solid and liquid electrolyte are potentially safer than current lithium-ion batteries, since uncontrollable thermal runaway reactions are prevented by the solid electrolyte, while the liquid electrolyte enhances the rate of the desired energy storage reactions. In addition, the protection by the solid electrolyte enables the safe use of lithium metal anodes, which dramatically enhances the energy density. However, the large interfacial resistance between the solid and liquid electrolytes severely limits the practical capacity achievable at the required C-rates, which hence prevents their commercial development [1].

In this work [2], we demonstrate a suitable approach to virtually suppress such interfacial resistance. On the example of a NASICON-type solid electrolyte in a variety of liquid electrolytes (ethers, DMSO, acetonitrile, ionic liquids, etc.), we show that the addition of water as electrolyte additive decreases the interfacial resistance from > 100 ohm cm² to a negligible value (< 5 ohm cm²). XPS measurements reveal that the composition of the solid-liquid electrolyte interphase is very similar in wet and dry liquid electrolytes, and thus the suppression of the associated resistance is tentatively ascribed to a plasticiser or preferential ion solvation effect of water, or to a change in the interphase morphology or porosity caused by water. Our simple estimates show that the improvement in the solid-liquid electrolyte resistance observed here could translate to an enhancement of 15-22 % in the practical energy density of a Li-S or Li-O₂ battery and improvements in the roundtrip efficiency of 21-28 percentage points.

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Electrochemistry Based and Coupled Characterization of Energy Storage Materials and Systems <u>Amy Marschilok</u>

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Lithium ion batteries represent a remarkable technological and commercial success, due to their lightweight and high energy density. However, to address future energy storage demands there is a need to understand and address life limiting mechanisms. This presentation will highlight progress achieved via electrochemistry based and coupled characterization of energy storage materials and systems, encompassing both positive and negative electrode investigations.

Synergistic Role of Functional Electrolyte Additives to Address Interfacial Chemistry and Phenomena in Lithium-Based Batteries Isidora Cekic-Laskovic

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It is common wisdom, that materials science in the field of electrochemical energy storage has to follow a systemic approach as the interactions between active materials, the electrolyte, the separator and various inactive materials (binder, current collector, conductive fillers, cell housing, etc.), are of similar or even higher importance as the properties and performance parameters of the individual materials only. In particular, of utmost scientific interest are the numerous chemical, electrochemical and mechanical interactions of all aforementioned components determining operation, safety and life of the given energy storage system.

Although batteries are considered the systems of choice for many portable, mobile and stationary applications, existing technologies still face diverse challenges limited by the fundamental behavior of the active and inactive materials used, among which electrolytes are often blamed as the shortest board in the bucket. Being the component bridging while interacting with all other active and inactive battery parts, the electrolyte plays a key role in terms of design and control of the redox processes as well as regarding material interactions, performance, long-term stability, cost and last but not least the safety of a battery. Although its role is often considered as trivial due to the superficial belief that energy is decided by electrodes only, the right choice based on criteria that differ depending on the battery chemistry and targeted application, is rather crucial. After many decades of research, the electrolyte, its ad hoc interfacial chemistry are still limiting and critical factors in the field of electrochemical energy storage systems. The development of novel and the advancement of existing electrolytes is by no means non-trivial because of the complexity of interactions, thus often leads to situations where specific targeted properties can only be improved at the expense of other relevant properties. For liquid electrolytes, a special focus is set on selection of adequate, commercially available as well as tailored syntheses of innovative and ultrapure electrolyte components, particularly (multi-)functional additives as effective and cost favorable approach towards desired advancements of electrolyte formulations. Different (multi)-functional electrolyte additives have already found their applications in advancing the performance and safety of liquid electrolytes, however not enough is understood about their function and effectiveness. Comprehensive characterization of resulting electrolyte formulations by means of emerging in situ and operando physicochemical, electrochemical, analytical, spectral and structural methods enables establishment of structure-property-performance relationships that provide insight in understanding and elucidation of main operation and failure mechanisms taking place in a battery comprising electrolyte | electrode interfaces and interphases. Due to the complexity involved in interface and interphase behavior, profound research and development require collaborative efforts involving the disciplines of chemistry, physics, materials science, nano-science/nanotechnology, engineering, as well as computational modeling/simulation that will beneficially impact the current lithium ion technologies and future generation solid state lithium and lithium ion batteries, based on ceramic solid electrolytes or polymer electrolytes.

This talk is an invitation to a journey of the scientific design, development, characterisation and comprehensive study of selected classes of (multi)-functional electrolyte additives and resulting formulations towards advancement of lithium-based battery chemistries for targeted applications.

Mastering Equilibrium at the Solid/Liquid Interface to Design Novel Intercalation Compounds Alexis Grimaud

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Intercalation chemistry lies at the center of a multitude of established and emerging technologies. Most centrally, mastery of intercalation materials has unlocked the concept of rocking chair lithiumion batteries. After more than 40 years of materials research, chances to discover new promising families are slim. We recently demonstrated that, through an electrolyte engineering approach, reversible lithium intercalation into transition metal layered tri-halides MX3 (with X = Cl, Br or I) previously studied for their magnetic and electronic properties could be achieved. In pursuit of that goal, mastering the high solubility of halides in polar solvent was critical. Using superconcentrated electrolyte based on low-dieletric dimethyl carbonate solvent, we found that the solubility of transition metal halides follows a bell-shape as a function of salt concentration, i.e. can be tailored. The key was to identify the formation of soluble adduct states in solution, formed either by chelation or by ligand exchange with the anion from the electrolyte, making the solubility to vary as function of the lithium salt concentration. The positive attribute of superconcentrated electrolytes against the solubility of intercalation compounds is thus rooted in a thermodynamic, and not kinetic, effect.

This proof of concept opens numerous avenues for continued design of novel halide compounds for battery applications with further improved performances, targeting higher capacity and cycle life. This goal will only be achieved by tackling intrinsic instabilities observed over prolonged cycling. Comparing halides intercalation compounds with Ni-rich NMC ones, we revealed that DMC-based superconcentrated electrolytes suffer from shuttling of species formed upon oxidation of DMC at the cathode/electrolyte interface. For that, dedicated workflows integrating capacity marching analysis with derivative voltage analysis were designed to assess the shuttling mechanism and guide the optimization of pre-formation cycles to stabilize the solid electrolyte interphase (SEI). Combining SEI pre-formation steps with a fine tuning of the chemical composition of superconcentrated electrolytes, performance for Ni-rich NMC cycled at high potential were stabilized.

We thus believe that the design of novel intercalation compounds will greatly benefits from knowledge of the physical/chemical properties of liquid electrolytes recently developed in the field. Nevertheless, optimization steps for these novel chemistries require the use of standardized protocols/workflows to reveal cross-talking mechanisms often responsible for the apparition of so-called "knee point" in capacity retention curves. The implementation of workflows can be easily automatized to feed machine learning algorithms and potentially move forward the advent of Al-assisted discovery of novel electrolytes and materials.

Recent Advances in Theoretical Methodology to Battery Interfaces Marie-liesse Doublet

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Controlling and mastering electrode/electrolyte interfaces is a central goal in energy storage applications to improve the performance, the lifetime and the safety of Metal-ion batteries. This implies understanding the microscopic mechanisms taking place at these interfaces during the battery operation. The large electric fields developing at these interfaces may alter the local properties of the solvent in the vicinity of the electrode surface. To account for the potential dependence of the interface reactivity, ab initio molecular dynamic simulations or classical MD with reactive force-fields should be the appropriate methods but are still far prohibitive for the complexity of these electrochemical interface. A Grand canonical DFT approach was then develop to elucidate the mechanisms at play in these complex system. The methodology was applied to several challenging issues of electrode/electrolyte interfaces to shed light on undesired phenomena such as electrolyte degradation/ageing or metal-dendrites growth. [1,2] The perspective of this work on the development of new electrolytes for post-Li technologies and/or on the functionalization of electrode surfaces will be discussed. [3,4]

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A Big-Map Approach to AI-Accelerated Discovery of Next-Generation Battery Materials and Interfaces <u>Tejs Vegge</u>

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Secondary batteries play a crucial role in the transition to a clean energy infrastructure, but until now, the development of novel, low-cost, and high capacity or high voltage electrode materials, has been very slow. Understanding and controlling the complex and dynamic processes in the electrodes and the electrolyte, particularly at the solid-liquid and solid-solid interfaces, is key to developing more efficient and durable ultra-high performance batteries. Here, we present some of the latest developments in the "Battery Interface Genome – Materials Acceleration Platform" (BIG-MAP) project under the European large-scale research initiative BATTERY 2030+, where we aim to accelerate the discovery process of future batteries using approaches such as autonomous workflows and generative deep learning models to understand and ultimately control these mechanisms. The models are trained on multiple sources of data, i.e., large-scale multi-fidelity data sets, multiscale computer simulations and databases, operando X-ray and neutron characterization from large-scale research facilities, high-throughput synthesis, and laboratory testing.

Computational approaches like atomic-scale simulations have reached predictive accuracy in critical areas of the design and characterization of battery materials. Here, we provide a number of examples of how density functional theory (DFT) simulations supported by machine learning (ML) and cluster expansion techniques can be used efficiently to identify the limiting thermodynamic, ionic, and electronic transport mechanisms in Li-ion and Li-S electrode materials, and alkali metaloxygen batteries. Fundamental and potentially performance-limiting interfacial reactions and processes like forming the Solid-Electrolyte Interphase (SEI) in battery cells, however, span numerous time- and length scales. Despite decades of research, the fundamental understanding of structure-property relations remains elusive. While density functional theory (DFT) and ab initio molecular dynamics (AIMD) generally provide sufficient accuracy to describe the making and breaking of chemical bonds at these interfaces, the calculational cost is often prohibitively high to reach sufficiently long time- and length scales to ensure proper statistical sampling. ML potentials offer a potential solution to this challenge. Still, the training of ML-based potentials capable of handling liquid (organic or aqueous) electrolytes remains a fundamental challenge since the potential must capture both intra- and intermolecular interactions in the electrolyte and during chemical reactions at the interface. We also present new approaches for ML/deep learning models to predict the spatio-temporal evolution of electrochemical interphases in batteries, such as Lidendrite formation. Finally, we discuss the development of methods for uncertainty quantification training and evaluating neural network ensemble models and AI-based optimal experimental design using models trained on multi-sourced and multi-fidelity data from multiscale computer simulations, operando characterization, high-throughput synthesis, and laboratory testing.

Techno-Economic and Environmental Analysis of Aluminium Batteries

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For any proper evaluation of next generation energy storage systems both technological, economic, and environmental performance metrics should be considered. Here conceptual cells, packs and systems are designed in silico for different aluminium battery (AIB) concepts, including both active and passive materials. Despite that all AIBs treated use high-capacity metal anodes and materials with low cost and environmental impact, their energy densities differ vastly and only a few concepts become competitive taking all aspects into account. Notably, AIBs with high-performant inorganic cathodes have the promise of superior technological and environmental performance, should they be more reversible and energy efficient, while at battery energy storage system (BESS) level costs become comparable or slightly higher than for AIBs with organic cathodes.

In more detail, the performance of various AlB concepts varies drastically; while the low volumetric energy densities hamper Al-graphite batteries, organic and inorganic cathode based AlBs remain promising. Yet e.g., Al-TiO2 has relatively poor technical performance, while the cell level material cost and resource usage are fair, but anyhow this means that both the system lifetime costs, and green-house warming potentials (GWPs) become prohibitive. We also note that most experimental AlB-studies use comparatively low areal capacity cathodes and combine these with a large excess of Al anode and electrolyte, while optimized electrolyte and electrode loadings truly ultimately are needed. Lean electrolyte conditions could, however, lead to severely reduced power performance, and the latter could give rise to current densities higher than optimal for the 2D-foil Al-anodes. The latter could, however, be mitigated by introducing 3D-anodes.

Even for the most promising AlB concepts the excellent performance at cell level still provides relatively minor improvements at the BESS level as compared to lithium-ion batteries (LIBs), both in terms of costs and GWPs. Modern LIB cell to pack designs, however, have improved the energy densities at pack level and alternative BESS designs optimized for AlBs could similarly provide relative benefits. Combined there are thus both significant promises and challenges for the various AlB concepts.

The motivation for this effort is the promises of AlBs to reach reasonable KPIs for stationary storage by 2030. As for now, all AlB concepts are based on materials of relatively low cost and environmental impact, but these promises still must be combined with really reaching sufficiently high energy densities, as will be shown e.g., for Al-PBQS and Al-MnO2. For example, AlBs based on organic cathodes do not at all meet the KPIs for the energy densities at cell level, but perform well for the economic KPIs, while Al-MnO2 both reaches the technological KPIs and has the best CAPEX at BESS level, but still falls behind in OPEX due to its lower energy efficiency.

Overall, the main benefit of the AlB concepts will likely remain their low critical resource demand, indicating not only that they could be more sustainable in long-term than LIBs, but also that the materials needed will be less susceptible to supply shortages during the expected huge growth in demand for energy storage. This implies that AlBs, with organic or inorganic cathodes, could provide sufficient performance for some applications, e.g., stationary BESSs, and become a complementary

technology to LIBs and readily enable a faster transition to a more sustainable global low-carbon energy system.

Ionic Liquid Electrolytes for Next Generation Sodium Batteries

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Lithium ion batteries are ubiquitous in our society with uses extending from personal electronics to EVs and stationary storage. However, due to the environmental and ethical issues of raw materials (i.e., lithium, high purity graphite and cobalt) and increasing demands for lower cost and high safety, emerging battery technologies such as those based on sodium chemistries are becoming more attractive. Sodium metal provides the opportunity for higher energy density devices while the possibility of carbonising waste biomass to produce hard carbons for Na ion batteries offers a more sustainable energy solution. Ionic liquid electrolytes have been investigated for over two decades as a safe alternative to traditional organic solvents, in particular for higher energy density, metal anodes. IL electrolytes based on fluorosulfonimide (FSI) anions have particularly favourable properties with respect to enhanced ion transport, high sodium salt solubility and the stable SEI formation and we are increasingly seeing that these electrolytes, the salt concentration, IL cation chemistry and molecular additives have a dramatic effect on the electrochemical performance of both Na metal and carbon anodes, as does the formation protocol on these electrodes. Using solid state NMR, SEM and XPS, we show that this is related to the SEI composition on the anode surface.

Fluoride Shuttle Batteries: Current Status and Prospects Takeshi Abe

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Since the fluoride shuttle batteries theoretically exhibit the higher energy density than lithium-ion batteries, much study has been done for these 10 years. In Japan, RISING Project, which began in 2009, verified the feasibility of constructing this battery system by using a thin-film battery. In the succession project of RISING2, we developed a bulk-type fluoride shuttle battery, and investigated various positive and negative electrode active materials and electrolyte materials. In addition, the reaction analysis of the active materials and the ionic conduction mechanism of the electrolyte were investigated in detail by utilizing advanced analytical techniques. In this conference, I will talk about our recent developments of fluoride shuttle batteries.

The Cathode Interfacial Evolution in Sulfide-Based Solid State Li Batteries Yong Yang

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The stability of electrode/electrolyte interfaces play a key role in the performance-determination of solid state batteries[1]. Such interfacial stability including not only the chemical/electrochemical stability such as side reactions, but also physical stabilitry such as stable physical contact between solid electrode and solid electrolytes which may not a big issue in liquid-type Li-ion batteries[2,3]. In this presentation, we will present some new progresses[4,5] in the characterization and undersstanding of the effects of interfacial behaviour on the electrochemical performance of the oxide-type or sulfide-type solid state batteries.

The electrochem-mechanical effects on structural integrity of the electrode material during cycling is a non-negligible factor affecting the cyclability and rate performance of all solid-state batteries (ASSBs). Herein, combined with in-situ EIS, FIB-SEM and ssNMR techniques, we compare the electrochemical performance and electrochem-mechanical behavior of conventional polycrystalline (LP-) NCM811 (LiNi0.8Co0.1Mn0.1O2), small-size polycrystalline (SP-) NCM811 and single-crystal (S-) NCM811 in Li10SnP2S12 based ASSBs during long charge-discharge cycles. Our results show that the deteriorating performance of both large and small polycrystalline NCM811 originates from their inherent structural instability at > 4.15 V, induced by the visible voids between the randomly oriented grains and microcracks due to the electrode pressing process and severe anisotropic volume change during cycling, rather than the lithium ions transport in the primary particle. In contrast, S-NCM811 with good microstructural integrity show remarkably high capacity (187 mAh g-1, 18 mA g-1), stable cyclability (100 cycles, retention of 64.5%) and exceptional rate capability (102 mAh g-1 at 180 mA g-1) in ASSBs even without surface modification. Moreover, 1 wt% LiNbO3@S-NCM811 has further demonstrated excellent initial discharge capacity and capacity retention. This work highlights the critical role of electrochem-mechanical integrity and offers an promising path towards developing mechanically-reliable cathode materials for ASSBs.

In addition, we also thoroughly investigate the bulk structure evolution of single-crystal LiNi0.8Co0.1Mn0.1O2 in ASSBs at different cycles, further correlated with its interface reactions and electrochemical performance. Operando X-ray diffraction detects the emergence of sluggish phase in ASSBs during the first charge process, which accumulates significantly as the cycle progresses, corresponding to the limited delithiation and rapid performance failure. Our results reveal that the surface chemistry has a great effect on the bulk structure evolution and such a surface-to-bulk effect is critical to the cathode design toward high-performance ASSBs. From this novel perspective, we demonstrate that the enhanced performance employing the surface coating on the nickel-rich materials is attributed to the suppression of sluggish phase.

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Asymmetric Delithiation and Lithiation of Li Layered Oxides under High Current Density Driven by SOC-dependent Charge Transfer Kinetics

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A few-minute-long fast charging capability of Li-ion batteries (LIBs) holds the key to the success of electric vehicles. For decades, it has been considered that the Li-ion diffusion in crystalline electrode materials governs the rate capability of LIBs. Extensive efforts, therefore, have been made to lower the activation barrier of Li-ion migration by tuning the chemical composition and lattice parameters and by reducing the length of Li-ion diffusion from bulk active materials to liquid electrolytes. However, recent discoveries show that the enhancement of the rate of solid-electrolyte charge transfer reaction, i.e., exchange current density, via surface modification or utilization of different electrolytes drastically improves the rate-capability of electrode materials. The results suggest us revisit the role of the charge transfer reaction which possibly affects the kinetics of (de-)intercalation reaction in batteries.

Here, we focus on lithium layered oxides widely used in LIBs. While the single-phase behaviors are well established near equilibrium, some operando diffraction studies have suggested phase separation during delithiation. Notably, the separation is not always observed, and never during lithiation. The discrepancy between delithiation and lithiation reactions have been attributed to irreversible processes during the first charge process (delithiation) or reversible concentrationdependent diffusion. However, these explanations are not consistent with all experimental observations such as rate and path dependencies and particle-by-particle lithium concentration changes. Using a combination of operando diffraction, ex situ nanoscale oxidation-state mapping, and a many-particle population model, we unambiguously explain the origin of asymmetric delithiation and lithiation processes of the single-phase material Lix(Ni1/3Mn1/3Co1/3)O2 (0.5 < x < 1) under high current density. We confirm that the apparent phase separation is a repeatable nonequilibrium process, but not the irreversible phenomenon observed only during the initial delithiation. We further show that the heterogeneous delithiation during the fast charge process induces severe degradation of the cathode materials and eventually increases the cell impedance. Our study suggests the importance of population dynamics in battery electrodes, to develop fastcharging batteries.

Liquid Madelung Potential as a Descriptor for Better Electrode Reactions Atsuo Yamada

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Improving the efficiency of electrochemical lithium (Li) plating/stripping is essential to maximise energy density of lithium-based batteries. Various technical solutions have recently been proposed. Among these, the most effective and promising strategy is upshifting the Li/Li+ redox potential (ELi/Li+) by electrolyte engineering. However, rationales behind the unexpectedly large potential upshift has remained unclear in the scientific community.

Herein, we resolve that the unusual upshift of ELi/Li+ is primarily dominated by the overall Coulombic energy penalty of Li+ in the electrolyte rather than the Nernst equation widely accepted by electrochemists. The energetics was verified and directly quantified by introducing the 'liquid Madelung potential' analogous to the conventional concept in solid-state science. Namely, positively charged Li+ is electrostatically more stabilised by electron-localised solvents while relatively destabilised by electron-delocalised anion.

The rational message of my talk will include,

(i) Well-established concept of Madelung energy in solid can be accurately applied to liquid.

(ii) Physicochemical origin is provided to the parametric activity coefficients appearing in Nernst equation, which cannot be understood by Debye-Hückel theory.

(iii) Identification of simple yet hitherto-overlooked descriptor 'liquid Madelung potential' leads to the better strategies for electrolyte design.

(iv) Replacing the ligand molecules from electron-localised to the electron-delocalised species is the firm technical guideline towards higher Coulombic efficiency.

More importantly, the concepts will better operate many of the industrial electrochemical processes with electrolytes under similar coordination environment matching the criteria (iv) above. Unique examples will be demonstrated as time permits.
Emerging Energy Chemistry at Li Metal Anode and Electrolyte Interfaces Qiang Zhang

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Building high-energy-density batteries is urgently demanded in contemporary society. Achieving a stable interface between electrolytes and highly reactive electrodes is prerequisite to construct a safe and powerful battery, in which electrolyte regulation plays a decisive role and largely determines the long-term and rate performances. The bulk and interfacial properties of electrolytes are directly determined by the fundamental interactions and the as-derived micro structures in electrolytes.

In this talk, we afford an overview of our recent attempts toward rational electrolyte design for safe Li batteries based on a comprehensive understanding of the cation—solvent, cation—anion, and anion—solvent interactions in electrolytes. The formation of cation—solvent complexes decreases the reductive stability but increases the oxidative stability of solvents according to the frontier molecular orbital theory. While the induction of anions into Li+ solvation shell has an opposite function in regulating solvent stability than cations. The competitive coordination of anions and solvents with cations directly determines the salt solubility in electrolytes and the formation of ion pairs and aggregates, which widely exist in high-concentration electrolytes and stabilize Li metal anodes. With a comprehensive and deep understanding of the fundamental interactions in electrolytes and the structure—function relationship, bottom-to-up engineering of Li battery electrolytes is expected to be achieved, accelerating the applications of safe and high-energy-density Li batteries. The general principles demonstrated in Li batteries are also supposed to be applicable to other battery systems and even universal electrochemistry in solutions, including fuel cells and various electrocatalysis.

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Resolving Complex Mechanistic Questions Related to Aqueous Batteries Using Analysis by EQCM-D

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The increased demands for safe and cost-effective energy storage lead to extensive research efforts in the development of stable aqueous batteries and supercapacitors. Significant progress toward practical use of these systems for large energy storage was achieved through the utilization of novel electrolyte solutions enabling significant suppression of the water splitting activity thus providing an expended potential stability window of more than 3V. Implementation of new electrodes' structures allowing reversible hosting of various mono and multivalence ions opens new directions for 'beyondlithium batteries' energy storage applications. The rising interest in aqueous batteries brings new scientific challenges regarding their charging mechanism and the corresponding ionic transport: unlike conventional Li-ion batteries that operate in aprotic environments, the presence of free protons and water molecules in the aqueous systems dramatically affect the electrodes charge storage behavior in aqueous batteries. Depending on the solvation nature of both anions and cations and the electrodes structures, insertion of ions into hosting electrodes' materials may be accompanied by co-insertion or de-insertion of water molecules or protons. The existence of water molecules within the electrodes may facilitate the insertion of multivalent ions by screening repulsive interactions with the host atoms, however, can also occupy active insertion sites. In similar manner insertion of protons result in increased electrodes' capacity on one hand, but may also lead to sluggish diffusion and poor kinetics on the other hand. Considering the above phenomena, it is necessary to develop effective methods that enable the real-time evaluation of the ions insertion/de-insertion dynamics in electrodes' structures upon their polarization. In this lecture, the use of electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) for understanding mechanisms of insertion electrodes and assessments of water molecules, and active ions fluxes in operating electrodes will be presented. The ability of this technique to provide in-situ gravimetric information about the identity of the inserted charge carriers and the influence of the confined water molecules on the charge storage performance in various inorganic and organic anodes and cathodes will be demonstrated. Analysis by EQCM-D includes all aspects of electrochemical processes, including gravimetric and viscoelastic behaviors. EQCM-D is capable to determine when a process has a neat gravimetric nature, so correlation between mass and charge exchanges can provide important and precise mechanistic insights. Most relevant systems are Na, Ca, Zn batteries with an emphasize on most abundant elements (as requested for large energy storage).

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A Rechargeable Calcium Battery With High Cyclic Stability

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Rechargeable calcium (Ca) batteries have the prospect of high energy and low-cost. With its electrochemical potential of -2.9 V vs. NHE, calcium is close to Li/Li+ (-3.0 V) in the electrochemical series so that electrochemical cells giving a good voltage are possible. However, the development of Ca batteries is currently impeded by the lack of electrolytes which can efficiently strip and plate Ca in non-aqueous solvents. We introduce new Ca salts with weakly-coordinating anions establishing the access to a new class of efficient Ca electrolytes. These electrolytes can be synthesized in one step from commercial materials and the reaction gives quantitative yield with the release of H2 as the only by-product. To our knowledge, the Ca[B(hfip)4]2 based electrolytes exhibits the electrochemical properties of a state-of-the-art Ca electrolytes in terms of high oxidative stability of 4.5 V, high ionic conductivity > 8 mS/cm and good capability of long-term reversible Ca deposition. These outstanding properties make the electrolyte well-suited for high energy calcium batteries.

We also demonstrate the feasibility and elucidate the electrochemical properties of calcium-tin (Ca– Sn) alloy anodes for Ca-ion chemistries. Crystallographic and microstructural characterizations reveal that Sn formed from electrochemically dealloying the Ca–Sn alloy possesses unique properties. As demonstration of the suitability of Ca–Sn alloys as anodes for Ca-ion batteries, we assemble coin cells with an organic cathode (1,4-polyanthraquinone) in an electrolyte of 0.25M calcium tetrakis(hexafluoroisopropyloxy)borate in dimethoxyethane. These electrochemical cells are charged/discharged for 5000 cycles at 260 mAg–1, retaining a capacity of 78mAh g–1 with respect to the organic cathode. The discovery of new class of Ca–Sn alloy anodes opens a promising avenue towards viable high-performance Ca-ion batteries.

Electrolyte, Cation Solvation Shell and Interphase for the Emerging Ca Metal Anode Battery <u>Alexandre Ponrouch</u>

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Various metals have been used as battery anodes in electrochemical cells ever since the birth of the batteries with Volta's pile and in the first commercialized primary (Zn/MnO₂, Leclanché 1866) and secondary (Pb/acid, Planté 1859) batteries. Li-MoS₂ cells, employing Li metal anodes, with specific energies two to three times higher than both Ni/Cd and Pb/acid cells, were withdrawn from the market due to safety issues related to dendrites growth. Instead, Ca are currently being considered as safer metal anode alternative. Pioneering work by Aurbach et al. in the early 1990's showed a surface-film controlled electrochemical behavior of Ca metal anodes in electrolytes with conventional organic solvents. The lack of metal plating was attributed to the poor divalent cation migration through the passivation layer.

Nevertheless, recent demonstration of Ca plating and stripping in the presence of a passivation layer has paved the way for assessment of new electrolyte formulations with high resilience towards oxidation. However, several challenges remain to be tackled for the development of Ca based batteries. Among these, the stronger cation-solvent and cation-anion interactions in divalent cation based electrolytes when compared with Li and Na systems convey significant implication in terms of mass transport within the electrolyte as well as desolvation energy barriers at both the anode and cathode interfaces with the electrolyte. Here, the recent advances on the impact of the electrolyte formulation on the composition/morphology and conductivity of passivation layer and on cation solvation structure and transport will be presented. In particular, after the recent identification of polymers containing borates as potential passivation layer component enabling Ca2+ migration, new boron containing salts, solvents and additives have been tested and will be discussed.

Engineering Graphite Interface for Enhancing Safety of Li-Ion Batteries Nae-lih Nick Wu

National Taiwan University, Taipei, Taiwan

The demand for high-energy-density and fast-rechargeable Li-ion batteries (LIBs) is escalated in recent years for meeting the rapid development of electric vehicles and sustainable energy storage applications. Graphite has been the major anode material for commercial LIBs and is anticipated to continuously play an important role in high-energy LIBs in the near future. The low electrochemical potential of graphite can be of two-edge: on one hand, a lower anode potential allows higher energy for a full cell; on the other hand, plating of metallic Li on the graphite anode surface could easily arise from either over-lithiation, due to heterogeneity in the negative electrode, or fast charging. Li metal deposition on an anode can rapidly deteriorate the LIB performance by, for instance, accelerating SEI formation, causing consumption of Li inventory and an increase in charge-transfer resistance. In particular, Li dendritic deposits can penetrate through the separator to trigger cell short-circuit and eventually thermal runaway. The fast SEI accumulation caused by the deposited Li metal, unfortunately, provides additional "fuel" to thermal runaway. Suppressing Li dendrite formation on two-dimensional (2D) current collectors, such as Cu and Li metal, has recently been drawing intensive attention because of Li metal anode applications; study on graphite anodes, which is of importance in improving the performances of the state-of-the-art LIBs, is scarce. A suitable dendrite-mitigating technique needs to be compatible with the existing graphite electrode manufacturing process. The technique needs to take into account the fundamental differences in ion diffusion, reaction kinetics, and surface chemistry between the 3D graphite particles and the 2D metal anodes. In this presentation, different approaches adopting polymeric coatings in modifying the surface properties of graphite and Si-graphite anodes are reported, showing profound effects on altering the Li metal deposition behaviors and battery performance.

Session III Thursday

Design of Next-Gen Cathode Materials With Both Cation and Anion Redox Shirley Meng

The University Of Chicago, Chicago, United States Argonne National Laboratory, Lemont, United States

Among all candidates of positive electrode materials for lithium ion batteries, the lithium rich layered oxides have gained growing research interests in recent years. Their energy density can reach closely to 700-900Wh/g (at materials level), making them the positive electrode materials with highest energy density among all known intercalation compounds for cathode materials. Combining both first principles computation, advanced electron and X-ray based imaging, we demonstrated that in the Li-rich materials oxygen vacancies are present and assist the transition metal ion migration through a facile mechanism. This means it is critically important to control the oxygen activities in these compounds for high voltage operations. In addition, the NiMn spinel oxides show little oxygen activities and under optimized synthesis condition the electrolyte/electrode interface showed superior stability. Combining the strengths of materials synthesis and the advanced characterization, I will discuss in details the strategies for stabilizing the anion redox for higher voltage electrode materials for lithium ion batteries.

BlueSolutions Achievements on the Way to GEN4 Batteries Margaud Lécuyer

Bluesolutions, Quimper Cedex 9, France

BlueSolutions has been the pioneer in commercializing all solid-state batteries in 2011, dedicated to mobile applications like EVs and buses but also stationary storage. The batteries are not only solid, but also manufactured thanks to a green process, namely extrusion, which avoids any use of organic solvent and allows to master the manufacturing of thin polymer films and homogeneous electrodes. By the way, BlueSolutions masters the production and handling of thin metal lithium foils.

BlueSolutions is hardly working on its future generation products that will match better with the expectations of the EV market. While the current battery is LFP-based and cycles at a nominal temperature comprised between 60 and 100°C, a lot of efforts are dedicated to improving the actual chemistry. Research programs are conducted on the development of a new positive electrode with higher energy density, new electrolytes that will be compatible with both high-voltage materials and lithium metal electrodes, with high conductivity at ambient and sub-ambient temperature. A lot of efforts are also dedicated to address the challenges related to the handling and cycling of even thinner lithium electrodes. The main achievements of this project will be shared during this conference.

Unveiling the Redox Mechanisms of KVPO4F1-xOx As Positive Electrode for K-ion Batteries

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K-ion batteries (KIBs) have been developed as future candidates for large scale and low-cost energy storage thanks to the high abundance of potassium, the low electrochemical redox potential of the couple K+/K and the possible use of graphite as negative electrode. Among all the positive electrode materials for KIBs, potassium vanadium phosphate fluoride (KVPO4F) and oxide (KVOPO4) are the most promising ones because of their theoretical capacity of 131 mAh·g 1 and average voltage between 4 and 4.3 V vs K+/K, corresponding to a theoretical energy density in the range of 520-560 Wh·kg-1, which is comparable to commercial LiFePO4-based Li-ion batteries.

KVPO4F and KVOPO4 crystallize in the KTiOPO4 (KTP) type structure and can be described by the general formula KVPO4X (X = O, F). The structure is built from corrugated chains made of cornersharing VO4X2 octahedra connected by phosphate groups. Two different octahedral sites exist for vanadium, where the two anionic sites X in VO4X2 octahedra alternate the cis and trans positions. Moreover, in KVPO4F, the octahedra along the chains are thus connected through fluorine anions, whereas in KVOPO4, they are connected though oxygen anions involved in highly covalent vanadyltype {V=O}2+ bonds. Even more complex is the structure of mixed anions vanadium phosphates such as KVPO4F0.500.5, which is made by alternating VO4F2 "ionic" entity and {V=O}O5 "covalent" vanadyl type units. Therefore, a detailed description of the redox mechanisms occuring in these materials is mandatory as their electrochemical properties strongly depend on the redox sequence of the vanadium centers. Being a site-specific and a local probe technique, operando V K-edge X-ray absorption spectroscopy is the unique tool providing information on the V oxidation state as well as its local environment evolution upon cycling in KVPO4F1-yOy (y = 0, 0.5, 1). The whole operando XAS dataset was analysed using a chemometric approach based on a combination of Principal Component Analysis (PCA) and Multivariate-Curve Resolution Alternating Least-Square (MCR-ALS), enabling the identification of the orthogonal components and their concentration upon cycling. While the two end-members KVPO4F and KVOPO4 undergo two components reaction pathways upon K+ extraction, three components are needed to describe the evolution of XAS spectra in KVPO4F0.500.5. Moreover, we found that ionic VO4F2 units oxidize before covalent {V=O}O5 units, which is surprising considering the inductive effect expected from F- anions. However, this result can be explained by considering the different redox potential observed for KVPO4F and KVOPO4. In a broader context, this work also sheds light at the chemical sensitivity of V K-edge XAS among ionocovalency, oxidation state and structure.

Multi-Modal Multi-Scale Characterization of Heterogeneities in Li-Ion Batteries by Neutron & Synchrotron Techniques Sandrine Lyonnard

Cea-irig, Grenoble, France

The in-depth understanding of the electrochemical processes that dictate battery performance require the monitoring of a variety of inter-related processes under operando conditions, i.e., acquiring data on a single cell during continual (dis)charge. Due to the extended range of length-scales involved, e.g. from atomic scale to device scale, tools capable of detecting key mechanisms at the appropriate scales are needed, as well as strategies to bridge these various scales to obtain a continuous description of processes during battery operation.

Synchrotron and neutron techniques provide unique insights into reaction and ageing mechanisms in battery components and interfaces across multiple length scales with, potentially, high time/spatial resolutions. Typically, the chemical, morphological and structural evolutions of negative and/or positive electrodes can be accessed in real-time by performing operando spectroscopic, imaging or diffraction/scattering experiments, using custom-made cells or, in some cases, commercial cells as pouch cells, coin cells or 18650. However, while a colossal amount of data have been already accumulated using these techniques, novel methodologies are still needed to extend the usual single-experiment practice towards more correlative characterization.

In this talk, we will illustrate the benefits and challenges of multimodal multi-scale characterization of batteries by focusing on the investigation of lithiation heterogeneities in composite anodes and high voltage cathodes, using advanced imaging and tomography techniques. We will present combined and/or coupled operando experiments performed on full batteries of different types, using both neutrons & x-rays, and/or both atomic scale and nanoscale techniques, focusing on the investigation of lithiation heterogeneities at the scale of electrodes. This is achieved either in the depth using spatially-resolved scanning microbeam experiments, or in 3D using neutron imaging and X-rays absorption and scattering tomography, and applied to a range of materials as hierarchical composite anodes based on silicon nanodomains or silicon nanowires, and layered intercalation compounds such as LNO. We will also show examples of detection of failure and defects in commercial-types batteries after long-term utilization. Last, we will describe integrated standardized experimental workflows as developed in the BIGMAP project, and highlight perspectives in battery research at large scale facilities by introducing new mechanisms, methods and organizations such as Al-aided modelling-driven strategies, coordinated beamtime allocations, and community-unified infrastructures.

Understanding the Correlation Between Structure – Morphology and Performance of All Solid-State Batteries

Oskar Thompson¹, Patrice Perrenot³, Ove Korjus³, Lucas Trassart¹, Adrien Fauchier-Magnan¹, Emmannuelle Suard⁴, François Fauth², Fannie Alloin¹, **Claire Villevieille**¹

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All-solid-state batteries have been presented as the ideal solution to address i) the safety limitations of conventional Li-ion batteries by suppressing the flammable organic electrolytes and ii) the problem of insufficient energy densities if coupled to Li metal. To date, two types of solid Li-ion electrolytes have been mainly studied, namely, sulfur-based and ceramic-based materials. As they are easy to process and they offer a high lithium ion conductivity in the range of 1-20 mS/cm [1,2], sulfide-based electrolytes such as e.g. thio-LISICONs and argyrodites are therefore regarded as suitable candidates to be used in lithium all-solid-state batteries.

Despite the progress in the development of superionic conductor, many aspects regarding their chemical and mechanical issues remain unsolved especially during electrochemical activities where the electrolyte is heavily decomposed [3]. If the electrode engineering i.e. composite electrode (mixture of electroactive material, conductive agent and solid electrolyte) is under intense investigation, the role of the solid electrolyte used as separator is so far poorly studied. As an example, if the sintering (even cold sintering) is not properly performed, the Li-ion conduction will not be optimal that could create kinetics problem, as well as if voids appear in the solid electrolyte pellet, it will lower the ionic conductivity and the voids could then evolve and propagate into cracks during electrochemical cycling. Increasing the temperature to improve the sintering is quite often proposed as a solution since the porosity is then decreasing in the pellet and the grains more easily being join reducing the grain boundaries resistance. However, the structural impact of the sintering is not yet fully understood, especially that the system Li-P-S is quite sensitive.

In this work, we are proposing an in depth (operando and postmortem) multiscale investigation of the parameter controlling the "shaping" of thiosulfate-based solid electrolytes and its consequence on the electrochemical activity. We gathered information from bulk to surface analysis using electrochemical (EIS, CV, etc.) X-rays (XRD, XAS, micro and nano-XRT, FIB-SEM, etc.) and X-ray/neutron-based diffraction techniques revealing the relationship between shaping, structure, morphology and electrochemical performance. The results obtained here should serve as a preliminary basis to develop better solid-state batteries using sulfide-based electrolyte. Session IV Thursday

Electrolyte Oxidation and the Role of Acidic Fluorophosphates in Capacity Loss for Lithium Ion Batteries Brett Lucht

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Cycling lithiated metal oxides to high potential (>4.5 V vs Li) is of significant interest for the next generation of lithium ion batteries. Cathodes cycled to high potential suffer from rapid capacity fade due to a combination of thickening of the anode solid electrolyte interphase (SEI) and impedance growth on the cathode. While transition metal catalyzed degradation of the anode SEI has been widely proposed as a primary source of capacity loss, we propose a related acid induced degradation of the anode SEI. A systematic investigation of LiMn2O4, LiNi0.5Mn1.5O4, LiNi0.6Mn0.2Co0.2O2, and LiNi0.8Mn0.1Co0.1O2 cathodes will be presented. The role of potential on the generation of soluble acidic fluorophosphates crossover species and the impact of these species on the structure and stability of the SEI will be presented.

The reason for this capacity fade for high voltage cathode materials has frequently been reported to be transition metal ion dissolution from the cathodes and their subsequent deposition on the anode destroying the anodes' protective SEI. However, the mechanism for transition metals degrading the anode SEI components is unclear.. On the other hand, oxidative decomposition of the electrolyte results in the generation of various acidic species including glycolic acid, formic acid, PF5, HF and OPF3. These species can be involved in cross over reactions which could facilitate the decomposition of the anode SEI components leading to capacity fade. This investigation focusses on the generation of the strong acid difluorophosphoric acid (F2PO2H) and has been quantified for two different cathode materials. There is an excellent correlation between the concentration F2PO2H, SEI degradation and the capacity loss of the cells

Imperfect Battery Materials: Impact of Structural Disorder in Cell Performance

Jon Serrano-Sevillano¹, Marine Reynaud¹, Damien Saurel¹, Montse Casas-Cabanas¹

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Innovation through structural design has been an effective mean for the realization of today's batteries. Indeed, our ability to master the atomic scale through the identification of host structures and chemistries able to intercalate lithium ions at convenient voltages has been rewarded by the deployment of the Li-ion technology and the ushering in of the portable electronics era. A massive effort is now devoted to the improvement of the selected group of materials that have reached commercialization and the development of new materials and chemistries. However, the development of the next generation of energy storage materials requires an unprecedented ability to understand and control all levels of organization of matter and its coupling with function, including disorder and defects, which have often been dismissed as assumed deleterious to performance. However, if understood and controlled, these can provide a depth of control and utility to design better materials.

Progress in the characterization of disorder is providing unprecedented insights into defect structures. In particular, recent models and tools applied to X-ray scattering techniques offer an accessible window for the observation and accurate parametrization of complex microstructural features. In this talk, two approaches targeting different length scales will be discussed. First, the use of the FAULTS program, which following the approach used in DIFFaX, allows to quantitatively describe planar defects like stacking faults and intergrowth structures from powder diffraction data. Next, in the higher limit of disorder, structural model descriptors that cover both the atomic and pore structures to describe the Small Angle X-ray Scattering (SAXS) signature of different disordered carbon materials will be shown. In both cases the capabilities of scattering techniques to reliably parametrize complex disordered structures critical to establish reliable correlations with performance will be described.

Synthesis by Design: A Framework to Manipulate Cathode Composition and Morphology

<u>Venkat Srinivasan</u>¹, Pallab Barai¹, Hakim Iddir¹, Juan Garcia¹, Mark Wolfman¹, Xiaoping Wang¹, Deepti Tewari¹

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With the increasing demand for batteries for transportation and grid, the role of critical battery materials, especially cobalt and nickel, have come to the forefront as a looming threat that can derail worldwide decarbonization goals. With this concern comes the need to rapidly move towards low Co materials, such as NMC-811, and low Ni materials, such as the Li- and Mn-rich NMCs. With these emerging changes, the importance of carefully controlling the composition of the cathode and the morphology of the primary and secondary particles is becoming clear. Examples include the need to minimize grain boundaries in high Ni cathodes to limit particle cracking and the need to minimize diffusion length in LMR-NMC cathodes to compensate for the slow diffusion coefficient of lithium in the structure.

In this talk, we will describe a recently developed methodology to understand synthesis pathways and use this understanding to mathematically predict the influence of synthesis conditions on the composition, size, and microstructure of primary and secondary particles. The methodology utilizes a combination of controlled synthesis, operando characterization during synthesis, and modeling across length scales. The focus is on co-precipitation to synthesis cathode active precursors and lithiation and calcination to form transition metal oxides.

The talk will explore the differing propensity for precipitation for the different transition metals and its impact on composition and the interplay between primary particle growth and aggregation during the coprecipitation process. We will also examine the role of surface oxygen during lithiation of high nickel content materials and the different synthesis pathway for NMC-622 vs 811 during calcination.

Anion Redox Mechanisms in Alkali-Rich Sulfides

Kimberly See¹, Joshua J. Zak¹, Seong Shik Kim¹, Andrew J. Martinolich¹, Eshaan Patheria¹

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Charge compensation by anion redox bypasses the theoretical capacity limits imposed by conventional intercalation chemistry but anion redox can cause significant structural deformations that impact reversibility. Sulfides are known to undergo reversible anion redox employing reactions like sulfide to persulfide oxidation. We will discuss alkali-rich metal sulfides not only as model systems for anion redox, but also as materials that use abundant elements while achieving energy densities that rival LiFePO4 chemistry. Li2FeS2, a material that has been known since the early 80s, can support reversible anion redox and delithiation up to 1.8 mol. We will discuss the mechanism of anion redox in Li2FeS2 and discuss chemical methods to tune the voltage of the anion oxidation. We will additionally discuss structural factors that enable oxidation to persulfides.

Session I Friday

Development of High Energy Battery Materials Without Natural Resource Constraints Hikari Sakaebe

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Demand for rechargeable batteries is widely spreading for electric vehicles, large-scale energy storage systems, and so on. State-of -the-art Li-ion batteries contain strategic metal like Co and Ni. And we have to reconsider the material development strategy for positive electrode materials or to establish the recycling process of used batteries in order to deal with such a situation.

Olivine LiFePO4 is a typical and rare electrode material that consists of iron and that have been commercialized. This material is so stable in Li-ion batteries to provide longer life, however, energy density is not enough for realization of high energy batteries.

Authors have developed novel iron materials for new battery systems with higher energy density (300 - 500Wh/kg). Li₈FeS₅ is one example of our achievement. This shows mode than 700 mAh/g and works with less amount of conducting carbon compared to S₈ electrode. We applied this material to liquid state Li-S battery and found severe side-reaction with electrolyte solution. Surface modification or use of solid electrolyte is effective way to improve the life.

FeF₃ also attracts the attentions because of its larger capacity. This material can be operated as both of Li-conversion and fluoride-shuttle system. Comparison of the electrochemical process will be discussed. In addition to iron containing materials, some topics for solid state battery application of novel material with less resource constrain will be presented.

Acknowledgement

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Speeding Up Electrochemical Reactions in Batteries Using Light Mediated Energy <u>Christopher Johnson</u>

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The growth in electrified transportation has benefited from the massive worldwide research efforts used to discover and improve electrode materials and electrolytes. Nevertheless, lithium-ion batteries still intrinsically suffer from a critical slow charging limitation. Recently, it has been demonstrated that under white light illumination LiMn2O4 cathodes undergo photo-accelerated fast charging, essentially improving the kinetics of delithiation without use of nanostructured active materials. In this work, we further probe the driving force behind photo-accelerated fast charging using LEDs to select discrete wavelengths of light and show that Mn d-d orbital transitions occurring under red light illumination are largely responsible for the increased charging rate. It is further demonstrated through X-ray absorption spectroscopy methods that LiMn2O4 undergoes a reduction in Mn-Mn bond distance as a result of this d-electron excitation. The shrinkage in the crystal volume from exterior light perturbation appears to beneficially contribute to delithiation kinetics by lowering the resistance to lithium-ion conduction. Advanced materials that can absorb light to modulate their structure may provide us with a new mechanistic pathway to pursue for increasing charge transfer rates.

Electrolyte Enabled Structural Evolutions of Na3V2(PO4)2F3 Electrode Upon Repeated Cycling and Their Influence on Degradation Mechanism of Na-Ion Cells.

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The growth of Li-ion batteries is enormous and their applications spread almost everywhere starting from small electronics to electric vehicles and grid energy storage devices. However, considering the limitations with lithium resources, we are in need of complementary energy storage devices, where the Na-ion batteries evolve as a suitable candidate. The progress in Na-ion battery technology is quite high in recent years and we are witnessing demonstration of Na-ion batteries for E-bikes and other applications by several start-ups and companies. Different Na-ion chemistries are in use at present, in which the positive electrode is selected from sodium layered oxides, polyanionic compounds ($Na_3V_2(PO_4)_2F_3$) and Prussian blue analogs with hard carbon (HC) negative electrode and non-aqueous electrolyte.

Among the different positive electrodes studied, polyanionic Na₃V₂(PO₄)₂F₃ (NVPF) exhibits good structural stability upon long cycling and exhibits a great advantage of high power rate capability, thereby making it attractive for high power applications. However, nearly 50% of NVPF redox happens at high potentials, around 4.2 V vs Na+/Na (4.5 V vs Li+/Li). Such voltage is very high for the oxidative stability of carbonate based electrolyte and also lead to the dissolution of vanadium from the charged NVPF. Such parasitic reactions are more pronounced at high temperatures thereby deteriorating the high temperature performance of the NVPF-HC cells. In addition, the reactivity of the NVPF with electrolyte leads to structural changes in the NVPF material that starts in the surface and propagates to bulk upon cycling. The parameters and the possible mechanism that lead to structural changes of NVPF will be discussed with respect to different electrolyte formulations. The possible solutions by tuning the electrode, electrolyte characteristics will be conferred with the goal to achieve the best electrochemical performances of NVPF-HC cells at all temperatures and harsh cycling conditions.

Influence of Pristine NMC811 Secondary and Primary Particle Surfaces on the Materials Reactivity

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The surface reactivity of Ni-rich layered transition metal oxides is instrumental to the performance of batteries based on these positive electrode materials. Most often, strong surface modifications are detailed with respect to a supposed ideal initial state. The study the LiNi0.8Mn0.1Co0.1O2 (NMC811) cathode material in its pristine state, hence before any contact with electrolyte or cycling, was performed thanks to advanced microscopy and spectroscopy techniques in order to fully characterize its surface down to the nanometer scale. Scanning transmission-electron microscopy-electron energy-loss spectroscopy (STEM-EELS), solid state nuclear-magnetic-resonance (SS-NMR) and X-rays photoelectron spectroscopy (XPS) are combined and correlated in an innovative manner. The results demonstrate that in usual storage conditions after synthesis, the extreme surface is already chemically different from nominal values. In particular, nickel is found in a reduced state compared to the bulk value and a Mn enrichment is determined in the first few nanometers of primary particles. Further exposition to humid air allows for quantifying the formed lithiated species per gram of active material, identifying their repartition and proposing a reaction path in relation with the instability of the surface. Modifying synthesis conditions impacts noticeably the previously identified surface particularities and, consequently, the materials reactivity.

Advanced Anode Materials for Li-Ion and Na-Ion Batteries

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The needed advancement in Li-ion and Na-ion batteries calls for the new anode materials, which can improve the performance of the batteries of today. Anode materials operating under alloying mechanism for a while seemed to be a great choice to replace the current set. However, their poor stability and fast performance decay impeded their use. The next generation represented by conversion/alloying materials provided a great alternative as they deliver a substantially improved capacity compare to the state-of-the-art. These materials operate under a complex mechanism resulting in a formation of the active species embedded in the inert matrix primarily occurring during a first cycle.

Such mechanism is key for the design of the future materials and understanding such is required for the future optimization and synthesis of new materials. The present talk will highlight the challenges associated with characterization and optimization of conversion/alloying materials for Li-ion and Na-ion batteries. Furthermore, this presentation will aim to demonstrate how the strong synergy between computer modelling and advanced characterization can be used to reveal the structure-property relationships of these promising battery materials.

Session II Friday

Recent Advancements in the Development of Magnesium Metal Negative Electrodes – Metallurgical Approaches Toshihiko Mandai¹, Hidetoshi Somekawa¹

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Magnesium metal rechargeable batteries (MRBs) are being studied intensively as one of the promising innovative batteries that can contribute to the achievement of the SDGs, because they can in principle store more than twice as much electric energy as lithium-ion batteries, in addition to having abundant resources of the constituent materials. In the past few decades, great research efforts have indeed been paid to achieve MRB materialization and a large variety of fascinating candidate electrode and electrolyte materials have been developed. As for electrode materials, in contrast to the remarkable development of positive electrode materials, little research has been reported on magnesium metal negative electrodes due to less research interests. In this talk, recent advancements and understandings of magnesium metal negative electrodes will be presented.

Novel metallurgical approaches revealed that the primary electrochemical processes, i.e. magnesium dissolution and deposition, should be grain-boundary mediated, hence the electrochemical activity would be improved by grain refinement. Alloying with appropriate doping elements can further enhance the activities probably owing to segregation of doping elements preferentially at grain boundaries and resulted perturbation of the free energy of the grain boundaries. The representative Mg-Ca (0.997Mg-0.003Ca) alloy exhibited remarkable electrochemical dissolution-deposition cycling performance with the corresponding over potential less than 30 and 50 mV at the current densities of 0.5 and 1.0 mA cm-2, respectively.

For practical MRB materialization, thin magnesium foil must be developed because the practical loading, i.e., thickness, of magnesium metal negative electrodes predominates the practical energy density of MRBs. The simple energy density estimation by the recently established energy density calculator indeed renders that thick magnesium metal, e.g. 100 μ m-thick, can lead significant loss in volumetric energy densities of the resulting cells compared to the cells with thinner magnesium metal, e.g. 40 μ m-thick, at the same amount of utilization. Although the poor formability of magnesium metal makes thin foils difficult, we have successfully fabricated ultrathin magnesium foils with a sufficient geometric size applicable to typical laminate-type cells by controlling the initial microstructure of the magnesium billet. The systematic metallurgical and electrochemical studies also revealed that the residual stress can be another determining factor of the electrochemical activities of magnesium metal negative electrodes.

Although the improvement in energy densities of MRBs upon utilizing the developed magnesium negative electrodes seems little, these strategies will open the door to the design of high-performance MRBs through simple metallurgical approaches.

Design of Lithium Metal Battery Electrolytes Based on Lithium-Ion Chemical Potential

<u>Yuki Yamada</u>

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Lithium metal is an ideal anode for high-energy-density batteries, but its critical problem is a low Coulombic efficiency (CE) with the reductive decomposition of electrolyte components caused by the strong reducing ability of lithium metal. To improve the CE, various electrolytes and additives have been proposed to form a stable solid electrolyte interphase (SEI) on lithium metal, which can kinetically suppress the electrolyte decomposition. However, the improved CE has not been understood quantitatively.

Here we report lithium electrode potential (E) as a quantitative and thermodynamic descriptor that dominates the CE. We measured E in 74 different electrolytes using ferrocene as an internal standard for electrode potentials. Then, we evaluated the CEs of lithium plating/stripping in the 74 electrolytes (without ferrocene). We found that the CEs are correlated with E. Higher E (thus lower reducing ability of lithium metal) leads to higher CEs due to diminished electrolyte decomposition.

Theoretically, E is linked to lithium-ion chemical potential (μ) in an electrolyte. Hence, E can be controlled by designing an electrolyte with focus on μ . Raman spectroscopy revealed that the formation of ion pairs is essential for increasing the μ and upshifting the E. This finding provides rational design of lithium metal battery electrolytes with focus on lithium-ion coordination states, μ , and E.

The Science and Engineering of Structural Batteries – But Are They a Practical Solution?

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There is an increasing interest in the development of structural batteries, especially in automotive applications, in order to take advantage of the considerable area and volume in vehicle structures. Structural batteries utilise materials and structures capable of carrying a mechanical load whilst also storing electrical energy, and their development is occurring two levels; embedding of standard prismatic batteries of varying size / capacity into structures, also known as multi-functional composite structures [1] or development of multi-functional materials [2,3] that can deliver mechanical strength whilst facilitating ion or electron transport within the electrolyte or electrode, respectively.

In the first instance, we have built a range of multi-functional composite structures to determine the effect of high structural bending loads on the flexural properties and electrical energy storage capacity of sandwich composites containing lithium-ion polymer (LiPo) batteries. Three-point bend tests which induce failure by plastic indentation or cracking of the foam core are performed on sandwich composites containing single or multiple LiPo batteries. The bending properties of the sandwich material are not changed significantly by embedding batteries within the core. The energy storage capacity of the sandwich composite can be increased by inserting multiple batteries without adversely affecting the bending properties. Furthermore, the internal electrical resistance and capacity of the batteries is not degraded when sandwich composites are damaged by high bending loads [4]. However, the use of multi-functional composites is not ideal, as the energy density of the structure is degraded due to the presence of the carbon fibre and resin composites and questions remain around safety of this approach.

Multi-functional materials are the preferred method for the design and build of structural energy storage devices. As an all-in-one solution, we are seeking to ensure that the electrode and the electrolyte can act provide the mechanical stiffness as well the electrochemical properties required. For electrodes, this is achievable using traditional electrode techniques with tweaks to the binder to further improve mechanical performance. The challenge remains in the design of electrolyte materials; mechanical stiffness does not equate to high conductivity in electrolytes

In this paper, we will describe our work in both multi-functional composite structures and materials and seek to understand whether this style of battery can deliver competitive energy densities, the required mechanical properties and safety for use in automotive applications.

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Poster Session I

3D Digital-Twin Based Anode Structure Modeling Considering Electrolyte Swelling for Lithium-Ion Batteries

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Digital Twin refers to a modeling technology that can simulate various physical phenomena by moving the shape of an actual object or system into a virtual space. It is widely used in research fields that require a lot of time and money to verify by experiment. Technological advancements have led to the use of digital twin studies to implement complex microstructures inside lithium secondary batteries.

In this study, we present an optimized silicon oxide (SiOx)/graphite composite electrode digital-twin structure that considers deformation during electrolyte swelling and presents an experimental parameter calculation method for determining the conformity of the structure. As a result, we discuss key results such as charge transfer pathway within electrodes and local stress by State-of-Charge through physical analysis and electrochemical simulation of 3D microstructure reflecting the swelling process.

There are two challenging points to obtain a three-dimensional structure during the electrolyte wetting process. First, it is difficult to know mechanical properties of each component in swelled state. During the swelling process, the binder expands in volume and at the same time the mechanical properties decrease significantly. Through these studies, a method for experimentally measuring the change in the properties of a binder is presented and applied to a three-dimensional microstructure. Stress and strain to electrode deformation were measured using non-destructive stress analyzers, MOSS (Multi-beam Optical Stress Sensors) and confocal microscopy, respectively. As a result of the measurement by our method, the volume expansion and Young's Modulus change during the process of impregnating the electrolyte into the SBR(Styrene-Butadiene Rubber) and CMC (carboxymethyl cellulose) binder were quantified.

The second challenging point is that it is difficult to experimentally verify variables to determine the reliability of the structure. Previous studies have been able to verify the conformity of the structure by experimentally obtained porosity, tortuosity, and electronic and ionic conductivity based on the dried state, but it is difficult to experimentally obtain the parameters in the state of being impregnated with electrolyte. Therefore, it is suggested that the effective stiffness of the electrode can be utilized as a major parameter for structural verification using the mechanical analysis method of this study.

A well fitted structure is applied to the electrochemical model to realize the complex electrochemical behavior in the electrode in real-time simulation. Consequently, the key factors of electrodes such as percolation pathway, effective contact area, and local mechanical stress are discussed. This study will be extended to the study of deformation during the electrochemical cycle in the future to improve the accuracy of the simulation.

3D Micro Structure Resolved Electro-Mechanical Simulations of a Full Battery Cell: A New Modelling Method and Its Verification With Time Resolved X-ray Tomography.

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Most commercially used electrode materials contract and expand upon cycling. This change in volume has an influence on the micro structure of the cell stack and with that on a range of performance parameters. Direct observation of these changes with operando experiments is challenging and limited by the constraints of the measurement. 3D resolved simulations enable the study of dynamic phenomena on much easier to acquire ex-situ (i.e. static) 3D micro structural datasets or artificially generated realistic micro structures. Furthermore, for acquired time resolved data, such simulations allow us to study the contribution of different theorized mechanisms on the whole dynamics of the measured data. Here we demonstrate the development of a new tool that combines 3D electro-chemical and mechanical modeling and that allows to simulate a range of materials either as individual components or combined in a full cell stack. We show the validity of this software tool by comparing the results of the simulation with time resolved x-ray tomography datasets from a graphite anode and a Li(Ni,Mn,Co)O2 cathode. We demonstrate that a full cell stack can be simulated giving new insight into to electro-chemo-mechanical behavior of the individual battery components during cycling. We show the potential of this new tool to provide a deeper understanding of battery aging, e.g. by analyzing the effect different expansion behaviors of the cathode material have on the entire cell stack.

A Comprehensive Study on the Effect of Washing on Nickel-Rich NCMs: Part I. Methodology for the Quantification of the Proton Content and the Li⁺/H⁺-Exchange Kinetics

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Due to their high specific capacity, the market share of nickel-rich layered lithium nickel cobalt manganese oxides (NCMs, LiNixCoyMnzO2, x+y+z = 1) as cathode active materials (CAMs) for lithium-ion batteries is constantly growing. With higher nickel content, the available capacity is increased; however, the higher reactivity of nickel increases the amount of unwanted contaminants on the surface of the NCM particles [1]. These contaminants comprise lithium salts (typically lithium carbonate and/or hydroxide), which remain from the lithium excess added during the synthesis of the CAM [2] or are formed during improper storage owed to the high sensitivity towards moisture [3]. In the cell, these compounds then lead to extensive gassing upon decomposition during the first charge/discharge cycles [4], to hydrolysis of electrolyte components [5], as well as to impedance build-up and, therefore, capacity fading during cell operation [6]. Due to these negative effects, these contaminants are commonly removed by washing the CAM in water; however, it was reported that this essential process is accompanied by the cation exchange of intercalated near-surface lithium ions from the NCM by protons from the solution when nickel-rich NCMs are exposed to liquid water [7] or to humid air [8]. To reveal the kinetics of this cation exchange as well as its implications on the electrochemical behavior, a comprehensive study on the exchange process during the washing is presented here for a nickel-rich NCM831205 (LiNi0.83Co0.12Mn0.05O2).

In the first part of this work, washed NCM samples were prepared under a wide variety of process conditions (e.g., washing time, water-to-CAM mass ratio, washing temperature) [9]. To determine the proton amount being introduced into the CAM and, consequently, describe the kinetics of the cation exchange, a variety of methods is applied which are all capable of independently quantifying the proton amount $x(H^+)$ (in units of mol%) exchanged into the CAM, using the unwashed CAM as baseline: i) By titrating the washing solution, its concentration of lithium hydroxide c(LiOH) is determined, what can be converted into $x(H^+)$ of the CAM. ii) During heating to 450 °C, the protonated NCM structure decomposes thermally and transforms into a rock-salt-type structure upon release of water and oxygen. Through thermogravimetric analysis coupled with mass spectrometry (TGA-MS), the observed mass loss can be converted into x(H⁺). iii) Upon irradiation with neutrons, the protons (as well as the atomic nuclei of the metals) in the NCM emit γ -rays with distinct energies, allowing to determine $x(H^{+})$ by prompt gamma activation analysis (PGAA). iv) As the protonated layered phase converts to a rock-salt-type structure upon heating, the amount of the rock-salt phase of a heated and washed NCM sample is determined by Rietveld refinement of the powder X-ray diffraction (XRD) data, from which $x(H^+)$ was obtained by the ratio of layered and rocksalt-type phase.

The x(H⁺) values obtained by the presented methods show good agreement, highlighting the reliability of each approach. For the various washed NCM samples, proton amounts between 0.5 mol% and 20 mol% are obtained, based on which the kinetics of the process are discussed. Finally, for NCM samples with well-defined proton content, the onset as well as the extent of the electrochemical release of the protons upon charge (i.e., delithiation) of the NCM is investigated by on-line electrochemical mass spectrometry (OEMS).

In the second part of this study [10], the impact of the protonation on the electrochemical behavior of the NCM is illuminated.

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A Comprehensive Study on the Effect of Washing on Nickel-Rich NCMs:Part II. Impact of the Li+/H+-Exchange on the Electrochemical Performance

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Due to their high specific capacity, the market share of nickel-rich layered lithium nickel cobalt manganese oxides (NCMs, LiNixCoyMnzO2, x+y+z = 1) as cathode active materials (CAMs) for lithium-ion batteries is growing continuously. With higher nickel content, the available capacity is increased; however, the higher reactivity of nickel increases the amount of unwanted contaminants on the surface of the NCM particles [1]. These contaminants comprise lithium salts (typically lithium carbonate and/or hydroxide), which remain from the lithium excess added during the synthesis of the CAM [2] or are formed during improper storage owed to the high sensitivity towards moisture [3]. In the cell, these compounds then lead to extensive gassing upon decomposition during the first charge/discharge cycles [4], to hydrolysis of electrolyte components [5], as well as to impedance build-up and, therefore, capacity fading during cell operation [6]. Due to these negative effects, the contaminants are removed by washing the CAM in water; however, it was reported that this essential process is accompanied by the cation exchange of intercalated near-surface lithium ions from the NCM by protons from the solution when nickel-rich NCMs are exposed to liquid water [7] or to humid air [8]To reveal the kinetics of this cation exchange as well as its implications on the electrochemical behavior, a comprehensive study on the Li⁺/H⁺-exchange process during the washing is presented here for a nickel-rich NCM831205 (LiNi0.83Co0.12Mn0.05O2). In the first part of this study [9], we quantified the proton content by titration, TGA-MS, and PGAA (prompt gamma activation analysis). In the present study, the impact of protons on the electrochemical performance is investigated.

To examine these aspects and to allow for a model surface without any inner surfaces, singlecrystalline NCM831205 was treated in accordance with our previous study [9], preparing samples with a proton content of 1.0 and 1.5 mol% H⁺. Electrodes with loadings of ~10 mgCAM/cm² were prepared and assembled in a three-electrode half-cell setup with a lithium reference electrode and were subjected to discharge rate tests with potential cutoffs controlled by the lithium reference electrode. During the first charge at a small C-rate, it was found that protonated materials exhibit a plateau-like overpotential until a charge of ~100 mAh/gCAM, which vanishes in the second cycle. Besides that, a relatively similar capacity is observed for both cycles and it is concluded that protonated materials can be cycled reversibly.

In a second set of experiments, the materials were cycled in coin full-cells using graphite as counter electrode for 200 cycles, applying different upper cutoff potentials that were chosen to be either below or above the estimated potential for the proton release (as indicated by online electrochemical mass spectrometry [9]). To elucidate the aging mechanism, impedance spectra were recorded with a three-electrode full-cell using a micro-reference electrode [11]. During long-term cycling, the presence of protons in the NCM material seems to have a detrimental effect on the capacity retention and the rate capability when compared to the as-received material, while also a rapid impedance build-up is observed. After cycling, the cathodes were harvested from the cycled cells and investigated by post-mortem experiments: The NCM cathodes were analyzed in half-cells at

slow rates and a dV/dQ analysis was performed. Finally, a mechanism will be postulated to explain the observations.

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A Multi-Layer Phase Field Model to Study Lithium Intercalation in Graphite: Focusing on the Coupling With Graphene Stacking Sequence

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During lithium intercalation in graphite, the active material undergoes phase separation between a succession of several stable phases, known as stages. This staging phenomenon corresponds to the appearance of an ordered sequence of intercalant layers separated by planes of the host-layered material. The stages are defined according to the number of host layers that periodically separates two successive intercalant layers. This phenomenon influences critical properties of graphite like its equilibrium potential, lithium diffusion or lithium insertion kinetics.

Here, thermodynamics and kinetics of stage formation are studied using a multi-layer free energy framework based on mean-field theory, accounting for both intra-layer and inter-layer interactions. More specifically, we go beyond the multi-layer Cahn-Hilliard framework by adding an order parameter to describe the local evolution of the stacking sequence of graphene sheets around lithium islands. The introduction of this order parameter enable the distinction between the liquid-like stage 2L and the stage 2. Key in this approach is the form of the underlying free-energy model and the associated intra- and inter-layers interactions between lithium ions and the host structure.

Following an empirical approach, we show that an inter-layer interaction between the lithium ions and the host-structure is necessary to counterbalance the enthalpy term of the lithium intra-layer energy and allow the formation of islands with intermediate concentrations, characteristics of the liquid-like phases as will be illustrated in the computed phase diagrams. The proposed interactions between the graphite structure and the lithium concentration let the stage 3, now in a dilute liquid-like form 3L, to appear at an average filling fraction around 0.2, a value that is closer to experiments than the value of 0.33 obtained without accounting for the graphene stacking order. Similarly, two stages of periodicity 2 are now solutions of the model. A dilute stage 2L with intermediate filled layers and a graphene staking sequence of the form /AB/BA, where carbon layers are staggered around empty layers, but eclipsed around filled ones and the ordered stage 2 where the graphene stacking sequence is of the form /AA/AA, where carbon layers are eclipsed around both filled and empty layers. This new framework therefore leads to a more complex phase diagram with the presence of the stages 3L, 2L, and 2. Interestingly, with the chosen parameters, the transition between the stages 2L and 2 disappears below 280 K, as reported in the literature.

Introducing the developed free energy model in Cahn-Hilliard's and Allen-Cahn's equations, we can also simulate the evolution of lithium concentration, as well as graphite stacking during spinodal decompositions and follow the emergence and evolution of these stages in a graphite particle. Staggered domains of lithium surrounded by different graphene stacking arise naturally with characteristics typical of stages 1', 3L, 2L, 2 and 1

A Nanoporous Polymeric Coating on Thin Metallic Lithium to Enhance Li-S Cell Cycle Life via Improved Deposition Behaviour

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Owing to their high energy density, the metallic lithium anode is regarded as a holy grail of electrochemical energy storage. The technology is plagued by poor cycle life and instability due to high reactivity however, and within lithium-sulfur (Li-S) cells specifically, critical issues related to the redox species present during cycling must be addressed to achieve long term cycling. The recent meteoric rise in lithium prices have reinforced the desire to achieve high gravimetric energy density cells without resorting to the use of vast excesses of lithium. In most cell configurations, metallic Li anodes experience rapid degradation due to uneven Li plating and stripping during operation. Lithium's reactivity results in unwanted side-reactions with the electrolyte as SEI is broken and reformed, resulting in an iterative capacity loss. Internal cell resistance rises as broken appendages termed 'dead lithium' accumulate, and most importantly as the increasing surface area of the lithium increases the rate of degradation increases. Direct coating of polymers onto lithium foils is an attractive prospective solution, owing to the potential scalability. Initial work on polymer coatings have been successful, and the field continues to develop. In this work, an nanoporous, superglassy, high FFV polymer (PTMSP) is described that may be cast directly on to lithium. The chemically and mechanically resilient coating exhibits unique polysulfide regulation properties owing to its intrinsic nanopores, and critically, improves the quality of lithium deposition, as verified via total anode mapping using SEM composite imaging. Cells coated with PTMSP exhibit improved stable cycling time, owing to the reduced surface area of the anode associated with even, smooth depositions. This reduced surface area provides fewer metallic Li – LiPS interactions, preventing the loss of charge contributing material and improving cycle life. While traditionally excesses on the order of 500-5000% of lithium metal are used in many cells, this obfuscate this important failure mechanism, and with lithium prices continuing to rise, addressing lithium excess has never been as pertinent. PTMSP@Li allows for the fabrication of cells with extremely low N/P ratios (>3) at practical loadings (4 mg cm-1) and cycled for more than 250 cycles at 0.2C.

A Systematic Study on Structure, Ionic Conductivity, and Air Stability of Li4SnS4–Li3PS4 Electrolytes for All-Solid-State Batteries

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Sulfide solid electrolytes (SEs) have attracted much attention because of their high ionic conductivity and deformability. However, sulfide SEs generate H2S gas when exposed to air. Therefore, the development of sulfide SEs with high air stability is required. The 75Li2S·25P2S5 (Li3PS4) glass has been used in all-solid-state cells as a typical SE due to the relatively high ionic conductivity of 3–4 × 10–4 S cm–1 at 25°C. Moreover, Li3PS4 exhibits the highest air stability in the Li2S–P2S5 system. In addition, Sn-based SEs such as Li4SnS4 show higher air-stability than P-based SEs because they contain air stable Sn–S bonds. However, Li4SnS4 exhibits lower ionic conductivity of ~10–5 S cm–1 at 25 °C. In the present study, we focused on the Li3PS4–Li4SnS4 system as a candidate for achieving high ionic conductivity and high air stability.

We prepared $xLi4SnS4 \cdot (1-x)Li3PS4$ glasses/glass-ceramics by ball-milling and evaluated their structure, ionic conductivity and air stability systematically. X-ray diffraction (XRD) patterns of asmilled samples with x = 0-0.5 and x = 0.6-1 showed hallo patterns and diffraction peaks of hexagonal Li4SnS4, respectively. Glass-ceramics with x = 0-0.5 were prepared by heat treatment of corresponding glass samples. On increasing the x value, lattice parameters of the glass-ceramics increased. Ionic conductivities of glass-ceramics with x = 0.1-0.3 increased to $8-9 \times 10-4$ S cm-1 compared with corresponding glasses. From the results of Raman spectroscopy and PDF analysis, glass-ceramics have ordered PS4 and SnS4 tetrahedra, suggesting that this ordered structure is one of the reasons of high ionic conductivity. To conduct air stability test, H2S gas generation from aqueous solutions of the prepared SEs was monitored. Air stability improved on increasing the amount of Li4SnS4. Moreover, the H2S amount generated from the samples with x = 0.3-1 remained unchanged both before and after the test. Therefore, glass-ceramic with x = 0.3 showed both high ionic conductivity and air stability. In addition, cyclic voltammogram of the asymmetric cell with the sample with x = 0.3 indicated that adding of small amount of Li4SnS4 to Li3PS4 did not degrade its electrochemical stability. To construct all-solid-state cells with dense SE layers and electrode layers consisting of LiNi1/3Mn1/3Co1/3O2 and SE, both layers were sintered at 200 °C. The cell using the glass-ceramic with x = 0.3 exhibited higher capacity than that with x = 0, suggesting that Li4SnS4added Li3PS4 showed high thermal stability to oxide positive electrodes.

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A Trade-off-Free Fluorosulfate-Based Electrolyte Additive Developed for Lithium-Ion Batteries Using Ni-Rich Cathode Materials

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Due to flammability of conventional organic liquid electrolyte, the safety of lithium-ion battery becomes continuously increasing problem to consumer applications of next-generation electric vehicles. Herein, a fluorosulfate-based additive with two symmetric phenylene fluorosulfate moieties is synthesized and it surely exhibits a trade-off-free behavior between flame-retardant and electrochemical performance even with 10 wt% content in the conventional liquid electrolyte of 1 M LiPF₆ dissolved in a mixture of carbonate solvents. The high-energy lithium-ion battery of LiNi₀₋₉Co₀₋₀₅Mn₀₋₀₅O₂(NCM955)||Li adopting the developed additive shows improved capacity retention, reduced interfacial resistance, and enhanced rate capability, compared with the case of triphenyl phosphate as a typical flame-retardant. By analyzing the results of electrochemical performance tests and cathode surface chemistries after cycling, it can be known that the additive significantly decreases the activation barrier of Li conduction to allow faster ionic conduction, and effectively passivates NCM955 surface with metal fluoride- and organics-rich species to protect NCM955 from transition metal dissolution, cracks, and electrolyte penetration into secondary particles, compared with the base electrolyte and triphenyl phosphate-containing cases.

Accelerated Degradation of SiO/Ncm Cell Quick Rechargeability Due to Li Dendrite Formation Caused by State-of-Charge Dependent Failure of SiO Electrode During Normal Cycle History Hyun-Seung Kim¹, Tae Hyeon Kim¹, Sung Su Park¹, Min Su Kang¹, Ye Rin Kim¹, Goojin Jeong¹

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The influence of the SiO electrode during low C-rate applied cycling on the ensuing rapid charge was investigated thoroughly. Significant mechanical and interphase degradation of the SiO electrode occurred with highly utilized SiO electrodes, which resulted in Li plating on the SiO surface under quick charge conditions because of the low open-cricuit voltage of SiO electrode and high charge transfer resistance, which are derived from the Li-trap at SiO and subsequent crack formation of the SiO electrode and SEI growth. At high C-rate applications, the deteriorated SiO electrode is prone to Li plating; hence, the pre-cycling condition of the SiO electrode effects the quick rechargeability of the SiO/NCM811 cell. As a result, to improve the durability of SiO-based quick rechargeable cells, the cycle range of SiO-based cells should be properly manipulated.

Accessing Degradation Mechanisms of Ni-Rich Lnca in State-ofthe-Art Cells for Electromobility

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Ni-rich cathode layered materials (Li[Ni1-xCoxAly]O2 with Ni > 0.5), so-called NCA, are one of today's key chemistries in lithium-ion batteries. They are commonly found in a wide spectrum of commercial applications including electric cars. However, ensuring a stable long-term production of such cells is complicated due to raw material extraction and geopolitical constraints. Therefore, prolonging cell life through exploring degradation mechanisms and adjusting the materials as well as cell design is essential for moving toward sustainable use of NCA-based cells. Generally, contributions of ageing mechanisms to Ni-rich cathode material ageing are evaluated by loss of conductivity (particle cracking, current collector corrosion), loss of active material (structural deterioration and transition metal dissolution), and loss of lithium-ion inventory (electrolyte decomposition). In the given study degradation of NCA material was studied for temperature and state of charge (SoC) dependent ageing processes in application relevant ageing conditions. We analyse commercial state-of-art 2170 cylindrical cells with NCA positive electrode (Ni = 0.9) extracted from Tesla Model 3. The results indicated the high importance of operational temperature and the SoC cycling window. Incremental capacity analysis of full cells verified with half cells has indicated that loss of active material on the positive electrode varied with cycling conditions. From analysing extracted electrodes we registered an increase of Li-ion diffusion resistance by incremental current interruption. Additionally, particle cracking was accessed by scanning electron microscopy and transition metal dissolution studied with inductively coupled plasma optical emission spectroscopy. The outcome shown the most significant degradation related to increase of operating temperature. Additionally, the study accessed ageing inhomogeneities within the cell. The results indicated higher material degradation towards positive cell tab and towards the cell casing within the electrode roll.
Accurate Gas Chromatography-Mass Spectroscopy Analysis of Li-Ion Battery Electrolyte

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Characterization of organic electrolyte components in Li-ion battery cells is important for understanding changes in the composition during cycling. Typically, the electrolyte in Li-ion cells is a mixture of organic solvents such as linear and cyclic carbonates, additives and conductive lithium salt - most commonly lithium hexafluorophosphate (LiPF₆). Organic components in the electrolyte are often characterized using chromatographic techniques such as liquid and gas chromatography. However, LiPF₆ is known to form hydrofluoric acid (HF) when exposed to trace amounts of water and due to the high concentration of the salt (often 1 M or higher), repetitive analyses can damage the detector. In order to protect the instrument, it is important to prevent the formation of HF. In this work, we attempted to remove the LiPF₆ salt from the electrolyte by precipitation using tetraphenylarsonium chloride (Ph_4AsCl). Ph_4As+ is able to form a precipitate with the PF_6- ions (Ph₄AsClPF₆), which can then be removed from the organic components in the electrolyte solution. We examined precipitation of the $LiPF_6$ salt from the electrolyte after dilution with different solvents. We studied the effectiveness of precipitation in three solvents which can be used to dilute the sample for chromatographic measurements - methanol, dichloromethane and dimethyl carbonate. A typical electrolyte in battery research (LP30 - 1.0 M LiPF₆ in EC/DMC=50/50 (v/v)) was used as a model electrolyte during method optimization. Inductively coupled plasma mass spectroscopy (ICP-MS) was used to detect traces of remaining LiPF₆ in the electrolyte. ¹⁹F nuclear magnetic resonance (NMR) was further used to confirm the removal of the conductive Li-salt. Lastly, several common additives were added to the model electrolyte and gas chromatography coupled with mass spectroscopy was employed to examine if the organic components in the electrolyte remained unchanged after precipitation. One commercial battery cell was finally analyzed and the method will be used to study its aging in the future.

Accurately Measuring Cathode Solid State Diffusivity Using Amidr, a Replacement for Gitt Mitchell Ball

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Ion transport within cathode materials is driven by diffusion. While fast cathode diffusion is desired, diffusivity is one of the most difficult cathode material properties to measure. It is, however, a very important property to understand as cathode capacity is often limited by kinetic hindrance in the form of poor diffusivity [1]. GITT (Galvanostatic Intermittent Titration Technique) is a common method used for measuring diffusivity. This technique is accomplished by applying a series of constant current pulses to a cell and then analysing the voltage response. While easy to use, this method has a series of flaws that can make it produce inaccurate results with sources of the error that are not immediately obvious. Notably, GITT assumes the active material takes the geometry of an infinite plane, makes a mathematical approximation in its derivation that requires an inequality condition that is often not formally checked, and doesn't account for the double layer capacitance or charge transfer resistance found at the cathode-electrolyte interface [2]. But most importantly, GITT does not verify that the voltage loss mechanism being observed is primarily due to solid state diffusion. Other techniques such as PITT (Potentiostatic Intermittent Titration Technique) and EIS (Electrochemical Impedance Spectroscopy) exist but come with their own issues. PITT is very similar to GITT but employs a constant voltage pulse rather than a constant current pulse and retains many of the same flaws [3]. EIS avoids many of the flaws of GITT such as not accounting for the double layer capacitance and charge transfer resistance, but is accomplished using alternating current as opposed to the direct current which is applied to cells in regular use cases [4]. This means that phenomena that require direct current to be produced are not observable with EIS.

AMIDR (Atlung Method for Intercalant Diffusion and Resistance) is a direct current method for accurately measuring solid state diffusivity and charge transfer resistance that accounts for and eliminates the flaws of GITT. Named after Sven Atlung, this method is founded on mathematics Atlung produced for a precise, analytic solution for particle diffusion in a spherical particle. Atlung's results were incorporated into an earlier version of this method made in this lab named AMID (Atlung Method for Intercalant Diffusion) [5]. AMID established the specifics of the experimental cell design, framework of the calculation program, and the decision to evaluate multiple data points at once by fitting them along a curve. This last element is essential for verifying diffusivity as the primary voltage loss mechanism as other loss mechanisms will produce poor fits. A series of alterations and additions were made to produce AMIDR including changing the cell testing protocol to a series of current pulses similar to GITT, processing of the data to remove the impact of ohmic resistance and double layer capacitance, and most importantly, expanding the mathematics of the model to measure solid state diffusivity and charge transfer resistance simultaneously. AMIDR is capable of being used on a variety of different cathode materials from LMO spinel to Ni-rich layered oxides and further work is underway to investigate the association between the charge transfer resistance and the cathode surface reconstructed layer.

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Addressing Key Challenges in the Development "Beyond Li-Ion" Chemistries <u>Giuseppe Antonio Elia</u>¹, Claudio Gerbaldi¹

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Renewable energy production is characterized by intermittent power output and requires large-scale applications to improve energy storage capability (currently, less than 1% of the electrical energy production can be stored). Developing low-cost and environmentally friendly electrochemical storage systems characterized by high performance is of fundamental importance for a sustainable energy economy. The currently most mature battery technology is the lithium-ion battery, considered one of the most appealing candidates as a power source for electric vehicle applications. However, the large-scale application of lithium-ion batteries is currently under discussion due to the limited lithium and certain transition metals such as Co and Ni resources. Several other metallic anodic materials such as sodium, potassium, calcium, magnesium and aluminium [1-3], characterized by a higher abundance of lithium, have been considered suitable candidates for electrochemical storage devices in replacing lithium systems. Notably, significant efforts are being devoted to understanding and addressing key challenges in developing these so-called "beyond Liion" chemistries, and substantial insights into their storage and failure mechanisms have been obtained over the past few years thanks to advanced characterization and computation/modelling techniques. An overview of our activity in "beyond Li-ion" batteries field and an evaluation of the capability of this technology will be presented. [4–8]

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Analysis and Modeling of Side Reaction Mechanisms Inside a Lithium-Ion Battery During Thermal Runaway Through the Design of Experiment With Combination of Battery Components <u>Minuk Kim¹</u>, Jaeyoung Jeon¹, Jongsup Hong¹

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Although a lithium-ion battery exhibits excellent performance compared to other secondary batteries, it has a safety risk of gas generation and fire upon thermal runaway when being used in various misuse conditions. If the internal materials of the battery are exposed to an abnormally high temperature, several side reactions occur, followed by gas generation and explosive heat generation. To diagnose and analyze the thermal runaway phenomena, it is essential to understand what side reactions appear inside battery materials such as a cathode, an anode, an electrolyte, and a separator. To do so, it is very useful to make a reliable model to analyze thermal runaway given the safety issue and high costs of large-scale experiments.

In this research, we conduct experiments through the design of experiment with combination of battery components and obtain the data of reaction temperature and calorific value by using a differential scanning calorimeter (DSC). Qualitative and quantitative analyses of gas generated from side reactions are ensured using an online thermogravimetry-mass spectrometer (Online TGA-MS). Based on these measurements, we identify the various side reactions inside the battery.

Using the experimental data, a variable indicating the reaction rates of individual reactions is secured using the Kissinger analysis. Applying the activation energy and the preexponential factor for Arrhenius equation, the transient 0-dimensional model is developed for simulating heat flow and gas generation rates. For the reliability of this model, it is validated compared to the DSC and TGA results. In addition, we analyze the variation of volume fractions of each phase inside the lithium-ion battery according to temperature for simulating electrochemical performance degradation depending on thermal runaway stages. Furthermore, the change of internal pressure is evaluated through gas generation using this reaction model.

As a result, there are four side reactions at the cathode side, such as vaporization of electrolyte, structure degradation of NCM, electrolyte combustion, and carbon combustion. Oxygen for these combustion reactions is generated through structure degradation of NCM. Also, at the anode side, vaporization of electrolyte, SEI decomposition and regeneration, and binder reaction with lithium-ion occur. Because of these consecutive reactions, the volume fraction of the active material and the electrolyte decrease continuously. However, the volume fraction of the gas phase increases at the same time, increasing the internal pressure under the fixed volume condition and finally making the battery pouch to be exploded in real situation. This reaction model is intended to be used in the side reaction-electrochemical coupled model of a lithium-ion battery, which can interpret thermal runaway in the future.

Anion-Polarisation–Induced Short-Range-Order in the Heterocationic Lithium-Ion Cathode Material Li2FeSO

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Short-range order in cation-disordered cathodes can have a significant effect on their electrochemical properties. Here, we report a combined computational and experimental study of short-range order in the cation-disordered antiperovskite Li₂FeSO, using density functional theory, Monte Carlo simulations, and synchrotron X-ray pair-distribution-function experiments. We predict partial short-range cation-ordering characterised by preferential OLi₄Fe₂ oxygen coordination, with a weak energetic preference for cis-OLi₄Fe₂ over trans-OLi₄Fe₂ oxygen coordination geometries. The preference for cis-OLi₄Fe₂ oxygen coordination and the presence of other non-OLi₄Fe₂ oxygen coordination geometries results in long-range disorder, in agreement with previous experimental data. This contrasts with the predictions obtained from a simple ionic "point-charge" model, which instead predicts almost exclusive trans-OLi₄Fe₂ oxygen coordination and corresponding long-range crystallographic order. The absence of long-range order in Li₂FeSO can therefore be attributed to the relative stability of cis-OLi₄Fe₂, and other non-OLi₄Fe₂ oxygen-coordination motifs, relative to the trans-OLi₄Fe₂ coordination favoured by point-charge electrostatics. We show that this effect can be attributed to the polarisation of oxygen and sulfur anions in polar coordination environments, with these resulting dipoles lowering the net electrostatic energy, and thereby stabilising polar anioncoordination geometries. We expect this effect to be generally applicable in cation disordered materials where the cations have different formal charges. This result shows how going beyond simple point-charge models can be necessary to predict or understand local structure in cationdisordered materials, and highlights the potential role of anion polarisation in these materials in directing short-range order and Consequently explaining the presence or absence of long-range order.

Atomic-Scale Investigation of Doping Effects in the Anti-perovskite Na3OCI Sodium-Ion Battery Material

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Solid-state batteries present potential advantages over their liquid-based electrolyte equivalents, including enhanced safety and increased energy density. In the search for novel solid electrolytes, the anti-perovskite family of materials are attracting growing interest. However, while there is significant work on Li-rich anti-perovskites, their Na-based counterparts and the atomistic effects of aliovalent doping on these materials are not fully characterised. Here, we investigate the effects on Na-ion conductivity of doping with divalent (Mg, Ca, Sr and Ba) and trivalent cations (Al and Ga), and of possible dopant-vacancy clustering in the anti-perovskite Na₃OCl by employing atomistic simulation techniques. Our results highlight the potential of Mg(2+), Ca(2+), Al(3+) and Ga(3+) doping due to their favourable incorporation and increased Na-ion vacancy concentration. Local defect clustering and binding energies are analysed, and such effects inhibit Na-ion conductivity in the doped Na3OCl solid electrolyte at operating temperatures. These results provide a framework to guide future work on anti-perovskites to enhance their solid electrolyte properties.

Atomistic Insights Into New Hydroxy Sulfate Polyanionic Insertion Materials for Li-Ion Batteries

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Iron-based polyanionic cathode materials for Li-ion batteries are possible alternatives to the currently used cathodes because of their earth-abundant elements and an easier synthesis protocol compared to Ni/Co-based layered oxides. Here, we investigated the electrochemical and electronic properties of the orthorhombic (o-) LiFeSO4OH cathode material using combined experimental and computational techniques. We synthesized the moisture-resistant o-FeSO4OH compound from earth-abundant sustainable precursors via a low-temperature hydrothermal synthesis route. This material functions as a robust 3.2 V Li-based battery cathode and provides a higher overpotential and moderate rate kinetics compared to the monoclinic-FeSO4OH reported previously. From the experimental structure of the o-FeSO4OH phase, we predicted the unknown lithiated structure using density functional theory calculations along with ab-initio molecular dynamics. We showed that intrinsic defects such as the Li Frenkel and anti-site (Li/Fe) pairs are unfavorable to form and unlikely to block Li diffusion. We then calculated the migration barrier height along different pathways. Our results suggest better Li mobility in two different directions due to lower energy barriers. These findings provide valuable information to guide the design of more sustainable cathode materials.

Ceramic-Coated Separator With Competitive Electrochemical Properties for Lithium-Ion Batteries

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To the present, polyethylene (PE) and polypropylene (PP) porous membranes have been used as separators for preparing lithium-ion batteries, which are manufactured through various dry or wet processes. Aligned with that, recent studies have revealed the beneficial use of ceramic-coated membranes that could open up a new chapter in manufacturing robust and safe separators and assist in enhancing the stability of the Li-ion batteries. In the other words, the high-temperature tolerance of separator membranes can be translated to the extension of their application for heavy-duty purposes by combining the heat resistance of inorganic powders with the characteristics of the membrane.

In this work, a novel ceramic-coated separator with reasonably high thermal stability has been successfully obtained through various coating techniques employing high purity alumina (HPA) particles with different particle sizes and morphology. A polypropylene separator is used as the coating substrate and the HPA and the PVDF-HFP are used as the inorganic coating and binder. To prepare a slurry, the mixing ratio of 10:1:44 wt% (HPA: PVDF-HFP: Acetone) was applied, under continuous stirring for 5 h at 50 °C. To prepare the wet coated separators, two different methods including blade coating, and spin coating were utilized. Depending on the chosen technique, particle size, and morphology the thickness of the as-prepared separator coating could be modified to a range of 5-30 mm. To evaluate the custom-coated separators the obtained results were compared with a ceramic-coated Celgard separator as the benchmarking reference. Scanning electron microscopy (SEM) and 3D optical profilometer are carried out to study the surface and cross-sectional morphology of the coated separators. Moreover, the cycling performance of the custom-coated separators was investigated using a high-energy Ni-rich Li-ion battery (Graphite | NMC811) employing carbonate-based electrolyte (1 M LiPF6 in EC: DMC (3:7 wt/wt) + 2% VC coin cells).

It has been shown that the HPA particle size, morphology, and coating technique have a significant impact on obtained surface morphology, thickness, and the cycling behavior of the samples. In addition, it was demonstrated that the ceramic coating can sensibly improve the heat resistance of the separators and reduce the separator shrinkage at a high temperature (120°C) to almost zero percent. Moreover, stable long-term cycling performance has proved a promising cycling behavior of the ceramic-coated separators in addition to a very similar rate capability performance to the references.

Complementary Operando Detection of Metallic Lithium Deposition in Lithium-Ion Batteries With High Sensitivity

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The specifications for automotive battery systems comprise partially contradictory aspects: a fastcharging capability and a long lifetime. To meet both, in the long run, metallic lithium deposition needs to be avoided while the lithium-ion battery is charged at maximum rates. In the first place, the process of and the prerequisites for lithium deposition need to be better understood. Known in the literature is, that the intercalation of lithium ions into the host lattice of the negative electrode is kinetically limited at high states of charge (SOC) and low temperatures. Under these conditions, high current densities lead to a surface film formation of metallic lithium on top of the graphite surface and finally on the SEI. Lithium deposition is partially reversible via chemical intercalation or stripping. Nonetheless, isolated (dead) metallic lithium and lithium chemically bound in new passivation films lead to an irreversible loss of cyclable lithium and hence an accelerated capacity loss.

To analyse the occurrence of lithium deposition and, in the best case, to observe its onset, the goal of this work is to detect metallic lithium deposition operando with a high sensitivity and with complementary non-destructive electrochemical methods. By means of these detection methods, the final goals are to avoid an accelerated aging at fast-charging processes and to learn on the limits of the charging current as a function of temperature, SOC, and state of health (SOH). If the rate capabilities according to the onset of lithium deposition are known, the performance of recuperation and fast charging can be extended while the charging times get further reduced.

The measures to detect lithium deposition can be grouped into two categories: retrospective methods that provide evidence of deposited lithium after the charging event, and introspective methods that deliver indications of the onset of or the ongoing lithium deposition during the charging process. For the retrospective approach we are using voltage measurements during the relaxation after fast charging events and a differential voltage analysis that looks for the occurrence of a characteristic minimum. The application of low current discharge immediately after the charging phase, and hence a stripping of plated lithium, enables a quantification of the reversibly deposited amount of metallic lithium.

Complementary to the simple voltage measurement we show that the measurement of the cell's impedance at characteristic and preselected frequencies during the relaxation yields a much higher sensitivity at shorter observation times. The impedance-based detection is supported by dynamic models of the relaxation behaviour after uncritical charging. Anomalies, i.e., deviations from the expected course of the impedance are observed and enable a detection of metallic lithium deposition. A second complementary approach is to measure the dilation of the cells during charging and relaxation. Graphitic electrodes present a difference in thickness if lithium ions get intercalated or form surface films. Especially the chemical intercalation of metallic lithium depositions leads to a distinctive change of the cell's thickness during relaxation. This behaviour can be used to detect metallic lithium deposition in the previous charging process with a sensitivity superior to the voltage relaxation analysis.

Measuring and analysing the impedance of the cells at characteristic frequencies during the charging process is, furthermore, used as a promising approach for an introspective detection. Tracking the

polarisation effects of single electrode processes in combination with an electrochemical model allows a mechanistic analysis of the occurring anomalies. A sophisticated algorithm is developed that leads to a detection with an even higher sensitivity compared to the retrospective methods. Additionally, the method enables an automated identification of the onset of lithium deposition during the fast charging of the cells.

To conclude, we elaborated different complementary, non-destructive methods for the detection of lithium metal deposition in lithium-ion batteries both retrospectively, i.e., immediately after the charging phase, and introspectively, i.e., during the charging phase. All presented methods are validated by extensive test series, have a high sensitivity and an applicability beyond lab experiments. The volage and impedance-based methods are ready to be employed in battery management systems of the next generation.

Comprehensive Study of the Impact of MoS2 Structure / Reactivity Relationship on the Polysulfide Conversion in Lithium Sulfur Batteries

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Nowadays, human activities are increasingly dependent on electricity supply for a wide array of transport and stationary applications, which implies to develop efficient ways storing electricity at large scale. Batteries are good candidates and are already ubiquitous in smartphones, laptops, or electric vehicles. To meet the requirements of these new applications, it is essential to increase the energy density. Unfortunately, current lithium-ion batteries are reaching their performance limits and the exploration of new chemistries is required. Among next-generations, Lithium-sulfur (Li-S) batteries are attracting increasing attention. Indeed, Li-S batteries owing to their high theoretical energy density (2600 Wh.kg-1) have the potential to store more energy (about 3 times practically) than Li-ion batteries. However, several challenges hinder their commercial development. Amongst those, the "shuttle-effect" is one of the major drawbacks. It consists of a back-and-forth movement between electrodes of the dissolved lithium polysulfides (Li2Sx $8 \le x \le 2$), produced during sulfur reduction (lithiation/ discharge), giving rise to low active sulfur utilization, poor coulombic efficiency, and rapid capacity decay. In literature, many strategies are proposed ranging from protective Li passive layers to electrolyte separator functionalization, via polysulfide entrapment in specificallydesigned host materials (e.g. carbon hollow sphere). For the latter, an interesting material is MoS2. Indeed, MoS2 materials has a large range of applications from catalysis (hydrotreatment reactions), to electrocatalysis, photocatalysis, sensors to tribology because of its excellent electrical, optical and magnetic properties. Its versatility enables to play on its structures and properties. It has proven also to be a good candidate for rechargeable batteries. Therefore, a synergetic effect may be effective by designing a carbon based host comprising MoS2.

Here, we proposed a systematic study of the impact of the structure / reactivity relationships of MoS2@porous carbon materials on the polysulfide adsorption. MoS2 morphology, type of edges, slab length, metal-support interactions are modified to improve the type and number of actives sites for polysulfides interactions. We aimed to better understand the polysulfides anchoring mechanism to design an optimized MoS2@ porous carbon structure to i) limit polysulfide shuttling and ii) favor their reduction into Li2S. The material characterizations, adsorption capacities as well as the electrochemical performances of the MoS2@porous carbon sulfur positive electrode will be presented.

Correlation Between Morphology, Surface Properties and Electrochemical Performance of Ni-Rich Cathode Active Material in Lithium Ion Batteries

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Ni-rich NCM is a promising cathode active material (CAM) for next-generation lithium-ion batteries (LIBS) due to its high specific capacity. However, high nickel contents lead to increased reactivity but thus enhanced degradation. This means that the interface between electrolyte and particle plays an important role for possible degradation processes. So, the particle morphology and thus the contact area to the electrolyte are highly relevant and significantly influence the capacity retention and electrochemical performance of Ni-rich CAMs. This also explains the increasing interest of industry in the use of single-crystalline materials instead of their polycrystalline counterparts, e.g. in electric vehicles.

In this study, we investigate the degradation mechanisms leading to degradation of NCM831106 depending on crystal morphology in liquid LIBs. By applying different synthesis parameters to the same precursor, a comparable material with different morphologies ranging from poly- to singlecrystalline shapes is obtained. A number of electrochemical methods including galvanostatic intermittent titration technique (GITT), impedance spectroscopy (EIS) and analytical methods are used to study the degradation mechanisms as function of the NCM morphology. Furthermore a coating of Al_2O_3 is applied to different morphologies by Atomic Layer Deposition (ALD) and its influence on particle cracking, loss of active material and impedance increase is evaluated.

The fundamental understanding of degradation mechanisms and the influence of properties of cathode active material allows to optimize them in order to improve the performance of LIBs. By observing the effect of the same protective coating on different morphologies a deeper understanding of the functional mechanisms of coatings is gained.

Cycling Performance and Safety Characteristics of NMC811/G-si Battery Cells With Optimised Electrolyte Formulations

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While current lithium ion battery technology is reaching a performance plateau in terms of achievable capacity, power, energy density and also safety [1], recent developments have shown that silicon could be a viable alternative anode material for enhancing the performance of nextgeneration LIBs [2]. Compared to the ubiquitous graphite anode (LiC6) with 372mAh g-1 specific capacity, Si has a superior specific capacity of 4200 mAh g-1 when fully lithiated (Li22Si5) and 3580 mAh g-1 for Li15Si4 along with other advantages such as abundance and low lithiation voltage (-0.2 V vs. Li/Li+). Lithium alloying (charging) and dealloying (discharging) of amorphous Si, however, is accompanied by large volume expansions of 280 % (Li15Si4) and 400 % (Li22Si5), respectively, and the resulting strain leads to mechanical problems of cracking, pulverisation, contact loss and ultimately capacity loss as a major shortcoming of Si anodes [3-5]. Various approaches have been taken in the past to alleviate these mechanical problems by designing composite electrodes, e.g. silicon in graphite composite anodes, and the use of nano-sized materials but these do not address remaining issues concerning the integrity of the solid electrolyte interphase (SEI) during long term cycling of Si anodes. One of principal approaches taken to stabilise the SEI layer formation are the blending of common electrolytes with 1-10 % of SEI forming and modifying additives [3, 6, 7] orthe use of ionic liquid electrolytes (ILELs)[8, 9].

In this work we report our performance evaluation of cycling classic carbonate-based electrolytes as well as ionic liquid based electrolytes (ILELs) in NMC811/Graphite -15% Silicon cells under various conditions, along with Differential Scanning Calorimetry analyses of electrode surfaces in contact with the electrolyte. Of the electrolytes, EC/EMC + 1.2 M LiPF6 formulations containing FEC/VC or LiFSI/VC combinations showed superior performance. Safer to operate ILELs were found to be compatible with the same electrode configuration and at moderate cycling rates, their discharge capacities were only 15% lower compared to the classic electrolyte formulations mentioned above.

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Data-Driven Tools for Accelerating Battery Innovation Across Spatio-Temporal Scales Arghya Bhowmik

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Batteries are complex electrochemical systems where performance, durability and reliability depend on a broad range of phenomena spread over many spatio-temporal scales. Thus data-driven approaches toward designing better batteries need to take a multi-modal approach covering experimental and computational data sources. Additionally, we must accelerate both materials and systems design. Here I discuss some specific examples of how we have used simple models (linear or gaussian regression) and complex architectured neural networks to accelerate materials design and battery system optimization - (a) graph neural networks for accelerated battery materials simulations at electron density level (b) symbolic regression for the discovery of ionic transport laws in battery electrolytes (c) differentiable sparse Gaussian process regression models for capturing local sensitivities in battery solid-electrolyte-interphase growth based capacity fade towards costeffective and uncertainty controlled multiscale simulations (d) Long short-term memory networks with epistemic and aleatoric uncertainty for early prediction of battery degradation trajectory and its application for accelerated battery development.

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- [4] DOI:10.26434/chemrxiv-2022-h1g21

Depth-Profiling the Li Intercalation in Graphite Electrodes for Li-Ion Batteries: Model and Experiment

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Li-ion batteries (LiB) are now ubiquitous, they already power a wide range of devices and are expected to play a key role in the incoming energy transition. In LiBs, several physico-chemical processes dictate the behavior of the Li ions as they travel from one electrode to the other, such as liquid-phase diffusion in the electrolyte, insertion reaction at the electrode/electrolyte interface, and solid-phase diffusion in the electrode active materials. These processes have to be correctly described to achieve accurate modelling of the behavior of the LiB, paving the way to predictive simulations of innovative cell designs for key operating conditions. However, some parameters of the model are hardly accessible independently and the model must be validated by comparison with experiments. In particular, predicting the distribution of the Li is relevant for two reasons: (1) heterogeneous distribution of Li can have adverse effects on the LiB lifetime and performances (e.g. due to local overpotentials), (2) thicker electrodes are needed to improve the overall energy density and larger electrical currents are needed for power performances (e.g. fast charging), yet these two effects will typically favor heterogeneous Li distribution.

In this study, we performed simulations and depth-resolved measurements of the Li concentration in a 80µm thick electrode made of graphite. The numerical model is based on the porous electrode formalism proposed by Newman coupled with a solid-solution model for lithium diffusion in the particles. Such a model cannot describe the multiple graphite phase transitions, yet it has already been shown to suitably capture some of the electrochemical behavior of LiB. In our case, the model predicted a triple succession of homogeneous and heterogeneous Li distribution across the thickness of the graphite electrode, with the maximum heterogeneities happening during the plateaus of the graphite equilibrium voltage curve..

In order to confirm experimentally this succession of heterogeneous/homogeneous distribution, we developed an operando XRD electrochemical cell that was used on ID13. Combined with the micronsized beam available on the microfocus endstation, the high photon flux of ID13 and the fast and large 2D detector, we could measure in real-time the local XRD patterns along the depth of the electrode during delithiation at C/5. We evidenced unambiguously the different stage composition during the delithiation. To obtain the local Li concentration, we used a statistical approach linking the mean distance between consecutive graphene sheets and the mean Li concentration.

For the lower concentrations, there was a remarkable match between the simulations and the measurements, with two successive homogeneous/heterogeneous Li distributions clearly observed. Yet, we could not observe experimentally the heterogeneous Li distribution that was predicted to occur at the stage 1 to stage 2 transition. This implies that the relative weights of transport in the electrolyte, insertion reaction at the graphite/electrolyte interface and diffusion in the graphite have to be different in that range of Li concentration. Bazant had shown the auto-catalytic or auto-inhibitory effect of asymmetrizing the usual Butler-Volmer description of the exchange current at the electrode material interface. We thus empirically reduced the exchange current in the high concentration range in our model, effectively slowering the deintercalation process in the high concentration range, and obtained a homogeneous Li distribution over the whole stage 1 to stage 2 transition. The modified model could thus achieve a good agreement with the experiment over the

whole lithiation range, spurring further research on the effect of C-rate, considering other electrode materials, and more advanced models for lithium diffusion and intercalation in multi-phase materials including phase-field.

Double Layer Chemical Structure Analysis via Advanced Electrogravimetry on Model LixMoO3 Electrode

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A major feature of the Electrolyte/Electrode Interface (EEI) that affects charge storage in Lithium-ion batteries is the electrical double layer (EDL), but most of the available experimental approaches for probing its structuration have limitations due to electrical field and redox reactions disturbances, hence explaining why it is frequently overlooked. Herein we show that this is no longer true by using an advanced Electrochemical Quartz Crystal Microbalance (EQCM) based method in the form of acelectrogravimetry. For proof of concept, we studied the effect of various solvent/salt combinations, differing in their dipole moment and size/weight respectively, on the structure of the EDL forming at the EEI of LixMoO3. We show that a significant amount of solvated lithium ions and anions contribute to charge compensation at the interface and by varying the nature of the solvents (cyclic vs. non cyclic), we provide a solid experimental proof of the direct relationship between the ions' solvation and solvent polarity. Moreover, we demonstrated a disappearance of the anionic motion in the less polar solvent (DMC) most likely due to plausible formation of contact ion pairs and agglomerates at the EDL level. Altogether, ac-electrogravimetry, when combined to classical EQCM, stands as an elegant and powerful method to experimentally assess the chemical structure and dynamics of the electrical double layer. We hope that the community will start to adopt it to better engineer interfaces of electrochemical energy storage devices.

Drawing the Landscape for Li+ Diffusion in Solid-State Electrolytes <u>Amber Mace</u>

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The development of novel cost-efficient multi-scale modelling strategies for modelling the ion diffusion in solid-state electrolytes can provide ground-breaking insight into the various (compositional and other) factors that govern the conduction mechanisms. This will also provide an understanding of the tuning strategies that control the transport mechanisms in these materials.

While systematic studies of large number of materials are needed for computational driven materials discovery the cost of (brute force) molecular dynamics, in particular for systems with low diffusion coefficients, can be prohibitively expensive. An alternative is to construct a statistical model by computing the hopping rates between adsorption sites using transition state theory and kinetic Monte Carlo. For large-scale screening this requires the automatic detection of the transition states between the adsorption sites along the different diffusion paths.

I will present my work on the development of an algorithm based on a topological analysis of the energy landscape felt by the mobile ion within a crystalline framework. This multiscale modeling approach is driven by a coarse-graining procedure that, in an automated approach, constructs a kinetic lattice model through an efficient and robust transition state search and that predicts the ionic conductivity of a material at an accuracy comparable to molecular dynamics, yet at only a fraction of the computational cost. I will further discuss how we are working towards extending this framework to non-crystalline solid-state electrolytes (i.e., polymer-based) as well as composites consisting of several phases.

Dynamically Disproportionating Structure, and High-Valence Doping of Prototype Model Cathode LiNiO2

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Nickel-rich layered cathodes, Li(Ni,Mn,Co)O₂ (NMC), project to be the workhorse of high-power electric-vehicle batteries in the coming decade. As such, understanding and extending their capacity and performance limitations rapidly translates to industrial impact. The performance, defect chemistry and limitations of NMC materials are driven by the chemistry of nickel, which motivates studies of the less stable prototype model cathode, LiNiO₂ (LNO). Because of its covalency, delicate synthesis, and ubiquitous antisite defects, understanding LNO remains a challenging problem.

Here, we report a comprehensive study of the dynamic electronic and magnetic structure of LNO. At room temperature and below, the material undergoes partial disproportionation and consists of three Ni species, with spins 1, 1/2, and 0, corresponding to formal charges 2+, 3+, and 4+. This disproportionation is frozen-in at low temperatures, dynamic on the picosecond timescale at room temperature, and melts to a uniform formal-3+ composition only at elevated temperatures. We present high-resolution ab initio molecular dynamics simulations including a first-of-a-kind visualization of vibration-coupled spin and charge transfer in LNO, and compare simulation results to bulk-sensitive core-level spectroscopy measurements.

This work reconciles many literature observations, such as the origins of lattice distortions and thermally activated p-type electronic conductivity in LNO. We provide a platform for the precise understanding of the nickel point-defect chemistry in industry-leading battery cathodes. We extend this work to describe the incorporation and phase-equilibria of high-valence dopants in LNO, such as W and Ta. Such dopants have seen success in improving the cycle life of Ni-rich cathodes despite their negligible solubility in the bulk layered oxides. We show that the incorporation of high-valence dopants is self-limited by the extensive Ni disproportionation they induce, but that surface phase equilibria are favorable to Li transport. Furthermore, co-doping with excess Li is favorable and provides an opportunity for increasing charge densities.

Electrochemical Characteristics and Degradation Analysis of NCM523 With All Solid State Three Electrode Cells

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Introduction

All-solid-state lithium-ion batteries (ASS-LIBs) have been studied because of their high safety standards and power characteristics. Although it is essential to clarify the degradation mechanisms of ASS-LIBs considering their practical application, there are few methods that can quantitively evaluate the degree of degradation. Electrochemical analysis used for conventional LIBs has advantages in quantitively evaluating battery performances with high time resolutions and versatility in a non-destructive manner. Especially, Electrochemical Impedance Spectroscopy (EIS) with three-electrode cells is a potent tool to separate each electrochemical elementary process in working electrodes and quantify them as the form of resistance and capacitance without the influence of counter electrode polarization. We fabricated reference electrodes valid for EIS measurements in the ASS-LIBs systems. In this study, we applied the reference electrodes to the all-solid-state three-electrode cells of LiNi0.5Co0.2Mn0.3O2 (NCM523), which is widely used as positive electrode material in LIBs, and examined the cyclability.

Experimental

Reduced lithium titanate (R-LTO) mesh reference electrodes were fabricated following the previous work. Then, we fabricated the all-solid-state three-electrode cells composed of the R-LTO as reference electrodes, lithium-indium alloy (Li-In) as counter electrodes, and NCM523 composites as working electrodes. The NCM523 composite electrodes were comprised of LiNbO3-coated NCM523, solid electrolyte (SE) (Li2S-P2S5-LiI (LPSI, glass-ceramics) or Li6PS5CI (LPSCI, argyrodite-crystalline), and carbon. Current collectors were aluminum foils for working electrodes and copper foils for counter electrodes. Electrochemical measurements were carried out with a multichannel electrochemical system (VSP-300, biologic).

Results and discussion

In the EIS measurements with the all-solid-state three-electrode cells, the combined impedance of the working electrodes and the counter electrodes agreed well with the cell impedance measured with the two-electrode connection in a wide frequency range below 1 MHz, which shows that we separated the cell impedance into two single-electrode components . It is noteworthy that Li-In counter electrode impedance affects cell impedance significantly. Nyquist plots of NCM523 composite electrodes showed several components. We assign RSE (intercepts) to ionic transport resistance in SE layers in the view of activation energy. The large semicircle around 1 kHz is asscribed to the charge-transfer resistance RCT at the SE | NCM523 interface because of its SOC dependency. The activation energy of RCT is lower than that of conventional LIBs. A small semicircle around 1 Hz (Rx) is probably assigned to contact resistance at the composite electrode | current collector interface.

In charge/discharge cycle tests, the resistance value of RCT+RX increased significantly, and the frequency-response changed. In addition, there were thick deposits on the LPSI|NCM523 interface in cross sectional SEM/EDS images of the degraded electrode, so we attributed the main

degradation factor of the LPSI-NCM523 systems to the oxidative decomposition at the LPSI|NCM523 interface and the increase of the resistance. We will also report the results of the LPSCI systems, which are more stable against oxidation than the LPSI systems.

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Elucidating the Morphology of Partially Lithiated Silicon Microparticles Using Transmission Electron Microscopy

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Because of its high theoretical capacity of 3578 mAh/g, silicon is one of the most promising negative electrode materials for next-generation lithium-ion batteries. One major drawback, currently hindering the widespread commercialization of silicon, is its large volume expansion of ~300% which is the root cause of the main degradation mechanisms of silicon anodes that limits its cycling stability.

Partial lithiation can limit the volume expansion of silicon; for example, using only 30% of its theoretical capacity decreases the volume expansion to only ~100%. This strategy drastically limits the degradation, enabling cycling of silicon microparticle (~2 - 5 μ m diameter) based anodes for over 200 cycles in full-cells. The partial lithiation of polycrystalline silicon microparticles results in a two-phase region of amorphous lithiated silicon and polycrystalline unlithiated silicon. It could be shown by X-ray diffraction analysis that even upon continuous lithiation/delithiation, this two-phase microstructure is maintained, so that it was postulated that an initially polycrystalline silicon microparticle would transform into a particle with a polycrystalline core and an amorphous shell. Furthermore, it was shown that if the lithiation potential stays above 170 mV vs. Li+/Li, the ratio of polycrystalline to amorphous silicon remains stable over extended charge/discharge cycling.

In this study we show the morphology of the amorphous and the crystalline phases in partially libilitated polycrystalline silicon microparticles. We investigate this by transmission electron microscopy, comparing lamellae cut from an electrode after one lithiation/delithiation cycle with lamellae cut from a pristine electrode. The Bragg diffraction induced contrast reveals grain boundaries within the polycrystalline microparticles and stacking faults inside the crystallites of the pristine and delithiated lamellae.

Using selected area electron diffraction (SAED), we can determine the orientation of different crystallites. After one partial lithiation and a full delithiation, we can see amorphous delithiated regions as homogeneous gray regions without bending contours. The amorphous structure was confirmed with SAED. The delithiated particles show a structure which is more complex than the postulated core shell model: the amorphous region was not only found around the outer surface of the polycrystalline microparticles, but also along grain boundaries and stacking faults.

These results give a deeper insight into the lithiation mechanism of partially lithiated silicon, which is more complex than previously expected.

Elucidation of Failure Mechanism and the Importance of Stack Pressure in the Li Metal Solid State Battery

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Solid state battery is long regarded as a promising candidate for a safer electrochemical energy storage device and intensive research has been conducted in recent years. Coupled with Li metal anode, achieving high energy density could be possible. Among the solid electrolyte, the sulfide solid electrolyte shows comparative Li-ion conductivity with non-aqueous electrolyte. However, the critical current density (CCD) is relatively low in the sulfide-based Li metal solid state battery (LMSSB), which is a big issue at present. Although the dendrite issue has been under investigation for a long time, there is still a lack of fundamental understanding and solutions for long stable performance are limited.

Here multi-characterization methods, including operando, in-situ scanning electron microscopy, and ex-situ focus ion beam scanning electron microscopy were employed to investigate the failure mechanism in Li6PS5Cl based LMSSB. The Operando method is a straightforward way to give us an insight view of the failure mechanism. Cracking of the solid electrolyte was identified as the dominant failure reason. Furthermore, we found that cracking was initiated during the plating process and the situation would be worse when an inhomogeneous plating occurred.

Due to a solid-solid contact of the Li/solid electrolyte interface, stack pressure is one vital parameter. In this report, we further give details of the relationship between the stack pressure and the battery performance, and some design principles. Our results unambiguously demonstrate that cracking could cause a disastrous effect on LMSSB, indicating that more attention should be paid on the mechanics of the solid electrolyte.

Evaluation and Improvement of the Stability of Poly(ethylene Oxide) Based Solid-State Batteries With High Voltage Cathodes

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Solid-state lithium-ion batteries (SSBs) are known to provide superior safety and increased energy density compared to conventional lithium-ion batteries (LIBs) with liquid electrolyte. However, for commercial applications SSBs based on poly(ethylene oxide) (PEO) have only been combined with LiFePO4 (LFP), a low-voltage active cathode material (CAM). With high voltage CAM such as LiNi1 x yCoxMnyO2 (NCM), which are essential for high energy applications, PEO-based SSBs experience "noisy voltage" related cell failure in the initial cycles. In our investigations, we confirm that poor mechanical properties of low molecular weight PEO are responsible for "noisy voltage" related cell failure independently of the applied voltage. This failure could be solved by a practical modification of the SPE using higher molecular weight PEO, resulting in improved mechanical properties and appropriate conductivities of the SPE. As a result, stable long-term cycling could be achieved for NCM-based SSBs. In contrast to several publications, no oxidative decomposition products could be detected by Fourier transform infrared spectroscopy (FTIR) in this case, indicating that PEO-based SPEs with high voltage cathodes are more stable than previously thought. However, we could show that cell leakage can lead to these undesirable oxidative degradation processes reported in the literature. Nevertheless, electrochemical impedance measurements in a three-electrode setup show that the NCM/PEO interface is still the Achilles' heel in PEO-based SSBs at high voltages. Overall, our results shed light on the apparent inconsistencies in literature and improve the stability of solid-state batteries based on poly(ethylene oxide).

Evolution of Spinel LiMn2O4 Single Crystal Morphology by Tuning Oxygen Partial Pressure

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Batteries are playing a pivotal role in sustainable development and conventional cathode materials (LiMO₂ where M= nickel, cobalt, and manganese) are in massive demand for electric vehicles (EVs). However, the scarcity of cobalt and nickel materials has sparked an interest in alternative cathode materials development, which may be needed for complete conversion to clean energy in the next decades. Recently, attention has shifted towards the development of cheaper cathode materials like LiMn₂O₄ (LMO) and LiFePO₄ due to their abundance, and the excellent safety of Li-ion cells that use them. To replace cobalt and nickel-containing cathodes, we need to address issues like moderate energy density and cyclic stability.

Major challenges in lithium manganese spinel (LMO) materials, especially poor electrochemical performance at elevated temperature ($>55^{\circ}$ C) due to manganese dissolution, can be tackled by developing large single crystal particles (SC) as ionic diffusivity is two orders of magnitude higher than conventional cathode materials. Large SC materials (free of grain boundary interfaces which could be a major cause of manganese dissolution) were developed as the degradation of any Li-ion cell is controlled by the electrode/electrolyte interface. By decreasing specific surface area the electrode/electrolyte reactions can be reduced. We have developed SC LMO with large crystallite size $(10\mu m - 15\mu m)$ and for the first time, we observed that the variation of oxygen partial pressure can change the morphology of LMO. We found a strong correlation between oxygen partial pressure, morphology, and elevated temperature electrochemical performance. To understand these unique phenomena we have used Electron Paramagnetic Resonance (EPR) which is sensitive to unpaired electrons as well as point defects and we realized that a certain oxygen deficiency generated at low partial pressure is triggering the morphology change in LMO. Optimizing oxygen partial pressure helped to developing large single crystals, which showed exceptional capacity retention at elevated temperature with low electrochemical impedance and better rate capability. We believe promoting single crystals and engineering their morphology could help resolve the ongoing challenges that prevent the wide adoption of LMO in Li-ion cellsBatteries are playing a pivotal role in sustainable development and conventional cathode materials (LiMO₂ where M= nickel, cobalt, and manganese) are in massive demand for electric vehicles (EVs). However, the scarcity of cobalt and nickel materials has sparked an interest in alternative cathode materials development, which may be needed for complete conversion to clean energy in the next decades. Recently, attention has shifted towards the development of cheaper cathode materials like LiMn₂O₄ (LMO) and LiFePO₄ due to their abundance, and the excellent safety of Li-ion cells that use them. To replace cobalt and nickel-containing cathodes, we need to address issues like moderate energy density and cyclic stability.

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Extending of Cycle Life of Nmc Cathode by Bn Surface Coating

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Layered cathode materials are widely used in the battery industry due to their high-energy-density properties. However, the bottleneck of layered cathode materials is low cyclic stability due to the unwanted side reactions between the cathode surface and liquid electrolyte. To overcome this limitation, we proposed coating the surface of the cathode material by using functionalized boron nitride (BN) material.

The synthesized BN powders are dispersed in an appropriate binder and dispersant media. NMC 532 cathode material is immersed in the BN solution with suitable coating/cathode ratios. After the solution was dried, various heat treatment temperatures were applied to obtain the best interface and to eliminate impurity phases between the cathode and coating layer.

The preliminary charge/discharge test results showed that the BN coating increased the cyclic life of the cathode and prevented rapid capacity fade of the cell. This may be attributed to the BN protective layer between the cathode and liquid electrolyte, which hinders the strong oxidation behavior of the layered cathode material.

Conclusively, the coating of BN onto the layered cathode surface has shown improved long-term stability compared to the pristine cathode. Optimum coating thickness, rate capability of the cell, impedance, and coating morphology will be investigated to observe cathode-coating interface chemistry and long-term cell behavior.

High-Energy and High-Flux X-rays to Investigate the Lithium Metal Electrode Inside the Cell

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We knew the economical and environmental importance of energy storage, and we are learning how strategic this domain is.

In this well-known context, secondary cells are meant to be crucial link in the energy transition pathway we must achieve and, among them, lithium-based system stay the most competitive together with the most promising.

One of the way to improve Lithium based batteries is to reach "beyond graphite" system for the negative electrode : huge progresses have been made in Si, Si-based or Sn-based electrode but the ultimate electrodes would be lithium metal itself.

Despite being studied for a long time now, those Li^o electrodes are still problematic because of the non-homogeneous plating they undergo, the endless SEI formation happening at their interface or the dendritic growth occurring during the plating process and that can lead to failure or safety issue.

Due to its low Z number, X-rays may not appear, at first sight, the method of choice for the study of lithium, but the synchrotron source, especially the ESRF "Extremely Brilliant Source", allow to reach high-enough flux to get exploitable data.

In realistic energy storage system, the lithium electrode thickness is typically comprised between 10 and 100 μ m, while most lithium grain size exceed 100 μ m. in other word, with a high energy micrometric X-ray beam, one can expect to see the signature of single grains of lithium when probing symmetric-cell or even full-cells.

We propose here to follow the behavior of single lithium grains in electrodes and, in the most favorable cases, to follow them operando.

The aim is to characterize the different mode of plating for the metal a the surface of the electrode and link them to the cycling conditions (current density, electrolyte, type of separator...), this, in order to reach a finer understanding of lithium metal electrode.

Influence of Anion Structure on Electrochemical Performance of Fluorinated Alkoxyborate Electrolytes for Mg Rechargeable Batteries

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Growing demands for world electrification are forcing scientists to research new, highly efficient energy storage systems that would provide high energy densities and combine the aspects of sustainable battery production. Metal Mg possesses a low redox potential, high gravimetric capacity, and bivalent character. At the same time, Mg is the eighth most abundant element in the earth's crust and is geographically evenly distributed, which additionally contributes to its potential as a candidate for future batteries. One of the main challenges of Mg batteries is the development of electrolytes. A few years ago, a significant breakthrough considering overpotentials, oxidative stability, and Cl-free character has been made with the introduction of Mg salts, containing weakly coordinated anions.¹,² Fluorinated alkoxyborate Mg[B(hfip)₄]₂ served as a pioneer salt showing that weakly coordinated anion with a high degree of fluorination enables large charge delocalization, decreases the anion – cation interaction and consequently reduces the ion-pair formation. All that contributes to the final electrolyte performing with Coulombic efficiency of Mg metal plating and stripping around 96% and overpotentials below 100 mV.

In our work, we synthesized Mg salts with different anion structures, where the hfip ligand was exchanged for various alcohols with a different number of binding groups, sterical properties, and degree of alcohol fluorination. To study the influence of anion structure on electrochemical performance, galvanostatic measurements were carried out. Results show that by tailoring the anion structure we affect different properties, which influence the overall electrolyte performance. With a selection of proper fluorinated alkoxy groups, Coulombic efficiencies over 99% are achievable. Additionally, oxidative stability of different fluorinated alkoxyborate electrolytes has been investigated. Since glymes solvents usually used for Mg electrolytes have limited stability, LSV measurements were performed in acetonitrile. Applying a 0.1 mV/s rate, anions are showing similar stabilities in a range from 0.2 to 0.4 V (vs. Ag/Ag+). This indicates that oxidative stability of fluorinated alkoxyborates is in general less dependent on ligand selection than Mg plating/stripping performance.

Study shows that tailoring the structure of fluorinated alkoxyborates with different alcohols allows further development of Mg electrolytes offering improved electrochemical performance compared to the model Mg[B(hfip)₄]₂ electrolyte and exposes the most promising candidates for the future design of high-performance Mg electrolytes.

1. Pavčnik, T. et al. Batter. Supercaps (2021)

2. Pavčnik, T. et al. ACS Appl. Mater. Interfaces (2022)

Influence of Protons on the Redox Chemistry of Verdazyl Radicals for the Application in Redox Flow Batteries

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Derivatives of verdazyl radicals have recently been applied as potential active material for symmetrical non-aqueous redox flow batteries (NARFBs). Non-aqueous electrolytes typically offer an electrochemical stability window of 3 - 4 V and can yield higher energy densities than their aqueous counterparts. So far, verdazyl radicals are used in symmetrical NARFBS, but only offer a potential difference of ≈ 1 V for Kuhn-verdazyl and ≈ 1.5 V for oxo-verdazyl radicals. This means that the main advantage of NARFBs cannot be utilized to its full extent at the moment.

Although aqueous redox flow batteries (ARFBs) provide a smaller electrochemical stability window of 1.23 V in theory, they offer lower costs coupled with higher safety and higher ionic conductivity. These characteristics of ARFBs in connection with the potentials of verdazyl radicals for NARFBs motivate the characterization in water-based electrolytes. However, before considering a final application, ARFBs with verdazyl radicals must be better understood and characterized. Watersoluble verdazyl radicals were already reported, but a comprehensive electrochemical characterization is still needed.

Herein, we demonstrate the chemistry of verdazyl radicals in aqueous electrolytes in the acidic pH range. We chose the 1,3,5-triphenylverdazyl radical as representative structure for this material class and evaluated the process of the radical disproportionation in acidic electrolytes electrochemically in an electrolysis cell. With this cell, we adjusted the redox state of the verdazyl species and performed an independent characterization of each of them by cyclic voltammetry (CV) and hydrodynamic linear sweep voltammetry. The number of transferred electrons was determined by the peak separation in the CV, as well as the oxidation / reduction experiments. pH-dependent CV measurements along with the analysis of the redox potential allowed to estimate the number of protons involved. Based on these findings, we propose the redox mechanism for the reaction of the aforementioned verdazyl species in acidic medium for the first time. Quantum-chemical calculations were performed to determine if the protonation is thermodynamically favorable within the used pH range. In addition, the positions of the protonations were determined and their thermochemistry compared, providing further evidence for the characterized species.

With these results, we gained a comprehensive understanding of the electrochemistry of the verdazyl radicals in acidic electrolytes. The fundamentals of the electrochemical behavior of verdazyl radicals in acidic electrolytes are a first step for their potential use in ARFBs. Investigations of derivatives with improved water solubility should be the next step towards the application of these materials for energy storage.

Interfaces Analysis in Lithium Solid-State Batteries Using Operando Auger, Xps and ToF-Sims.

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Lithium solid-state batteries (SSBs) are a promising technology for electrochemical energy storage systems. So far, performance of SSBs are governed by the diverse solid/solid interfaces and their electro-chemo-mechanical evolution upon cycling and storage. However, these interfaces are buried in the battery stack so that their thorough analysis remains a challenge. Indeed, cross-sectioning of the battery stack remains often required to reveal and analyze these buried interfaces but it is not a trivial task. If reliable and reproducible cross-sections can be obtained, then ex situ analysis of the solid/solid interfaces is the preferred method so far. In situ (i.e. sequential analysis and electrochemical cycling) and operando (i.e. analysis during cycling) analysis are also attracting much interests in the recent literature.

In this presentation, it will be showed that cross-sections of polymer-based SSBs can be obtained with high reliability using argon ion milling at liquid nitrogen temperature. Moreover, the interest of operando analysis using the electron beam present in the XPS, ToF-SIMS (flood gun or charge neutralizer) and Auger (primary beam) apparatus will be presented. In that case, the electron beam is directly used to flood the surface, thus creating a potential difference followed by lithium migration, SEI formation and Li platting. The main advantage of this approach is to remove the need for dedicated electrochemical cells. Here, this operando Auger is very attractive due to its fully adjustable electron beam and its ability to follow both morphology and chemical environments evolution at the nanoscale. Comparison with operando XPS and ToF-SIMS results will be discussed. Overall, this work should greatly benefit to all researchers working on interfaces analysis in SSBs.

Interfacial Engineering for Stable Interphase to Realize High-Voltage Ni-Rich Cathode

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The demand of advanced lithium ion batteries with high energy density for electric vehicles is driving the development of layered nickel-rich LiNixMnyCo1-x-yO2 (NMC) cathode materials. It is inevitable to charge at high voltage in order to make the capacity limit close to the theoretical value. However, the high-voltage stability of Ni-rich cathodes still has not met the requirements of power batteries due to the intrinsic structural instability and electrolyte degradation. Various approaches such as surface coating, bulk doping and morphology tailoring as well as electrolyte optimization have been attempted to enhance the cycling stability of Ni-rich cathodes with different degrees of success, but it still remains highly challenging to realize long-term cycling of Ni-rich NMC at high voltages (> 4.3 V vs Li/Li+). [1,2]

Here, we demonstrate that stable cycling at a high cut-off voltage of 4.5 V (vs. Li/Li+) on a singlecrystalline NMC811 cathode can be achieved through using small amounts of electrolyte additives in the commercial carbonate-based electrolytes, such as LP40. Both the Li||NMC811 (3 - 4.5 V) half cells and graphite||NMC811 (2.8 - 4.4 V) full cells retain close to 90% of initial capacities after 200 cycles at 0.5 C (1 C = 200 mA g-1) after adding the additive at room temperature. The improved cycling performance is ascribed to the robust cathode-electrolyte interphases (CEIs) on the singlecrystalline NMC811 cathodes. Through comprehensive experimental efforts, it reveals that a robust and protective interphase is formed by the additive decomposition thus inhibiting the detrimental surface reconstruction at the surface of the NMC811 cathode. Consequently, the growth of interfacial impedance is largely mitigated and remains stable during charge-discharge cycling at high voltage. The underlying mechanism of forming a robust CEI and various experimental details at the high voltage will be presented.

Investigation of Charge Compensation Mechanism in Co-free Materials for Na-Ion Batteries

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Sodium-ion batteries attract great interest because of wide range of their potential applications and sodium abundance. In order to make Na-ion batteries competitive, the research in Na-ion batteries focuses on the development of new electrode materials, offering higher specific charges and voltages to reach higher energy density and performance comparable to or higher than those of state-of-the-art Li-ion batteries. Therefore, we are searching for novel Na-ion Co-free materials with high specific charge, preferably mainly based on earth-abundant elements like Mn. One promising approach to achieve this goal is the substitution of one of the transition metals by lithium, which not only increases energy density due to its low molar mass but also, as additional positive ion in the structure, it would lead to the increase of manganese oxidation state. In conventional intercalation cathodes, Na-ions can move in and out of a layered material with the charge being compensated by reversible reduction and oxidation of the transition metal ions. Since Mn4+ ions are not likely to change their oxidation state in the voltage range of cycling, anionic redox reaction on oxygen is likely to be the only accountable resource for the observed reversible capacity. This can increase the battery's energy density by storing charge on both the oxygen and manganese, rather than on the transition metal alone.

The aim of this work was to study the influence of Li-substitution degree on charge compensation mechanism, crystal structure and gas evolution in Mn-based materials, Na0.6Li0.1Mn0.9O2 and Na0.6Li0.2Mn0.8O2. To achieve this goal, materials have been synthesized using solid-state synthesis approach and characterized using electrochemical methods, operando XRD, Online Electrochemical Mass Spectrometry (OEMS) and X-ray Absorption Spectrometry (Swiss Light Source, SuperXAS beamline).

Na0.6Li0.1Mn0.9O2 showed excellent initial capacity of 180 mAh/g, and oxygen evolution at high voltages during first charge was suspected from the shape of the potential profile. Na0.6Li0.2Mn0.8O2 had a lower capacity of 140 mAh/g without showing no oxygen evolution characteristics in potential profile. The material with lower lithium content exhibited also an irreversible phase transition during first charge as detected by operando XRD. The gas evolution at voltages above 4.2 V suggests that irreversible oxygen redox reactions actually take place in case of Na0.6Li0.1Mn0.9O2. Additionally, XAS measurements revealed rather a peculiar behavior of Mn oxidation degree upon first charge for this material. The decrease of oxidation state of the transition metal at voltages seems to correspond well with the irreversible oxidation of O2- ions and loss of oxygen from the structure during first cycle, which was confirmed by OEMS. The influence of different degrees of Li-substitution in sodium manganese layered oxides onto the oxygen redox activity will be discussed.

Kinetic Study of Organic Cathodes in Multivalent Batteries Enabled by Quasi-symmetric Cells

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Rechargeable batteries that employ energy-dense multivalent metals as anodes could represent a major step forward in the transition to a renewable energy economy. When coupled with low-cost and environmentally friendly organic cathodes, batteries utilizing multivalent metal anodes can realize their full potential. Despite research efforts, organic cathodes face myriad challenges when coupled with multivalent charge carriers, especially in terms of achievable capacities. Therefore, to improve existing cathodes and design better ones, a comprehensive kinetic study of organic materials is a necessity. Electrochemical impedance spectroscopy has proven to be an invaluable tool in this regard. However, the phenomena observed in the final impedance spectra are a consequence of the complex interplay of various processes and cannot be attributed to a single battery component. To investigate the kinetic limitations of particular electrode material, it is important to distinguish between the contribution of the cathode and the anode to the final response. Several strategies can be used for this purpose, including the three-electrode setup and the conventional symmetric approach. The former is severely limited by the artifacts of the chosen reference electrode. The second approach, on the other hand, requires complicated and timeconsuming cell assembly and disassembly. The introduction of quasi-symmetric cells circumvents both problems since this approach does not require a reference electrode and at the same time involves a rather simple assembly procedure. Another advantage is the potential difference greater than zero between two electrodes at different charge states, which allows galvanostatic cycling and even rate capability testing in cases where passivation of the metal anode does not allow reversible cycling. This setup has proven to be a simple but effective tool for the comprehensive study of organic cathode kinetics and opens the doors for enhanced multivalent-metal organic batteries.

Li+ Transport Phenomena in a Compositesolid-State Electrolyte

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In the context of all solid-state lithium batteries, we focus on lithium ion transport phenomena at the solid-solid interfaces. Using Molecular Dynamics techniques, we study an interface composed of Li+ conducting ceramic (LLZO) and polymer (PEO or PTMC) materials. Interestingly, although a lot of attention has been dedicated to study lithium-ion transport phenomena in such composite solidstate electrolytes, there are plenty contradictory findings and hypothesis concerning Li+ transport mechanisms in literature. For example, both an increase and a decrease in ionic conductivity has been observed when inserting ionic conductive ceramics to a polymer electrolyte matrix. These phenomena are also related to the type of composite components and the overall composition. Such controversies highlight that some fundamental questions remain unanswered. What is the ionconducting phase? When is it more beneficial to use a composite electrolyte in comparison to a single-phase system? In this presentation, our strategy to study these complex but fascinating solidsolid interfaces will be discussed. A sensitivity analysis of different relevant simulation parameters provides us with a good base for further exploration of such complex solid-solid interfaces, and the general approach to this sensitivity study is discussed in detail. In particular, the possible impact of some simulation parameters on the outcome of a simulation will be explained together with preliminary results on ionic transport behavior and structure-dynamic properties. Considering that atomistic studies concerning an interface of a Li+ conducting ceramic and a polymer are scarce, the work will hopefully spark more in silico activities to enhance the perspectives on Li+ transport phenomena in composite solid-state materials.
Lithiation Heterogeneities at High Cycling Rates in LiNiO2/Graphite Full Cells Monitored by Multimodal Operando Characterizations: Combining Neutron Imaging and Micro-Xrd.

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Mastering fast charging of high energy density Li-ion batteries is key to accelerate market penetration of electric vehicles (EV). This will be achieved by better understanding lithium concentration heterogeneities developing under high current densities, due to limited Li charge transfer rate or diffusion in porous electrodes. Disentangling these effects is possible by spatially resolving lithiation heterogeneities as a function of the electrode thickness and current density. However, this requires operando characterisation capable of quantifying lithium concentration at the micron scale in solid (electrodes) and liquid (electrolytes) phases within minutes. Along that line, we report correlated operando high-resolution neutron imaging (NI) and depth resolved micro-X-ray diffraction (μ -XRD) on a LiNiO2/graphite full cell using the same operando cell. Neutron are strongly absorbed by 6Li, hence neutron imaging offers the unique opportunity to track Li concentration in both liquid and solid phases with a 5 micron resolution and in minutes at D50/NeXT (ILL). Similar resolution is achieved with μ -XRD (ID31-ESRF) having the advantage of monitoring local crystal structure evolution and hence Li content with a greater accuracy. Using a standardized cell for both experiments circumvents the well-known issue of limited reproducibility over different cell designs especially at high cycling rate, and hence, allows a direct comparison of the data sets to achieve a better description of Li heterogeneities. In a nutshell, neutron imaging shows substantial Li heterogeneities in the graphite electrode at C/5, C and 5C, but with different characteristics depending on the C-rate. At low C-rate, Li concentration gradients across the electrode thickness show three maximums during charge, presumably corresponding to the three biphasic transitions while only one maximum is observed at higher C-rate. Regarding the LiNiO2 electrode, much weaker concentration gradients at the limit of neutron imaging resolution can be observed at C or 5C. A more accurate determination of Li concentration in LiNiO2 using cell parameters determined form μ -XRD is performed. Lithiation gradients at C are found to be generally weak with however, spikes at the high-voltage H2-H3 biphasic transition of ≈ 0.1 Li and ≈ 0.05 Li across the depth of the electrode during the charge and discharge, respectively. In conclusion, operando neutron imaging and μ -XRD were successfully employed to provide a qualitative and quantitative measurement of Li heterogeneities, giving new insight about electrode engineering to improve high rate performance. We believe this multimodal operando characterisation strategy, performed in the context of the BIG-MAP European project (part of Battery 2030+), paves the way towards acquiring high-fidelity data essential to build better models and understand operating batteries.

Local Disorder Hindering Fast Ionic Transport: Case Study on Nanocrystalline and Amorphous Li10GeP2S12 – Poster Presentation

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Solid electrolytes with extraordinarily high Li-ionic conductivities are key for high performance allsolid-state batteries. In many sulfide materials nanosizing via ball-milling increases the ionic conductivity. So far, the thiophosphate Li10GeP2S12 (LGPS) belongs to the best Li ion conductors with an ionic conductivity exceeding 10 mS /cm at ambient. There are many studies investigating the effects of ionic substitution on the ionic conductivity in LGPS. However, the effect of reducing the grains size to the nm-regime has not been investigated experimentally. Recent molecular dynamics simulations predict that the ionic conductivity of LGPS can be further enhanced by a factor of three if the crystallite size is reduced to the lower nanometer regime. A change in local ion coordination, hence local disorder, has been assumed to facilitate Li diffusion in the ab-plane of LGPS. Here, we synthesized nanocrystalline LGPS experimentally by different steps of high-energy ball milling in varying intensity. We characterized differently modified samples with regard to their structure and Li+ ion transport parameters. X-ray powder diffraction and high-resolution ³¹P and ⁶Li magic angle spinning nuclear magnetic resonance (NMR) spectroscopy helped us to determine morphological changes and local structures upon milling. To precisely follow the changes in Li+ ion dynamics we applied broadband conductivity spectroscopy in combination with electric modulus measurements. Surprisingly and against the behavior of other electrolytes, ionic conductivity turned out to decrease with increasing milling time, finally leading to a reduction of $\sigma(20^{\circ}\text{C})$ by a factor of 25 in the bulk. This decrease affects both, bulk ion dynamics and total conductivity, which also comprises Li+ transport across grain boundary regions in LGPS. As could be shown by NMR, ball-milling leads to a structurally heterogeneous sample with the nm-sized LGPS crystallites embedded in an amorphous matrix. This amorphous phase is also responsible for the reduced performance of the milled LGPSelectrolyte. Importantly, careful separation of the amorphous and (nano)crystalline contributions to the overall ionic conductivity revealed that even in the nanocrystalline regions Li+ ion dynamics is slowed down compared to untreated, coarse-grained LGPS. By means of solid-state NMR relaxometry we confirmed that elemental Li-ion jump processes in the bulk have higher energy barriers in the ball-milled, disordered structures. In conclusion, defects introduced into the LGPS bulk structure via ball milling have a negative impact on ionic transport. We postulate that such kind of structural disorder is detrimental to fast ion transport in materials, whose transport properties rely on crystallographically well-defined diffusion pathways.

Mass and Charge Transport in Li1- δ CoO2 Thin Films – A Defect Chemical Perspective

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The three archetypal cathode material classes of spinel, layered oxide and olivine all belong to the class of mixed ionic and electronic conductors (MIECs) and as such all exhibit ionic, electronic, and chemical capacitive contributions to the ambipolar solid-state diffusion process. Moreover, these elementary material parameters critically depend on the cathode's state of charge. Measuring all these transport properties as a function of Li content is far from trivial and data are often deduced from porous and geometrically complex electrode systems relying on simplifying assumptions. Most of the relevant thin film literature has been limited to the evaluation of the chemical diffusion coefficient D as the inverse time constant of Li diffusion. However, D is not an elementary material property, but a composite parameter that, for Fickian diffusion, is comprised of ionic conductivity and chemical capacitance. The variation of D along the charge curve can therefore only be understood by deconvoluting these two individual contributions as a function of stoichiometry. The underlying thermodynamics of electrochemical Li storage may be considered in terms of point defect concentrations (electron holes and Li vacancies for cathode materials) as a function of Li activity and chemical potential, as proposed by Maier.

In this work, we present a comprehensive impedance study of sputter-deposited polycrystalline Li1- δ CoO2 thin films for a wide stoichiometry range ($0 \le \delta \le 0.4$) that includes the transition region around 3.9 V vs. Li+/Li, where the most pronounced changes of the electrochemical properties are observed. Full sets of material parameters are extracted at various states of charge, including the ionic conductivity, chemical capacitance, ambipolar diffusion coefficient and interfacial charge transfer resistance. For this purpose, we adapt an anomalous diffusion equivalent circuit element according to Bisquert within a modified version of Randles circuit to model the impedance response. The evolution of all material parameters along the charge curve is discussed and their separate contributions to the total electrode resistance are evaluated. Finally, we provide a defect chemical perspective on the observed trends in terms of chemical potential, Li activity and point defect concentrations.

Mediated Lithium-Air Batteries: What Can We Learn From Cyclic Voltammetry?

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Lithium-air batteries are appealing candidates for high-energy electric vehicle applications. Not only are they generally cheaper than other types of batteries, but they have a unique feature: they "breathe" oxygen present in the air, which makes them much lighter than lithium-ion batteries and ideal for electric vehicles. Despite their promising potential, there are many challenges to overcome before technology deployment. They are composed of a lithium anode and a porous conductive matrix (usually carbon-based), where oxygen is reduced during discharge and oxidized during charge. One of the major issues is the high overpotentials needed to recharge the battery due to the isolating nature of the discharge product, lithium peroxide (Li₂O₂). Recently, incorporating redox mediators (RMs) for the discharge and charge reactions has gained popularity because it can increase energy efficiency and minimize electrolyte degradation. These molecules act as soluble catalysts: during the discharge, the RM molecule gets reduced at the surface of the cathode, it then diffuses through the solution where it can react with solubilized oxygen to form big deposits of Li_2O_2 . In the case of charge, the RM molecule gets oxidized at free surface of the cathode that is not blocked by Li₂O₂, and then chemically reacts with it to release O₂. Thus, RMs allow decoupling the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) from the electron transfer reactions at the electrode, giving the charge transfer an alternative path to the electrically insulating Li2O2.

These molecules need to have an adequate electrochemical potential, fast charge transfer kinetics, and readily react with either oxygen or lithium peroxide to be able to establish a steady state and avoid the accumulation of intermediate species hindering the catalytic activity. Cyclic voltammetry is a very useful tool to probe the kinetics both of electrochemical reactions and, indirectly, chemical reactions. The rate of the chemical reactions is not affected by electrochemical potential, and their effect can be evidenced only if the timescale of the experiments is comparable with the half-life of the reaction. Thus, it is possible to decouple the influence of these two types of processes by varying the scan rate: At very fast scan rates, where the timescale of the experiment is much faster than that of the chemical reactions, only the redox activity of the mediators is evidenced, while at slower scan rates the effect of the catalytic behaviour becomes important.

In this work, we aim to decouple the electron transfer kinetics from the rate of homogeneous catalysis by RMs employing cyclic voltammetry in the absence and presence of oxygen. Firstly, the electrochemical behaviour of two typical RMs in an inert atmosphere was studied. 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) and lithium iodide were used as discharge and charge redox mediator models, respectively. For that, 10 mM solutions of the respective molecules with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as supporting electrolyte dissolved in tetraethylene glycol dimethyl ether (TEGDME) were studied. The experiments were run in a three-electrode cell with a Pt disc working electrode, a Pt coil counter electrode, and a LiMn₂O₄/Li₂Mn₂O₄ reference electrode. By modelling the cyclic voltammograms, we obtained diffusion and kinetic parameters for the iodide/triiodide/iodine couples, as well as for the DBBQ in its different oxidation states. From this, it is possible to extract further information about the comproportionation equilibria present in these solutions. The effect of lithium concentration on the redox activity of these molecules was also

analyzed and related to the ionic association in the solution and stabilization of negatively charged species.

Once a benchmark was established for the RMs in an inert atmosphere, the behaviour of the iodide in TEGDME was studied in the presence of O_2 . This way, we showed that the effect of the chemical reaction between triiodide and Li_2O_2 to produce iodide and O_2 in a catalytic manner becomes more important at slow scan rates (<1 mV/s). Using this approach, we were able to probe the timescales of the catalytic behaviour of triiodide and relate it to the performance of iodide-mediated lithiumoxygen batteries at different charge rates.

The advantage of this approach is that it is easily generalizable to other kinds of RMs, without the need of following specific functional groups that depend on the structure of the molecule. Further modelling of the results complemented by validation using spectroscopic characterization will allow quantitative information to be obtained about the kinetics of the catalytic behaviour, and aid the understanding of more complex mechanisms such as the ones involved in lithium-air batteries with LiOH as the discharge product.

Metal-Organic Framework Based Solid Electrolyte With High Magnesium-Ion Conductivity for Solid-State Magnesium Batteries

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The rapid development of electronic devices has spurred the exploration of different battery technologies in different applied fields. Thanks to the earth abundance and divalency of magnesium, magnesium-ion batteries (MIBs) have been considered as one of the most promising alternatives for the well-developed lithium-ion battery technologies with low cost and high energy density. However, the divalency of magnesium ions can act as a double-edged sword which simultaneously leads to strong Coulombic force between the Mg2+ and the host material, leading to rather slow kinetic properties in both electrolyte and lattice of host materials, making it extremely hard for the exploitation of the functional materials. Especially, efforts have been made in the searching of MIB electrolytes with high ionic conductivity, high cathodic/anodic stability and importantly, non-corrosion to the battery components, and progress has been achieved by the successive development of Grignard reagents, non-nucleophilic salts, fluoroalkoxyborate salts and even aqueous electrolytes. In this context, solid electolytes (SEs) with high safety also appear to be a family of promising candidates.

Here, we present a new promising hybrid SE material for Mg-ion conduction. The ionic liquid (magnesium bis[(trifluoromethyl)sulfonyl]imide, Mg(TFSI)2, dissolved in 1-ethyl-3methylimidazolium bis[(trifluoromethyl)sulfonyl]imide, [EMIM][TFSI]) was incorporated into the metal-organic framework (MOF, UiO-66), which has large inner surface area as well as rich porous structure. Comparably high ionic conductivities of 5.7 · 10-5 S cm-1 and 2.4 · 10-4 S cm-1 could be achieved at room temperature and at mildly elevated temperature (60 oC), respectively. Apart from the good ionic conductivity, the prepared SE also exhibits good chemical and electrochemical stability against metallic Mg. Moreover, in Mg metal electrode symmetric cells, stable Mg plating and stripping can be achieved for 200 cycles without dendrite formation yet comparably large overpotential could be observed. The interfacial reaction between the Mg metal anode (MMA) and the SE is characterized to seek the possible origin of the large overpotential. Via time-of-flight secondary ion mass spectroscopy (ToF-SIMS), a fluorine- and oxygen-rich interface containing both organic and inorganic components can be observed. The high Mg migration barrier in the surface degradation products inevitably causes the large interfacial resistance and thus high overpotential in consequence. Even so, by pairing the MMA with an aromatic organic material, perylenetetracarboxylic dianhydride (PTCDA) as cathode material, a solid-state Mg battery (SSMB) can work reversibly at 60 oC at a small current density. Future work including MMA surface engineering as well as the SE component optimization could further decrease the voltage hysteresis and enhance the electrochemcial properties of the SSMBs. The presented results suggest that the MOF-based material can indeed be a good template for the functional design of SEs for future SSMBs. We also hope that the presented results can be useful to define the strategies to deal with MMAs in SSMBs.

Modelling Oxygen-Redox and Structural Rearrangements in a Lithium-Rich Layered Cathode

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Lithium-rich oxide cathodes exhibit high reversible capacities from a combination of transition metal ion and oxygen-redox, but are plagued by hysteresis and voltage fade, due to structural rearrangements during cycling. These oxygen-redox driven rearrangements, which involve hostframework disordering and oxygen-dimerisation are not fully understood at the atomic-scale. One reason for the lack of clarity of oxygen-redox mechanisms is the current limitations in computational modelling of lithium-rich cathodes. Atomistic computational modelling requires knowledge of the crystal structure. However, these structural changes during cycling mean that the structure of the oxygen-redox cathode beyond the early stages of the first charge is not known a priori. The rearrangements mean there is an enormous configurational space of possible structures that the cathode could take. To obtain reliable models of the charged cathode, which can then be analysed to understand the mechanisms of oxygen-redox, this space needs to be comprehensively searched. In any search, the kinetics and thermodynamics of transformations should be accounted for. To date, no strategies have existed to systematically search this space.

Here, we use two techniques: long-timescale ab initio molecular dynamics and cluster-expansion, to show that the kinetics and thermodynamics of oxygen-redox driven structural changes can be fully resolved. We show that in layered Li_{1.2}Mn_{0.8}O₂, there is kinetically favourable reaction pathway via metastable superoxide and peroxide intermediates to form thermodynamically stable O₂ molecules in the bulk during charge. The O₂ formation is coupled with Mn migration, which results in the growth of voids with nanometre length scales, containing pockets of O₂ molecules. The molecules in the voids have a fluid-like character, comparable to compressed liquid O₂, with implications for long-range oxygen transport in the charged cathode. This work demonstrates new strategies for computational modelling of oxygen-redox cathodes, and in doing so, develops new understanding of the mechanisms and processes that limit their application.

Molecular Understanding of Li-Ion Diffusion in Dual Doped Ga^{3+}/Sc^{3+} Li_{7}La_{3}Zr_{2}O_{12}

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Garnet Li_{7}La_{3}Zr_{2}O_{12} (LLZO), in its high conductive cubic phase, is among the most promising solid electrolytes for next-generation all-solid-state Li-ion batteries. It can prevent the safety issues associated with highly flammable and toxic organic liquid electrolytes and, in principle, overcome the complications associated with replacing existing carbon-based anodes by metallic lithium, significantly increasing energy density. Pure cubic LLZO is not stable at room temperature; thus, aliovalent substitutions must be performed to promote disorder within the lithium sublattice and to stabilize the cubic phase. Recently, a dual substitution with Ga[{]3+} and Sc[{]3+} at the Li[{]+} (tetrahedral Li_{24d} and octahedra Li_{96h}) and Zr^{4+} sites, respectively (stoichiometry Li_{7-3x+yGa {x}La {3}Zr {2-y}Sc {y}O {12}), was shown to provide an exceedingly high conductivity of 1.8 mS/cm for x = 0.15 and y=0.10. However, the precise content of Sc^{3+} at which the conductivity is maximized is yet to be determined, as well as the underlying physics behind this enhancement has to be explained. In this work, we thoroughly examine Li^{+} diffusion in Li_{7-3x+yGa_{x}La_{3}Zr_{2-y}Sc_{y}O_{12} over the range of Sc compositions (0 < y < 0.2) by using classical molecular dynamics in combination with a novel material-specific first principles-based force-field developed within this study. The analysis of the dynamics relies on the innovative machine learning-based clustering approach, which traces the correlation between the local environment of each individual lithium-ion and its mobility in the course of a simulation, thus allowing us to attribute the changes in ionic conduction to the distribution of Ga^{+3} in tetrahedral Li {24d} and octahedra Li {96h} sites, as well as the distribution in the concentration of Sc. This work rationalizes the experimental observations and puts forward a novel machine learning methodology for interpreting molecular dynamics in solid-state electrolytes.

Multi-Scale Modelling of Li-Ion Batteries – Demonstration of Advanced Features on the Lfp Material

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A strong demand for simultaneous increases in energy and power densities, as well as a prolonged lifetime, and increased safety of batteries, at low battery costs, imposes significant development challenges. A huge variation space of material selection and geometrical characteristics from the nano- to the macro-scale as well as the resulting reaction and transport phenomena inherently requires multi-scale modelling and simulation support to create high fidelity virtual prototypes, which are one of the enablers for achieving the listed objectives. With such advanced modelling tools, it is possible to approach engineering limits with higher certainty in shorter times and with less effort, which are key KPIs in the modern development process.

The authors' contributions address the outlined challenges through a proprietary advanced multiscale multi-domain battery modelling framework covering the entire chain from crystal lattice structure over mesoscopic intra-secondary particle phenomena to the electrochemical cell level. Moreover, the integration of selected degradation mechanisms allows for intra-cell spatially and temporally resolved virtual analyses of degradation and also of safety phenomena. Furthermore, modelling framework is set up in a generic manner to cover simulations of arbitrary DC and AC operating conditions. The latter enables detailed virtual analyses of EIS spectra at different scales, i.e., intra-particle level, single particle level and electrochemical cell level.

Due to its phase separating nature, fast diffusion in one dimension and complex mesoscale topology of the secondary particles, LixFePO4 (LFP) material represents a very challenging material for indepth simulation analyses. The advanced multi-scale multi-domain battery modelling framework is therefore demonstrated on LFP material and LFP-Li cells.

Multi-scaling starts with the advanced thermodynamically consistent application of the regular solution theory that considers crystal anisotropy and thus the crystallographic structure of the LFP to derive the dependency of the chemical potential as a function of particle lithiation by considering the mechanistically derived enthalpy of mixing and the phase boundary gradient penalty. This upscaling, based on sequential linking from statistical physics to the phase field model, was consistently transferred to the particle level, thereby obtaining a high fidelity chemical potential model at the macroscopic scale.

Another important aspect of advanced battery simulation is the plausible topological representation of the electrodes. An advanced computationally efficient approach, reaching beyond standard P2D models, was developed to more credibly represent electrode topology at the macroscopic scale. Inspired by TEM and SEM imaging of the LFP electrode, this insightful approach pushes the boundaries on two scales, i.e. a) on the intra-secondary particle level by applying quasi-3D transport model and b) on the intra-electrode level by applying advanced porous electrode modelling framework based on more consistent virtual representation of the electrode topology. Both approaches enable straightforward virtual generation of electrode topology through determining an adequate multi-particle size distribution and particle-to-particle connectivity.

Such an advanced porous theory based model that consistently considers lower scales enables, compared to the current state-of-the-art, modelling experimentally observed LFP characteristic

phenomena that were previously not consistently modelled by macroscopic cell level models. This is demonstrated by simulating: a) voltage vs. capacity curves for a wide range of C-rates and providing clear reasoning for the reduced Li utilization at higher rates despite the very short characteristic diffusional times of particles, b) the memory effect and c) relaxation-induced polarisation. In addition, lower scale models reveal several unexploited phenomena, as for example: a) discovery of inductive effects in bulk active phase separating materials and b) uncovering specific fingerprints of material properties in the EIS spectra.

To further comply with the objectives stated in the opening, advanced porous theory based model framework incorporates also a heat generation functionality, a model of electrochemical SEI formation at the anode and its thermal decomposition. This interaction allows for modelling intracell spatially and temporally resolved degradation phenomena. In addition, with such a modelling framework it is possible, due to its computational efficiency, to study long term degradation phenomena. The model is thus capable of simulating the capacity decrease and overpotential increase due to the loss of cyclable Li being incorporated into the SEI and higher losses due to the transport through the thicker SEI respectively. Further on, interaction of the thermal domain and intra-cell phenomena such as SEI decomposition and other irreversible and reversible heat sources enables modelling the onset of thermal runaway due to SEI decomposition within the proposed modelling framework.

The presented advanced multi-scale multi-domain battery modelling framework, therefore, represents a contribution to the advanced virtual development of batteries and virtual testing of new materials, while developed models can serve also as advanced virtual sensors.

NMR Spectroscopic Investigations of the Performance Limiting Mechanisms of Lithium-Sulfur Batteries

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During the past decades, the development of alternative energy sources has become increasingly important as the growing consumption of non-regenerative fossil energy poses a threat to the environment. Hence, the development of next-generation batteries featuring high capacity, reduced costs and improved safety, such as in lithium-sulfur batteries, is of utmost importance. These advantages of lithium-sulfur batteries have led to a widespread effort to understand the fundamentals of the sulfur redox chemistry that drives their operation. Therefore, the involved local structural changes that correlate with the (electro)chemical processes need to be unveiled during the operation of Li/S batteries, suitably by in situ and in operando methods. This poster will demonstrate the development and application of one such (operando) technique: nuclear magnetic resonance (NMR) spectroscopy. NMR spectroscopic measurements allow the probing of the structural changes that occur in a battery during electrochemical cycling. In particular, the application of a non-invasive experimental setup, which can follow the reaction inside the battery in operando is highly desirable as it provides real-time structural information compared to ex situ analysis.

Lithium-sulfur batteries contain two NMR-active nuclear isotopes ⁷Li and ³³S, which allow the following of the reversible chemical reaction during the charge-discharge mechanism. This mechanism includes the transition between elemental sulfur and polysulfides on the cathode side, and the formation of the solid-electrolyte interface (SEI) as well as the metal plating and stripping on the anode side. Herein, we use a combination of ⁷Li and ³³S in operando NMR spectroscopy to reveal a fundamental understanding of the reaction pathways of the lithium-sulfur battery during discharge and charge. ⁷Li NMR spectroscopy is a powerful technique to apply to batteries, as demonstrated by many previous investigations on different Li battery systems, since it enables the detection of the chemical environments of Li species during electrochemical cycling and parasitic reactions in the cell. The great advantage of in operando ⁷Li NMR spectroscopy is that the ⁷Li signals of the anode and the deposited metal differ due to the bulk magnetic susceptibility effects and the surface area, bringing the skin depth effect into play. Thus, this investigation enables a time-resolved and quantitative evaluation of the electrochemical metal deposition during cycling or electrochemical plating. Therefore, it is possible to investigate a key problem that leads to a reduction in cell performance – the formation of lithium dendrites. This lithium deposition is particularly problematic if it occurs in an uncontrolled and inhomogeneous manner. It has already been established that the controlled formation of microstructures depends on the SEI, but the exact mechanism of nucleation and propagation of dendrites is not yet fully understood. Previous studies have shown that the etherbased electrolytes lead to an intensification of the nucleation density, a reduction in the dendrite size and a better coating of the Li electrode, especially when using LiTFSI-based electrolytes as used in lithium-sulfur batteries. Thus, the formation of microporous and dendritic lithium could be quantified and related to the electrolyte composition. Hence, we vary the composition of the electrolyte, in particular additives, like LiNO₃ or biomolecules, and soluble polysulfides, to investigate the influence on the metal plating. From this, conclusions can be drawn as to which electrolyte composition leads to an optimal SEI and accordingly results to uniform plating and stripping at the Li electrode at commercially relevant current densities. The interpretation of the diamagnetic signal in the in operando ⁷Li spectra is much more difficult because of the overlapping signals. Therefore, in

situ ³³S NMR spectroscopy supports the identification and quantification of formed species during the discharge-charge-mechanism. Hence, we developed an in operando method, that allows the detection of the formation of sulfur species in which the sulfur atom is located at sites of high electronic symmetry, such as Li₂S. This technique provides complementary results to the ⁷Li NMR studies. Our developed in situ NMR spectroscopic setup is a powerful analytical method, since the qualitative and quantitative detection of different sulfur and lithium species in real-time is crucial for understanding the electrochemical process in sulfur batteries. These new insights at the molecular level are essential to accelerate the development of lithium-sulfur battery technologies.

Novel Organic Cathode Material for Rechargeable Aqueous Zinc-Ion Batteries

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Aqueous zinc-ion batteries show great potential for sustainable large-scale energy storage systems. Inorganic cathode materials such as manganese dioxides, Prussian blue analogues and vanadium oxides enable high capacities but experience capacity fading due to strong electrostatic interactions with a rigid lattice, large structural deformations and material dissolution. Recently, several studies have shown that organic cathode materials possessing flexible design features, high capacity and sustainable production could present a viable alternative to inorganic cathode materials. Hexaazatrinaphthalene (HATN), a small organic cathode material, and its derivatives have already been explored as cathodes in aqueous zinc batteries demonstrating very high specific capacities. Herein we present a novel HATN based small organic cathode material derived by synergistical combination of hexaazatriphenylene (HAT) core and hydroquinone motif enabling increased theoretical capacity of 669 mAh/g. The material exhibits one of the highest reported initial capacities of 420 mAh/g at 100 mA/g. Similar to other small organic materials it suffers from fast capacity fading (71 % capacity retention after 20 cycles at 100 mA/g).

On the Relative Importance of Li Bulk Diffusivity and Interface Morphology in Determining the Stripped Capacity of Metallic Anodes in Solid-State Batteries

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In solid-state batteries with a lithium metal anode, the lithium bulk self-diffusion is too slow to sustain large current densities at the interface with the solid electrolyte so that the formation of voids on stripping is a major limiting factor for the power density of the battery. Recently, lithium alloys have shown a better morphological stability in contact with the solid electrolyte and they have been successfully employed as anodes or as interlayers. The improved stability of such lithium alloys has often been attributed to a faster lithium diffusion in the alloy than in pure lithium metal. However, only a few lithium diffusivity studies exist and most of them employ electrochemical titration methods in liquid electrolytes, which show inconsistency in the reported values. Amongst various lithium alloys, the Li-Mg system has attracted particular interest because of the wide lithium solubility range in Mg and of its high energy density. However, contrasting information on the lithium diffusivity in Li-Mg alloys can be found in the literature, with diffusion coefficient values ranging from 10-7 to 10-11 cm2·s-1 depending on the different methods and experimental conditions used. In this study, the lithium diffusivity in Li-Mg alloys with up to 30 at. % Mg is investigated by an isotope tracer method, employing SIMS to directly track the lithium diffusion. Our diffusion coefficients agree with the more conservative literature values, and we show that the presence of magnesium in the alloy slows down the diffusion of lithium compared to lithium metal self-diffusion. This would suggest a slower lithiation and delithiation kinetics of such alloys. To confirm this, we study the stripping behaviour of lithium and Li-Mg electrodes in contact with a lithium garnet solid electrolyte. We demonstrate that indeed, for large stripping current densities the delithiation is diffusion-limited, so that a pure lithium metal electrode yields a larger capacity than Li-Mg alloys due to the difference in lithium diffusivity. However, for lower current densities a larger capacity can be extracted from the Li-Mg electrode rather than from pure lithium. We attribute this behaviour to the ability of the alloy to maintain a diffusion path to the solid electrolyte surface so that the effective lithium diffusivity is improved. Instead, in a pure lithium electrode large voids limit the effective diffusion of lithium to the solid electrolyte. This was revealed by cryogenic PFIB imaging of the electrode-electrolyte interface. Our study challenges the widespread notion that the alloy's morphological stability at the solid electrolyte interface is due to a faster lithium diffusivity.

One-Pot Solvent-Assisted Synthesis of All-Solid-State Composite Cathodes Using Li3PS4 and LiFePO4

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Solid electrolytes with high Li-ionic conductivities are the key to high-performance all-solid-state batteries. For such electrolytes, the fine-tuning of their properties, let alone the integration into batteries is most challenging. The ionic conductivity, as one of the central properties, is often enhanced by introducing defects in the crystal structure, be it vacancies or local bond distortions that are beneficial for ionic conductivity. Obtaining defect-rich or, in the extreme, even X-ray amorphous solid ion conductors, is, however, typically based on post-synthetic treatments such as high-energy ball-milling. Liquid-assisted synthesis routes, in contrast to conventional solid-state synthesis routes of these materials, can directly lead to amorphous materials without the need for time and energy-consuming thermal treatments such as sintering, followed by post-synthetic modifications. Outstandingly, the liquid-assisted synthesis approach offers a path for a one-pot synthesis and mixing of composite cathodes, thus significantly easing the production of all-solid-state cathodes.

We synthesized the promising Li+ conducting Li_3PS_4 in an amorphous form starting from Li_2S and P2S5 using tetrahydrofuran (THF) in the liquid-assisted synthesis route and studied the influence of annealing temperatures on ionic conductivity. For a better understanding of these influences, samples were analyzed by X-ray powder diffraction to analyze the crystallinity. Additionally, we used magic angle spinning NMR spectroscopy of ³¹P, and ¹H to gain insight into the local structural aspects of the samples. Finally, we used this synthesis approach to produce composite cathodes with the solid electrolyte Li_3PS_4 and carbon-coated active material LiFePO₄.

Vacuum drying of Li₃PS₄ at only 80 °C yielded an X-ray amorphous solid with low conductivity in the range of 3×10–5 S/cm and significant local disorder as judged by ³¹P MAS NMR. Distortions of the PS₄-tetrahedra give rise to a large distribution of local magnetic fields, resulting in rather broad NMR linewidth even under MAS conditions. Drying at temperatures up to 120 °C leaves the local disorder mostly intact as judged by XRPD and MAS NMR, but led to a fourfold increase in conductivity compared to the sample annealed at 80 °C. Annealing the samples only 50 °C higher, namely at 170 °C, caused the crystallization of the material as well as an even further increase in the ionic conductivity. This increase went along with significant relaxation of the PS₄-tetrahedra, as highlighted by ³¹P MAS NMR spectroscopy. 1H MAS NMR revealed the presence of trace amounts of organic material stemming from remnant THF. In conclusion, the annealing of the material and the concomitant relaxation of the amorphous material up to its crystallization leads to a fourfold increase in ionic conductivity. Finally, the direct one-pot synthesis of Li₃PS₄-LiFePO₄ composite cathodes showed a similar trend regarding the crystallinity of Li₃PS₄ and the conductivity of the composite.

Operando Atr-IR Spectroscopy: An Appropriate Tool to Characterize Metal-Organic Batteries

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Organic materials are receiving an increasing amount of attention as cathode electrode materials for future post lithium-ion batteries due to their versatility (application of different counter ions such us Li, Na, K, Mg, Al) and sustainability. However, their electrochemical reaction mechanism has seldom been investigated. This is a direct consequence of a lack of straightforward and broadly available analytical techniques. So far, the electrochemical reaction mechanism inside of organic battery cathodes has been mostly investigated by ex-situ measurements, such as XRD, NMR, Raman and IR spectroscopy. However, there are certain limitations to these techniques; XRD is limited to crystalline samples, Raman is troublesome due to fluorescence and laser-induced sample damage, NMR and IR have been so far mostly limited to the analysis of ex-situ samples. Thus, development of new characterization methods is needed for further progress of organic cathode materials.

IR spectroscopy can be a non-destructive and straightforward probing tool in the battery research. However, its application has been limited due to the difficulties related to the handling and interpretation of ex-situ samples along with the lack of widely applicable in-situ and operando cells. Herein, we develop an operando ATR-IR characterization method for organic cathode materials in a spectro-electrochemical cell with Si wafer window. Si window enables us continuous measurements of ATR-IR spectra on the cathode composite and electrolyte degradation, while subtractive normalization allows visualization of all IR bands in the composite that are changing during electrochemical characterization. The operando ATR-IR characterization method was applied to study the electrochemical mechanism of poly (anthraquinonyl sulfide) (PAQS) and polyanthraquinone (PAQ) in Li-, Mg- and Al-organic battery system. During the reduction/oxidation process of the organic cathode material, not only the conversion of both C=O groups into C-Ospecies is observed, but also the formation of an intermediate semiquinone radical anion as an intermediate product. Moreover, we were able to observe pronounced variations between the difference IR spectra of PAQS in Li and Mg batteries for ring vibrations, which are connected to differences in the polarization between magnesium and lithium ions and conformational changes of the polymer structure. Conclusions done by the operando results were complemented by synthesis of model compounds and density functional theory calculation of infrared spectra. In the Al-organic battery, the electrochemical mechanism is proven to be the reduction of carbonyl bonds in anthraquinone groups during discharge and charge and become coordinated by AlCl2+ species.

Operando Haxpes Probing Solid Electrolyte Interphase Growth Through Ultra-Thin Film Electrodes

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Metallic lithium electrodes hold promise for increasing the energy density of Li-ion batteries, and when used in conjunction with solid electrolytes, adverse safety implications associated with dendrite formation in organic liquid electrolytes can be overcome. To better understand the stability of solid electrolytes when in contact with lithium and the reactions that occur, requires experimental approaches to access the chemistry of the buried electrode-electrolyte interfaces. All solid-state batteries are typically assembled and studied within 'inert' glovebox environments, however in practice trace contaminants alter the surfaces of battery materials with carbonate/hydroxide surface layers often formed. Such contamination has been observed to affect the cycling performance of solid electrolytes increasing interfacial resistance, acting as a barrier to lithium-ion transport. Additionally, these contaminants react with cycled, disassembled surfaces studied by ex-situ methods masking the true nature of reactions occurring at the interface.

We thus present an experimental approach for preparation and cycling of cells in an ultra-high vacuum environment, in the absence of these trace contaminants. Cell preparation consists of evaporation of an ultra-thin (30-60 nm), X-ray transparent lithium film, to study the Li-electrolyte interface. Such a cell, in conjunction with hard X-ray photoelectron spectroscopy (HAXPES) allows operando measurements of the buried electrode-electrolyte interface. The long inelastic mean free path of photoelectrons through alkali metals allows photoelectron so escape through the Li electrode. By changing the incident X-ray energy, the photoelectron escape depth varies, providing a depth resolved study (up to 100 nm) of the interfacial layering between the electrolyte and the electrode. Herein, we discuss the detection of different chemical species formed during the first lithium metal stripping and plating cycles of an all solid-state lithium ion battery. Consequently, identification of species at different charge states and different locations within the solid-electrolyte interphase whilst cycling is possible, including reactive intermediates which cannot be observed by ex-situ studies. This approach is shown to be applicable to most solid electrolyte materials and is expected to elucidate the nature of the interfacial layers and degradation processes occurring in new and promising solid-state electrolytes.

Operando Study of Phase Transitions and Defect Imaging of Single Crystal Cathode Particles With Scanning X-ray Nanodiffraction Microscopy

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Study of cathode materials at the single crystal scale allows to improve our mechanistic understanding of phase transitions and paves the way for improvement of their electrochemical performance. Scanning X-ray Diffraction Microscopy (SXDM) is a diffraction-contrast imaging technique. It has been applied at the ID01 nanodiffraction beamline of ESRF, the European synchrotron. The diffraction patterns are measured at different positions on the sample with a nanofocused X-ray beam. These maps are collected over a narrow range of angles covering the diffraction peak of a microcrystal, resulting in a 3D reciprocal space map at each point of the crystal. These maps are extremely sensitive to: (1) the local lattice d-spacing which allows mapping crystallographic strain across a sample and (2) local lattice misorientation, which allows the identification of mosaic domains and their crystallographic rotation/tilt.

This technique can be used to image crystal defects. Li-ion battery cathode active materials produced using different synthesis methods often exhibit broadly divergent performance and cycling stability, despite no obvious differences in morphology, purity, and crystallinity. SXDM reveals how commercial single crystalline LiNi0.6Mn0.2Co0.2O2 (NMC 622) particles possess large internal nanostructural heterogeneities even in the pristine state, which are difficult to detect using standard analytical techniques, but which could play detrimental role for the electrochemical performance of the battery.

SXDM also allows for relatively quick measurements of particles over wide range of sizes (100nm - 10µm) which makes it perfect for operando experiments. Operando SXDM imaging follows the (de)lithiation at the nanoscale to determine the link between strain, mosaicity, cationic ordering, and the dynamics of the phase transitions during battery operation. Local lattice displacement fields inside the particle which are directly influenced by the local lithiation state could be imaged with extreme sensitivity down to 10-4 Å. As the lithiation dynamics in many battery cathode materials remain poorly understood because of the difficulty in differentiating between inter- and intraparticle heterogeneity, SXDM could be an important tool for advances in this area of research.

Operando SXDM study was conducted with LiMn1.5Ni0.5O4 (LMNO), high voltage spinel cathode material which is considered to be a part of the next generation lithium-ion battery technology. LMNO operates at a high voltage of 4.7 V vs Li+/Li with a relatively large theoretical capacity. Despite impressive rate capability, LMNO cathodes also exhibit two phase reactions which can compromise cycling stability and reversibility. Furthermore, the interplay between two-phase and solid-solution transformation mechanisms present in such materials is still poorly understood.

The SXDM measurement allowed to observe two distinct phase transition in LMNO during charging that are determined by the difference in strain and mosaicity structure on a scale of single crystals.

During the first phase transition we followed the evolution of metastable domains of solid-solution phase during delithiation. Persistent strain gradients that were observed inside the single crystals during the first phase transition (Li1 - Li0.5) suggest that the shape and size of solid solution domains are determined by lattice defects. These defects are considered to originate at the boundaries of the misorientated mosaic domains, the evolution of which was also imaged during charging. The strain evolution during the second phase transition (Li0.5 - Li0) appears to be much more dynamic, which indicates redistribution of Li ions between phases inside the particle.

Nanodiffraction microscopy is a promising, but underutilized imaging method well-suited for investigating nanostructural evolution in battery cathode crystals. This simple but information-rich strategy represents a powerful platform for investigating strain dynamics and phase transitions inside cathode single crystals.

Operando Swelling Measurement of Si-C/G Based Anode in Pouch Cell: Effect of External Pressure and Impact of Cathode Material

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Silicon lithiation induces a high material expansion up to 280% which leads to significant swelling and mechanical pressure at the anode and cell level. In this study, the swelling behavior of bilayer pouch cell with high performance silicon carbon graphite (Si-C/G) anode material is investigated. Operando swelling was measured using an in-house compression set-up designed for 10 cm² pouch cell and able to apply pressure from 0.1 to 10 MPa with simultaneous pressure and thickness recording as well as dynamic pressure regulation system with an overall precision of 100 nm. This high precision gives a clear access to the graphite and silicon state of lithiation while from voltage profile it is not so obvious. Combining this unique experimental technique and a 1D electrode model based on materials expansion in function of the state of charge give access to the anodes porosity changes. While a particle rearrangement is clearly occurring at the first cycle with progressive stabilization, it can lead to very different anode porosity range in function of the external pressure. In particular, below an external pressure value, a continuous anode porosity increase is observed cycle after cycle. The pressure is not enough to recover the initial anode thickness. On the contrary, above this external pressure level, the cell swelling is reversible and the anode porosity is directly linked to this external pressure while continuous SEI growing could also contribute. The cathode active material signature on the cell swelling behavior is finally visible at the end of charge. While LCO has a small expansion, NMC shows a shrinking which is more and more pronounced with the nickel content. This is finally other argument for high Ni content NMC material to contribute to energy density increasing at cell level as it can partly buffer the anode swelling.

Operando Synchrotron-Based Fourier Transform Infrared (Sr-FTIR) Microspectroscopy for Battery Materials

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Operando synchrotron radiation-based characterization techniques applied to energy storage materials are becoming a widespread characterization tool as they allow for non-destructive probing of materials through spectroscopy, scattering, and imaging techniques. The use of operando techniques has intrinsic advantages, as they enable the detection of metastable intermediates, if any, and ensure characterization under real conditions avoiding the risk of ex situ sample evolution during its preparation. Compatibility between the electrochemical cell designs and the experimental set ups may force some specific design features and care has to be taken to ensure that these do not perturb the electrochemical response of the materials under investigation.

Organic material-based rechargeable batteries meet the specifications in terms of sustainability, abundance and scalability required to address the global energy transition towards net zero emissions. However, their development has been in part limited by the lack of straightforward and broadly available analytical techniques that are able to follow the reduction/oxidation processes that non-crystalline organic polymeric materials undergo upon cycling. Infrared spectroscopy allows the visualization of chemical changes at the molecular level of all infrared active bands that occur as consequence of redox processes.

Operando synchrotron-based Fourier Transform infrared (SR-FTIR) Microspectroscopy takes advantage of the high brilliance of synchrotron radiation that allows collecting high quality spectrums in the milliseconds range with a spatial resolution below ten microns squared. The combination of both, high temporal and spatial resolution enables operando mapping of electrode surfaces in real-time upon battery operation upon demanding cycling rates.

Here we will present an Operando SR-FTIR Microspectroscopy study on polyimide type organic polymer positive electrode material applied to lithium and post-lithium technologies, Na, Mg and Ca. Focusing especially on the experimental operando setup and the instrumental and measurement conditions.

Organic Cathode Materials for Multivalent Rechargeable Batteries

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Rechargeable multivalent (Mg, Ca, Al) batteries are highly perspective battery technology. Their application is envisioned through use of metallic anode and high capacity cathode materials, which each on their own present a specific challenge. Metallic multivalent metals are incompatible with conventional electrolytes known from Li-ion battery technology due to the fact that passive layers typically do not allow transport of multivalent ions, unlike in case of Li solid electrolyte interphase. On the cathode side, inclination towards conversion reaction, slow solid state diffusion and energy demanding desolvation of multivalent ions present a major challenge in the development of cathode materials.

Rapid development of new multivalent electrolytes in the last years, especially in the field of Mg and Ca electrolytes, has opened a path towards exploration of new types of cathode materials such as organic compounds and sulfur. Organic active materials offer a possibility to circumvent most of the limitations encountered in inorganic ones. However, organics typically contain electrophilic centers inside organic electroactive groups. Hence, they need to be combined with non-nucleophilic electrolytes. Additionally, organic active materials often suffer from dissolution of active material into electrolyte, which leads to rapid capacity fade. Dissolution can be effectively mitigated through preparation of insoluble polymers. Our studies show that combination of suitable organic polymers and non-nucleophilic electrolytes offer long-term cycling stability of multivalent metal–organic batteries with capacity retention of several hundreds of cycles.

Electrochemical mechanism of organic cathode materials is investigated through various techniques like operando ATR-IR, ex situ X-ray photoelectron spectroscopy (XPS), X-ray Raman scattering (XRS) and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS). A complementary toolbox of these techniques allows us to monitor changes in organic cathode material as well as active multivalent cation species during electrochemical cycling. Organic cathode materials display good electrochemical reversibility, although they often suffer from incomplete capacity utilization. During cell discharge ion-pairs take part in the electrochemical mechanism, which can lead to significant decrease in energy density of the cell. These findings offer future guidelines for research, which should be directed in improving multivalent ion-pair dissociation and moving closer towards full capacity utilization of organic cathodes.

Pre-lithiation of Silicon-Based Anodes Using an Electrochemical Bath

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Increasing the volumetric and gravimetric energy of lithium ion batteries (LIBs) for mobile electronic devices and electrification of the transport sector in particular is a major driving factor for intense research in the field of electrochemistry. Applying high capacity active materials as silicon (Si) (3579 mAh g⁻¹, Li₁₅Si₄) for the negative electrode is one strategy to increase the specific energy on active material level. However, Si negative electrodes exhibit huge volume expansion during lithiation causing high strains, loss of active material and continuous formation of bare Si surface. Thus, formation of the solid-electrolyte interphase (SEI) causing irreversible cathodic currents and loss of active lithium is more pronounced compared to typical graphite negative electrolyte design, loss of active lithium remains one of the major obstacles for practical application of LIB full cells using negative electrodes with higher Si-content. Pre-lithiation is an effective method to compensate active lithium loss and therefore a promising concept to overcome this challenge.

This work is focused on Li-metal-free pre-lithiation via electrolysis of the electrolyte salt in an electrochemical bath (electrolytic pre-lithiation). Pre-lithiation using Li metal is considered to have potential safety issues due to the high reactivity of Li metal, and features high costs or worse controllability and homogeneity regarding contact pre-lithiation methods. As electrolytic pre-lithiation using cheap lithium salts may be performed in a continuous roll-to-roll process, it is appealing for large scale-application and enables a higher safety compared to other pre-lithiation methods.

Herein, electrolytic pre-lithiation is investigated via electrochemical and analytical techniques. Filmforming and electronic passivation abilities of the alternative electrolytes based on lithium chloride and γ -butyrolactone used for electrolytic pre-lithiation are evaluated and optimized. The efficiency of pre-lithiation is validated in three-electrode setup, and the performance of pre-lithiated electrodes is evaluated in LIB full cells. The impact of pre-lithiation on the interphase formation of Sibased negative electrodes is systematically analyzed by X-ray photoelectron spectroscopy.

Probing the Interface of Thin Film Battery Materials Using XAS and XPS

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To encourage wider adoption and uptake of electric vehicles significant improvements to battery capacity, cost and cycle life are required. Nickel-rich LiNi0.8Mn0.1Co0.1O2 (NMC811) are promising cathode materials providing high energy density and low-cost benefits over conventional cathode materials such as lithium cobalt oxide. However, transition metal (TM) ion dissolution (particularly Ni and Mn) from the cathode and subsequent incorporation into the anode solid electrolyte interphase (SEI) plays a key role in promoting SEI layer growth. TM dissolution has been correlated with detrimental battery performance impacting cycle life and causing rapid capacity fade.

Thin film transition metals deposited via physical vapour deposition onto Cu foil substrates are used as model electrode surfaces cycled vs. Li/Li+ to model the effects of TM incorporation into the anode SEI in lithium-ion batteries. XAS and XPS reveal potential induced formation of passivation products on the TM electrode interface. This provides insight into the decomposition products of battery electrolyte (1M LiPF6 dissolved in EC/DMC 1:1, v/v) under electrochemically reducing conditions, and the extent of decomposition and products formed varies for different TM species. This will inform the development of novel materials, cell design and develop strategies to mitigate this degradation mechanism.

Probing the Operation of Non-graphitizable Carbons in Na-Ion Batteries by Nuclear Magnetic Resonance (NMR)

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The development of batteries is currently one of the most active areas of research. In this area, the researchers want to understand what happens during charging and discharging, i.e. during the battery operation. Of particular interest are their mechanisms and degradation processes. Lithiumion batteries (LIB) due to the combination of their high energy and high power density currently remain the most desirable energy storage system for electromobility. On the other hand, shifting from the use of fossil fuels to renewable sources and their successful integration into the grid, sufficient energy storage systems are required. Among these sodium-ion batteries (SIB) are ideal, due to the high availability of sodium, its low cost, and suitable redox potential. One possible negative electrodes for SIB comprise non-graphitizable carbons. Intercalation and deintercalation of Na ions into and from non-graphitizable carbons is the focus of many recent studies. The mentioned battery system is a relatively new and precise mechanism of its operation and degradation is as of yet under debate. Often the species present in the batteries contain motifs that do not exhibit long-range order.

NMR spectroscopy is an extremely powerful technique, as it allows the study of local structure in the vicinity of many pre-selected types of atoms, however it has rarely been used as an in-situ or operando technique. The main reason for this is that it is quite difficult to manipulate samples in a very limited space and in a very strong magnetic field. We implemented operando measurements with nuclear magnetic resonance at the NMR center spectrometer at the National Institute of Chemistry and supplemented them with ex-situ NMR measurements.

NMR spectroscopy study of SIB started with an ex-situ approach. By rotating the sample at a magic angle (MAS) to the direction of the magnetic field the normally broad lines of the measured signal are narrowed, increasing the resolution and simplifying the understanding of the spectrum. The batteries were sodiated or desodiated at a certain potential and analyzed. This method provides information on the resulting morphologies, crystal structures and electrochemical reaction products. However, this method can be invasive and potentially severely alter the state of the battery inside. In addition, various metastable, intermediate and / or short-term phases that are not detected by the ex-situ method are likely to occur during electrochemical reactions in the cell. Therefore, recent research is going in in-situ and operando directions. In these two techniques, the battery is not destroyed during operation, but rather non-invasive methods are used to observe the battery in operation and thus provide information on dynamic structural changes and processes in real time. Magic angle rotation is not possible for in-situ/operando measurements. However, these measurements are very welcome as they allow us to observe the battery during operation. Mentioned approaches are thus complementary and allow the necessary data for clarifying the degradation mechanisms. As references in assigning individual NMR spectra for different containing nuclei, we measured the initial battery condition before the first discharge and its individual components, such as the electrolyte, separator and non-graphitizable carbon. This makes it easier assigning individual NMR spectra in the cycled batteries. By measuring ²³Na NMR spectra, we obtained information about sodium intercalation in active material, results in a moving of NMR peak

during the sodiation process, the formation of a solid electrolyte interphase (SEI) on the electrode surface in the form of NaF and Na_2CO_3 and the potential formation of metal sodium dendrites.

Probing the Phase Evolution Between High Voltage Spinel Cathode and Coatings

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The spinel LiMn2O4 (LMO) cathode and its substituted variant LiMn1.5Ni0.5O4 (LMNO), owing to their three-dimensional structure, have high-rate and high-power capability with moderate energy density. Structurally, the phase diagram of Li-Mn(Ni)-O is complicated with many possible crystal structures with varying Mn oxidation state and lithium content. For high voltage LMNO cathode (Ni2+/Ni4+ 4.6-4.7 V vs Li), non-availability of suitable high voltage stable electrolyte further creates challenges. With conventional electrolytes, surface TM undergoes reduction forming thin binary or layered ternary oxide when oxidised beyond 4.2V (vs Li), further restricting the Li ion movement and compromising the accessible capacity. This along with Mn dissolution by HF (generated by reaction with liquid electrolyte at the electrode surface) restrict the long-term application of spinel phase – without appropriate surface coatings or doping in practical LIBs.

To achieve near theoretical energy and power density from high voltage cathode containing Li based batteries, coatings (or artificial interface) are more promising compared to doping of bulk structures. It has been successfully demonstrated that coating with binary (Al2O3, ZrO2, TiO2) and ternary metal oxides (LiNbO3, LiTaO3) can help in mitigating the electrolyte degradation and structural reconstruction over cathode surface. However, these coatings, in solid as well as liquid electrolyte systems, as such can be very dynamic and evolve during processing stages or during electrochemical cycling.

In this work we have investigated the interphases between cathodes (LMO, LMNO) and coatings (LiNbO3 and Al2O3) by using two different approaches. In first approach, epitaxial film of cathode material was deposited using pulsed laser deposition (PLD) followed by controlled thin layer deposition of Al2O3 via atomic layer deposition (ALD) or LiNbO3 via PLD. The epitaxial nature and crystal structure of deposited thin films are confirmed using thin film X-ray diffraction. The effect of deposition conditions and electrochemical cycling is evaluated using X-ray absorption spectroscopy by focusing on Mn L-edge and Al K-edge. Elemental distribution from surface to the bulk of thin films is also evaluated using X ray photoelectron spectroscopy (SOXPES+HAXPES). In second approach, the formation of interphases between cathode and coating is induced by sintering cathode and coating under high temperature and pressure using spark plasma sintering (SPS). Structural characterisation of the prepared composites is performed using powder X-ray diffraction, where structural degradation of spinel cathode into layer and rock salt type phases was identified. These structural transformations were further confirmed using Raman and solid state Nuclear magnetic resonance (ssNMR) spectroscopy. These combinations of techniques provide in depth long range and short-range changes occurring in the pristine high spinel cathode system with and without coatings.

Quantifying Dissolved Transition Metals and Understanding the Metal Solvation Shell With Magnetic Resonance Spectroscopy

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Although lithium nickel manganese cobalt oxide (NMC) finds widespread use as a relatively safe and energy dense class of cathode materials for lithium-ion batteries, one issue associated with its use is the dissolution of transition metals (TMs) into the electrolyte solution. TM dissolution alters the positive electrode structure as the material compensates for cation site vacancies and changing oxidation states of remaining metal species, which may cause irreversible capacity loss. Furthermore, dissolved TMs may migrate to, and deposit on, the negative electrode, becoming incorporated into the solid electrolyte interphase. This leads to further detrimental effects, including solvent reduction, impedance growth, and capacity loss. It is therefore important to explore the dissolution and deposition mechanisms of battery-relevant dissolved metals, to understand and mitigate the negative impacts on cell performance.

This work considers how nuclear magnetic resonance (NMR) spectroscopy may be applied to study TM dissolution. Solution NMR is often used in battery research to study lithium solvation and electrolyte degradation reactions. The method is also suitable to study dissolved TMs because most dissolved TMs are paramagnetic. The unpaired electrons in paramagnetic species induce distancedependent paramagnetic relaxation processes in nearby nuclei, resulting in more efficient nuclear relaxation. Paramagnetic solutes also cause chemical shift changes, from both bulk magnetic susceptibility (BMS) effects and hyperfine interactions. The effects of dissolved Ni(II), Mn(II), Co(II), and Cu(II) bis(trifluoromethanesulfonyl)imide (TFSI) complexes are characterised with ¹H and ¹⁹F NMR. Longitudinal (T_1) and transverse (T_2) relaxation times of these nuclei in conventional electrolyte solutions have a significant dependence on the TM species and concentration, and may be used to estimate the TM concentration in solution. ¹H BMS shifts are also used to successfully quantify dissolved TMs, and we show that the BMS shift reveals valuable information about the metal oxidation state, spin state, and coordination number. Lastly, through the combined use of NMR relaxometry and pulsed electron paramagnetic resonance spectroscopy (pEPR), we identify key components of the Mn(II) solvation shell, observing critical differences between its coordination in pristine and degraded electrolyte solutions as it preferentially coordinates to degradation species. This study of metal oxidation states and solvation shells provides insights into dissolution and deposition mechanisms and can be readily applied to any system from which paramagnetic metals dissolve.

Real Time Observation of Structure Changes in LiNiO2/Graphite Cell During Fast Cycling

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The energy density and rate capability of Lithium-Ion Batteries (LIBs) are very significant in expanding LIBs application from electronic devices to electric vehicles. Many effort has been done towards improving rate capability of LIBs, e.g. using nanoparticles for cathode materials, surface coating to improve ionic and electronic conductivity of cathode materials.[refs] However, the insight into structural changes of cathode materials during fast (de)lithiation in real time is still limited, as ultrafast data collection is quite hard to meet for some operando techniques (e.g. neutron/laboratory X-ray diffraction or total scattering). [refs]

Recently, metastable phases in LiFePO4 and LiNi1/3Mn1/3Co1/3O2 has been detected during high C-rate (> 10 C) cycling using synchrotron time-resolved X-ray diffraction (TR-SXRD) methods.[refs] Both reports demonstrate that the phase transformation of respective cathodes during high C-rate cycling behaves differently from those recorded during low C-rate cycling. These findings are informative and motivate us to explore structural changes of LiNiO2(LNO) during fast (de)lithiation in real time using TR-SXRD.

The reason for particularly choosing LNO is based on present and future importance of this material with low cost and high energy density. It is widely accepted that LNO undergoes a sequence of reversible phase transitions, i.e. H1 (pristine LNO) \leftrightarrow M \leftrightarrow H2 \leftrightarrow H3 (H and M represent rhombohedral and monoclinic phases, respectively), accompanied with large volume change (~ 10 %) during (de)lithiation.[refs] However, in these references, operando studies on LNO were performed under low C-rate cycling (1/10 C - 100/C). To the best of our knowledge, the insights into structural evolution of LNO during fast (de)lithiation in real time is still absent in state-of-art research. To fill this blank, we have collected operando SXRD patterns on LNO/Graphite electrodes assembled in an Argonne's multi-purpose in situ X-ray (AMPIX) cell during 1/2, 1, 5 and 10 C-rate cycling within a voltage range of 2.5 - 4.3 V. We reveal that, as hypothesized, the phase evolution of LNO under high C-rate cycling behaves very differently compared to previous studies on low C-rate cycling (1/10 - 1/100 C)[refs]. In the initial cycle at 1/2 C, the phase transitions are not reversible: during charging, H1 converted to H2 via a solid-solution reaction cover a range of LixNiO2 (0.4<x<0.8) composition bypassing the nucleation of M phase. This reaction heterogeneity indicates different reaction state for LNO particles, which is raised by passive surface layers such as Li2CO3[ref]. During the discharging, the phase transition sequence is consistent with previous reports except LNO is not fully lithiated to H1 at the end of discharging while reaches a mixture of H1 and M phases instead. This indicates kinetics limitation of LNO during fast cycling, particularly more pronounced at higher C-rates (1, 5, 10 C).

For graphite, we managed to observe stage transition of graphite during lithiation/delithiation from shift of reflection (00l). At ½ C, the observed stage transition of graphite is in good agreement with previous reports. Towards higher C rates, the reaction becomes inhomogeneously as expected, which multiple phase regions (dominated by two or more LiCx phases) cover wider ranges.

Sensitivity Analysis of Sei-Based Capacity Fade Model for Lithium-Ion Batteries

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Accurate battery models are important to maximize the utilization of batteries in modern societal energy storage devices spanning from electronic devices to electric vehicles. However the validation of the fidelity of these models still remains a challenge. Here we present a sensitivity analysis of a pseudo-two-dimensional battery model coupled with a capacity fade model based on the formation of solid electrolyte interphase and the corresponding irreversible charge loss for Li-ion batteries. The proposed method is based on training an inexpensive differentiable surrogate Gaussian process regression model on observed input-output pairs and analyzing the surrogate model to learn about the global and local sensitivities of the original system. Based on our studies, we are able to show that the proposed method is capable of identifying the most global sensitive input parameters as well as the exploration of local sensitivities around specific sets of inputs providing insights to the governing electrochemical process. Moreover, we identified a strong correlation between the growth of the solid electrolyte interphase and the irreversible charge loss at different current densities.

Synergies and Differences at the Alkali Metal/Electrolyte Interface

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In a world where lithium but also more abundant alternatives such as sodium and potassium should be used as metal anodes in batteries to increase the energy density, there is still a fundamental gap in the understanding of the reactivity of alkali metals with the electrolyte. This study of the solid electrolyte interphase (SEI) is based what is known in case of lithium batteries and translates this to sodium and potassium to identify similarities but also differences at the metal electrode/electrolyte con-tact.

Here, we schematically investigate how commonly used battery electrolyte solvents and carbonatebased electrolytes affect the surface of Li, Na, and K. The SEI layers formed under these conditions are studied using X-ray photoelectron spectroscopy (XPS). In addition to surface analyses, changes in the liquid electrolytes are also investigated using high pressure liquid chromatography (HPLC) and gas chromatography (GC). Different dominant SEI species are present depending on the alkali metal used.

This work provides important insights into the initial SEI formation on alkali metals. The data on the alkali metal surface after contact with solvents and electrolytes can also serve as input for theoretical models on the metal anode/electrolyte interface. Through this comprehensive characterization, improved approaches for batteries with metal electrodes and further understanding of their electro-chemical performance can be obtained.

Tem Lamella Preparation and Subsequent Atomic Resolution Imaging From a Pure Li Metal Using Inert Gas Transfer Workflow From DualBeam to Tem

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To be able to design lower cost, more efficient, and more flexible batteries, it is crucial to build strong fundamental understandings on battery components and materials at microscopy level. Techniques such as site-specific DualBeam (FIB-SEM) lamella preparation and subsequent TEM analysis have always been the key steps to unlock atomic resolution for materials science studies. However, due to the air and moisture sensitivity associated with various battery components, it used to be a very challenging task to keep sample integrity during the workflow, especially during sample transfer between different instruments.

In the current study, the Thermo Scientific IGST (Inert Gas Transfer) workflow solution was used to enable a DualBeam to TEM workflow by protecting both the bulk sample and the prepared lamella in Ar atmosphere with a CleanConnect[™] transfer module.

Using the CleanConnect module, a bulk Li-metal piece was successfully transferred from glovebox to a Helios 5 Hydra DualBeam without signs of surface oxidation. Due to the low melting point of lithium, the entire TEM lamella preparation process, including bulk milling, lift out, attach to TEM grid and final thinning were carried out at cryogenic temperature (-178°C) with a Thermo Scientific cryo-stage and cryo-EasyLift nano-manipulator. To achieve minimal ion damage to the final lamella, all the ion milling processes were carried out with Ar plasma focused ion beam from a Helios 5 Hydra multi-ion species plasma FIB.

The prepared lamella was then transferred back to glovebox under Ar gas protection using CleanConnect transfer module. Inside the glovebox, the lamella was loaded to a MelBuild double tilt LN2 Atmos Defend Holder, which allows lamella transfer from glovebox to a Talos F200X CFEG TEM under Ar gas protection.

The lamella was then analyzed in TEM. It is evident that the whole workflow successfully protects the lithium metal lamella from oxidation during transfer between multiple instruments. The lithium metal lamella stays crystalline with minimal signs of surface oxidation. Atomic resolution TEM images from lithium metal were successfully acquired. According to literature survey, this could be the first DualBeam prepared lithium lamella which gives atomic resolution in TEM analysis.

The study successfully shows the capability of the workflow by achieving atomic resolution from Limetal, which is one of the most challenging samples in terms of air, moisture, and temperature sensitivity. The success of the workflow also enables new methods to study other trending topics in the battery world such as characterization of SEI layer evolution, post-mortem analysis in higher resolution whilst keeping the sample in its original state.

The Atlung Method for Intercalant Diffusion (Amid) – A Reinvented Diffusion Measurement

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One limitation of Ni-rich cathode materials in lithium-ion batteries is their rate capability, especially in the kinetic hindrance regions, which leads to a high apparent irreversible capacity [1]. This motivates the need for an accurate measurement of the chemical diffusion coefficient of lithium ions in intercalation materials at different voltage ranges. GITT, PITT, and EIS are standard methods to measure the diffusion coefficient of lithium ions at various states of charge [2],[3]. However, these methods contain inaccuracies from the following sources: determining the electrochemically active surface area of an electrode, choosing appropriate pulse times, currents, and relaxation time periods. Our group developed a novel method, based on equations from Atlung's paper in 1979, which relate ion concentration at particle surfaces to the fractional capacity achieved in a charge or discharge step at various rates [4]. By using a signature curve protocol [5] that contains a series of variable C-rate constant current charge or discharge steps, we fit our measured capacities to the theoretical Atlung curve for spheres and extract a diffusion coefficient [6], [7]. Our method, called the Atlung Method for Intercalant Diffusion (AMID) only requires the particle radius to be known, rather than the active surface area, and we believe this generates more reliable and repeatable diffusion measurements. This poster will show the method development of AMID, including experimental electrode-level and cell-level considerations to achieve reliable measurements, particularly minimizing the cell's internal resistance to ensure it is operating in a diffusion-limited regime. We use single crystal NMC622 as an example material throughout this method development and compare AMID results to GITT.

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The Role of Trapped O2 in O-redox Cathodes

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The energy density of Li-ion batteries can be improved by storing charge at high voltages through the oxidation of oxide ions in the cathode material. However, oxidation of oxide ions triggers irreversible structural rearrangements in the bulk and an associated loss of the high voltage plateau, which is replaced by a lower discharge voltage, and a loss of O₂ accompanied by densification at the surface.

High resolution resonant inelastic X-ray scattering (RIXS), ¹⁷O nuclear magnetic resonance (NMR), neutron pair distribution function (PDF), and density functional theory (DFT) were employed to investigate the O-redox reaction in Li-rich cathodes. These techniques reveal that oxide ions are oxidized to O_2 which is trapped in voids formed in the bulk by reorganization of transition metal ions within the structure. The trapped molecular O_2 can be reduced on discharge back to oxide, but this process occurs at a lower voltage compared to the first charge, giving rise to voltage hysteresis. Furthermore, we show that it is possible suppress the formation of O_2 , trapping hole states on O and obtaining reversible, high voltage O-redox.

Time-Resolved Electrochemical Heat Flow Calorimetry for the Analysis of Highly Dynamic Processes in Lithium-Ion Batteries

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To meet the current requirements for lithium-ion batteries (LIBs), research focus has shifted towards high-energy-density active materials. Lithium- and manganese-rich NCMs (LMR-NCMs) are examples of such cathode active materials, with a superior energy density compared to conventional NCMs. However, their large voltage hysteresis between charge and discharge, even under open circuit voltage (OCV) conditions, results in a reduced energy efficiency during operation and in an increased heat evolution compared to conventional NCM or NCA cathode active materials. As a result, the study of the heat generation in these active materials is important for the optimization of operating conditions and for the prediction of the cell and battery temperature during operation. Electrochemical calorimetry can be used in combination with electrochemical characterization methods, such as impedance spectroscopy, incremental OCV cycling, and entropy measurements to distinguish different sources of heat generation. This distinction enables a better understanding of the impact of parasitic processes and their dependencies on factors such as the electrolyte composition, operating voltage, and active material particle morphologies. Recent research has shown the application of isothermal microcalorimetry to cells during high cycling rates, for example fast charging. However, the limitation of isothermal microcalorimetry is the low-pass characteristic of the measured heat flow, introduced by the thermal inertia of the setup and the calorimeter itself. To solve this problem, we introduced an optimized cell holder design and a novel data processing method for a time-resolved measurement of highly dynamic heat flow profiles. Our proposed method is calorimeter device independent due to a calibration procedure. Using a dummy cell with matched thermal properties to an actual half-cell, the time-resolution of the setup was characterized and the resulting dynamic correction method based on the obtained parameters will be presented. The setup and method was validated using a synthetic power profile applied to the dummy cell. Experiments on a graphite-lithium half-cell illustrate the improvement of the method and the optimized cell holder when compared to the state-of-the-art setup. Our proposed setup showed a 3.6 times faster time response, enabling a quasi-SOC-resolved analysis at C-rates up to 1C. Further improvement was made by implementing our post-processing deconvolution method. It was shown that the measured heat flow features appeared at the same SOC at different C-rates and that they were in excellent agreement with the features displayed by the derivative of the potential with respect to the capacity dV/dQ versus capacity curve. In addition to an analysis of features in the graphite lithiation, another possible application of highly time resolved calorimetry could be the detection and analysis of lithium-plating during fast charging. Furthermore, the separation of contributions to the heat flow can be performed more precisely for signals with a good SOC resolution, as the current dependency is a way to identify the reversible heat flow Q⁻ rev contribution (\propto I). The origin of certain features in the heat flow could be better analyzed by this method and attributed to different sources of heat. For example, one could distinguish a parasitic process, which occurs at a specific SOC, from one which occurs at a specific potential. Furthermore, this method could enable a better understanding of high-energy next-generation active materials, which produce significant heat upon cycling as a result of their large voltage hysteresis (e.g., LMR-NCM, silicon). In summary, the improved time resolution provides the acquisition of more detailed features than currently shown in the literature and allows an accurate correlation of the thermal
signals to electrochemical features, which can be applied to many critical areas in the field of lithium-ion battery research.

To Improve the Li/Solid Electrolyte Interphase of Halide Solid Electrolytes by Formation of In Situ LiF Sei Layer

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All Solid-State batteries are being researched widely owing to its safety and higher energy density that can be achieved by using Li metal Anode (3803 mAh/g). Solid state batteries are classified broadly into 2 types, viz., Inorganic and Polymer based electrolytes. Inorganic ceramic electrolytes are divided into oxides, sulphides and halides depending on their chemical and physical properties. Although Oxide based electrolytes show better conductivity and stability, their mechanical nature and higher sintering temperatures are their major drawbacks. Sulphides, on the other hand, are mechanically very stable and show promising conductivity in the order of 10-2 S/cm. However, their chemical stability and oxidation potential makes it challenging to work with. Recently, a breakthrough by Asano et al. on halide based solid electrolytes (Li3YCl6 and Li3YBr6) showed very good cycling stability with LCO and an ionic conductivity of 10-3 S/cm at RT. The work by Asano et al. has led to various studies on other halide-based electrolytes namely Li3InCl6, Li3YBr6, Li3YCl6, Li2ZrCl6, LiAlCl4 etc. Li3InCl6 not only showed a higher conductivity in the range of 10-3mS/cm but also outstanding stability with water.

Although, halide based solid electrolytes have very good cathodic stability, mechanical properties, good ionic and electronic conductivities, their stability with Li metal anode is still a concern and is being studied. Recently, Janek et al. have shown the anodic instability of halides using in situ XPS and impedance study. Usually, a Li6PS5Cl layer at the interface is used to overcome the interface issue. However, having this layer would increase the cost of production. Hence, improving the anodic stability of halides, especially chloride based solid electrolytes are of prime importance.

Of all the halides, Li2ZrCl6 is of interest, attributing to its low cost, cathodic stability and abundance compared to other halides. Recent reports have shown better conductivity and good cathodic stability of Li2ZrCl6 with LCO and high voltage cathode like NMC 811 with good cycling stability over 100 cycles. However, since the halide anodic instability is known, they are usually fabricated either with Li6PS5Cl or a Li-In alloy, which are economically not feasible. There are various ways to improve the interface stability viz., by adding additives, ionic liquids or by forming an in situ stable SEI layer.

Herein, Li2ZrCl6-xFx as Li ion conducting solid electrolyte with improved electrochemical stability and humidity tolerance was demonstrated owing to the formation of stable in-situ LiF SEI layer. Li Stripping/Plating studies show stable cycling at 38 μ A/cm2 for Li2ZrCl6-xFx upto 1000h as compared to the pure compound i.e., Li2ZrCl6. Critical Current Density (CCD) studies show stable cycling up to 192 μ A/cm2 from 19.2 μ A/cm2. This improved stability is attributed to the presence of LiF layer that suppresses dendrite formation and enhances the critical current density. SEM-FIB, SIMS and XPS studies confirm the presence of LiF at the interface for Li2ZrCl6-xFx. Thus, LiF layer at the interface has shown an increase in electrochemical stability, air stability and can be applied for stabilizing the solid electrolyte for commercial applications with Li metal anode.

Transition Metal Deposition, Electrochemical Activity and Cell Capacity Fade

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Nickel-rich layered oxide cathodes, such as lithium nickel manganese oxide (NMC) and lithium nickel manganese aluminum oxide (NCA), are the leading high-capacity cathode technologies, but suffer from degradation phenomenon, such as electrolyte oxidation, oxygen release and transition metal dissolution from the cathode. These degradation pathways are coupled and are best understood in context of each other and their subsequent reactivity with the electrolyte and anode. Electrode cross-talk, where metallic and acidic species are generated at the cathode and migrate to the anode can be particularly problematic, since these species can disrupt the solid electrolyte interface (SEI). Transition metal (TM) ions released from the cathode are believed to be particularly harmful as they are believed lead to catalytic degradation of the SEI.

Here we present results from a variety of experiments that together present a coherent picture of the nickel and manganese deposition process on graphite anode, their subsequent electrochemical activity and finally their impact on cell degradation. Experiments where preformed graphite anodes were soaked in electrolytes spiked with TM ions showed that the anodes have a huge capacity for taking up the TM ions, which is independent of the anode potential. Cyclic voltammetry experiments showed that the nickel and manganese reduction peaks are shift to lower potentials in the presence of a SEI. Together, these results are strong evidence that TM deposition principally is governed by through exchange with lithium in the SEI rather than through direct reduction of the ions.

X-ray absorption spectroscopy (XAS) measurements on both the electrolyte and the graphite anodes support the Li/TM exchange mechanism. The XAS measurements also show that the both nickel and manganese are attached to carbonate ligands, either as inorganic salts or polymeric species, on delithiated graphite. Similar to earlier reports on manganese deposits on graphite anodes, neither the manganese or nickel appear to reduce onto the anode as metallic clusters upon charge, rather they form a yet to be identified reduced species.

Finally, graphite anodes with either nickel or manganese directly spiked into their SEI were tested using a long term cycling protocol in cells against NMC811. It was found that only the introduction of manganese decreased the discharge capacity during the long term cycling, while the capacity fade from cells with nickel introduced had no measurable effect compared to control samples.

Visualization of the Accelerated Sulfur Redox Processes on Atomic Zn-N2 Sites for Room-Temperature Na-S Batteries Daliang Fang

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Metal-sulfur (M-S) batteries are promising next-generation energy-storage devices for their high energy densities and low costs. Rational design of advanced catalysts is critical for realizing the practical application of M-S batteries. However, the micro-level understanding of the sulfur catalytic mechanisms is still lacking due to the difficulty to characterize the sulfur catalytic conversion process at the nanoscale. In-situ transmission electron microscopy (in-situ TEM) is a powerful tool to reveal the real-time microscopic reactions in the electrode materials, but it is difficult to be applied into M-S field due to the highly mobile and easy sublimation nature of sulfur molecules under high-energy electron beam (200 kV). By developing a novel sulfur host consisting of atomic Zn-N2 sites and N-rich microporous graphene (Zn-N2@NG) into room-temperature sodium-sulfur (RT Na-S) batteries as a model, this research first demonstrates that the stability of sulfur under high-energy electron beam can be greatly enhanced through decreasing its size into 20~30 nm and chemical bonding with a conductive substrate simultaneously. This striking discovery unprecedentedly enables the successful operation of in-situ TEM to clearly visualize the accelerated S redox evolution (S8 \leftrightarrow Na2S) under the catalysis of atomic Zn-N2 sites: During sodiation process, S nanoparticles on the surface Zn-N2@NG quickly convert into Na2S, faster than S molecules in the micropores, which contributes to effectively inhibit the shuttle effect and improve the sulfur utilization efficiency. Up the following desodiation process, the formed Na2S can be oxidized back to S, realizing a highly reversible reaction. The superior directional catalysis of atomic Zn-N2 sites on sulfur conversion is further confirmed by other ex-situ methods and theoretical calculations. As a result, even with a high sulfur content of 66 wt%, Zn-N2@NG/S cathode still exhibits the state-of-the-art sodium-storage performances: high reversible capacity of 894 mA h g-1 at 0.1 A g-1, unprecedented high-rate capability (467 mA h g-1 at 5 A g-1) and ultra-long cycling stability for 6500 cycles with an ultralow capacity decay rate of 0.0062% per cycle. This research should be of interest to the broad audience. It not only makes a great step forward the practical application of RT Na-S batteries, but also opens a new avenue towards the future application of in-situ TEM into the insightful mechanism investigation of M-S batteries at the nanoscale.

Worflows for Detecting Cross-Talking Mechanisms for Ni-Rich Coumpounds

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To quickly screen high energy density intercalation compounds or more stable electrolytes for Li-ion batteries, metrics such as capacity retention or coulombic efficiency are often used. These metrics are efficient at assessing initial degradation of the battery performance. Nevertheless, more than the linear degradation of battery performance with time, the battery lifetime is often regulated by the appearance of the so-called "knee points" in capacity retention. Knee points are the indication of a change of degradation mechanism or associated rate and are often followed by capacity rollover, during which the capacity retention abruptly degrades to lead to the sudden death of the battery cell. Capturing complex chemical and mechanical events which when cascading lead to capacity rollover is challenging, especially for cross talking mechanisms during which degradations at one electrode directly disrupts the functioning of the second one. Indeed, cross talking events often happen simultaneously to "classical" degradation modes occurring at sole electrode such as impedance raise, higher lithium loss inventory and loss of active material, complexifying their detection.

In this work, Ni-rich layered compounds were studied, LiNiO2 and LiNiO.8Mn0.1Co0.1O2, in full cell configurations. By varying the electrolyte chemistry and the cycling conditions (cutoff potential and temperature), cross talking mechanisms are pinpointed by the introduction of dedicated protocol workflows combining derivatives curves (dV/dQ & dQ/dV) and charge/discharge capacity endpoints. Applying these workflows to graphite/NMC811 chemistry using 5M LiFSI in DMC electrolyte, we demonstrate that super concentrated DMC-based electrolytes are plagued by cross-talking events, albeit good capacity retention is recorded in full cell. Furthermore, we show that SEI formation at high temperature (>55°C) is efficient to alleviate cross-talking phenomena. Overall, we propose novel workflows for detecting complex mechanisms. We believe that their implementation is of prime importance to go beyond our understanding of classical aging mechanisms.

Poster Session II

Advanced Rechargeable Aqueous Zinc Ion Batteries by Electrospun Ferroelectric Polymer With Hierarchically Porous Structures <u>Bo Keun Park¹, Ki jae Kim¹</u>

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Recently, rechargeable aqueous Zinc ion batteries (AZIBs) have received considerable attention due to their attractive properties such as low cost, environmental benefits, high safety, and high theoretical capacity. Accordingly, AZIBs are considered candidates to solve the several limitations of lithium ion batteries and alternate some portions of them. Nevertheless, the conventional use of AZIBs was restricted by several obstacles, including dendrite growth, Zinc metal corrosion, and hydrogen evaluation. Here we report an advanced protection strategy for Zinc metal with a protective layer of ferroelectric polymer. The protective polymer layer prepared via a simple electrospinning method on Zinc metal has a porous structure and strong polarizability due to the electric field (20 kV) applied during electrospinning. This protective layer suppresses dendrite growth and side reactions with aqueous solvents, and at the same time improves electrolyte accessibility owing to the pore space in the polymer layer. Furthermore, ferroelectric polymers affect the ion solvation structure of Zinc ions in electrolyte, thereby contributing to the improvement of electrochemical stability. As a result, the proposed zinc anode exhibits significant improvement under various current conditions in the symmetric cell and, also exhibits more stable cyclability than bare Zinc in the full cell. We believe that our work will accelerate the commercialization of AZIBs and lead to dendrite-free Zinc metal anode and high performance AZIBs.

Analysis of Lithium-Ion Batteries Seriously Degraded Under Floating-Charging Conditions

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Lithium ion batteries (LIBs) have been used as power supply in portable applications such as smartphones and PCs because of their high energy density, high power density, high chargedischarge efficiency and high safety standards. In recent years, LIBs have been utilized in large-scale applications such as backup power supply where fully charged states are constantly maintained (float charging). Such continuous charging could result in thick resistive film formation at the electrodes and cause cell degradation. By operating LIBs under float charging with periodic discharging, it is possible to utilize nighttime power, and also to avoid the continuous charging, which could improve the battery life.

In this study, we investigated the effect of the combination of the float charging and occasional discharging on the battery life by analyzing charge-discharge curves and operando neutron diffraction measurements. With the operando neutron diffraction measurements, it is possible to analyze the structural transitions of the positive and negative electrodes during the charging and discharging processes, which changes in the course of the cell degradation. The degradation tests were conducted using commercial 18650 LIBs, consisting of LiNixCoyAlzO2 (NCA) and graphite electrodes, under float-charging, continuous cycling, and floating-cycling (float-charging with occasional full discharge once per day).

We specifically expected that occasional discharging releases the cell from continuous float charging, reduces the side reactions, and extends battery life. However, we found that the combination of float charging and cycling had a negative synergistic effect on the cell lifetime to cause significant capacity loss. The dV/dQ curve analysis and neutron diffraction revealed that the degradation with the float charging and cycling was caused by the conventional loss of lithium inventory due to the side reactions at the graphite negative electrode. In contract, the dV/dQ curves of the floating-cycling cell were drastically changed from the original cell. It was difficult to determine the cause of the degradation only from the dV/dQ analysis. The operando neutron diffraction and half-cell measurements showed that the main cause of the degradation was the increase in the resistance of the NCA positive electrode which seriously limited the level of charging. Cross-sectional SEM/EDS images of the NCA electrode removed from the degraded cell showed that the active material particles were significantly cracked and the electrolyte-derived products were deposited between the cracked particles, suggesting that the decomposition products of the electrolyte generated by the float charging accumulated between the cracks formed by the charge-discharge cycles.

Anion Effect on the Transport Properties of Ternary Ion-Gel Electrolytes

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Gel polymer electrolytes (GPEs) encompassing polymerized ionic liquid (PILs) as polymer host matrix, ionic liquids (ILs) as plasticizers, and lithium salts, also known as ternary ion-gel electrolytes, are possible candidates for application in lithium metal polymer batteries. Herein, we report the fundamental properties of some representative ternary ion-gel electrolytes, based on poly(diallyldimethylammonium) (PDADMA) as PIL-backbone, 1-propylpyrrolidinium (PYR13) as IL cation, and with three sulfonamide anions, namely bis(fluorosulfonyl)imide (FSI-), bis(trifluoromethylsulfonyl)imide (TFSI-) and the asymmetric anion (fluorosulfonyl)(trifluoromethylsulfonyl)imide (FTFSI-). The GPEs are supported on poly(vinylidene fluoride) (PVDF) nanofiber mats as mechanical reinforcement. The aim of the study is to understand the effect of the anion's chemistry on the transport properties of ion-gel electrolytes. The thermal properties, ion association behavior, ion diffusivity, and charge-transport properties of the electrolytes were studied by differential scanning calorimetry (DSC), Raman spectroscopy, solid-state nuclear magnetic resonance (ss-NMR), and by standard electrochemical characterization techniques, respectively. DSC shows that replacement of the TFSI- anion leads to a decrease of the glass transition temperature (Tg), with the full-FSI- electrolyte having the lowest Tg. This indicates that FSI- based GPEs are characterized by higher flexibility and faster local motion. Raman spectroscopy indicates lower association degree for the full-FSI- electrolyte, compared to the full-TFSI- system. Replacement of TFSI- leads also to an increase of the total ionic conductivity and of the lithium transference number. Finally, ss-NMR shows that full-FSI- electrolytes have higher lithium diffusivity, thus corroborating the results of the electrochemical characterization. Altogether, the results indicate that replacing TFSI- with FSI- in ion-gel electrolytes leads to a considerable enhancement of the transport properties. The overall favorable transport properties, combined to the mechanical strength provided by the PVDF nanofiber mats, render these materials promising candidates as electrolytes for safe, room-temperature lithium metal batteries.

Architectural Aspects of Silicon Nanowires and Its Effects on the Performance of Li-Ion Batteries

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Silicon in all its forms, like film, micron/nano-sized particles, composite with carbon, is being utilized for anodes in Li-ion and Na-ion batteries. These studies aim at maximizing the percentage of silicon in the anode so as to gain the advantage of its high energy density, meanwhile, reducing the effects of huge volume expansion that it undergoes during the charge-discharge process. Among these silicon nanostructures, silicon nanowires (SiNWs) grown directly on the current collector reduce the number of processing steps for anode fabrication, and provide high energy density while maintaining good contact with the current collector after multiple charging-discharging steps. These SiNWs comprise of a composite structure having a crystalline Si core and an amorphous Si shell. The architecture of SiNWs can be varied to have a microcrystalline or an amorphous shell, the orientation of SiNWs on the current collector can be perpendicular or random or the crystalline core to amorphous shell ratio can be tuned.

These changes in the architectural aspects of SiNWs play an important role in determining their stability, capacity and rate capability as an anode. The effect of the changes in microstructure and architecture of SiNWs on their electrochemical performance has been studied in our work. The work here will show the variations in the geometrical orientation of SiNWs, variation in crystalline core diameter while keeping the amorphous shell thickness constant and variations in the amorphous shell thickness while keeping the crystalline core diameter constant. The growth of these SiNWs has been tuned by using the hot wire-assisted VLS growth mechanism and the SiNWs have been grown on copper foils at a temperature of 400°C. The work presented here gives detailed insights into the behavior of Si as an anode that can be used for applications in alkali metal ion batteries as well as in all-solid-state batteries.

Charge Rate Dependence of Delithiation Mechanism in High Nickel Content Layered Materials for Li-Ion Batteries

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The possibility to fast charge batteries with higher capacities is key to enable the rise of electrical vehicles. Layered oxides are the current high energy density materials, especially the materials family of general formula LiNi_xCo_yAl_zO_2 or LiNi_xMn_yCo_zO_2 (NMCxyz). Even if these materials have been investigated over the past two decades, the exact lithiation process is still contested, especially for the higher nickel stoichiometries that provide the best capacities. Indeed, the lithiation or delithiation mechanism of NMCxyz is described either as a succession of three phases depending on the lithium composition, or as a solid-solution mechanism during the whole lithium extraction.

Comparing the results of different studies remains a challenge due to various experimental conditions such as different electrolytes, pressure, material supplier, the probing technique itself, etc. Among these differences, the charge rate is a key parameter since it is correlated with the evolution of the material phases. Indeed, during fast charge, the chemical potential is influenced by distinct phenomena such as lithium diffusion hindrance in the material or transport limitations in the electrolyte, both lowering the effective battery capacity. Based on these observations, a study binding the impact of charge rate and the material structure is needed to get a full picture of material evolution during such demanding conditions.

In this objective, operando experiments with synchrotron radiation are appropriate for resolving materials structure during charge and discharge. Nevertheless existing studies reported different behaviours on same or similar materials, and yet the impact of the beam on the electrodes is not always explicitly considered or assessed.

To tackle these questions, we performed a series of experiments in the framework of the ESRF-ILL-CEA Battery HUB to follow the structural evolution of NMCxyz during lithiation and delithiation by combining lab-scale and synchrotron operando X-ray diffraction (XRD). We used different stoichiometries of NMCxyy with x from 0.6 to 1 to highlight the effect of nickel content on material structure. The impact of charge rate was evaluated by increasing the current from C/100 to 2C implying the need of synchrotron radiation to achieve a sufficiently high temporal resolution. We used the exact same experimental settings, such as the setup or cycling conditions to be able to compare our samples and to avoid side effects on the insertion mechanism. The reproducibility and reliability of our data is guaranteed by pressure-monitored full pouch cells with industrial grade electrodes. The measurements were performed in transmission mode with a moveable 2D CdTe detector on BM32 at ESRF. Finally, to complete our study, we varied the X-ray dose absorbed for same or very similar electrodes to understand the effect of exposing battery materials to hard X-ray beam.

In summary, we report here on the lithiation mechanisms and crystal structure evolution as function of the charge rate for different stoichiometries of NMCxyz. We further carefully evaluate the X-ray beam damage as a function of dose. We also note that this approach lends itself to be further applied to other dense electrode materials of interest.

Chemical Fire Extinguishing Materials Embedded Microcapsules for the Safety Enhanced Lithium-Ion Batteries

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Since the safety problem of lithium-ion batteries (LIBs) has not yet been resolved, there is a limit to developing and utilizing LIBs in our lives. In this work, we confidently announced the thermally activated fire extinguishing microcapsule for the improvement of LIBs safety. The microcapsules were triggered by thermal degradation of shell, which decomposition began just over melting point. At the point, the shell began to melt and allowed the inner fire extinguishing agent to contact with the fire. And then fire extinguishing materials can obstructs fire reactions, so we can prevent fire and explosion accidents occurs from LIBs systems. As a results, the microcapsules were described as the core-shell structure with particle sizes of about 2 ~ 5 microns. And from self-extinguishing time (SET) tests, fire extinguishing agent embedded microcapsules were proved their fire extinguishing effects.

Computational Design of High Voltage Li-Rich Sulphide Cathode Materials.

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The design and discovery of new cathode materials with higher energy density, using Earthabundant elements is in high demand. Oxide cathode materials deliver high energy density but experience issues with voltage hysteresis and capacity fade as a result of oxygen evolution. Conversely, sulphide materials mitigate these issues, but suffer from low voltage and hence, a lower energy density. Here, we present a new Li-rich sulphide cathode material with an improved voltage compared to similar materials. We also report our computational insight on two phase behaviour during charging. It allows us to access most of the potential charge capacity associated with the Lirich nature of this material. We employed a range of computational techniques such as density functional theory (DFT), cluster expansion (CE), and ab initio molecular dynamics (AIMD), to examine structural, electronic, and redox properties of the designed materials.

Dendrite Growth in Lithium Metal Solid-State Batteries

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Lithium metal solid-state batteries using ceramic solid electrolytes promise a step change in cell energy density. However, there are significant challenges to charging and discharging these cells at high current densities in the range of several mA/cm². At high rates of charge, dendrites (filaments of lithium metal) are observed to crack through ceramic electrolytes, leading to critical failure of the cell. The realisation of lithium metal solid-state batteries therefore depends on understanding how a soft metal such as Li can create cracks in a stiff ceramic electrolyte. Using a combination of X-ray computed tomography and FIB-SEM we have made observations which reveal both how Li dendrites crack Li_6PS_5CI electrolytes and how these dendrite-cracks propagate across the solid electrolyte. We have made the finding that dendrite-cracks propagate whilst partially filled, driven by Li at the back of the crack not the tip. This has enabled advances in understanding dendrites in ceramics and the factors that influence them and their progression to a short-circuit.

Designing Prussian Blue Analogues for High-Energy-Density and Long-Life K-ion Batteries

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K-ion batteries (KIBs) have recently attracted much attention as potential high-voltage and highpower batteries. Among positive electrode materials reported so far, KxMn[Fe(CN)₆]1-y \Box y (KMnHCF, 0 < x ≤ 2, \Box = [Fe(CN)₆] vacancy) is a promising material because of 4 V-class operation and large capacity. We recently reported that [Fe(CN)₆] vacancy-rich (~15%) KMnHCF exhibited a larger reversible capacity and superior rate capability due to faster ionic diffusion in the lattice than almost vacancy-free KMnHCF when their primary particles are micrometer size. Thus, the impact of [Fe(CN)₆] vacancy, whose negative aspects are generally highlighted, should be worth revisiting for Prussian blue analogues as K-insertion hosts. An important open question is the impact of vacancies on the cycle performances because the vacancy would affect the structural change during charge– discharge and increase the crystal water content. In this study, we investigated the effect of the vacancy on the electrochemical performances, structural evolution, and cyclability of KIBs to provide a design strategy for Prussian blue analogues for KIBs.

Almost vacancy-free samples with small (~100 nm) and large (~3 μ m) particle sizes precipitated in 0.2 and 1 M potassium citrate solutions, respectively, and a vacancy-rich sample with large (~3 μ m) particle size was obtained by Na+/K+ ionic exchange method. Hereafter, these samples will be denoted as vacancy-free(VF)-small(S)-KMnHCF, VF-large(L)-KMnHCF, and vacancy-rich(VR)-L-KMnHCF, respectively.

All samples have monoclinic structures (P21/n), and no crystalline impurities were found. Rietveld refinement and ICP-AES revealed that the composition of VF-S, VF-L, and VR-L-KMnHCF were $K_{1.9}Mn[Fe(CN)_6]_{1.0}$ ·0.28H₂O, $K_{1.8}Mn[Fe(CN)_6]_{0.99}\square_{0.01}$ ·0.18H₂O, and $Na_{0.1}K_{1.6}Mn[Fe(CN)_6]_{0.85}\square_{0.15}$ ·0.92H₂O, respectively.

In K-metal half cells, all electrodes showed good capacity retention. Especially, VR-L-KMnHCF exhibited no capacity decay over 80 cycles. Operando XRD measurements revealed that the VF-sample exhibited the structural evolution from monoclinic to tetragonal through the cubic structure during K+ ion extraction. In contrast, the VR-L-KMnHCF did not show the tetragonal phase formation even at the fully depotassiated state. This result indicates that the presence of vacancies suppressed the cooperative Jahn-Teller effect. In the presentation, we will also discuss the impact of crystal water in the lattice on the electrochemical performances of KIBs.

Differential Electrochemical Mass-Spectrometry (Dems) for In-Situ Gas Evolution Studies on Solid-State and Sodium-Ion Batteries

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In situ studies of gas evolution in batteries provide mechanistic understanding of various processes related to formation, operation, and degradation of the battery components. To this end, differential electrochemical mass spectrometry (DEMS) and online electrochemical mass spectrometry (OEMS) setups adapted to batteries have been developed, and over the past years, a good understanding of the origins and intricacies of gas evolution in lithium-ion batteries has been gained.

After a short introduction about instrumentation and gas evolution mechanisms in lithium-ion batteries, we will discuss the future of the in-situ gas evolution studies based on three DEMS examples from the fields of solid-state batteries and sodium ion batteries. This is to emphasize that understanding the gassing of NCM cathode active material (CAM) is not the end by now, but the beginning for a broader range of DEMS/OEMS experiments on novel materials and cell concepts. We also demonstrate how the combination of DEMS experiments with complementary techniques helps to gain deeper mechanistic insights and to arrive at the right conclusion.

First, a comparative study on gas evolution in solid state batteries with different solid electrolytes is presented. In particular, cells containing LiNbO3 coated NCM622 and either crystalline Li6PS5Cl or glassy 1.5Li2S-0.5P2S5-Lil solid electrolytes were investigated using DEMS. In contrast to CAM gas evolution studies in which low gas evolution at given SOC/potential indicates material stability, herein we show that higher gas evolution is related to reduced reaction between the gasses released by the CAM and the respective solid electrolyte. Considering gas species compositions, the cells with glassy electrolyte generate lower amounts of O2, but also form additionally SO2 which indicates oxidation of sulfides. In combination with electrochemical results, XPS and ToF-SIMS, it is surprisingly found that even though a stronger degradation is observed, this likely stemmed from a closer contact and thus better conductivity of the glassy electrolyte.

Next, a series of P2-type layered oxide sodium ion CAMs of different configurational entropy is characterized and compared using DEMS. The materials show a varying degree of phase transition upon desodation. Based on DEMS results, an activation-like first cycle including oxygen redox is analyzed. Unexpected gas evolution at low potentials is explained and serves as an example for similarities and differences between lithium ion and sodium ion battery gassing.

Lastly, gas evolution of a Prussian Blue Analogue CAM for sodium ion batteries is characterized and serves as an example of DEMS application for next generation materials. The observed gassing can be understood starting from the known mechanisms in NCM CAMs but requires additional interpretation. The observation of cyanogen formation can be attributed to the same concept as the evolution of oxygen from NCM: The oxidative dimerization of lattice anions at high potentials. Based on the initial experiments, future experimental possibilities and considerations, especially towards surface residues, synthesis conditions and material composition are presented. The presentation is finally concluded with a brief summary of possible DEMS/OEMS applications and complementary experiments.

Dry Battery Electrode Manufacturing Using a Twin-Screw Extruder for Continous Powder Granulation

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Electrode manufacturing is a cost- and energy-intense process that in industrial scale usually relies on the use of a hazardous and expensive solvent, N-methyl-2-pyrrolidone (NMP), for cathodes. After coating the battery-slurry to a current collector, the solvent needs to be evaporated to obtain a porous electrode suitable for the use in a Lithium-Ion Battery, meaning that the solvent is a processing material and unwanted in the final product. Nevertheless, the utilization of NMP in largescale applications demands costly labor protection and explosion safety measurements during mixing and coating and necessitates a highly energy and floor-space demanding drying step using thermic drying ovens of up to 100 meters. For ecological and economic reasons, NMP is not emitted in large-scale production facilities, but condensed and recovered by an elaborate distillation process to receive battery-grade NMP. The NMP-recovery system adds additional floor space and energy demand to the production site. The drying and solvent recovery can account for up to 39% of the total energy demand of a Lithium-Ion Battery Cell production and therefore produce significant CO2 emissions. A solvent-free, dry electrode manufacturing that eliminates the use of solvents hence reduces the floor space, energy demand and cost of a Lithium-Ion Battery production and eases safety and environmental concerns. Different approaches have been reported in the literature to put dry coating into practice, yet most strategies, including electrostatic spray deposition, brush coating or sieve coating, lack of a feasible implementation into large scale production. In contrast, a dry coating approach that is sometimes referred to as the Maxwell-Process is, according to media reports, currently installed at Tesla's Gigafactory in Berlin. Compared to the state-of-the-art electrode manufacturing process, dry coating requires different polymeric binder systems that form spiderweb-like structures of fine fibrils connecting the electrochemical active particles and the conductive additive particles. The fibril-network is primarily formed by a high-shear dry mixing process. The powder mixture is then compressed to a free-standing electrode film (powder-to-film) by a heated rolling mill (calender) and the resulting film is ultimately laminated to a current collector foil (film-to-foil). We demonstrate that a twin-screw extruder can be used to tune the degree of binder-fibrillation during dry-mixing of NMC-based cathode mixtures and show a superior cyclingstability of dry-coated cathodes in single-layer pouch cells compared to wet coated reference electrodes of likewise composition and electrode design. Additionally, the requirements towards current collectors to guarantee a sufficient adhesion of the free-standing films and low contact resistances between the electrode-layer and the current collector were studied in detail.

Effect of Anion Chaotropicity in the Expansion of Electrochemical Stability Window in "Water-in-Salt" Electrolytes Zahid Ali Zafar

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Electrochemical energy storage systems (EESS) with high energy density, safety, low cost, and low carbon footprint have become indispensable in the modern era of ubiquitous electronics, electric vehicles, and grid storage. Current EESS lack these characteristics due to the utilization of critical materials that are precious, flammable, difficult to recycle, and pose a threat to the environment. Whereas aqueous electrolytes offer higher safety and lower cost. Nevertheless, their biggest bottleneck is the narrow electrochemical stability window (ESW) that is preventing them from attaining higher energy and power densities in most of the aqueous EESS. For instance, multivalent metal-ion-based aqueous rechargeable batteries promise high energy density due to the multivalent redox chemistry of metal ions (Al3+, Zn2+etc.) but they exhibit much lower energy density in real experiments due to the limited ESW of the aqueous electrolytes. The water-in-salt (WIS) electrolytes can potentially eliminate this barrier by offering a larger ESW. However, an anion's nature, i.e., kosmotropic (water structure-maker) or chaotropic (water structure breaker) plays an important role in the expansion of the ESW in WiS-electrolytes. In general, the kosmotropic anions have a negative impact on the ESW by disturbing the solvation shell of the counter cations. On the other hand, chaotropic anions increase the ESW by limiting the fraction of free water in the electrolytes by pushing water molecules into the solvation shells of the cations.

We demonstrate WIS-electrolytes of metal-perchlorates (metal: Al, Zn, etc.) containing strong chaotropic anion (ClO4-). As a result, the WiS-electrolytes of Zn- and Al-perchlorates demonstrate expanded ESW of 2.80 V and 4 V, respectively. The electrochemical tests of the electrolytes are performed using carbon-based redox-active electrode materials. We employ the new electrochemical systems in aqueous rechargeable multivalent dual-ion batteries, revealing superior performance to standard aqueous electrolytes. Our findings provide new possibilities for widening the ESW and enhancing the energy and power density in aqueous EESS, especially for grid storage applications

Effect of Sintering Conditions on Ionic Conductivity of Na3Zr2(SiO4)2(PO4)

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All-solid-state batteries are to be investigated due to its high safety as well as its potential for higher energy density compared to batteries containing liquid electrolyte. In that content, sodium ion batteries are paid more and more attentions as the natural abundance of sodium is 3 orders of magnitude higher compared to that of lithium thus a sodium-ion battery may be fabricated cheaper than a lithium-ion battery.

In the present study, Na3Zr2(SiO4)2(PO4) (NZSP) is selected because it is one of the most promising materials as a sodium ion conducting electrolyte for an all-solid-state battery. First the influence of sintering condition of NZSP was investigated for the purpose of producing batteries with higher charge-discharge performance. NZSP powders are prepared through the solid-state reaction method and it is mixed with Na2B4O7(NBO)-10H2O that is a sintering aid material, which percentile of the mixture from 5 to 15% in weight. The powder mixture of NZSP and NBO was first compressed and then sintered by spark plasma sintering method in argon gas atmosphere which was slightly below the atmospherics pressure. The sintering temperature and the uniaxial pressure on the sample during the sintering were arbitrary varied as from 500 to 700 oC and from ca. 60 to 130 MPa. The sintering process of NZSP with NBO was then evaluated by X-ray diffractometry and scanning electron microscope. The impedance spectroscopy was also applied to extract the ionic conductivity and its activation energy measured by an electrochemical measurement device under the various temperature conditions. Additionally, the bulk density of each sintered NZSP was also obtained by measuring the size as well as the weight.

The results showed the followings; In the case of samples which NBO content is 10% and the sintering temperature is 500 °C, the bulk density was ca. 2.2 g/cm3 and the ionic conductivity was about 1.5×10-5 S/cm at 25 °C. In the case sintered at 700 °C, the bulk density was from 2.5 to 3.0 g/cm3 and the ionic conductivity was about 2.2×10-4 S/cm at 25 °C. As the sintering temperature increases, the bulk density is increased and the ionic conductivity also increases. In the case of samples sintered with uniaxial pressure of ca. 60 MPa at 700 °C, the bulk density was about 2.5 g/cm3 and the ionic conductivity was about 1.0×10-4 S/cm at 25 deg. C. In the case of samples sintered with uniaxial pressure of ca. 130 MPa at 700 °C, the bulk density was about from 2.4 to 3.0 g/cm3 and the ionic conductivity was about 1.2×10-4 S/cm at 25 °C. As the uniaxial pressure increases, the bulk density is increased and also the ionic conductivity increases. In the case of samples which NBO content is 5% in weight with uniaxial pressure of ca. 130 MPa at 700 deg. C, the bulk density was about 2.5 g/cm3 and the ionic conductivity was about 3.4×10-4 S/cm at 25 deg. C. In the case of samples which NBO content is 15% in weight with uniaxial pressure of ca. 130 MPa at 700 deg. C, the bulk density was about 3.2 g/cm3 and the ionic conductivity was about 4.6×10-4 S/cm at 25 deg. C. Same as the sintering temperature and uniaxial pressure, as the percentile of NBO increases, the bulk density is increased and the ionic conductivity also increases. It is interesting to note that when the bulk density is above ca. 2.5 g/cm3, the ionic conductivity does not increase with the increase in bulk density. Moreover, NZSP mixed with 15% NBO and sintered at 500 deg. C and NZSP mixed with 5% NBO and sintered at 700 °C have about the same bulk density, however, their ionic conductivity is different about one order of magnitude. The reason is explained by the impedance spectroscopy measurement results as well as the SEM images in the relation between

the bulk conductivity, the grain boundary conductivity and tortuosity factor of ionic conducting path depending on the sintering temperature and the percentile of NBO mixed with NZSP.

This work is based on results obtained from a project, JPNP14004, commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

Electrophoretic Deposition of Electrodes for Flexible Batteries David Stark

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The growing demand for consumer electronics coupled with advancements in research and production techniques pushes the battery technology for better and innovative approaches. Fabrication and design limitations pose somewhat of stagnation for the industry to bring inventive power sources such as custom-shaped flexible batteries.

We present a unique, single-step method for the preparation of a membrane-electrode assembly [1].

Concurrent electrophoretic deposition (EPD) of positive and negative battery electrodes (LFP and LTO) on opposite sides of a commercial nanoporous membrane (Celgard 2325) results in the formation of a three-layer-battery structure. The cell comprising this electrophoretically deposited structure ran for more than 150 cycles with 125-140mAh/g capacity, which approaches the theoretical value of lithium iron phosphate. The electrodes can be deposited either cathodically or anodically by replacing the interchangeable charging agents, like polyethyleneimine and polyacrylic acid. These polyelectrolytes, when adsorbed on the particles of the active material, serve also as the binders.

With environmental and economic issues in mind, we also present our latest experimental results for the EPD of LTO from water-based suspension made possible by a square-wave and triangular AC deposition.

The simultaneous EPD, which we developed, can be used for the simple and low-cost manufacturing of a variety of cathode and anode materials on nanoporous polymer- and ceramic ion-conducting membranes for energy storage devices.

Electrospun Hierarchical Vanadium Oxide Nanostructures As Electrode Materials for Post-lithium Batteries

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Driven by the need for economical and sustainable energy storage devices and the limited global resources of lithium, magnesium batteries emerged as the long-term potential energy storage systems. In particular, batteries based on magnesium ions represent one of the most attractive alternatives to Li and Na ion batteries due to their multivalent-ion chemistry, which can be extrapolated to high theoretical capacity. Besides, Mg batteries can offer improved safety, thanks to the dendrite-free Mg deposition. However, the strong electrostatic forces induced by divalent Mg2+ ions hinder the ion insertion and transport, resulting in kinetically sluggish redox reactions and low charge storage capacity of the electrode. To mitigate this problem, this work explores the advantages of advanced nanostructured electrodes that can offer high surface area and a short iondiffusion path, which can enhance the electrochemical activity of the electrode material during the Mg2+ ion insertion/extraction processes. For this purpose, we attempted to design free-standing and binder-free electrodes through the electrospinning method, a widely known technique in the nanotechnology field due to its simplicity, low cost, high productivity, and reproducibility. Besides, low density, extremely high surface area to weight ratio, high pore volume, and controllable pore morphology of the nanofibers obtained through the electrospinning process have made this technique an important approach for designing high-performance electrodes for rechargeable batteries. We have considered vanadium oxides as the active materials for charge storage owing to their high operating voltage and high theoretical capacity to demonstrate the advantages of electrospun electrode materials. The fabrication of the electrode involves the immobilization of a soluble polyoxovanadate precursor to a polymer matrix followed by electrospinning and thermal annealing, forming a nanocomposite of vanadium oxide and carbon fiber. The nanofibers' composition, morphology, and thermally induced structural rearrangements are confirmed through detailed physicochemical characterization.

Electrospun Nanofiber Mesh Cathodes for Ultrathin Flexible Batteries <u>Edi Mados-Kantor¹</u>, Diana Golodnitsky¹, Amit Sitt¹

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Nanofiber meshes are a promising platform for constructing light, flexible, and mechanically robust batteries for a range of applications including wearable electronics, healthcare services, and energy devices. This is due to their large surface-to-volume ratio, highly porous structure, lightweight, and the ability to perform even under significant mechanical deformation.

In this work, meshes of Polyethylene glycol (PEO) polymeric nanofibers loaded with lithium iron phosphate (LFP) (LiFePO4) nanoparticles and C65 nano carbon black were formed via electrospinning. The LFP containing meshes were tested as a cathode to evaluate the ion transport properties of ultrafine electrospun meshes and assess the potential of this fabrication technology for ultra-thin flexible lithium-ion batteries.

In particular, we examined the effect of dispersion and grain size of the LFP particles on the cathode performance. When cycling the cells at a c/20 rate, fibers that were loaded with ball-milled nanosized LFP demonstrated an improved initial discharge capacity compared to non-milled micron-sized LFP (133 vs. 115 mAh/g LFP). Both cathodes demonstrated high reversible capacity retention and stable performance. These preliminary results indicate that the spun meshes hold a great potential for the formation of flexible batteries, towards the goal of fully electrospun flexible batteries in the future.

Enabling Uniform Li Plating/Stripping for Long-Life Thin Li Metal Batteries via Li2O/LiOH-Rich Passivation Layer

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The growing use of electric vehicles and portable electronic devices imposes strong requirements for developing high energy-density rechargeable batteries. In this context, lithium metal anode remains one of the most appealing alternatives to graphite, given its more than ten-fold higher capacity of 3860 mAh/g versus graphite (372 mAh/g). However, substantial challenges still impede the practical application of Li metal anode. Among the crucial issues is the unstable solid electrolyte interphase (SEI) formed due to the side reactions between Li and the organic electrolytes. These continuous reactions result in electrolyte consumption and the formation of dead Li, which further causes low coulombic efficiency, high overpotential, and a rapid fading of the cell. The other barrier is the uneven Li plating/stripping during the electrochemical cycling, which leads to dendrite growthrelated battery failure. Multiple strategies have been developed to address these issues, including electrolyte additives, organic/inorganic passivation layers, and recently the introduction of solidstate electrolytes. Among the promising approaches to increase interphase stability and homogenize the Li plating/stripping process are inorganic surface passivation layers. On the one hand, Li fluoride, Li nitride, Li phosphate, and Li alloys are examples of inorganics species that have the potential to extend the cycle life of Li metal. On the other hand, species like Li2O and LiOH are less investigated and it remains unclear whether they have an intrinsically beneficial function as a protective passivation layer for metallic lithium.

In this study, we fabricate a Li2O/LiOH-rich layer as a passivation layer for the thin lithium metal anode of 50 µm deposited on a Cu foil. The experiments were carried out in an ultra-high-vacuum (UHV) surface preparation reactor connected directly to the X-ray photoelectron spectroscopy (XPS) system. The Li2O/LiOH-rich layer is formed by exposing the thin metallic lithium to a Radio Frequency N2 plasma using Li3PO4 as a target. The in-situ XPS at the C1s and O1s core levels demonstrate that the native Li2CO3 is converted to Li2O/LiOH as major components on the surface due to the highly oxidative environment of the plasma. The formed ~700 nm Li2O/LiOH-rich layer shows textured surface and particle agglomeration, as shown by scanning electron microscopy (SEM). From ex-situ X-ray absorption spectroscopy (XAS) carried out at the O K-edge, Li2O and LiOH are detected in both total electron yield (TEY) (probing depth ~10 nm) and total fluorescence yield (TFY) (probing ~100s of nm), confirming that Li2O/LiOH preserve their integrity underneath the surface. The Li2O/LiOH-rich metallic Li symmetric cells cycled for about four times longer than the as received thin Li in the ether-based electrolyte, reaching 1200h (400 cycles) with a current density of 1 mA/cm2 and an area capacity of 1.5 mAh/cm2. Li2O/LiOH-rich metallic Li symmetric cells also show a low overpotential of 12.4 mV (cycled after 200h), indicating high stability of plating/stripping process. At the end of Li plating after 20 cycles, ex-situ SEM and XPS measurements showed much smaller and uniform plated Li clusters and thinner SEI formation, respectively, indicating a regulated plat-ing/stripping process and better electrolyte stability thanks to the Li2O/LiOH-rich passivation layer.

Evaluating Charge Transport Bottlenecks in Composite Cathodes of All-Solid-State Batteries

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As an energy storage device with high energy and power density, ASSBs (all-solid-state batteries) have recently received increased attention. Their key component is a solid electrolyte and among the plethora of available materials, thiophosphate-based solid electrolytes such as Li6PS5Cl are very promising because of their high lithium-ion conductivity. Furthermore, their malleable nature makes them easily processable at room temperature.

Replacing liquid electrolytes by rigid solid electrolytes in composite cathodes poses different challenges such as insufficient charge transfer between cathode active material and solid electrolyte due to low contact areas. Sufficient ionic and electronic transport pathways in composite cathode structures are essential because cathode active material particles that are either electronically or ionically isolated cannot contribute to the charging or discharging process. Because ASSB cathodes rely solely on solid-to-solid contacts, achieving percolation is more difficult, than by infiltration of porous electrodes with a liquid electrolyte. The challenge of achieving complete ionic percolation is amplified for composite cathodes containing high amount of cathode active material, which is necessary for obtaining high energy density. Additionally, residual porosity that blocks charge transport of ions and electrons has to be minimized. Thus, optimizing cathode microstructures becomes increasingly important for the improvement of all-solid-state batteries.

In this study, we investigated both ionic and electronic percolation in composite cathodes made of LiNi0.6Co0.2Mn0.2O2 and Li6PS5CI. Different cathode microstructures were created by varying the volumetric content of cathode active material and solid electrolyte between 20% and 70%. Partial conductivities were used to evaluate the effectivity of the electronic and ionic conduction pathways. To quantify the respective partial conductivities, we used electronically as well as ionically blocking electrodes with which to carry out electrochemical impedance spectroscopy measurements.

From the obtained partial conductivities, we calculated tortuosity factors and correlated them to cell performance with complementary cycling data of all-solid-state batteries in order to determine charge transport bottlenecks. By FIB-SEM tomography of a composite cathode we could generate a detailed 3D reconstruction of the cathode microstructure and found the particle size of the solid electrolyte to influence the electrochemical performance of composite cathodes containing high amounts of cathode active material.

Evaluation of γ-Butyrolactone-Based Electrolytes for Fast-Charging Polymer-Based Dual-Ion Batteries

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Lithium ion batteries (LIBs) possess various properties, which make them the most favourable cell system for various applications. Especially in terms of their specific energy and their energy density, they outrival other cell technologies. However, LIBs still face some challenges with regard to their sustainability, safety, abundancy of the used materials and their rate capability.

Redox-active polymers are based on a simple working mechanism compared to the complex intercalation mechanisms in LIBs. This results in a fast de-/insertion of the respective ions into the polymer electrode and thereby to a high rate capability. In addition, polymer-based electrodes are easy to manufacture and the absence of toxic metals make them an environmental-friendlier alternative compared to e.g, layered transition metal oxides. Since polymers with conjugated polymer chains bear disadvantages, such as voltage sloping within ongoing cycling, polymers with isolated redox-active units represent a promising approach for polymer-based batteries. One example for this type of polymer is the radical poly(2,2,6,6-tetramethylpiperidinyl-N-oxyl methacrylate) (PTMA), which is also the focus of this study.

This work presents the influence of the rate performance of PTMA||Li metal cells in dependency on different electrolytes. Previous investigations revealed a positive effect of γ -butyrolactone (GBL) as electrolyte solvent compared to standard electrolyte solvents. Therefore, various lithium salts are used in combination with GBL and are investigated regarding their rate capability and long-term cycling stability at different specific currents (e.g., 100 mAh g-1 (\approx 1C) and 1000 mAh g-1 (\approx 10C)). Particularly, lithium difluoro(oxalate)borate (LiDFOB) in GBL has an advantageous effect on the rate performance of PTMA||Li cells, resulting in a specific discharge capacity of 92 mAh g-1 compared to 23 mAh g-1 for 1M LiPF6 in ethylene carbonate:ethyl methyl carbonate (3:7 by wt.) when the cell is charged and discharged with a specific current of 5000 mA g-1 (\approx 50C).

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Fast Na Ion Dynamics in Nb5+ Bearing Na3+xZr2Si2+xP1-xO12

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Electrochemical systems such as Li-ion batteries have become an integral part, not only in the affluent societies, to power mobile devices. Over the next years they will also be used to stationary store electricity converted from intermittent energy sources such as wind, tidal or solar power. Considering electric vehicles or small electronic devices, Li-ion batteries clearly dominate the market. However, socio-economic considerations do already point away from the Li-ion technology to batteries relying on other charge carriers such as Na+, being small enough to be quite mobile in condensed matter. The high natural abundance of Na allows the development of sustainable large-scale stationary storage systems. Compared to the current ones using Li+, Na-ion batteries are facing the same safety problems if flammable, liquid blends are used as electrolytes. While ceramic, i.e., solid, Na+ electrolytes are expected to be much safer, they usually suffer from significantly lower ionic conductivity as compared to their liquid counterparts. Fortunately, the group of ceramic Na superionic conductors (NASICONs) comprises many intriguing candidates with high Na+ ion conductivities, being almost on a par with some liquids.

NZSP (Na3+xZr2Si2+xP1-xO12) ranks among the most promising NaSICON materials to develop allsolid-state Na+ ion batteries. Importantly, its moderate ionic conductivity in the order of 0.1 mScm-1 can be increased further and fine-tuned by varying its original composition and by taking advantage of clever substitution strategies. Here, we systematically analysed the influence of aliovalent substitution on ionic conductivity of mechanosynthesized Na3+xZr2Si2+xP1-xO12. For this purpose, we partly replaced Zr4+ by Nb5+ and studied the resulting effect on the Na+ ionic transport properties with broadband impedance spectroscopy, electric modulus spectroscopy and nuclear magnetic resonance (NMR) operating at both micro- and macroscopic length scales.

We found that increasing the Na content from x = 0 to x = 0.4 enhances the bulk, that is, the intragrain conductivity, resulting in a total conductivity of approximately 0.4 mS cm-1. The exchange of Zr4+ by 2 % Nb5+ leads to a further significant increase of the bulk conductivity to 6.5 mS cm-1; the total conductivity turned out to be in the order of 1.6 mS cm-1 (20 °C). Local Na ion hopping barriers (0.31(3) eV and values as low as 0.09(1) eV) as determined by 23Na NMR will be compared with those from conductivity measurements being sensitive to macroscopic transport. Importantly, the 23Na NMR spin-lattice relaxation rates (1/T1) reveal a shallow rate peak (log(1/T1) vs 1/T) near room temperature pointing to extremely rapid 23Na spin fluctuations comparable to those in thiophosphates such as Li6PS5Br.

Flexible Biodegradable Electrolytes for Custom-Shaped Batteries

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The progress made in flexible electronics would receive a strong stimulus with the development of free form-factor flexible batteries. Our research pioneers simple one-step extrusion of recyclable battery with a multi-shell architecture comprising biodegradable polymer electrolyte.

As in the conventional battery, high ionic conductivity of extruded electrolyte and compatibility with electrode materials are the essential properties for enabling high performance of the battery.

The electrolytes are composed of LiTFSI, polyethylene oxide (PEO), which is a known lithium-ion conductor, and one of the thermoplastic recyclable and biodegradable polymers- polylactide (PLA) or polyurethane (TPU) - for enhanced mechanical properties and high-temperature durability.

The extruded electrolytes of varying PEO-to-PLA and PEO-to-TPU ratios and salt content were characterized by means of ESEM imaging, mass spectroscopy, differential scanning calorimetry (DSC) and electrochemical impedance spectroscopy (EIS). The structure and electrochemical properties of extruded and printed electrolytes were compared with cast films. It was found that extrusion process promotes longitudinal orientation of polymer macromolecules. Both thermoplastic polymers not only improve the mechanical properties of neat PEO-based polymer electrolyte, but also form complexes with lithium salt and serve as conducting medium.

Flexible all-solid LiTFSI-based PEO-PLA blended electrolyte showed bulk ionic conductivity of 8.1*10-5 S/cm, and that of PEO-TPU – 2.6*10-4 S/cm at 90°C. This difference is much more pronounced at room temperature. Plasticization of the electrolytes by LiTSI-Pyr14TFSI increases bulk conductivity by an order of magnitude. The mechanism of ion transport in both electrolytes will be discussed.

High-Throughput Experimental Automated Module for Battery Materials Exploration

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The global demand for sustainable rechargeable batteries is expected to increase drastically in the next decade as applications continue to take off. Li-ion batteries (LIBs) are the most powerful of the high-capacity rechargeable batteries on the market today, but they have almost reached their energy density limit and, therefore, exploration of new systems and chemistries is mandatory.

Taking up this challenge requires new disruptive approaches and better tools to accelerate the discovery and understanding of new electroactive materials. Several strategies have been proposed by different groups to theoretically identify new potential candidates more efficiently, but the experimental validation stage often reveals to be the limiting step of the new material discovery process.

In this work, a novel automated high-throughput experimental module for the preparation of labscale samples of electrode materials will be presented. This module is designed to handle and mix solutions of precursors in appropriate stoichiometries that will be evaporated before a solid-state annealing treatment. This approach enables to build a set-up compatible with a wide range of synthesis routes such as sol-gel, Pechini, co-precipitation-based syntheses, etc, which in turn enable for size and morphological control and/or in situ carbon coating of the particles to enhance the ionic conductivity.

Hydrogen Bond Assisted Ultra-Stable and Fast Aqueous NH4+ Storage

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Aqueous ammonium ion batteries are regarded as eco-friendly and sustainable energy storage systems. And applicable host for NH4+ in aqueous solution is always in the process of development. On the basis of density functional theory (DFT) calculations, the excellent performance of NH4+ insertion in Prussian blue analogues (PBAs) is proposed, especially for copper hexacyanoferrate (CuHCF). In this work, we prove the outstanding cycling and rate performance of CuHCF via electrochemical analyses, delivering no capacity fading during ultra-long cycles of 3000 times and high capacity retention of 93.6% at 50 C. One of main contributions to superior performance from highly reversible redox reaction and structural change is verified during the ammoiation/de-ammnoiation progresses. More importantly, we propose the NH4+ diffusion mechanism in CuHCF based on continuous formation and fracture of hydrogen bonds from a joint theoretical and experimental study, which is another essential reason for rapid charge transfer and superior NH4+ storage. Lastly, a full cell by coupling CuHCF. In brief, the outstanding aqueous NH4+ storage in cubic PBAs creates a blueprint for fast and sustainable energy storage.

Impact of Structure and Interface Properties on Charge Distribution and Transport in Composite Solid Electrolytes

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To decarbonize the transport sector, a widespread switch to battery electric vehicles is needed. Current drawbacks of battery electric vehicles include the large size and weight of the Lithium-ion batteries (LIBs) to achieve attractive driving ranges. To tackle this challenge, the energy density of LIBs needs to be increased. All-solid-state-batteries (ASSBs) have the potential to increase the energy density, as they enable the use of metallic Lithium anodes among other advantages. Challenges around ASSBs include the formation of a well conducting and stable interface between the solid electrolyte (SE) and the electrodes, as well as achieving high ionic conductivities and therefore decent C-rates in the application. To achieve high ionic conductivities and longevity, uniform current densities within the SE are desirable.

SEs can be divided in three major classes: ceramic, polymer, and composite electrolytes. Ceramic electrolytes offer the highest ionic conductivities, good prevention against Lithium dendrite growth, high voltage operation as well as thermal, chemical, and mechanical stability. However, they are brittle, expensive, challenging to manufacture, and cannot adapt to volume changes during battery operation. Polymer electrolytes are easy to manufacture, cheap and sufficiently flexible to ensure good interfacial contacts during battery operation. Yet, they have limited ionic conductivity, especially at room temperature. Combining polymer and ceramic in a composite SE, combines the benefits of both materials: the ceramic particles facilitate rapid ionic transport and enhance the mechanical strength of the electrolyte while the polymer facilitates good interfacial contact during operation and adapts to volume changes. Also, composite electrolytes allow cost effective, slurry-based manufacturing on large scales.

In composite SEs, Li-ion transport through and along the polymer-ceramic interface is known to be a key factor in ionic transport; however, detailed understanding of the relative importance of bulk and interface transport is missing. To understand this, we apply x-ray tomography to quantify the structure of composite SEs made of Al-doped LLZO (LLZO) and Polyethylene oxide (PEO) with varying LLZO volume fractions (15, 25, 40 vol. %) and particle size distributions. With these 3D reconstructions, we perform ionic transport simulations with varying assumptions of specific interfacial resistivity and temperature. The simulations allow us to study the relative contributions of the LLZO, PEO, and their interfaces to the transport as a function of structure and different operating conditions. In particular, we consider the distribution of current density within the composite SEs. These findings guide the selection of materials and interface treatments for the composites SEs. For example, we find that surface treatments decreasing interfacial resistivity are critical above 15 vol% LLZO, particularly in the case of smaller LLZO particles, to enable uniform and higher current densities throughout the SE.

Increasing the Cycle Life of Anode-Free Li-Metal Batteries and Li-Metal Batteries by Addition of Ceramic Nanoparticles to the Electrolyte

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Because of their higher energy density, compared to lithium-ion batteries, rechargeable lithiummetal batteries (LMB) have been considered one of the most attractive next-generation energystorage systems (ESS). A promising approach to improve LMB performance, that has gained interest in recent years, is the use of anode-free lithium-metal batteries (AFLMB). Such battery configuration enables elimination of the problem of using excessive amounts of lithium (Li) in LMBs, hence increasing the specific energy and the safety.

This work explores the beneficial effects of integrating metal-oxide nanoparticles (MONPs) into the liquid electrolyte of AFLMB and LMB. It was found that the addition of low concentrations of MONPs significantly improves coulombic efficiency (CE), capacity retention (CR) and the Solid-Electrolyte-Interphase (SEI) properties. SEM images revealed a smoother lithium morphology for MONPs cells and XPS analysis indicated, in some cases, no "dead Li" formation. The resistance of the cell components, extracted via electrochemical impedance spectroscopy (EIS), has been significantly lowered due to the addition of MONPs. It was also found that conducting EIS at early cycling stage has deteriorative effect on the cyclability of AFLMB.

The performance of the AFLMB, without MONPs, was 97.1% CE and CR of 70% within 12 cycles, while cells with 1% In2O3 or 1% ZnO addition resulted in 99.6% and 99.2% CE, and CR of 70% within 46 and 39 cycles, respectively. Combination of these MONPs showed 99.9% CE, which is among the highest found in the literature for AFLMB.

Increasing the Cycle Life of Silicon-Anode Lithium Ion Battery

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Because of their higher energy density, compared to common graphite-anode lithium-ion batteries (GLIB), rechargeable silicon-anode lithium ion batteries (SLIB) have been considered as one of the most attractive next-generation energy-storage systems (ESS). Silicon is a low-cost and environmentally friendly material, and is the second most abundant element in the Earth's crust. Its theoretical capacity of 4200mAh g-1, is an order of magnitude greater than that of graphite. Nevertheless, the main and most important challenge with this anode is the short cycle life due to very large expansion and contracting during cycling. This work explores the beneficial effects of integrating metal-oxide nanoparticles (MONPs) into the liquid electrolyte of these systems. It was found that the addition, to the electrolyte, of low concentrations (0.1 to 5%) of MONPs improves coulombic efficiency (CE) capacity retention (CR) and the SEI properties. For example, addition of 2% nano TiO₂ reduces the capacity loss per cycle by 28% and increases the CE from 99.2 to 99.7%.

Inductive Heating as a Recycling Preatreatment for the Recycling of Li-Ion Electrodes

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In view of the growing demand for stationary and mobile energy storage applications, the recycling of Li-ion cells is an important opportunity to make resource use more sustainable, reduce greenhouse gas emissions and lower cell costs.

In addition to Li-ion cells that have reached their end of life, rejects are already generated during the cell manufacturing process. These rejects also contain valuable materials and need to be recycled. Due to a multitude of cause-effect relationships within the manufacturing process that are not fully understood, the reject rates in Li-ion cell production of approx. 5 to 10 % are significantly higher than in other areas of industrial production.

Production rejects from Li-ion cell production differ from end-of-life cells because these have not yet undergone any material ageing and can be regarded as effectively pristine. In addition, the material composition is known. These circumstances require the development of processes specially designed for the recycling of production rejects. Valuable scrap battery materials should be treated in-house and reintroduced directly into the process chain. In this way, long transport routes and extensive recycling routes can be avoided and the material cycle can be closed within production.

With this background, an inductive heating of coated current collector foils is being investigated as a thermal pre-treatment for the recycling of lithium-ion cathodes. For this purpose, production rejects are heated in a continuous process in order to heat the polymer binder above melting point or decomposition temperature and thereby weaken the adhesion of the coating and the current collector foil. The cathode materials and the foil are then separated in a cutting and impact mill.

The main objective of the investigations was to assess the feasibility of the process. To evaluate the process, the separation efficiency of the coating material and film as well as the degree of contamination of the recyclate were determined. From this, the recycling rate for the cathode material was calculated and correlated with the temperatures approached.

In addition, the recyclate was examined by XRD with view to its crystal structure and by XPS for possible passivation of the active material as a result of binder decomposition.

Innovative Polymer-Based Electrolytes for Advanced Li Metal Batteries

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The pressing demand for long-lasting, high-power portable electronics and the emerging large-scale diffusion of electric vehicles (EVs) and energy storage from renewable sources require batteries with improved energy density at reduced cost, along with enhanced cycle life and safety. The most striking solution at present is to switch on all solid-state designs exploiting polymer materials, films, ceramics, etc., particularly in alkali metal-based batteries. Considering their intrinsic properties, polymer electrolytes are considered one of the most promising solutions among different solid-state electrolyte possibilities. There are several approaches to outperform the capabilities of current energy storage devices including the in-situ preparation of polymer electrolytes along with crystallinity reduction by means of addition of plasticizers, ceramic fillers, functionalization and proper crosslinking. In addition, to fulfill all the stringent requests in terms of higher energy density and improved stability at the electrolyte/electrode interface, specific family of solid-state polymer electrolytes namely polyanions were developed. Because of their single-ion nature, the lithium transport number values approach unity; this accounts for remarkable benefits to the electrochemical performance, because Li+ ions are predominantly engaged in the redox reaction while anions remain relatively inactive. In the present talk, an overview of the recent developments on advanced polymer electrolytes for Li-based batteries will be offered. The novel solid-state polymer electrolytes were thoroughly characterized in terms of physical-chemical and electrochemical properties. The novel polymer electrolytes demonstrated greatly enhanced performance towards the state of the art of solid-state systems in terms of mechanical properties, electrode compatibility and electrochemical performance. The lab-scale Li metal cells assembled with the different electrode materials (e.g., LiFePO4, NMC, etc.) showed highly reversible charge/discharge characteristics with full specific capacities, limited capacity fading upon very longterm reversible cycling and stable operation for hundreds of cycles.

In-Operando Structural Stability and Electrical Performance of Spark-Plasma-Ablation Derived Porous Films Based on Cathode Nanomaterials for Li-Ion Batteries

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In the last years, Li-ion batteries have been attracting growing interest, mostly focused on cathode material modification as its performance limits to the cell potential and capacity. Desirable features comprise structural stability, good kinetics, good cycling ability, etc. Efforts for solving these issues repose on nanostructured design, among others.

Spark ablation is a powerful new, low cost, and efficient method enabling easily controlled synthesis of clean nanoparticles. By coupling a spark ablator with a vacuum-driven impaction-deposition chamber we have been able to start from metal electrodes to derive films with high specific surface area and complex morphology. Within this research we seek to expand our understanding of ablation synthesis of nanomaterials into deposited films with well-defined porosity, surface composition, structure, and morphology. From a wide range of wide range of single and mixed metal-to-metal oxide materials we prepare those that have proven applicability in Li-ion batteries, however prepared by other methods.

Also, we have conducted in-operando investigation of the simultaneous DC electric performance and synchrotron diffraction of well-known cathode spinel systems prepared using our refined method of deposition and implemented in a Li-ion battery, in sandwich configuration, ready for transmission experiment, in closed and layered coin-cells.

We checked the possibility of pinpointing the desired composition for a certain combination of starting electrode(s) for the ablation deposition, as well as organization of the prepared films, while maintaining the porous morphology.

We checked the possibility of pinpointing the course of the deposition to specific electric behaviour of the films. From this, we are able to better understand phenomena affecting operative functionality and the performance.

Keywords: Li-ion-batteries; Nanomaterials; Spark-Plasma-Ablation-Deposition; In-operando testing

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Interlayer Expansion of Layered Transition Metal Oxides by Alkylamine Functionalization and Its Effects on Lithium Ion Intercalation

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The electrochemical intercalation of ions in layered host electrode materials is the basis of important electrochemical energy storage devices, such as the lithium-ion battery (LIB). Several layered transition metal oxides have been well established as suitable host electrodes for the reversible (de-)intercalation of lithium ions into their interlayer vacant sites.

An important task of the scientific community is to improve the diffusion kinetics of the intercalating ions in the layered oxides to enhance the rate handling capabilities of the electrodes. Several strategies have been suggested to fulfil this aim. For example, one possible route is a nanostructuring approach to minimize diffusion lengths for intercalating ions in the host lattice. However, this often results in low tapping densities of the resulting materials and increased parasitic reactions of the electrodes with the electrolyte due to the increased surface area. Therefore, alternative avenues to increase the kinetics of intercalating ions in layered host materials must be explored.

In this contribution, we demonstrate an approach to manipulate the intrinsic properties of layered transition metal oxide host lattices via interlayer-functionalization. Due to relatively weak van der Waals interactions holding the layers together, layered materials offer the possibility of adjusting their interlayer properties, such as interlayer chemistry and distance, making them very versatile. Such modifications in the structure translate into changes in the intrinsic electrochemical ion intercalation performance of the materials.

The interlayer distance and environment of layered transition metal oxides are tuned using alkylamines as pillaring molecules. Amine molecules of different lengths are inserted into layered oxide host structures via a wet chemistry process, resulting in an expansion of the interlayer distance as shown by XRD. We investigate their electrochemical properties in a Li-ion storage system by cyclic voltammetry and galvanostatic charge-discharge cycling, allowing us to formulate structure-property relations. The morphology of the resulting functionalized structures is also discussed. These studies can pave the way for future research enabling interlayer expansion by organic pillars with the aim of enhancing the power capabilities of common intercalation-type battery materials.

Investigating Thick Positive Electrodes for Li-Ion Batteries Produced by 3D-Printing

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The Li-ion battery is nowadays the leading technology for electrochemical energy storage. The first reason is its superior energy density compared to other technologies (lead, Ni-Cd, Ni-MH...). Second, in the last decade, the Li-ion battery has become the cheapest battery technology (Euro/Wh). However, there is a constant need to increase the energy density of the batteries and decrease their cost. Aside from the development of new battery materials, one possibility is to improve electrode engineering. Thick electrodes are expected to increase significantly (at least 33%) the proportion of active material in a battery cell, thus increasing the energy and the Euro/Wh cost at cell level and beyond. However thick electrodes produced by the standard coating method on metallic foils suffer from weak strength, delamination, high tortuosity, sluggish kinetics and poor rate performances.

In recent years, 3D printing (also labeled as "additive manufacturing") has attracted great interest with the promise to overcome these limitations. Thick electrodes produced by 3D-printing can reach high areal capacities as reported by different research groups. However, the use of this technology for the battery application is still in its infancy and too many unknowns remain to obtain competitive electrodes for real-life applications.

We have decided in VITO to screen the different parameters (materials, electrode composition & morphology...) influencing the properties of 3D-printed electrodes for Li-ions batteries. For example, our recent work focus on lithium iron phosphate (LFP)-based electrode made by 3D printing. The corresponding LFP- loading is superior to 20 mg/cm² with an areal capacity of ca. 3.5 mAh/cm².

Ionically Conducting Inorganic Binders: A Paradigm Shift in Electrochemical Energy Storage Shivam Trivedi

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Binders are one of the key components in a battery. They play a crucial role of interconnecting active materials & conducting carbon together with each other and with the current collector. State of the art binders like polyvinylidene fluoride (PVDF) necessitate the use of use of toxic and expensive solvents like n-methyl pyrrolidone (NMP). As an alternative several water processable binders like carboxymethyl cellulose (CMC), alginate etc. have been investigated. These binders do not have any intrinsic ionic conductivity and are not thermally stable. Taking this as a background, we revealed the potential of several ionically conducting phosphate and silicate based inorganic binders1. These binders are not only ionically conducting, but also water processable, thermally stable (>1000°C), chemically compatible, eco- friendly and safe to use. These binders outperform standard PVDF and CMC based binders in their electrochemical performance. The unique ionic conductive properties of these binders together with binding abilities enabled the flexible fabrication and functioning of solid-state batteries. Twelve such inorganic binders were investigated with six different class of electrode materials for sodium and lithium ion batteries.

Low Voltage Operation and LiFSI Salt Enable Long Li-Ion Cell Lifetimes at 85oC

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Recently, Aiken et al. 1 demonstrated exceptional lifetime (<6 months) for single crystal NMC532/graphite pouch cells balanced for 3.8 V operated continuously at 70oC. These cells contained LiSFI electrolyte salt and 2% VC electrolyte additive in an EC:DMC 3:7 mixture. The cells with LiFSI vastly outperformed identical cells with LiPF6 salt1. The keys to the success of these cells are:

1. Low voltage operation which limits parasitic reactions at the positive electrode;

2. The use of LiFSI salt which is more thermally stable than LiPF6 salt

3. Low voltage operation which avoids aluminum corrosion in the presence of LiFSI.

It is worth mentioning that these NMC532/graphite cells have a larger energy density than LFP cells in spite of being balanced for only 3.8 V.

We had been moving to test Li-ion cells to sequentially higher and higher temperatures in our laboratory to try to accelerate the failure of very good Li-ion cell chemistries to enable lifetime extrapolations to room temperature1–3). We were extremely surprised by the incredible lifetime shown by the cells described above at 70oC. Therefore, we decided to increase the testing temperature to 85oC, the limit of the homemade temperature chambers that we use.

Figure 1a shows the fractional capacity versus time for single crystal NMC532/graphite pouch cells with 1.0 M LiFSI in EC:DMC 3:7 with 2% VC and 1% DTD additives tested at C/3 between 3.0 and 3.8 V. 265 cycles are shown, Figure 1b shows the absolute capacity time for the same type of cells, but tested instead at 1C/1C, 2C/2C, 4C/ 4C and 6C/6C between 3.0 and 3.8 V at 85 C. The numbers of cycles reached are 372, 710, 1405 and 2101 for the 1C, 2C, 4C and 6C cells, respectively. It is our belief that never before has such an incredible lifetime been demonstrated for Li-ion cells operating at 85oC. The data for these cells will be updated at the meeting.

Other cell chemistries, including LFP/graphite and Li[Ni0.83Mn0.06Co0.11]O2/graphite, have also been tested at 85oC and also show exceptional lifetime, provided appropriate electrolytes are used. This will be detailed at the meeting.

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Mechanism of Action of the Tungsten Dopant in LiNiO2 Positive Electrode Materials

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Many researchers have been studying Ni-rich layered oxide material because of its high specific capacity. However, materials with a very high Ni content show faster degradation such as microcracking of secondary particles during charge discharge cycling. The addition of tungsten (W) has been reported to be particularly effective to improve the cycling stability of Ni-rich and Li-rich materials. However, the underlying mechanism for the action of W remains puzzling. Therefore, a close examination of the location of W in LiNiO2 and the corresponding mechanism that is responsible for improving charge-discharge capacity retention is urgently required.

In order to examine the location of W, electron energy loss spectroscopy (EELS) was performed on LNO with 1mol%W, denoted as W1-LNO, synthesized by coating nano-sized WO3 on Ni(OH)2 by a dry particle fusion method previously reported by our group, followed by heating with LiOH·H2O. W-containing Ni(OH)2 precursors were also prepared by co-precipitation and then were subsequently heated with LiOH·H2O.

EELS shows that W is present at the surfaces of the secondary particles and all the grain boundaries of the primary particles. Given that the WO3 was only coated on the surfaces of the Ni(OH)2 precursor in the samples made by dry particle fusion, finding W deep within the secondary particles means that the W phases wet the LNO surfaces well. This provides a coating on the primary and secondary particles which may aid in capacity retention. In addition, EELS also shows that W was mostly concentrated at the grain boundaries between primary particles for W1-LNO whose precursor was prepared by coprecipitation, which supports that W is not preferable to dope into layered oxide structure. In our opinion, W prefers to stay in LixWyOz phases instead. The LixWyOz phases hinder primary particle growth as temperature increases. The smaller primary particles, the less their absolute shrinkage would be and therefore less microcracking should happen. Besides, LixWyOz phases possibly appear to act as a "glue" to increase the resistance of the secondary particles to microcracking under applied stress and during charge-discharge cycling, therefore improve the cycling stability of LNO.

Microscale-Silicon Anodes With High Silicon Content Fabricated by Water-Based Slurry Processing for Use in All-Solid-State Batteries <u>Gioele Conforto^{1,2}</u>, Hubert Gasteiger^{1,2}

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In order to enable the market introduction of all-solid-state batteries, some major challenges must be overcome. In particular, several anode concepts are under investigation to increase the energy density compared to graphite anodes, while maintaining longer stability. At the same time, the production costs must be the same or even reduced in comparison with classical lithium-ion batteries. Besides lithium metal as anode material, which still poses significant technical challenges, more and more interest is being directed towards materials that form lithium alloys, particularly silicon, which has a theoretical capacity of 3579 mAh/g.

Silicon-containing anodes are already being introduced in classical lithium-ion batteries. For that system, the lithium ion conduction across the anode electrode is mainly provided by the liquid electrolyte that fills the pores of the electrode, while the electrical conduction is enhanced by the addition of graphite and/or conductive carbon additives, because crystalline silicon is only a semiconductor. As is well known, the major issue with silicon anodes is the volume expansion of 300% upon lithiation of the silicon particles, inducing severe cracking of the silicon particles as well as continuous solid electrolyte interphase (SEI) growth, both of which lead to a fast capacity fading.

An analogous anode configuration is usually pursued for all-solid-state batteries, whereby the silicon particles are embedded by solid-electrolyte (SE) particles to produce a silicon/SE composite with or without conductive carbon additives. However, the drawback of the volume expansion/contraction upon lithiation/delithiation of the silicon particles is even more accentuated in this case because of the gradual loss of contact between the solid electrolyte and the silicon particles over extended charge/discharge cycling. A possible alternative is the utilization of the silicon particles are present in the anode electrode. This approach is possible since silicon-rich anodes are very thin due to the high specific capacity of silicon. In this case, the lithiation would start at the interface of the silicon particles with the solid electrolyte separator, and the loss of lithium into the SEI should be minimized due to the limited silicon/SE contact area. On the other hand, it is likely that a complete utilization of the silicon in the electrode requires the addition of conductive carbon additives for efficient electrical conduction. While the formed silicon-lithium alloy shrinks to its original volume during the delithiation, it has been observed that it assumes a columnar morphology that could guarantee the mechanical integrity of the electrode even upon extended cycling.

In this work, anodes with >90w% silicon are prepared by coating water-based slurries which contain a microscale silicon (ca. 2-5 μ m diameter) as active material, the rest being made up of LiPAA as binder and C65 carbon as conductive additive. The combination of the water-based process and the microscale dimension of the silicon particles make this electrode concept easily scalable and costeffective. To reach a competitive areal capacity in the range of 2-6 mAh/cm2, with the full utilization of the silicon, only a thin layer is needed (delithiated thickness of 3-9 μ m, lithiated thickness of 10-29 μ m). Therefore, this results in volumetric and gravimetric energy densities that are comparable with lithium metal. The thickness variation and the anode morphology is being investigated by examining cross-sectional SEM images at different states of charge. Cycling half-cells with InLi as counter and as reference electrode, the stability and the rate capability of the prepared silicon anodes will be compared when cycled at different cell compression pressures and for electrodes with different amounts of conductive carbon. In particular, the possible increase in the anode impedance due to anode degradation can be monitored by differential capacity plots and impedance spectroscopy measurements during cycling; on the other hand, the mechanical degradation of the anodes will be examined by post-mortem SEM images of the anodes.

Modeling of Dehydration Reactions in a Synthesis Process of High Ni-Based Cathode in Li Ion Battery

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Dehydration reactions of precursors such as lithium hydroxide monohydrate (LiOH·H2O) and transition metal hydroxide (NixCoyMnz(OH)2) have a poor impact on prediction of temperature distribution and temperature control in synthesis process. Roller Health Kiln (RHK) are mainly used in a synthesis process which consists of heating-isothermal-cooling sections. The dehydration reactions occur in heating section where the temperature increases from room temperature deviation, which interrupts temperature control in RHK. This is one of the reasons causing the quality difference of produced cathode materials. Also, moisture generated in the synthesis process could remain on the cathode surface due to the insufficient temperature control. Residual moisture forming residual lithium compounds on the cathode surface is one of the major side effects, and it adversely affects electrochemical performance such as electrode capacity and resistance.

In this study, the dehydration reactions were analyzed and modeled using a random pore model method. In-situ x-ray diffraction (In-situ XRD) and thermogravimetric analyzer/mass spectrometer (TGA-MS) were used in analyzing the dehydration reactions of each precursor in high-Ni based cathode synthesis. There were four reactions identified at Ar atmosphere where three reactions resulted in water vapor but the other resulted in only oxygen. In LiOH·H2O precursor, two dehydration reactions were classified as 'dehydration of lithium hydroxide monohydrate (LiOH·H 2 $O \rightarrow \text{LiOH} + \text{H}_2 \text{O})'$ and 'decomposition of lithium hydroxide (LiOH $\rightarrow 1/2$ Li $_2 \text{O} + 1/2$ H $_2 \text{O})'$. Meanwhile, in NixCoyMnz(OH)2 precursor, 'dehydration of transition metal hydroxide Ni x Co y Mn_z (OH)_2 \rightarrow Ni_x Co_y Mn_z O_1.25 +3/4H_2 O+1/4H_2)' was confirmed and the other reaction was identified as 'decomposition of transition metal oxide (Ni_x Co_y Mn_z O_1.25 \rightarrow Ni_x Co_y Mn z O+1/8O 2)'. In order to calculate kinetic parameters of dehydration reactions and perform random pore modeling, structural parameters and isothermal TGA data were attained. Structural parameters, which feature initial pore structures of each precursor, were secured by using mercury porosimetry. Moreover, isothermal TGA experiments of each precursor were performed at five temperature points of each reaction to calculate the intrinsic kinetic parameters and conduct random pore modeling. The random pore model was validated using 4°C/min programmed TGA experiments with respect to different precursors ratios, where they were set the same condition as RHK.

The understanding of the dehydration reactions in the cathode synthesis suggests strategies to control much uniform temperature field, considering the effects of generated moisture. This work will be extended by applying the dehydration reactions to the RHK model. Therefore, it is expected that it is possible not only to predict and precisely control the temperature distribution but also to produce the cathode materials of better quality.

Modelling the Redox Chemistry of Lithium-Rich Sulphide Cathode Materials

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Advances in cathode materials are critical for the development of lithium-ion batteries for energy storage applications in portable devices and electric vehicles. Li-rich oxide cathodes offer high energy densities by allowing redox chemistry involving both the transition metal and oxide ions. Issues such as voltage hysteresis, capacity fade, and oxygen loss, however, have hampered the practical application of oxygen-redox cathodes. In this context, Li-rich sulphides have attracted interest due to the possibility of complex multielectron redox chemistries, but practical use is limited by low voltages. We have used a range of computational techniques, including machine-learning accelerated screening protocols, density functional theory (DFT), cluster expansion (CE), and ab initio molecular dynamics (AIMD) powered by intelligent workflows written in AiiDA (Automated Interactive Infrastructure and Database for Computational Science), to examine structural, electronic, and redox properties of new Li-rich sulphide cathode materials with both high voltage and high charge capacity. We also show that incorporation of Earth-abundant transition metals further improves the electrochemical performance of these materials by activating anionic redox processes.

New Experimental Binder for Si-Based Anode

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Battery for EV cars need to keep improving in terms of energy density to remove range anxiety and allow broader and faster adoption. Adoption of Silicon anode is one of the most powerful techno strategies to increase battery capacity and therefore energy density. Silicon (Si) has been extensively studied as anode active material due to its high theoretical specific capacity (3600 mAh/g), much higher than the incumbent anode active material, graphite (<400 mAh/g). Unfortunately, silicon undergoes high volume change (~400%) during lithium uptake that results in mechanical fractures and electrolyte consumption. One widely adopted strategy in the battery market is to use a limited amount of silicon oxide (<10%) mixed with graphite as active material. This strategy mitigates the detrimental impact of silicon on electrode mechanical integrity however, the achieved improvement in energy density, proportional to the amount of silicon, is quite limited. The binder used at anode with current active material (graphite with low Si amount) is not adequate for silicon rich anode (>10%) because it is not sufficiently rigid and has weak interaction with active material particles: it is a combination of a styrene butadiene rubber (SBR) with a cellulose derivative (CMC). The interest of the academia and industry is moving to lithiated poly acrylic acid (Li-PAA) for fabricating silicon anode. Li-PAA in fact demonstrated good cycling stability in Si anodes, however it suffers from severe mechanical issues, low adhesion to copper and cohesion, especially at high loading electrodes and thus making it very challenging to achieve high energy density systems.

In this communication, we report a recently developed aqueous lithiated binder that has excellent mechanical properties and addresses the issue of Si rich (20% SiOx) anode. Unlike conventional anode binders, SBR/CMC and Li-PAA, the Solvay lithiated binder allows for high energy density cells without compromising physical properties and electrochemical performance. Solvay lithiated binder exhibits far better full cell capacity retention than conventional SBR/CMC and Li-PAA binders and imparts excellent mechanical properties at significantly high loading, where the Li-PAA binder fails.

New Hybrid Solid Electrolytes Based on Metal Organic Frameworks

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Solid state electrolytes for battery systems represent a fast developing research field. [1] Here, we focus on a new class of solid state electrolytes based on metal organic frameworks (MOFs). An endless number of linkers and metal centres can be used to build a tremendous variety of different MOFs with tuneable physical and chemical properties. MOFs are a thus a versatile platform to develop solid state electrolytes.

In this study, MIL-121 (Al centres linked by pyromellitic acid) was synthesized by a hydrothermal route [2] and post synthetically modified with lithium acetate and sodium acetate. After the lithiation and sodiation step, the samples were soaked with LiClO₄ or NaClO₄ in propylene carbonate in order to increase the ion content even further.

X-ray powder diffraction (XRD) revealed that the structure of pristine MIL-121 could be largely maintained after lithiation or sodiation. At 303 K, a high Na ion conductivity of 0.12 mS/cm was measured. This fits nicely to the only very few previous investigations on different MOF structures as solid state electrolytes. [3,4] Low activation energies of 0.28 eV (above 323 K) and 0.36 eV (above 283 K) for Li and Na, respectively, were found in the higher temperature region. NMR spectroscopy confirmed the mobility of both ions.

Moreover, a crossover at 323 K (Li) and at 283 K (Na) from correlated to almost uncorrelated motion at higher temperature is proven, which is in line with Ngai's coupling model. Alternatively, in accordance to the jump relaxation model of Funke, at low temperature only a fraction of the jump processes are successful as lattice rearrangement in the direct vicinity of Li (or Na) ions is slow. ¹H NMR unambiguously shows that Li ions are the main charge carrier.

In conclusion, successful modifications (lithiation, sodiation) lead to encouraging ion conductivities in MIL-121 Al-based MOF. [5] These findings pave the way towards development of easily tuneable and rationally adjustable high-performance MOF-based hybrid solid-state electrolytes. Nevertheless, there is plenty of room to further improve this very young and very promising class of solid-state ion conductors.

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Oligoethylene Oxide Functionalized Vinylphosphonic Esters As Solid Polymer Electrolytes With Intrinsic Flame Retardancy and Adjustable Flexibility

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Solid-state polymer electrolytes show great potential for next-generation high-energy rechargeable lithium batteries due to the advantages of high safety, good mechanical flexibility, and easy filmformation ability. Among all the polymers, polyethylene oxide (PEO) is demonstrated to be a feasible polymer host, based on its high dielectric constant and strong lithium salt dissolving ability. However, the practical application of PEO in the all-solid-state lithium batteries is limited mainly by its low ionic conductivity at room temperature, which is a result of its semi-crystalline character as the ion conduction mainly takes place in the amorphous regions of a polymer electrolyte. There have been many attempts to reduce the crystalline domains in these polymer electrolytes including copolymerization, addition of plasticizers, development of gel polymer electrolytes and introducing inorganic fillers with various advantages and disadvantages to each approach. In this study we synthesized a solid polymer electrolyte based on a vinyl phosphonate backbone functionalized with oligoethylene oxide side chains. Hereby, the side chains are responsible for the ionic conductivity, while the phosphonate polymer backbone contributes to a high chain flexibility, electrochemical stability and flame retardancy. The resulting polymers are characterized via nuclear magnetic resonance spectroscopy (NMR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and size-exclusion chromatography (SEC). Consequently, polymer films are prepared by solution-casting with LiBF₄, LiClO₄, LiPF₆, LiOTf and LiTFSI as conducting salts. The resulting polymer films are analyzed by X-ray diffraction (XRD), and electrochemical impedance spectroscopy (EIS). The catalytic polymerization of these oligo(ethyleneoxy) vinylphosphonate monomers features a livingtype character leading to molecular weights up to 1000 kg/mol featuring narrow polydispersities. The polymers are thermally stable up to 260 °C and exhibit a low glass transition temperature (Tg) of -67 °C while no melting temperature (Tm) is observed, therefore lacking any crystalline domains. The fully amorphous character of the polymers is confirmed by XRD measurements. Furthermore, the morphology does not change with the addition of lithium salts in the free-standing polymer films. Hereby, the polymers exhibit a good solubility of the lithium salts showing complete dissolution in a monomer to Li+ ratio of 1:1. With the precisely adjustable catalytic polymerization the synthesized polymers can be optimized in their mechanical and electrochemical properties by introducing various side chains at the phosphonate unit without affecting the polymerization procedure. The completely amorphous character of the free-standing polymer films is one major advantage over pure poly(ethylene oxide) (PEO). In addition, the low Tg indicates a high chain flexibility and therefore results in high ionic conductivity already at room temperature. With the thermal stability up to 260 °C and the phosphonate group as flame retardant feature a SPE based on vinylphosphonic esters enhances the intrinsic safety feature in battery applications.

Optimized Cathode Active Materials for Llzo Based All-Solid-State Lithium Batteries

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Bulk-type all-solid-state lithium batteries (ASBs) with thick composite cathodes consisting of a solidstate electrolyte (SSE) and a high-capacity cathode active material (CAM) are promising candidates for futures energy storage systems. They solve the nowadays challenges of conventional lithium-ion batteries (LIBs) by providing higher energy densities and intrinsic safety. However, the fabrication of such ceramic batteries is challenging due to the necessary high processing temperatures which lead to material compatibility issues. Especially, high-capacity CAMs, like LiNixCoyMn1–x–yO2 (NCM), show insufficient material compatibility toward the solid electrolyte, Li6.45Al0.05La3Zr1.6Ta0.4O12 (LLZO:Ta), during co-sintering of dense composite cathodes. Thus, the thermodynamic stability of NCM towards LLZO:Ta at elevated temperatures, needs to be improved. Regarding to this, in this work NCM cathode materials are tailored by doping. We synthesized B- and Ru-doped NCM via a hydroxide co-precipitation route and fundamentally studied the impacts of the small sized B3+, in comparison to the lager, highly charged Ru5+ on the lattice, the morphology, and electrochemical performance of NCM811. Finally, we investigated the thermal compatibility between different NCM compositions (NCM111, Ni-rich NCM811, B- and Ru-doped NCM) and LLZO:Ta, to assess the impact of the transition metal composition and doping on the material compatibility during fabrication of ceramic composite cathodes for ASBs. The experimental investigations by XRD, DTA/TG/MS, SEM, TEM, EDS, TOF-SIMS, and nuclear reaction analysis were supported by DFT calculation. By the combination of experimental and theoretical findings, surprisingly, Ni-rich NCM811 was found to be the most promising CAM for the combination with garnet-type LLZO:Ta in composite cathodes of ceramic ASBs. Therefore, a fully inorganic ASB based on a Li-metal anode, an LLZO:Ta separator, and a composite cathode, consisting of Ni-rich NCM811, LBO, and LLZO:Ta, could be successfully manufactured. This battery exhibits one of the highest specific areal capacities (0.7 mAh/cm²) reported so far for garnet-type ASBs based on Ni-rich NCM811 as active material.

Organic Batteries and Four Electron Reaction

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Organic batteries are new battery technology which could in the future revolutionize our energy storage. Compared to state of the art Li-ion technology, they are more sustainable as they don't contain toxic and strategic metals such as Nickel and Cobalt, their production is less energy demanding, can be produced from organic waste and are less prone to thermal runaway. Moreover organic electrode materials offer much higher specific capacities than inorganic ones, can be used in aqueous batteries and can be used in multivalent batteries (Mg, Zn, Al, etc.) which is another advantage if we want move away from relatively rare and strategic lithium metal.

In this study we will present range of hydroxybenzenes from mono to hexahydroxy and explain why 1,2,3,4-tetrahydroxybenzene is the best candidate in terms of specific capacity and cycle stability. Three model compounds were synthesized: reduced MH4, partially oxidized MH2 and fully oxidized M. Their CV curves in 0.1 M HClO4 in water were identical which means they can be electrochemically converted from each other and this is a proof for reversible four electron reaction.

To enable stable battery cycling we have also developed polymer nanoparticles with high theoretical capacity 631 mAh/g, based on poly(2,3,4,5-tetrahydroxystyrene) and tested it as organic positive electrode in Li-battery. However very low capacity 111 mAh/g was obtained without visible redox peaks. It seems that this polymer works well only in acidic water electrolytes and could be not used with classical Li-organic electrolytes. The same was also observed with previous model compounds MH4, MH2 and M and is known from the literature of catechols, where it is explained as complicated side reactions of reactive radical anion with electrolyte or catechol itself. According to this results poly(2,3,4,5-tetrahydroxystyrene) could be used in proton batteries, potentially delivering very high specific capacity 631 mAh/g owing to it's four electron redox reaction.

P3-Type Mn and Fe-Based Layered Oxide Positive Electrode Materials for Sodium-Ion Batteries

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Sodium-ion batteries (SIBs) have been proposed as an alternative energy storage technology to lithium-ion batteries with increasing concerns on the world's lithium supply. Layered transition metal oxides of the general formula NaxTMO₂ (where TM stands for transition metals such as Ni, Co, Mn, Fe and combinations thereof) have become prominent positive electrode active materials for SIB applications. They can be classified into the P2, O3 and P3 polymorphs which can be differentiated according to their Na ion coordination environment, number of TMO₆ sheets in a single unit cell and oxygen stacking sequence. The P3-type materials remain largely underexplored despite offering the advantage of lower synthesis temperature compared to the P2 and O3. Owing to their abundance and low cost, layered oxides containing Mn and Fe are attractive as layered oxide positive electrode materials. Their application in practical batteries, however, is hampered by challenges brought about by the Jahn-Teller activity of high spin Mn3+, ion migration to the tetrahedral sites in the Na layer, poor electronic conductivity, and air-sensitivity. The recently reported P3-type Na0.9Mn0.5Fe0.502 (MF 55) shows promise as a low-cost and earth-abundant positive electrode material for SIBs. It delivers a high first cycle discharge capacity of 160 mAh g-1 at an average working voltage of 2.8 V when cycled over a large potential window of 1.5 V to 4.4 V vs Na+/Na. However, this electrochemical performance suffers from severe capacity and potential fading upon cycling. In this study, the electrochemical performance and air stability of MF 55 were improved through combined Cu and Ti substitution of Mn and Fe, and varying the potential windows during cycling in a sodium half-cell. Operando X-ray diffraction was employed to understand the phase transformations during cycling of the active materials. The results of the study provide an effective strategy to improve the electrochemical performance of P3-type Mn and Fe-based layered oxide positive electrode materials for SIBs.

Probing the "Adsorption-Intercalation-Pore Filling" Mechanism in Corncob Derived Non-graphitizable Carbons

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Sodium ion batteries (SIBs) are considered as one of the alternative materials to replace lithium ion batteries (LIBs) in the large scale energy storage application. Due to the inability of graphite to form binary graphite intercalation compounds with sodium, non-graphitizable carbons are currently the most viable option as negative electrode materials in SIBs because of their low price, high storage capacity and cycling stability. Non-graphitizable carbons exhibit two distinctive regions where sodium storage occurs, namely the sloping region at high voltages and a plateau region at low voltages. Several mechanisms describing the sodium insertion into non-graphitizable carbons have been proposed. However, due to the complex microstructure obtained from various precursors, a consensus on the exact mechanism has not been reached yet. More recently, Bommier et. al. proposed a three-stage mechanism consisting of adsorption of sodium ions in the sloping region followed by intercalation between the graphene layers in the plateau region. Finally, sodium atom clusters formation in nanopores takes place at very low voltages. In this study, corncob derived nongraphitizable carbons were prepared via two-step carbonization process. The second step was implemented to various final temperatures of heat treatment. Structural, textural and morphological properties were determined by employing techniques such as X-ray diffraction (XRD), Raman spectroscopy and transmission electron microscopy (TEM). Additionally, small and wide angle X-ray scattering (SWAXS) and electron energy loss spectroscopy (EELS) measurements were performed to provide additional insight on the "adsorption-intercalation-pore filling" mechanism. Descriptors providing information on the pore-pore interactions as well as the curvature and long-range ordering of the graphitic layers were successfully obtained and the results were correlated with the electrochemical performance of studied materials. Moreover, the sp^2/sp^3 ratio was determined with EELS and the influence on the electrochemical performance was investigated. Overall, the investigated materials followed a trend of increased ordering of the carbon structure with the increased final temperature of heat treatment. In this study, the physical and electrochemical properties of corncob derived non-graphitizable carbons were established and additional contributions on the "adsorption-intercalation-pore filling" were presented.

Quasi-simultaneous Operando Waxs and Saxs Investigation of the Charge Dynamics Between Graphite and SiOx Particles

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Targeting higher energy density in Li-ion batteries requires changing electroactive materials, which might affect the aging mechanisms of the battery. Graphite-based silicon anodes are seen as a candidate for future commercial negative electrode, but still suffers from the large volume expansion of the silicon particles and the enhanced SEI formation. To better understand the lithiation and degradation mechanisms occurring in the complex composite electrode materials, techniques able to investigate these processes simultaneously and at the different length-scale at which they take place are necessary.

In this contribution, I will present how wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) can be employed to monitor the aging processes of graphite-based silicon anodes during galvanostatic cycling. Using a Swagelok-style cell and liquid carbonate-based electrolyte, we investigated in operando the charge distribution between graphite and SiOx particles during the first, second, and 30th cycle. With this approach, we are able to monitor the formation of the Si-inclusions in the SiOx matrix during the first cycle (formation cycle) and identify the contribution of both graphite and Si-inclusions to the charge dynamics in the early stages of cycling (second cycle) and after long cycling, when the specific capacity decay is observed.

The analysis of vertical line scans through the cross-section of the composite electrode during cell operation allows for the charge distributions depth profiling. We observed inhomogeneities in the lithiation process of graphite and SiOx particles already at early cycling stages, inhomogeneities which intensify during the cell relaxation. Our study highlights the importance of controlling kinetics parameters in biphasic composite electrodes, especially when interruptions in the device operation are foreseen.

Safe, Flexible, and High-Performing Gel-Polymer Electrolyte for Rechargeable Lithium Metal Batteries

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With the boom of flexible and wearable electronics, the safety issues and operation stabilities of the batteries have attracted worldwide attention. The main factor to blame for the safety problems is the commonly used liquid electrolyte, which is quite flammable. The replacement of liquid electrolytes with solid-state electrolytes offers an opportunity to improve the safety and energy density of batteries. Unfortunately, due to some issues such as the poor interfacial contact and/or low ionic conductivity at room temperature in the absence of liquid components the all-solid-state batteries suffer from severe handicaps. In this scenario, the use of gel polymer electrolytes (GPEs) is of great interest to build high-performing rechargeable lithium metal batteries (LMBs) at room temperature owing to the combination of the good electrochemical properties coming from the liquid and improved safety of the polymer host. Herein, a GPE based on the non-flammable polyethylene glycol dimethyl ether (PEGDME) plasticizer in a poly(vinylidenefluoride-cohexafluoropropylene) (PVDF-HFP) polymer matrix is reported. The developed GPE exhibits excellent properties in terms of safety (non-flammability and thermal stability up to 250 °C), outstanding electrochemical properties (σ_{25} = 3.4×10–4 S/cm) and presented good mechanical strength making it easy to handle. Finally, the GPE was tested in a battery delivering good C-rate response and high capacity (ca. 1 mAh/cm² at C/10). Notably, the prototype pouch cell (ca. 19 mAh at C/10) provides remarkable safety, mechanical flexibility, and strong tolerance towards bending and cutting. These results suggest that the prepared GPE is a promising candidate for the development of highperformance, flexible and safe LMBs that operate at room temperature.

Si Nanowires Based Materials for Lithium-Ion Battery Anodes

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Silicon (Si) is the most promising anode candidate for the next generation of lithium-ion batteries. Its great abundance, its reasonable working potential of 0,4V vs Li/Li+ and its high theoretical specific capacity of 3579mAh/g are its main advantages. However, due to the formation of an alloy with lithium ions up to the Li15Si4 phase, the silicon undergoes a strong volume expansion of almost 300%. Various solutions are described in the literature, such as the use of nano-sized silicon particles and the combination with carbon materials.

Nano-sizing helps in avoiding the mechanical pulverization however the improvement depends highly on the quality of the Si dispersion and on the size and shape of the nano-silicon. We investigated the impact of the size/shape of Si on the electrochemical performance of conventional Li-ion batteries thanks to the use of scalable synthesis processes of both nanoparticles (SiNP) and nanowires (SiNW) in the 10–100 nm size range. In cycling lithium metal batteries, the initial specific capacity is significantly higher for nanoparticles than for nanowires. We demonstrated a linear correlation of the first Coulombic efficiency with the specific area of the Si materials. In long-term cycling tests, the electrochemical performances of the nanoparticles fades faster due to an increased internal resistance, whereas the smallest nanowires show an impressive cycling stability. Finally, the reversibility of the electrochemical processes is found to be highly dependent on the size/shape of the Si particles and its impact on lithiation depth, formation of crystalline Li15Si4 in cycling, and Li transport pathways. As the first Coulombic efficiency remains low in comparison with commercial graphites and it is difficult to process nanomaterials to prepare batteries electrodes, we prepared a Si nanowires-grown-on-graphite one-pot composite (Gt-SiNW) via the same simple and scalable route used for SiNW. The uniform distribution of SiNW and the graphite flakes alignment prevent electrode pulverization and accommodate volume expansion during cycling, resulting in very low electrode swelling. Our designed nanoarchitecture delivers outstanding electrochemical performance with a capacity retention of 87% after 250 cycles at 2C rate with an industrial electrode density of 1.6 g cm-3. Full cells with NMC-622 cathode display a capacity retention of 70% over 300 cycles. These results were obtained with a synthesis process relying on gold nanoparticles as the SiNW growth catalyst. Thus, we considered low-cost substitutes. Tin, an efficient silicon-growth catalyst, is interesting for its catalytic capacity at lower temperature than gold, and the inexpensive and air-stable sources available, such as SnO2 or SnS. However, contrary to Au catalysts, Sn-based catalysts offer little control on SiNW size, a structural feature that proved key for the cycling performance and long-term stability of silicon-rich lithium-ion battery anodes. We studied the synthesis of SiNW composites from commercial SnO2 nanopowders, with a precise control on the SiNW diameter by rationalizing the reagent ratios and the addition of an inert gas. We obtained electrochemical performances similar to those demonstrated with gold with the possibility to tune the SiNW diameter by adjusting two parameters of the growth process. Increasing the SnO2 loading leads to increased SiNWs diameters, while adding an inert gas (Argon) in the reactor leads to reduced SiNW size. This allows for chosing a trade-off between high first Coulombic efficiency (favored by large sizes) and high stability in long-term cycling (favored by small sizes). Further work is ongoing to control the chemical composition of the composite at the interface with the electrolyte, in particular at the silicon surface, to reduce its reactivity and the extent of SEI formation.

Silicon Nanowires Grown on a Stainless Steel Fiber Cloth as a Flexible and Robust Anode for Lithium-Ion Batteries

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Silicon nanowires (Si NWs) are a promising anode material for lithium-ion batteries (LIBs) due to their high specific capacity [1]. Achieving adequate mass loadings for binder-free Si NWs is restricted by low surface area, mechanically unstable and poorly conductive current collectors (CCs), as well as complicated/expensive fabrication routes [2][3]. Herein, a tunable mass loading and dense Si NW growth on a conductive, flexible, fire-resistant, and mechanically robust interwoven stainless-steel fiber cloth (SSFC) using a simple glassware setup is reported. The SSFC CC facilitates dense growth of Si NWs where its open structure allows a buffer space for expansion/contraction during Li-cycling. The Si NWs@SSFC anode displays a stable performance for 500 cycles with an average Coulombic efficiency of >99.5%. Galvanostatic cycling of the Si NWs@SSFC anode with a mass loading of 1.32 mg.cm−2 achieves a stable areal capacity of ≈2 mAh.cm−2 at 0.2 C after 200 cycles. Si NWs@SSFC anode transmission electron microscopy to examine the effects of Li-cycling on the morphology. Notably, this approach allows the large-scale fabrication of robust and flexible binder-free Si NWs@SSFC architectures, making it viable for practical applications in high-energy-density LIBs.

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Single Crystal P2-Na0.67Mn0.67Ni0.33O2 Cathode Material With Improved Cycling Stability for Sodium Ion Batteries

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Sodium ion batteries (SIBs) are known to be potential alternatives to the expensive and unsustainable lithium ion batteries (LIBs) for grid storage and low speed electric vehicle applications. Among the main cathode materials studied for SIBs, layered oxide cathodes show promising performances needed for large-scale commercialization due to their high specific capacity, ease of large-scale synthesis and low cost. However, their low energy density, physicochemical instability and poor cycling stability delaying the transition. To address these issues, in this work, we synthesized polycrystalline (PC) and single crystal (SC) P2-Na0.67Mn0.67Ni0.33O2 (NMN) cathode materials by solid state method and evaluated their chemical, electrochemical and thermal properties. It was found that SC-NMN cathode with a mean primary particle size of $6.2 \pm 1.9 \,\mu m$ exhibited high cycling stability, with 47% higher capacity retention than PC-NMN after 175 cycles at 1C rate in the potential window 4.2–1.5V. This could be due to the effective mitigation of parasitic side reactions at the electrode/electrolyte interface and suppressed intergranular cracking induced by anisotropic volume changes, thereby reducing the irreversible structural degradation. Moreover, both the cathodes exhibited good chemical stability against air and water, allowing storage and handling in ambient atmosphere, also making them suitable for aqueous processing, which could potentially lead to significant cost reductions in electrode manufacturing. Additionally, SC-NMN cathode displayed higher thermal stability compared to PC-NMN. In summary, the strategy of developing micron-sized single crystal cathodes for SIBs should become mainstream research as they offer high microstructural stability and long cycle life, as in the case of Ni-rich NMC layered cathodes for LIBs.

Spherical Templating of CoSe2 Nanoparticle-Decorated MXenes for Lithium-Sulfur Batteries

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2D material MXene was shown to have competitive performances in various applications. However, MXene nanosheets are known to aggregate and restack, limiting application performance. Furthermore, in more complex electrocatalytic reactions like the multi-step sulfur reduction reaction in lithium-sulfur batteries (LSBs), MXene alone is insufficient to ensure that the optimal reaction pathway is taken, resulting in the need for further functionalisation.

Inspired by previous works on spherical templating of MXene nanosheets, we propose the loose templating of sulfur nanospheres using MXene nanosheets decorated with polymorphic CoSe₂ nanoparticles. These spheres were further incorporated in LSBs, allowing various electrochemical analyses to take place that demonstrate the superiority of our material. DFT calculations also show that multiple pathways can be taken during each intermediate reaction of the discharging process, emphasising the compounded effects of incorporating more complex nanoparticles with MXene.

Study of Limiting Factors of Power Performance Within Li-Ion Batteries

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Li-ion battery is a mature technology widely applied as a power source for consumer electronic devices, and nowadays, their use is expanded towards electric vehicles and stationary applications. However, improvement of current battery systems is needed to meet the requirements of the transport sector in terms of energy density, safety, cycle life, and costs. Among the strategies to increase battery autonomy, one focuses on electrode loading to increase the ratio of active materials (negative and positive electrode thickness) to inactive components (separator, current collector...). However, by doing so, the output power density becomes strongly limited by the charge transport within the composite electrodes. Thus, our objective is to optimize the battery design to find the best compromise between energy and power density in Li metal-based batteries.

In this work, we studied Li-battery capacity as a function of the current density with respect to electrode loading, formulation, porosity, microstructure, temperature, and ageing. For this purpose, LFP (LiFePO₄) and NMC-811 (LiNi₀₋₈Mn₀₋₁Co₀₋₁O₂) based electrodes were formulated at different loadings (from 0.4 to 3.4 mAh/cm²), compositions (Active material %wt, Carbon %wt, PVDF %wt), and calendered to reach different porosities (from 20 to 50 %). The microstructure of electrodes is investigated using SEM and BET to determine their specific area. Subsequently, the power performance is fully captured and analyzed using a time-saving methodology. The limiting current density, Jlim, is obtained through capacity vs discharge current curves, which allows us to determine an effective diffusion coefficient of the limiting transport process (Deff) via the Sand equation.

Finally, Deff is compared to the diffusion coefficient obtained using the conventional Galvanostatic Intermittent Titration Technique (GITT) to assess the nature of the limiting phenomena such as Li+ diffusion within the solid phase and/or Li+ diffusion in liquid phase through electrode porosity. The coupling of the various processes, as well as the correlation between design parameters and Jlim, are discussed.

Sustainable & Safe Energy Storage; From Electrolyte to Electrode to Full Cell Martin Karlsmo

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Energy storage solutions for medium/low-demanding electrical applications and stationary energy storage can and should favour low cost, low environmental impact, and safety, and thereby supplement high performant solutions such as lithium-ion batteries. The choice of materials complying with these demands are highly restricted and should furthermore consider every cell component; salt(s), solvent(s) and additives of the electrolyte; active materials, conductive carbons and binders of the electrodes; as well as the separator and the current collectors. In this regard, aqueous electrolytes and organic active materials are especially attractive as both expensive metals and flammable organic solvents are avoided. This can be further leveraged by using sodium-based battery concepts and focusing on non-fluorinated compounds.

Figure 1: a) Walden plot and b) Raman spectra peak deconvolution in the O-H stretching vibration region of Na2SO4-based aqueous electrolytes. $\frac{1}{2}$ A data use half the molar conductivities.

Here we present aqueous sodium-based energy storage solutions by virtue of a medium concentrated aqueous hybrid electrolyte consisting of simple inorganic sodium and magnesium salts, showing favourable physico-chemical properties (Fig. 1). The limited availability of "free" water suppresses the common problem of dissolution of the organic electrode material, here perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), during cycling and enables high capacity retention, rate capability, and Coulombic efficiency (Fig. 2).

Figure 2: PTCDA electrode a) galvanostatic charge/discharge curves and b) rate capability test with the hybrid electrolyte.

Finally, a truly all-organic aqueous Na-ion hybrid supercapacitor of PTCDA//activated carbon (AC) was created, with technical performance suited for safe, low-cost, and sustainable energy storage solutions (Fig. 3), and in addition it was post-cycling tested with respect to biodegradability.

Figure 3: a) Rate capability test, b) GC stability test, c) Ragone plot, and d) Nyquist plot of the Na-HSC with an equivalent circuit. Inset in (b) shows the corresponding charge/discharge curves of the 100th cycle.

Synergistic Investigation of P2- and P3-Type Layered Transition Metal Oxide Cathodes for Potassium-Ion Batteries

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Li-ion batteries (LIBs) dominates the electrochemical energy storage sector owing to their high energy and power densities, cyclability, and reliable performance. Nonetheless, the rising energy demand, safety concerns and limited availability of lithium resources provide impetus to explore alternative post-Li-ion batteries. In this context, development of potassium-ion batteries (PIBs) having similar energy densities, low cost, and operational similarity is an imperative step in ensuring a sustainable energy future [1]. K-ion battery (PIB) is still in its infancy with limited reports on potential cathode materials with high reversible capacity, rate kinetics and long cyclability.

Among all reported PIB cathode materials, alkali ion intercalated P-3 type layered oxide compounds impart high volumetric energy density, cycling stability capable of (de)insertion of considerable number of K+ ions via topotactic reactions. P-3 type phases are always non-stoichiometric (typically x~0.5) and largely deviate from the third Pauling's rule [2-3]. In the present work, we have adopted a theoretical screening approach or Density Functional Theory (DFT) calculations using strongly constrained and appropriately normed (SCAN) meta-GGA exchange-correlation functional to screen the chemical space of K0.5MO2 (M= 3d transition metal) systems [4]. We have calculated the average intercalation voltage, electronic structure, K+ (de)insertion mechanism and thermodynamic stability (0 K convex hull of ternary K-M-O systems). We will demonstrate the dependency of transition elements on ordering in K-metal layer.

Building further upon the knowledge of single transition metal system, mixed transition metal-based P-3 system K0.5M'xM"1-xO2 (M',M" = 3d Transition elements) was developed using facile solid-state synthesis [5]. Furthermore, the structural ordering in transition metal layers, electronic properties (density of states) and electrochemical performance have been extensively investigated. At ambient temperature, it serves as a novel ~3.2 V (vs. K/K+) cathode for PIBs. Importantly, it demonstrates efficient electrochemical activity even at elevated temperatures (ca. 40-50 °C). Synergising experimental and theoretical tools, we will demonstrate novel P-3 type insertion materials for potassium-ion batteries.

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Temperature and Stack-Pressure Dependence of the Critical Current for Voiding in Lithium and Sodium Anode Solid-State Batteries

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Solid-state batteries using an alkali metal anode and a ceramic electrolyte promise to improve the energy density and safety of cells. However, cycling such cells at practical current densities in the mA/cm² range often leads to cell failure. While much attention has been devoted to understanding dendrite penetration on charging (plating the anode), the formation of voids on discharge (stripping the anode) also has an important role in failure. We have investigated the processes of stripping lithium and sodium metal anodes as a function of current density, stack-pressure and temperature, revealing the importance of metal creep on void formation and cell failure. To explore this, we have used a combination of 3-electrode cells, scanning electron microscopy and X-ray tomography. We reveal that there is a critical current density on stripping above which voids will accumulate on cycling at the metal anode/solid electrolyte interface, eventually leading to cell failure. The necessity to strip the metal anode below this current density is limiting, as discharging above this critical rate leads to high local currents that can trigger dendrite penetration on subsequent charges. However, we demonstrate that cycling solid-state batteries under moderately elevated stack-pressures and temperatures increases the critical current for voiding by promoting creep in the metal anode.

The Challenge of Polyanion Redox in Oxalates

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Recently, polyanionic compounds have received great interest as alternative cathode materials to conventional oxides due to their various advantages in cost, safety, structural stability, as well as being environmentally friendly. However, the vast majority of polyanionic cathodes reported so far rely primarily upon the redox reaction of the transition metal for lithium/sodium transfer.

The development of multielectron redox-active cathode materials is a top priority for achieving high energy density with long cycle life in the next-generation secondary battery applications. Triggering anion redox activity is considered to be a promising strategy to successfully enhance the energy density of polyanionic cathodes for Li/Na-ion batteries. In addition to transition metal redox activity, the oxalate group itself also shows redox behaviour enabling reversible charge/discharge and high capacity without gas evolution.

Recently, our group reported dual ion redox in the lithium iron oxalate, Li2Fe(C2O4)2 in which both the iron and the oxalate group appear to exhibit reversible redox activity.

Different characterisation techniques such as Raman spectroscopy or XANES analyses make it possible to show this phenomenon experimentally. First-principles calculations also help to understand the interactions between the transition metal and the oxalate group as the main factor that modulates the cationic and polyanionic redox couples in these materials.

Our current results suggest that this phenomenon is not unique to this compound and could be widespread among transition metal oxalates, including those of sodium and potassium.

Moreover, the oxalate anion is a particularly versatile species and may be monodentate, bidentate, tridentate, or even tetradentate, giving rise to a huge range of possible compounds and a very rich structural chemistry. It is important to establish the structural requirements that give rise to polyanion redox behaviour and a range of materials are being synthesised and characterised by our group. In addition to pure oxalates, it is possible to prepare materials with mixed polyanions e.g., oxalate/phosphate.

In our work, we demonstrate that oxalate has a role as a family of cathode materials and suggests a direction for the identification and design of electrode materials with polyanionic frameworks.

The Hydrotropic Effect of Ionic Liquids in Water-in-Salt Electrolytes

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Lithium-ion batteries (LIB) have become ubiquitous in our daily life, ranging from batteries for handheld devices to batteries for electric vehicles and grid-scale energy storage applications. With the increasing deployment and energy content of such batteries, safety concerns receive a high attention. Aqueous LIBs based on water-in-salt (WIS) electrolytes come with the promise of combining the longevity of the lithium-ion technology and the safety of non-flammable aqueous electrolytes. However, the limited lithium salt solubility results in a relatively narrow electrochemical stability window of ca. 2.5 V for single-salt WIS electrolytes and prevents the use of most commercial Li-ion electrode chemistries.

In this contribution, we show that the electrochemical stability window of WIS electrolytes can be ex-tended by increasing the lithium salt solubility through the hydrotropic effect of ionic liquids. This effect boosts the lithium bis(trifluoromethanesulfonyl)imid (LiTFSI) solubility up to 60m (moles per kilogram of water). Overcoming the solubility limitations allows the design of tailored electrolyte properties. For example, an electrolyte containing 40m LiTFSI and 20m of the ionic liquid 1-ethyl-3methylimidazolium TFSI (EMImTFSI) still displays a relatively high conductivity of 1.2 mS/cm despite the low water-to-lithium molar ratio of 1.4, which greatly contributes to the enlarged electrochemical stability window of >3 V of this electrolyte. Especially the improved reductive stability enables cycling of commercial Li₄Ti₅O₁₂ (LTO) anodes when coated with a layer of niobium oxide. Furthermore, we exploit the reduced water content of the WIS/ionic-liquid hybrid electrolyte and demonstrate compatibility with LiNio.8Mno.1Coo.1O2 (NMC811) cathodes. For full cells based on the LTO/NMC811 electrode couple, we obtain relatively high Coulombic efficiencies for such an aqueous high-voltage battery of 99.4% and 99.2% at rates of 1C and C/2, respectively. The hydrotropic effect is not unique to ionic liquids, but also occurs with polar molecules such as urea or succinonitrile, which opens a great toolbox for tailor-made electrolyte design that further closes the gap between organic and aqueous LIBs.

Three-Dimensional Porous Flower-Like CoMoO4 As Cathode for Li-O2 Batteries

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Lithium oxygen batteries (LOBs) are considered to be the next-generation energy storage system due to their high energy density. However, the insulating and bulk lithium peroxide discharge product causes sluggish decomposition, increasing overpotential and reducing cycle stability. Here, Three-Dimensional Porous flower-like CoMoO4(3DF-CM) was synthesized via a universal and low-cost hydrothermal method, which is to be used as an efficient electrocatalyst in an oxygen electrode for high-performance LOBs. Morphologically, the 3DF-CM with high electrical conductivity has a large surface that can improve charge transport and promote delithiation during recharge compared to nano-sheet CoMoO4(NS-CM) and nano-cube CoMoO4(NC-CM) and thus plays a critical role in the facile decomposition of lithium peroxide. The 3DF-CM as cathode exhibited a lower overpotential of 1.48 V, a high specific discharge capacity of 21521 mAh g–1 at a current density of 200 mA g-1 and long cycle stability of 210 cycles at 200 mA g-1 with a limited capacity of 1000 mAh g-1.

Tuning the Transition Metal (Tm) Layer Composition of 'Layered' Na-Tm-Oxide Cathode Materials for Na-Ion Batteries Towards Enabling Water-Stability, High Capacity and Cyclic Stability Bachu Sravan Kumar¹, Anagha Pradeep¹, Animesh Dutta¹, Amartya Mukhopadhyay¹

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Among the potential cathode material classes for Na-ion batteries, O3-type 'layered' NaxTMO2s (TM => transition metal ion) are of importance due to their high starting Na-content (of ~1 per formula unit; x). However, the O3-type NaxTMO2s suffer from multiple structural phase transformations during electrochemical charge/discharge cycles, TM-dissolution into electrolyte and, more importantly, inherent sensitivity to moisture. The moisture sensitivity of these 'layered' NaxTMO2s necessitates the usage of toxic/hazardous non-aqueous solvents like N-Methyl-2-pyrrolidone (NMP) during electrode preparation. Against this backdrop, a carefully designed composition-cumstructurally tuned O3-type 'layered' NaxTMO2 has been developed in this work, which addresses the aforementioned problems, in particular, the air/water-instability. Partial/complete substitution of Tiion for Mn-ion in the Na(Li0.05Mn0.5-yTiyNi0.30Cu0.10Mg0.05)O2 eliminated the presence of Mn3+ (which dissolves in electrolyte) at the particle surface, supressed increment in impedance and voltage hysteresis during electrochemical cycling and, thus, significantly improved cyclic stability of Ti-substituted O3-type layered NaxTMO2s. The Mn-containing Na-TM-oxides were found to be extremely unstable in terms of phase/structure retention upon exposure to air and water; progressively evolving O'3 and P3 phases due to spontaneous Na-loss and thereby forming undesired NaOH and Na2CO3 phases on the particle surface, causing increase in electrochemical impedance. By contrast, no phase/structural change occurred upon partial/complete Ti-substitution (for Mn-ion), even after 40 days of air-exposure and 12 h of soaking, as well as stirring, in water (viz., very stringent hydration condition). Such excellent stability against hydration, which was partly due to reduced Na-ion 'inter-slab spacing' in the presence of Ti-ion, was not reported earlier for O3-type Na-TM-oxides. The excellent stability of the optimized O3-type NaTMO2 enables the usage of environment/health-friendly and economical 'aqueous-binder' (viz., Na-alginate) and water (as solvent) for electrode preparation; without compromising on the overall electrochemical behaviour/performance, including long-term cyclic stability. This work, as published in [Kumar et.al., J. Mater. Chem. A, 8 (2020) 18064-18078], has established important correlations between the composition, structure (viz., reduction in 'inter-slab spacing'), stability against hydration (viz., in air and water), feasibility for health/environmental-friendly 'aqueous processing' of electrodes, electrochemical impedance, stability of average voltages and cyclic stability of O3-type Na-TM-oxide based cathode materials for Na-ion batteries. On similar lines, i.e., regulating the Na-layer 'inter-slab' spacing by tuning the TM-layer composition has also opened-up the feasibility (as a universal strategy) towards designing high Na-containing P2-type Na-TM-oxide cathode materials (which are usually Na-deficient, otherwise), for Na-ion 'full cells' [Patent for a part of this work has been filed as; Indian Patent Application No.: 202121053254, dated: 19/11/2021].

Understanding and Applications of Phosphate-Based Electrode Materials for Aqueous Na-Ion Batteries

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Aqueous Na-ion batteries are considered to be among the promising candidates for the new generation of truly sustainable stationary

energy storage technologies. In addition to finding suitable electrode materials, there are also issues related to the stability of the aqueous electrolyte/electrode interface to be solved before their full potential

could be utilized. Some of our recent contributions in terms of understanding and enabling Mn- and V-based phosphate framework materials for the use in aqueous

Na-ion batteries are summarized. The thermodynamic limitations in terms of phase formation, electrochemical stability issues, and the origin of these effects in NASICON-structured Na₁+₂xMnTi₂- $x(PO_4)_3$

 $(0.0 \le x \le 1.5)$ and Na₃-xV₂-xTix(PO₄)₃ ($0.0 \le x \le 1.0$) and several other mixed-phosphates systems as potential cathode materials for aqueous Na-ion batteries are discussed in detail.

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Understanding Molecular-Scale Dynamics Inside Composite Polymer Electrolyte

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The state-of-the-art Li-ion battery is showing limitations regarding its principal application as energy storage device for electric mobility. In fact, the liquid electrolytes used in those devices is a brake to reach both higher energy density and safety standards of the market. Overcoming these limitations could be possible by using solid-state electrolyte inside Lithium metal batteries. Those types of electrolytes could limit Lithium dendritic growth, hence allowing the use of Lithium metal as the negative electrode and increase the cell energy density. Safety issues would also be solved by avoiding the use of flammable solvents.

In this context, composite polymer electrolytes for solid-state applications are highly appealing materials as they could combine the best properties of organic and inorganic phases, assuring excellent performances and process compatibility with low cost industrialization. In this study we use poly(trimethylene carbonate) (PTMC) as the polymer matrix and alumina nanoparticles as the filler. Compared to the typical poly(ethylene oxide)-based electrolyte, PTMC brings the advantage of wider electrochemical stability window and weaker coordination strength with Li+ ions. The former feature allows considering the use of high potential active material, while the latter reduces the immobilization of Li+ ions from the polymer. PTMC-based electrolyte can therefore reach high energy density with appropriate Li+ transport properties.

In PEO-based composite electrolyte, the blending with alumina fillers enhances the overall performances of the electrolyte, especially Li+ ion conductivity and cycling ability. This enhancement is due to the beneficial interaction between the filler surface and the polymer-Li salt system. It is generally accepted that appropriate surface chemistry of the filler can increase the amount of free Li+ ions density or trap counter-ions in the electrolyte. Particles also create faster conduction pathways surrounding them by changing the PEO structure and mobility. This happens through either larger size of free volumes or stabilization of the polymer into fast conducting PEO6:LiX ordered phase.

We observed similar performance enhancement with our PTMC-based composite electrolyte filled with alumina, e.g. a ten-fold increase in conductivity, a stabilized interface with Li metal and a potentially longer stripping-plating. However, the role of the filler in the enhancement mechanism might differ from PEO composites, because of the fully amorphous state of PTMC electrolytes and the distinct chemistry of carbonate units. To unravel the mechanisms behind these better performances induced by alumina fillers in PTMC-based composites, we performed quasi-elastic neutron scattering (QENS) experiments combined with complementary structural characterizations.

Quasi-elastic neutron scattering is well suited to probe dynamics inside soft-matter materials as polymer-based electrolytes. We carried out multi-resolution QENS experiments at ILL (on IN5 and IN16b) and compared several formulations of our material, along with reference samples of pure

polymer and polymer electrolyte without filler. We observed that the addition of salt and fillers affect the quasi-elastic contributions, therefore indicating that the dynamics inside the polymer electrolyte and the composite differ from pure polymer matrix. Our results show that the intrinsic motion of PTMC is hindered by the presence of Li salt in the polymer electrolyte sample. This motion is then recovered in the composite samples containing alumina filler.

We believe these changes in dynamics are a starting point to explain the enhanced performances of our composite material. We will discuss this assumption by relating molecular-scale dynamics inside the electrolyte to its structure and composition in the light of complementary characterization as synchrotron nanotomography, SAXS, DSC and FTIR. Fine-tuning of the composite electrolyte formulation is challenging and it requires understanding of the material behavior to envision Lithium metal batteries in the future.

Understanding the Redox Behaviour of Na+/Li+ Exchanged T2/O2-Li0.67+xNi0.33Mn0.67O2 Cathode Materials for Lithium-Ion Batteries

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As lithium-ion batteries have become a major cornerstone of the transition towards renewable energy sources and emission-free mobility, fulfilling all expectations as a truly sustainable technology is of utmost importance. This includes the complete substitution of critical elements, especially cobalt, by abundant and environmentally benign alternatives such as manganese. However, the development of high-performance cobalt-free and manganese-rich layered oxide cathode materials remains a challenge, due to the structural instability of these compounds. Although these issues can be addressed by careful structural tuning towards T2/O2 stacking orders, as for instance known for T2-Li0.67Ni0.33Mn0.67O2, such materials still suffer from initial Li+ deficiency and their limited Li+ extraction during the first charge, yielding practical capacities far below the theoretical values in any potential graphite-based full-cell.

Herein, we introduce a new synthesis concept to overcome this limitation by increasing the Li+ content in T2-Li0.67Ni0.33Mn0.67O2, initially obtained by a Na+/Li+ ion-exchange process. Based on a reductive treatment this approach is shown to be capable of significantly enhancing the first charge capacity of such materials and, thus, compensate their Li+ deficiency. Furthermore, it is demonstrated that the variation of the synthesis environment results in surprising differences regarding the shape of the voltage profiles with a significant impact on cycling stability. To understand the underlying mechanism of the lithiation process and the nature of the additionally incorporated lithium, an in-depth investigation was performed, combining several operando and in/ex situ techniques. A particular focus was set on the differentiation between surface and bulk contributions and the distinct origin of the increased capacity during the first charge. The results provide a very comprehensive understanding of the underlying mechanisms and the important impact of the synthesis conditions.

Unraveling Cation-Anion Redox Mediated Electrochemical Lithium (De)insertion on Novel Layered Manganese Oxychalcogenides

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The most widely used cathode materials in commercial rechargeable lithium-ion batteries (LIB) are intercalation compounds, which have intrinsic capacity limitations by the amount and the extent to which the redox species can change valence. This limitation is circumvented in conversion and displacement reactions, leading to a greater capacity. In conversion reactions, metal binary compounds such as MxXy (such as M = Mn-Cu, X = O, S, etc) are lithiated and the metals are reduced to their elemental state ultimately leading to complete reorganization of the electrode structure. Displacement reactions as commonly observed in Cu-Sn and Cu-Sb intermetallic alloys that can function as the negative electrode materials are related to conversion reactions but usually some part of the framework is preserved during the (de)lithiation processes. Interestingly, a handful of cathode materials can undergo combined conversion displacement reactions (CDI) during LIB operation. Cu2.33V4O11 and CuTi2S4 undergo Li intercalation following CDI reaction associated with extrusion of elemental Cu and reduction of cation e.g. V5+/V4+ or Ti4+/Ti3+ redox couples. On the other hand, the electrochemical reaction of CuCr2S4 with Li also occurs through a CDI reaction, with the reduction of S- anion and extrusion of Cu. In this presentation, I will explore the new family of LIB cathodes which follows both cation and anion redox changes including the CDI mechanism.

My presentation will begin with the investigations of Li reaction chemistry with oxysulfides, e.g., Sr2MnO2Cu2m- δ Sm+1 (m = 1, 2 and 3, δ ~ 0.5). These materials consist of alternating perovskitetype [Sr2MnO2] sheets and antifluorite-type [Cu2S] slabs of varying thickness in which Cu+ ions occupy tetrahedral sites. These materials were initially studied because of the potential of achieving materials that coupled some of the best properties of oxides and sulphides, namely higher redox potentials and higher Li+ mobilities, respectively. Sr2MnO2Cu3.5S3 (m = 2) composition shows optimum electrochemical activity in 1.1-2.7 voltage regime considering cycle life and capacity. Previous studies have concluded that upon lithiation, Cu+ and Mn2.5+ are reduced to Cu metal and Mn2+, respectively, so in total 4 Li+ ions are inserted into this composition. However, the reaction mechanism accompanying electrochemical insertion of Li and extrusion of Cu has not been explored in detail. Charging up to 2.7 V (vs Li/Li+) is observed to be insufficient to extract all 4 Li+ ions, whereas the details of the delithiation mechanism, when charged upto 2.7 V have not been explored so far. Moreover, the device performance in the upper voltage range (> 2.7 V) and the associated mechanisms are unknown. In this presentation, I would explain a detailed investigation of the electrochemical behaviour of Sr2MnO2Cu3.5S3 upon lithiation and delithiation. The structural changes during both discharge and charge processes will be discussed in detail by in situ diffraction methods, and ex situ X-ray Absorption Near Edge Structure and 7Li NMR measurements. Our results show that the Sr2MnO2 layer is far more than merely a structurally rigid "spacer", and is indeed redox-active and redox chemistry is controlled by the upper charging voltage.

While the CDI reaction with oxysulphides involving the extrusion of elemental Cu is interesting, it still suffers from Cu dendrite formation and following degradation induced capacity loss. To circumvent this problem, I will present our recent findings directed towards making of Cu free-oxysulphide structure following its Li intercalation-deintercalation activity and reaction mechanism. This
presentation will highlight the differences and similarities between the device performance and Li reaction pathways between Cu-rich and Cu deficient oxysulphide structures. In the end, I will present our ongoing effort of tuning the cation-anion redox activity of these oxysulphides by varying the polychalcogenides compositions.

Unveiling the De-/Lithiation Mechanism for Monoclinic Nb2O5 As High Performance Li-Ion Anode

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The net-zero target accelerates the transition from internal combustion engines to electric vehicles powered by lithium-ion batteries (LIBs). To further support this transition, however, further improvement concerning the eventual driving range and the possibility to rapidly charge the battery is needed. The latter limitation is mainly related to the graphite-based negative electrode, which is characterized by rather sluggish lithiation kinetics and the risk of lithium plating at high current densities. Accordingly, there is great interest in searching for alternative anode materials. One alternative that offers much faster charge rates is Nb2O5. Depending on the eventual calcination temperature, Nb2O5 has a monoclinic, tetragonal, or orthorhombic crystal structure. Among them, monoclinic Nb2O5 with a Wadsley-Roth crystallographic shear structure provides a high specific capacity of more than 200 mAh g-1 and, consequently, a relatively high specific energy at the full-cell level. However, the cycling stability is inferior to the other phases.

Herein, we present our investigation of the origin of this inferior cycling stability – for the common, rather narrow voltage and an extended voltage range down to 0.01 V, reaching specific capacities up to almost 400 mAh g-1. For this purpose, we combined a set of highly complementary techniques such as operando XRD and dilatometry as well as ex situ XPS to gain fundamentally new insights into the reaction mechanism. Eventually, we obtained a capacity retention of about 86% after 4,000 cycles at 2 A g-1 when setting the cut-off voltages to 0.8 V and 3.0 V, rendering the monoclinic phase at least as interesting for high-performance lithium-ion batteries as the other crystal structures.

Very High Rate-Capable, Electrochemically Stable and Safe Biphase Na-Titanate Based Composite Anode for Na-Ion Batteries

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The 'workhorse' anode material for Li-ion batteries, graphitic carbon, cannot reversibly store Na-ions in its lattice. Hard carbon has been widely explored as anode material for Na-ion batteries. However, the Na-insertion potential in hard carbon is too close to that of Na-plating; thus, causing serious safety concerns and operational hazards. Hence, the upcoming Na-ion battery system, lacks in terms of the availability of a safe, electrochemically stable and high 'rate-capable' anode material. In this scenario, the present work reports bi-phase Na-titanate based anode material, which is safe, which exhibits excellent rate-capability and long-term cyclic stability, even at very high current densities. The 'bi-phase NTO', with Na2Ti3O7 as the primary phase (~66%) and Na2Ti6O13 as the secondary phase (~34%), exhibits contributions from both the constituent phases towards electrochemical sodiation/desodiation (as confirmed via operando synchrotron X-ray diffraction studies) and is more electrochemically stable than phase pure Na2Ti3O7. Additionally, 'Bi-phase NTO' also has safe and favourable Na-insertion/removal potential in terms of operation as anode. The addition of functionalised multiwalled carbon nanotubes (MWCNTs) further improves the electrochemical performance of 'bi-phase NTO', leading to a reversible Na-storage capacity of ~162 mAh g-1 at C/5 and excellent cycling stability. The stable 'charge-averaged' discharge/charge voltages and minor increment in impedance over multiple electrochemical cycles support the excellent stability of 'biphase NTO'/MWCNTs composites. More importantly, even at a very high current density corresponding to 50C, 1st cycle reversible Na-storage capacity of >140 mAh g-1, and capacity retentions of ~83%, ~65%, 58% after 100, 1000, 2000 cycles, respectively, can be obtained with the as-developed 'bi-phase NTO'/MWCNTs based electrodes. In fact, a negligible capacity fade from the 300th cycle onwards at 50C, indicating the feasibility for long-term cycling at very high current densities, can be noted. Overall, this will allow the development of Na-ion cells possessing outstanding rate-capability and cyclic stability; thus, addressing the major concerns associated with the same. A part of this work has been published as Pradeep et al., Electrochim. Acta 362 (2020) 137122.

Which Contamination Do Cathodes for Lithium-Ion Batteries Tolerate?

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In the past three decades, the performance of lithium-ion batteries was steadily improving. Nowadays the technology is reaching its chemical and engineering limits and the next necessary and important step, the recycling of spent battery cells and the reusing of materials thereof is in the focus of research activities. The reprocessing of cathode active materials from spent cells has the consequence of bringing contaminants, above all Mn, Ni, Co, Cu, Al, and Fe, into the cell production process. In order to minimize the recycling cost, it is important to know the maximum concentrations of the respective contaminants which can be tolerated. Of course, there is an interplay with other contaminants like H2O and HF (from the reaction of H2O with the electrolyte salt LiPF6). The poster presents a systematic work on the influence of the contaminants in the electrolyte on the performance of positive electrodes based on NMC811. More specifically, electrolyte solutions were intentionally contaminated with M(H3CCOO)2, MSO4, and MCO3 (M = Ni, Co, and Mn). In some cases, different concentrations of water were added to the test solutions to understand the influence of the so generated HF on the cell behavior. Apart from electrochemical cycling, electrolyte conductivity data were collected and the contaminated electrolytes and electrodes (fresh, aged, and from cycled cells) were analyzed with suitable methods including GC-MS, NMR, HF titration, I2 titration (to determine the oxidation state of the transition metals in the oxide), and DEMS. In the poster the results will be summarized and recommendations for further work given.

Y-TEC's Lithium R&D and Industrial Activities: From the Resource to the End Customer

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The history of YPF is the modern history of Energy in Argentina. Today YPF is a leader in exploration and exploitation of Oil & Gas resources, petrochemical refining, fuels and lubricants, service stations. It is the local oil company that is leading in actions related to a context of energy transition, from the generation of renewable energy and the incursion into the lithium value chain.

Since its creation in 2013, YPF Tecnología (Y-TEC) as part of YPF has consolidated a team focused on innovation in lithium and in this journey, it has been supported by various teams from the national S&T system. Some researchers who specialized in lithium-ion battery in CONICET (National Scientific and Technical Research Council) institutes joined us and work in R&D projects in our company. As a Y-TEC Lithium Group, we intend to lead the process of lithium technologies in the South American region, with high technological standards, according to the most advanced international industry. We are focused on the development of the local lithium value chain and cell manufacturing adding the largest proportion of local inputs and/or components in these processes. Also, we are involved in the development of an industry of storage systems, based on lithium-lon batteries.

R&D activities: Fine-tuning of work capabilities: we have a unique capacity in the country, the possibility of designing new materials for lithium-ion battery cells in the laboratory, scaling them up and evaluating them in the cell electrode pilot plant itself. We are working on a method for direct extraction and purification of lithium rich brines, incorporating sustainable techniques. Also, in development and scale-up of LiPF6 electrolyte salt production.

Industrial activities: UNILIB Lithium-ion cells and batteries industrial plant in La Plata city is under construction in an UNLP (National University of La Plata) area, and it will start production of Li-ion cells and batteries by the end of Q4 2022 with a total capacity up to 9 MWh/y. The Li-ion batteries to be produced there will supply renewable energy storage facilities, demanded by public and government sectors (eg. Rural schools, isolated small villages, Armed Forces teams, etc.).

Zirconium Substitution in Ni-Rich Nmc Layered Cathode Material for High-Energy Lithium-Ion Batteries

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Currently, Ni-rich layered oxides LiNi1-x-yMnxCoyO2 (NMC, x=0.1 and y=0.1) are considered promising cathode materials due to their high-energy density in lithium-ion batteries (LIBs). However, those suffering a severe capacity loss upon long cycling. Elemental substitution or coating of Zr has been considered as an attractive approach for Ni-rich NMC layered cathode materials to overcome the capacity fade during long term cycling. Herein, a small amount of Zr dopant is added to the NMC811 material synthetized via the co-precipitation method following two alternative pathways: 1) During formation of the transition metal hydroxide precursor at the co-precipitation step (C-Zr-NMC811) and 2) during the lithiation at the solid-state synthesis step (S-Zr-NMC811). The presence of Zr has been confirmed, for both cases, by X-ray Absorption Spectroscopy (XAS) in fluorescence mode and, for C-Zr-NMC811, it suggests that Zr is octahedrally coordinated into the transition metal (TM) site. The chemical environment of Zr in S-Zr-NMC811 appears to be different. Furthermore, for S-Zr-NMC811 XRD shows the existence of multiple extra-phases formation such as: Li2ZrO3 and Li4ZrO4 (Zr-based) whereas they are absent for the C-Zr-NMC811 leading to a clean single-phase formation. In this work, cycling stability and gravimetric capacities are correlated with the C-Zr/S-Zr-NMC811 structure. The electrochemistry of the C-Zr-NMC811 by co-precipitation method shows enhanced specific capacity and improved cycling stability. Upon 100 cycles at 1C, CZr-NMC811 has a lower degradation trend and higher specific capacity as compared to S-Zr and undoped NMC811 whereas the S-Zr-NMC811 shows only improved specific capacity.

Virtual Posters Session

Conversion-type Metaphosphate Electrodes for Lithium/Sodiumion Batteries: Working and Degradation Mechanisms

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The development of novel high-performance electrodes is crucial for the next generation of lithium/sodium-ion batteries (LIBs/SIBs) that can charge rapidly while maintaining high lithium/sodium storage capacity. One of the major research directions to achieve improved energy/power densities of LIBs/SIBs has, thus far, focused on electrode materials that can store Li+/Na+ through conversion reactions. Our group has discovered and systematically studied a new family of conversion-type electrode materials, the transition metal metaphosphates [M(PO3)n (M =Mn, Fe, Co, Ni and Cu; n = 1, 2 and 3)]. Unlike traditional conversion-type monoanionic compounds such as oxides, nitrides and fluorides which rely on nanomaterials engineering, these metaphosphates can achieve full capacities and fast Li+/Na+ diffusion kinetics from micro-sized samples synthesised by conventional solid-state methods. We studied their conversion reactions and electrochemical degradation mechanisms using a combination of in situ x-ray powder diffraction (XRPD), in/ex situ X-ray absorption near-edge spectroscopy (XANES), and ex situ high resolution transmission electron microscopy (HRTEM). During the initial discharging, these compounds convert into amorphous ceramic composites with high electrochemical activities in which fine transition metal nanograins are embedded in a glassy LiPO3 matrix. Glassy LiPO3 is an excellent Li+ conductor due to the low iconicity of PO3-, and it can buffer the volume change of the electrode to maintain its integrity, thus leading to much better electrochemical reversibility and cycling stability than monoanionic compounds. In the following first charge, the electrode converts back to a metaphosphate in terms of its composition but does not recrystallise. In subsequent cycles, the metaphosphate electrodes in an amorphous form continue to react with Li+/Na+ reversibly.

Cow Hair Based Biochar As Sulfur Host for Lithium-Sulfur Batteries

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Argentina is the 4th largest producer and exporter of leather worldwide, with an average annual production of around US\$1 billion. This not only implies a great economic impact but also a huge generation of waste associated with this industry. In this work, we will focus in particular on cow hair - which represents one of the main leavings from the leather industry. Every ton of salt-wet cowhide can produce around 85 kg of waste hair. The accumulation of large quantities of hair waste causes a huge waste of resources and deterioration of the environment, the reason why it should be solved urgently.

Biochars have attracted much attention due to their promising role in many environmental management issues. They can be produced from different organic materials such as plant tissue, anthropogenic sources, raw pine chips, peanut hulls, and agro-industrial biomass – presenting different properties depending on the thermochemical conditions used to pyrolyze it. Traditionally, the main application of biochar has been its application to agricultural soils to increase crop production. However, in the last few years, biochar-based materials have been studied as excellent candidates for applications in adsorption, catalysis, and energy storage. In particular, porous biochar-based materials impregnated with sulfur have been applied as cathode materials for post-lithium technologies since their micropores can adsorb the migrating polysulfides, while mesopores can facilitate lithium-ion transport and ensure appropriate access to the electrolyte during the electrochemical reactions involved.

Combining these two fields, in this study, we analyze the properties of cow hair waste produced in leather production and then, we used it to prepare porous biochars. The influence of chemical activation and different carbonization processes on the properties of the biochar is optimized. After that, the biochar is used as support for sulfur impregnation to create an active material for Li-S cathodes. After optimization, biochars with areas as high as 2287 m²/g were obtained and impregnated with sulfur. As cathodes in Li-S batteries, these composite materials present capacities of 519 mAh/g after 100 cycles at 0.1 A/g and 462 mAh/g at 2.0 A/g. The improved behavior of the material is explained not only by the big area and microporosity but also due to the presence of remnant ash to enhance the electrochemical performance.

Graphene-Based Activated Carbon Composite for High-Performance Lithium-Sulfur Batteries

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The increasing demand for electrical energy storage requires the exploration of alternative battery chemistries that overcome the limitations of the current state-of-art lithium-ion batteries. In this scenario, lithium-sulfur batteries stand out for their high theoretical energy density, as well as the low price, high availability, and environmental friendliness of sulfur. However, their practical deployment is still hindered due to the presence of various inherent challenges, including the lithium dendrite/mossy growth, electronically insulating nature of S8 and its lower-order reduction product (Li2S), the shuttling soluble long-chain polysulfides (PS) between cathode and anode (i.e., shuttle effect), low sulfur utilization, etc. Those issues have become top pressing priorities and need to be addressed so as to meet the stringent requirements of such technologies (e.g., long-term cycling stability, superior rate capability, and high sulfur utilization). Herein, we report the synthesis and characterization of a novel activated carbon, prepared through resorcinol/formaldehyde condensation in the presence of graphene oxide (called ResFarGO). The developed porous structure not only features excellent individual properties but also presents outstanding battery performance, related to its superior conductivity and polysulfide trapping ability, allowing to obtain improved rate capability and high sulfur loading cycling. Additionally, the scalability and the practical application of this tailored nanomaterial were further demonstrated by the preparation of a high-loading pouch cell, which delivered a stunning sulfur utilization and incredible high total capacity (ca. 90 mAh at C/10). Therefore, these results demonstrate that the developed ResFarGO material is capable to solve many of the inherent drawbacks of Li-S technology, becoming a potential candidate for the development of practical high energy density Li-S batteries.

Maximizing the Triple Phase Boundary Area in Sodium-Oxygen Batteries

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Lithium-ion batteries (LiBs) have led the portable electronic market in the last 30 years due to their great cyclability. However, the current energy demand, forced by the rapid advance of technology or the transition to the electric vehicle, is pushing the limits of LiBs in terms of energy density (100 -265 Wh kg-1), cycle life (1000 cycles at > 80% of capacity) and charge/discharge rate capabilities (1C). Aprotic sodium-oxygen batteries (Na-O2) are promising devices to resolve such energy demands due to their much higher theoretical energy density (1086 Wh kg-1 based on NaO2 discharge product). However, this technology is still in its early stages and several challenges such as their cyclability at high capacities must be tackled. One of the most important components for longlasting and reversible cycling is the air-cathode. The electrons flowing into the cathode reduce O2 gas (Oxygen Reduction Reaction, ORR), which react with the sodium ions present in the electrolyte on Na-O2 batteries. Thus, solid sodium oxides are formed as solid discharge products, which are redissolved back during charge in the backward process (Oxygen Evolution Reaction). The kinetics of these reactions depend significantly on the boundary points between the solid-liquid-gas reaction phases, known as triple phase boundary (TPB). Because of the much larger oxygen diffusion coefficient in gas than in liquid phase, electrodes with mixed electrolyte wettability could create phase boundaries by ensuring the coexistence of gas and liquid phases in the pore network. Perfluorinated polymers are known to enhance oxygen transport and therefore they could favour the diffusion of gaseous components in detriment to liquid electrolytes when added to the cathode formulation. Adding perfluorinated polymer will increase the oxygen transport through nonwetted pores but, on the other hand, too many nonwetted pores will decrease the ionic conductivity of the electrodes. The manufacture of air-cathodes with mixed electrolyte wettability will open the possibility to maximize the battery efficiency by adjusting the density of TPB points on the electrode.

In this work, the effect of adding polytetrafluoroethylene (PTFE) and/or fluorinated ethylene propylene (FEP) polymers on the oxygen transport of Na-O2 battery cathodes is studied.

Graphene nanoplatelets (GNPs) are selected as active material due to their good electrochemical performance and easy processability. The critical physical properties affecting the formation of the TPB have been identified and correlated to Na-O2 battery performance. The electrochemical performance of the cathodes containing 10% PTFE exceeded that in literature. The mixed wettability cathode yields good discharge capacity (4.51 mAh cm-2) and large cycle life by delivering 142 cycles at 0.5 mAh cm-2. Besides, high cycling efficiency (100 %) and low overpotential (< 0.3 V) is achieved at a high current density (0.2 mA cm-2). The key properties to modulate the oxygen diffusion within the cathode structure have been identified for the first time for aprotic metal air devices. This approach is of outmost importance for the development or efficient electrochemical storage devices where oxygen gas is involved.

Power Capabilities in Lithium-Ion Capacitors

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Lithium-ion batteries face limitations in specialised uses where an ability to produce a high current on demand or possess a high power density is desired from an electrochemical cell. Other types of electrochemical energy storage cells are appropriate in such applications, and lithium-ion capacitors have been previously highlighted as possible candidate cells delivering excellent high rate performances and power densities. Lithium-ion capacitors are hybrid devices achieved by combining a battery-type negative electrode from a lithium-ion battery (usually graphite) and an activated carbon from an electrochemical supercapacitor in one cell. It is expected in the academic literature that lithium-ion capacitors have energy and power densities intermediate between lithium-ion batteries and supercapacitors.

In this contribution, we revisit the high rate characteristics of lithium-ion capacitors. Using both commercially available cells and Swagelok-type cells fabricated in-house in our laboratory, we evaluate rate capabilities and power densities in these cells. Direct experimental comparison with electrochemical supercapacitors is undertaken. It follows from our data that power densities (or specific power) of lithium-ion capacitors are usually superior to those of supercapacitors, in contrary to well-established opinions in literature and the majority of review papers in the field. Furthermore, the power metrics of lithium-ion capacitors can be further enhanced in a slow charge regime, which is correlated with the intercalation behaviour of lithium ions in graphite.

The Effect of Cu (II) Substitution on Material and Electrochemical Properties in Sodium Deficient Manganese-Based Oxides

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Sodium ion batteries (SIBs) have seen rapid development in recent years as low-cost and sustainable energy storage systems and are poised to play an important role in grid-scale energy storage. For positive electrode materials in SIBs, extensive studies have focused on layered transition metal oxides (NaxTMO2) due to their high capacity and energy density. Among different structures, P(')2type materials are one of promising candidates as their low energy barrier for Na+ hopping compared to that of O(')3-type compounds, enabling higher rate capability. Most of NaxTMO2 necessitate at least binary systems to enhance electrochemical properties. Cu-Mn binary system is of interest because of its compatibility with the NIBs' philosophy and previous studies in our group show unique properties originating from Jahn-Teller active Cu (II) substitution for Mn. For example, experimental and theoretical investigation propose the Cu substitution for Mn in NaMnO2 is a way to stabilize β -phase. The enhancement of electrochemical properties derived by the substituted Cu has been shown in P'2-type Na0.67Mn0.9Cu0.1O2 and P2-type Na2/3Mn2/3Ni1/4Cu1/12O2, studied in our group and other compounds investigated by other groups. In addition, P2-type Na0.67Cu0.28Mn0.72O2 is reported to exhibit oxygen redox without voltage hysteresis that has been only observed in the compounds having a specific ordering in 3d-TMO2 slabs. In ternary or quaternary systems consisting of 3d-TMs, the substituted Cu has been reported to be essential to stabilize oxygen redox via enhancing TM-O covalency as proposed in Li-rich layered oxides with 4dand 5d-TMs. Despite of the peculiar properties related to oxygen redox, the role of Cu substitution has not been fully understood.

As part of our ongoing studies on understanding the effects of Cu substitution for Mn on material properties and electrochemical performance, two series of P'2-type Na0.67CuxMn1-xO2 (x = 0, 0.125, 0.15, 0.20, called as o-OCu, o-12.5Cu, o-15Cu, o-2OCu, respectively) and P2-type Na0.67CuxMn1-xO2 (x = 0, 0.15, 0.20, 0.33, denoted as h-OCu, h-15Cu, h-2OCu, h-33Cu, respectively) are systematically investigated, focusing on the cooperative Jahn-Teller (JT) distortion. The solubility of Cu in Mn is found to be 0.125 and 0.20 for P'2 and P2 phase compounds, respectively. o-OCu consisting of high concentration of Jahn-Teller active Mn (III) shows stepwise voltage profile. The Cu substitution renders smooth voltage profiles and the phase transformation to another P'2 having different cooperative Jahn-Teller distortion occurs at lower voltage by increasing Cu substitution: from 2.3 V to 2.16 V for o-OCu and o-20Cu, respectively. Without Cu substitution, adopting P2 phase smoothens voltage profile as shown in h-OCu. All P2-type samples exhibit a reversible plateau at around 2.1 V, corresponding to the biphasic region of P2 and P'2. Different from the P'2-type samples, Cu2+/3+ redox is activated between 3.4-4.2 V (vs Na/Na+) when more than 20% Cu is substituted.

P2-type Na0.67Cu0.2Mn0.8O2 (h-20Cu), showing reversible Mn3+/4+, Cu2+/3+, and oxygen redox, is selected for deeper investigation, along with the two compounds, representing 10% Cu replaced with Mg (P2-type Na0.67Cu0.1Mg0.1Mn0.8O2, h-10Cu10Mg) or Zn (P2-type Na0.67Cu0.1Zn0.1Mn0.8O2, h-10Cu10Zn). We unveil that the nature of substituent(s) for Mn has no impact on the activation of oxygen redox. In contrast, the type, and the concentration of substituted

element(s) influence structural evolution during charge and discharge. Upon charge, partial or complete phase transformation to O2 phase occurs for h-10Cu10Mg or h-10Cu10Zn, respectively, while the initial P2 phase is retained for h-20Cu. The well-maintained P2 structure for h-20Cu in bulk and local suppresses voltage hysteresis when oxygen redox is activated. Upon discharge, all the three compounds converse to P'2 and the higher Cu concentration of h-20Cu leads to largely distorted P'2 than the others, reducing capacity retention.

Ultrasonically Assisted Wasted Cathode Leaching Process

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The fraction of metals recovered from spent batteries ranges between 3 and 5% as of 2022. Lithium and cobalt prices constantly increase for geopolitical and technical challenges while demand grows.

In this scenario, the recovery of valuable metal from wasted batteries is a valuable option to avoid the metal supply being the bottleneck in the batteries market while also helping to reduce greenhouse emissions.

The current industrial processes used to recover valuable metals are strongly limited by the time required for the cathode leaching. The leaching process involves the dissolution of spent cathodes (a mixture of lithium, cobalt, nickel, and manganese oxide) in an acid solution to precipitate valuable metals. This step is currently executed with strong inorganic acids, such as sulfuric or hydrochloric acid. It requires characteristic time scales in the order of hours to get to the saturation limit of the solution. This work aims to improve the leaching process, sensibly reducing the time scale for cathode dissolution and moving toward using a weak organic acid. The dissolution kinetics acceleration is enabled by applying ultrasound at specific frequencies to the solid/liquid mixture.

The phenomenon responsible for the improvement is ultrasonically induced cavitation (UIC). UIC is a physical process based on the propagation of high-frequency pressure waves in a liquid medium to trigger the nucleation of vapour cavities. A vibrating probe generates waves with a frequency higher than 20 kHz. Due to wave propagation, the liquid medium experiences a fluctuating pressure field. The low pressure experienced cyclically triggers the formation of vapour bubbles. Once formed, bubbles start oscillating, growing, and finally collapsing. The bubble collapse is associated with extremely high pressure and temperature in confined areas of nanometers. In addition to extreme conditions generated by bubble collapse, UIC favours the formation of micro-jets and waves. Micro-jets and waves also favour the leaching process because of two factors. First, they enhance the mixing between solid and liquid phases, and second, strong jets can mechanically break solid particles increasing the contact area between the two phases exponentially.

The new technology was demonstrated in a lab-scale setup able to process up to 200 lt per hour of liquid.

The UIC reactor consists of a reaction chamber and a pump able to circulate the mixture. The solid was loaded in the aqueous medium and let circulate for a given amount of time. The shape of the ultrasonic probe was designed to favour the formation of bubbles having a diameter of approximately 20 microns on average during the sonication process when processing aqueous substances.

The temperature of the reactor approached 40 C during the process although the solution was periodically quenched in the reservoir that was kept at ambient temperature. The exposition time to the region experiencing cavitation was approximately 0.5 s.

The leaching efficiency was calculated by filtering the solution and weighting the filters after letting them dry in an oven at 80 C.

Cobalt and lithium were deposited by adding NaOH and Na2CO3 subsequently in order to separate salts of lithium and cobalt. The solids obtained were then characterized by XRD technique.

A weak organic acid solution of acetic acid in water was used as a liquid medium. Lithium Cobalt Oxide (LiCoO2) was used as a surrogate for the spent cathode. A series of experiments were run, testing three acetic acid concentrations, solid-liquid ratios, and time of UIC treatment. The dissolution of LiCoO2 approached the thermodynamic equilibrium after 3 minutes of processing resulting in an improvement compared to the state-of-the-art.

To conclude, the newly developed continuous ultrasonically assisted leaching process was proved to be a valuable mechanism to improve the standard leaching process, reducing the characteristic process time and allowing to move toward a weak organic acid solution, thus avoiding the safety concern related to strong acid utilization.

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