Conference program and abstract book

Empa Academy, Dübendorf
August 29-31 2022

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Exhibition

Exhibitor stands are located in the foyer of Empa Academy from Monday 12:00 To Wednesday 15:40.

Dear participants,

Welcome to the 4th edition of the Swiss Battery Days. This is the first in-person event since 2019 and we are looking forward to three days of stimulating presentations and discussions.

We would like to thank the international advisory board, the scientific committee, local organizing committee, and battery associations and initiatives for their support in preparing and promoting this event. We would also like to thank our sponsors and exhibitors for their interest in our event and their support. A big THANK YOU also to all our invited speakers for accepting our invitation and to everyone that submitted an abstract.

Remember that the aim of this event is to provide young researchers, active in the field of battery materials research and cell manufacturing, a platform to present their results and to connect to renowned battery researchers from Europe. So enjoy this in-person networking opportunity!

We will kick off the event on Monday with a session focusing on metal anodes followed by the official poster session and the welcome apero. Posters will stay up during the entire duration of the event, so feel free to have discussions there with your colleagues.

On Tuesday, we will have a session focusing on recent trends in battery materials research, followed by the conference banquet in the evening. Please do not forget to bring the ticket for the conference banquet to the event. You will receive it already on Monday at the registration desk upon checkin.

On Wendesday morning, we are hosting an exciting industry session focusing on the topic of solid-state batteries. This event is co-organized and chaired by the Swiss Battery Association iBAT. In the afternoon the Horizon 2020 LC-BAT-5 battery project cluster organized a session with talks on Gen3B lithium-ion batteries from their various projects.

If you have any questions or concerns during the event, please stop by the registration desk or get in touch with us directly. We hope you have a great meeting experience and enjoy your time at the event!

Dr. Sigita Trabesinger PSI
Vice-chair Swiss Battery Days 2022

Dr. Corsin Battaglia Empa
Chair Swiss Battery Days 2022

Conference organization

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Poster session information

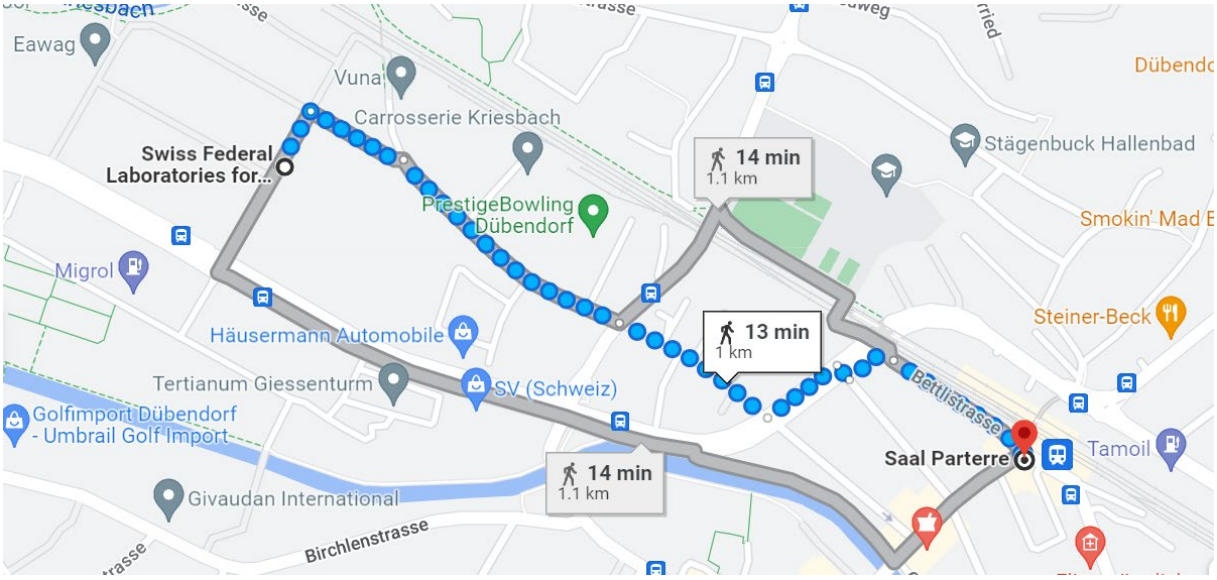
The poster session takes place in the atrium (entrance hall) of the NEST building located just next to the Empa Academy on Monday 15:30-19:00. Please make sure to mount your poster before the session starts and please be present at your poster during the session to answer questions of your colleagues. You can leave your poster for the duration of the conference, but are requested to remove your poster lastest by Wednesday 16:00. Poster that are not picked-up will be sent to paper recycling. Abstracts and posters are ordered by the first author's last name in alphabetical order.

Welcome apero information

The welcome apéro takes place in the atrium (entrance hall) of the NEST building located just next to the Empa Academy starting on Monday 17:00. Enjoy this great networking opportunity with refreshing beverages and finger food.

Banquet information

The conference banquet takes place at Restaurant Saal in Dübendorf, a short walk from Empa and just next to Dübendorf railway station starting on Tuesday 18:00 (see map below). Please do not forget to bring your ticket received at registration.



Technical program

Monday August 29 afternoon

12:00 Registration, lunch and exhibition

13:30 Welcome address
Corsin Battaglia, Empa and Sigita Trabesinger, PSI

13:40 (Invited) Electrochemo-mechanics of metallic lithium anodes
Mauro Pasta, University of Oxford, Faraday Institution

14:20 Unravelling lithium nucleation and dissolution in lithium-metal batteries
Eric Winter, T. J. Schmidt, S. Trabesinger, PSI

14:40 Why potassium half cells fail to deliver reliable results
Iurii Panasenko, Leonie Wildersinn, Franziska Allgayer, Julia Maibach, Fabian Jeschull, KIT

15:00 Free standing thin flexible artificial polymer composite SEI to increase the performance of lithium-sulfur batteries
Nico Grotkopp, Annelise Jean-Fulcrand, Georg Garnweitner, TU Braunschweig

15:30 Poster session and refreshing drinks

17:00 Apero riche

Tuesday August 30 morning

08:30 Coffee and exhibition

09:00 (Invited) Electrode kinetics in solid-state batteries
Jürgen Janek, Justus Liebig University Giessen, KIT

09:40 Interface evolution of the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2/Li_6PS_5Cl$ solid-state battery cathode during cycling
Barthélémy Lelotte, Carlos A. F. Vaz, Camelia Borca, Thomas Huthwelker, Vincent Pelé, Christian Jordy, Lorenz Gubler, Mario El Kazzi, PSI, SAFT

10:00 Polymerized-ionic-liquid-based polymer electrolyte for 4 V and 5 V class solid-state lithium metal batteries
Chenyin Fu, Gerrit Homann, Rabeb Grissa, Daniel Rentsch, Wengao Zhao, Tom Gouveia, Anais Fagayrat, Rongying Lin, Sébastian Fantini, Corsin Battaglia, Empa, Solvionic

10:20 Coffee and exhibition

10:50 (Invited) Understanding imperfect battery materials
Jon Serrano-Sevillano, Marine Reynaud, Damien Saurel, Montse Casas-Cabanas, CIC energiGUNE, Ikerbasque

11:30 Mechanism of Li_2S formation and dissolution in lithium-sulfur batteries
Christian Prehal, Jean-Marc von Mentlen, Sara Drvaric Talian, Alen Vizintin, Robert Dominko, Heinz Amenitsch, Lionel Porcar, Stefan A. Freunberger, Vanessa Wood, ETHZ, National Institute of Chemistry Slovenia, University of Slovenia, Graz University of Technology, Institut Laue-Langevin, IST Austria

11:50 Electron microscopy study of intragranular cracking mechanism in nickel-rich transition metal oxide cathode for lithium-ion batteries
Jedrzej K. Morzy, Wesley M. Dose, Per Erik Vullum, May-Ching Lai, Amoghavarsha Mahadevogwda, Michael De Volder, Caterine Ducati, U Cambridge, Faraday Institution, University of Leicester, Norvegian University of Science and Technology

12:10 Conference picture

12:20 Lunch and exhibition

Tuesday August 30 afternoon

13:40 (Invited) Eletrolyte-electrode interphases in high-voltage aqueous lithium-ion batteries
Jie Lie, Xu Hou, Helmholtz-Institute Münster, Forschungszentrum Jülich, Politecnico die Milano

14:20 The hydrotropic effect of ionic liquids in water-in-salt electrolytes
Maximilian Becker, Ruben-Simon Kühnel, Corsin Battaglia, Empa

14:40 The synergistic role of functional electrolyte additives containing phospholane-based derivative in NMC811/Si-graphite cells
Bahareh A. Sadeghi, Christian Wölke, Martin Winter, Isidora Cekic-Laskovic, Hemholtz-Institute Münster, Forschungszentrum Jülich

15:00 Coffee and exhibition

15:30 (Invited) Autonomous workflows for an accelerated design of battery electrodes
Ivano E. Castelli, Technical University of Danemark

16:10 Plasmonic based fibre optic sensors as in-situ battery diagnostic technique
Christopher Gardner, Elin Langhammer, Joe Fleming, Alexander J. Roberts, Rohit Bhagat, Tazdin Amietszajew, Coventry University, Insplorion

16:30 Characterization of lithium-ion cells degradation through deconvolution of electrochemical impedance spectroscopy
Pietro Iurilli, Claudio Brivio, Vanessa Wood, CSEM, ETH Zürich

18:00 Conference banquet

Wednesday August 31 morning

08:30 Coffee and exhibition

09:00 **Welcome address industry day**
Andreas Hutter, CSEM, iBAT and Corsin Battaglia, Empa, iBAT

09:10 (Invited) Automotive OEM views on solid-state battery technology
Hansen Michael Chang, Mercedes-Benz

09:40 (Invited) Perspectives on automotive all-solid-state batteries
Aron Varga, BMW

10:10 Coffee and exhibition

10:40 (Invited) Printing of all-solid-state batteries
Petrachai Srimuk, Andy Fiedler, Marcel Zwahlen, David Flaschenträger, Blackstone Technology, BFH

11:10 (Invited) Alternative manufacturing process for new solid-state electrolyte
Sebastian Heinz, Markus Stichnote, Günther Hambitzer, High Performance Battery Holding, High Performance Battery Technology

11:40 (Invited) Northvolt R&D strategy and progress for next generation battery development
Hwamyung Jang, Matteo Ambrosetti, Léo Duchêne, Northvolt

12:10 Poster award

12:20 Lunch and exhibition

Wednesday August 31 afternoon

13:30 **Welcome address Horizon 2020 LC-BAT-5 battery project cluster session**
Ruben-Simon Kühnel, Empa, SeNSE project

13:40 (Invited) A novel carbon material as conductive additives for slurry formulations
Florian Klunker, Steven D. Lacey, M. Schauer, Francesco Bizzotto, Ruben-Simon Kühnel, Corsin Battaglia, Huntsman Advanced Materials, Nanocomp Technologies Inc, Empa, SeNSE project

14:10 Graphite-based anodes with recycled silicon for lithium-ion batteries
Guiomar Hernandez, Ane Muguruza, Iratxe de Meatza, Jekabs Grins, Gunnar Svensson, Mads Heints, Marthe Emilie M. Buan, Anne-Karin Soiland, Uppsala University, CIDETEC, COBRA project

14:25 Pre-lithiation additives for the positive eletrode to compensate for active lithium losses in Si-based lithium ion battery cells
Aurora Gomez-Martin, Maike Michelle Gnutzmann, Egy Adithma, Lars Frankenstein, Bastian Heidrich, Martin Winter, Tobias Placke, MEET, University of Münster, Helmholtz-Institute Münster, Forschungszentrum Jülich, SeNSE project

14:40 Multifunctional ethoxy(pentafluoro)cyclotriphosphazene additive enables safe carbonate electrolytes for silicon-graphite/nickel-rich NMC lithium-ion batteries
Sufu Liu, Gerrit Homann, Rabeb Grissa, Konstantin Egorov, Yuanye Huang, Corsin Battaglia, Ruben-Simon Kühnel, Empa, SeNSE project

14:55 Development of in-situ monitoring tools for prototype cell performance and safety mapping
Tazdin Amietsajew, Alexander J Roberts, Conventry University, SeNSE proj

15:10 Coffee and exhibition

Wednesday August 31 afternoon (continued)

15:40 Temperature-driven chemical segregation and doping in cobalt-free lithium-rich layered oxides and its influence on electrochemical performance

Kunkanadu Rajappa Prakasha, Jekabs Grins, Aleksander Jaworski, Thomas Thersleff, Gunnar Svensson, Leif Olav Josang, Anne Dalager Dyril, Andreas Paulus, Dries De Sloovere, Jan D'Haen, Marlies K. Van Bael, An Hardy, Hemesh Avireddy, Joan Roman Morante, Jordi Jacas Biendicho, IREC, Stockholm University, Ceramic Powder Technology, Hasselt University, Imec, COBRA project

15:55 Environment friendly water-based cathode production from cobalt-free lithium-rich layered oxides for pouch cells testing

Hongmei Wang, Vassilios Siozios, Reinhard Mörtel, Andreas Würsig, Fraunhofer ISIT, COBRA project

16:10 High-areal-capacity nickel-rich NMC water-based electrodes with excellent long-term cycling stability

Yuri Surace, Nicolas Eshraghi, Damian Cupid, AIT, SeNSE project

16:25 Innovative hybrid high-voltage electrodes based on LNMO/LFP materials for lithium-ion batteries

Roberto Colombo, Daniele Versaci, Julia Amici, Silvia Bodoardo, Carlotta Francia, Federico Bella, Nadia Garino, Politechnico di Torino HYDRA project

16:40 Closing remarks

17:00 End of conference

Poster 1

Challenges and Strategies Towards More Realistic Application of the Li Metal-based Pre-lithiation Technique on Si Anodes

Egy Adhitama[1,2,*], Frederico D. Brandao[1], Iris Dienwiebel[1], Marlena M. Bela[1], Atif Javed[1,2], Feleke Demelash[1], Lukas Haneke[1], Marian C. Stan[1], Martin Winter[1,3], Aurora Gomez-Martin[1], Tobias Placke[1]

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[1]*University of Münster, MEET Battery Research Center, Institute of Physical Chemistry, Germany*

[2]*University of Münster, International Graduate School for Battery Chemistry (BACCARA), Germany*

[3]*Helmholtz Institute Münster, IEK-12, Forschungszentrum Jülich GmbH, Germany*

Lithium ion batteries (LIBs) do not only dominate the small format battery market for portable electronic devices but have also been successfully implemented as the technology of choice for electric vehicles.[1] However, for successful consumer acceptance and broad market penetration of electric vehicles, further improvements of LIBs in terms of energy density and cost are required. The practically usable energy density of LIB cells is reduced by parasitic side reactions including electrolyte decomposition and formation of the "solid electrolyte interphase" (SEI) at the surface of the anode, as this process is related to the consumption of active lithium. Especially high-capacity silicon-based anodes suffer from ongoing lithium losses and rapid capacity fading.

Pre-lithiation is considered as a highly appealing technique to compensate for active lithium losses and, therefore, to increase the practical energy density. A critical parameter for a pre-lithiation strategy is to establish a technique for achieving lithiation of the active storage material at the most uniform lateral and in-depth distributions possible. Despite extensive exploration of various pre-lithiation techniques, controlling the lithium amount precisely while keeping an even lithium distribution remains challenging.

In our previous publication, the thermal evaporation of lithium metal as a novel pre-lithiation technique for silicon (Si) anodes has been successfully developed that allows both, *i.e.*, precise control of the degree of pre-lithiation and a homogeneous deposition at the electrode surface.[2] Pure Si thin film | lithium metal interface and SEI characterization show that this approach enables the preserved Li to be consumed for the formation of a pre-formed SEI and creates moderate mechanical cracks by volume changes. The highly uniform Li metal on Si thin films is beneficial for increasing capacity retention and significantly suppressing active lithium losses. The phase changes are evaluated and the terms dry-state and wet-state pre-lithiation (without/with electrolyte) are revisited. A series of electrochemical methods are also validated where the active lithium losses were compensated and improved electrochemical performance of Si thin film anodes.

Further, one major question arises whether all of the improvements from this pre-lithiation technique on pure Si thin film can be translated into a more realistic electrode format *e.g.*, composite-based Si. This study reports the feasibility of pre-lithiation by use of Li metal in half-cell and full-cell setups using composite Si anodes. Firstly, the Li utilization is examined which is highly affected by particle size and surface area of electrode materials. Secondly, the anode potential behavior is investigated. Thirdly, the impact of pre-lithiation on the electrochemical performance is thoroughly examined. This study contributes to navigating the research direction in regard to the Li metal-based pre-lithiation technique on Si anodes in a wider sense.

References:

(1) Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M. Performance and cost of materials for lithium-based rechargeable automotive batteries. *Nat. Energy* **2018**, *3* (4), 267-278. DOI: 10.1038/s41560-018-0107-2.

(2) Adhitama, E.; Dias Brandao, F.; Dienwiebel, I.; Bela, M. M.; Javed, A.; Haneke, L.; Stan, M. C.; Winter, M.; Gomez-Martin, A.; Placke, T. Pre-Lithiation of Silicon Anodes by Thermal Evaporation of Lithium for Boosting the Energy Density of Lithium Ion Cells. *Adv. Funct. Mater.* **2022**, 2201455.

Horizon 2020 LC-BAT5 battery project cluster session

Development of *in-situ* monitoring tools for prototype cell performance and safety mapping

Tazdin Amietszajew*[1], Alexander J Roberts[1],

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Thermo-electrochemical monitoring of state-of-the-art rechargeable Li-ion batteries during operation is critical for safety and reliability, yet it remains quite limited, relying on conventional full cell measurements with in-situ techniques lagging behind. However, energy storage cells are complex multi-component devices. To unlock the full battery performance without jeopardising safety, live in-cell thermodynamic characterization is needed.

Within the SeNSE project we utilise a combination of developments on miniature quasi-reference electrodes and micron-scale temperature sensors facilitating internal thermal mapping. A small array of these sensing elements can be placed on a single assembly, adaptable to a range of cell formats and chemistries for installation into prototype, commercial or other industrially relevant cells.

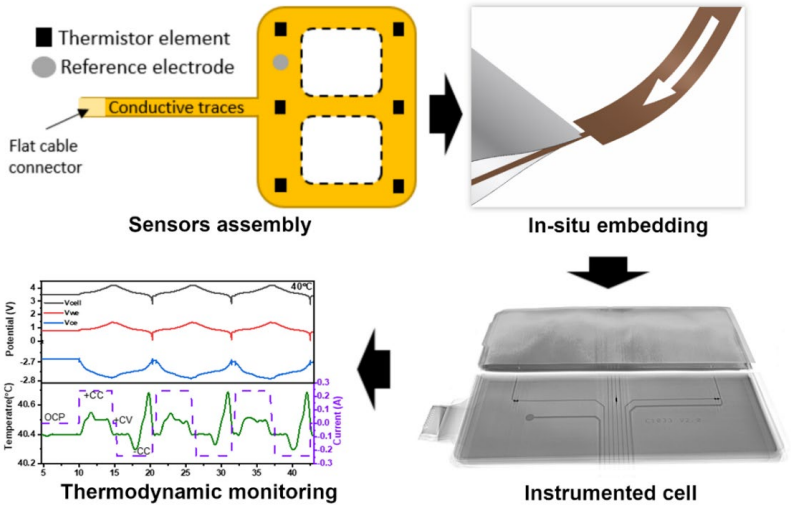

Figure 1: Advanced cell diagnostics methodology

Here we demonstrate the feasibility of incorporating Au, LiFePO4, and TiO2 quasi-references into prototype pouch cells, report a long-term stable Ti-based reference electrode, and a new design enabling impact-free implementation into pouch, in conjunction with thermal probes to track the cell behaviour during galvanostatic cycling at varying operating temperatures[1,2]. Collectively, these complementary techniques can offer valuable insights and improved battery management approach for next-generation of lithium-ion energy storage systems.

References:

[1]Ahmed, Z., Roberts, A. J., & Amietszajew, T. (2021). *Energy Technology*, *2100602*, 1–7. https://doi.org/10.1002/ente.202100602

[2]Ahmed, Z., Roberts, A. J., & Amietszajew, T. (in print) *Energy Technology*, (in print) https://doi.org/https://doi.org/10.1002/ente.202200248

Poster 2

Stabilizing thin metallic lithium anode by LiI surface passivation layer for high energy density Li-ion batteries

Adil Baiju[1*], Marco Carboni[2], José-Antonio Gonzalez[2], Tian Liu[1], Mario El Kazzi[1]

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[1]*Electrochemistry Laboratory, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland*

[2]*Belenos Clean Power Holding Ltd, 4452 Itingen, Switzerland*

Thin lithium metal anodes hold the promise of increasing the energy density of Li-ion batteries over 400 Wh/Kg. This is possible thanks to its high theoretical capacity of 3860 $mAhg^{-1}$ and lowest negative electrochemical potential of -3.06 V vs. Standard Hydrogen Electrode. However, lithium metal anodes suffer from uncontrolled dendrite growth which causes capacity loss and increased safety hazard in batteries.[1] The Li metal anode surface passivation with organic or inorganic layers have shown improved cycling stability and mitigation of the dendrite growth.[1] Among them, Li halides demonstrate low energy barriers for Li^+ at the anode and promote uniform plating and stripping during cycling.[2] Furthermore, Li halides also have a high Young's Modulus (29-126 GPa)[3] to effectively suppress dendrite growth.[1] Compared to other Li halides, studies on lithium iodide (LiI) as a passivation layer using liquid-based electrolyte remains scarce. In this work, we report on (i) the formation of a homogeneous LiI passivation layer on a thin Li foil achieved by a solid-gas reaction and (ii) its beneficial effect on improving the cycling performances.

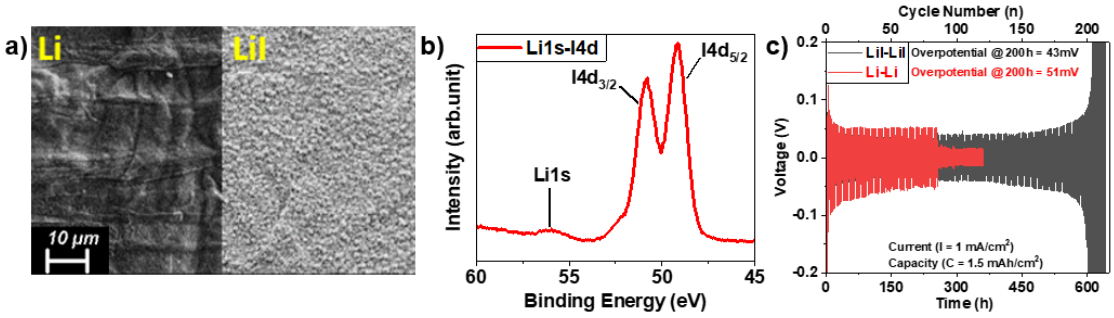

Figure 1: a) SEM micrographs of the as received 50 µm Li foil and of the deposited LiI passivation layer, b) XPS core level spectra for Li1s, I4d, c) galvanostatic charge-discharge performed on Li symmetric cells with and without the LiI passivation layer at a current density of 1 mA/cm^2 and areal capacity of 1.5 mAh/cm^2.

The LiI deposition is achieved by sublimating iodine vapor from an I_2 crystals onto a 50 µm thick Li foil coated on Cu in an airtight stainless steel container inside a muffle furnace. A homogeneous LiI layer can be seen from the SEM micrographs when compared to the as received Li foil (Fig. 1a). XPS spectra (Fig. 1b) show well defined $I4d_{5/2}$ and $I4d_{3/2}$ core levels peaks at 49 eV and 51 eV with a distinct Li1s peak at 56 eV. XPS quantification indicates a surface composition mainly consisting of LiI and small amounts of Li hydroxide (LiOH) and Li carbonate (Li_2CO_3). The galvanostatic charge-discharge in ether-based electrolyte performed on Li symmetric cells with the LiI passivation layer shows a stable cycling up to 600 hours (~200 cycles) (Fig. 1c) when is cycled at a current density of 1 mA/cm^2 and with an area capacity of 1.5 mAh/cm^2. The presence of the LiI demonstrates the enhanced cycle life compared to the as received Li which fails after 255 hours (~85 cycles) (Fig. 1c).

References:

[1] X.B. Cheng, R. Zhang, C.Z. Zhao, Q. Zhang, Chem. Rev. **2017**, 117, 10403-10473

[2] M.D. Tikekar, S. Choudhury, Z. Tu, L.A. Archer, Nat. Energy. **2016**, 1, 1-7

[3] J. Wang, M. Deng, Y. Chen, X. Liu, W. Ke, D. Li, W. Dai, K. He, Mater. Chem. Phys. **2020**, 244, 122733

Poster 3

Unveiling the surface and bulk degradation of P2-type sodium layered oxide cathode material operating at high-voltages

Dominika Baster[1*], Carlos A. F. Vaz[2], Adam H. Clark[2], and Mario El Kazzi[1]

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It is well known that cathode materials with the P2 crystal structure undergo multiple types of phase transitions upon charge and discharge, which lead to sever capacity fading, especially under high-voltage cycling conditions (> 4.2 V vs. Na^+/Na).[1] However, the influence of the surface degradation on the capacity deterioration of P2-type cathode materials remains less explored.

In this work, the origin of the capacity fading in P2-$Na_{0.67}Mn_{0.6}Fe_{0.25}Al_{0.15}O_2$ cathode material cycled at high operating voltages (4.5 V vs. Na^+/Na) is investigated (Fig.1a) with a combination of surface and bulk-sensitive advanced characterization techniques such as soft X-ray absorption spectroscopy (XAS) in total electron yield (TEY) detection mode with a depth sensitivity of 10 nm and hard X-ray absorption spectroscopy in transmission mode, together with X-ray diffraction.

From the Mn L-edge spectra, the oxidation state of the manganese at the surface is observed to be reversible at the end of the first charge and discharge, and determined to be +4 and +2/+3 respectively. However, after long-term cycling (15 cycles), reduced manganese species (Mn^{2+}/Mn^{3+}) are detected at the surface of the fully charged cathode (Fig. 1b). These results imply that the surface suffer from sever structural degradation and formation of an electrochemically inactive reduced layer. Moreover, the Mn and Fe K-edges (Fig. 1c) show that Mn redox reactions in the bulk are not fully reversible because Mn is less oxidized on charge in the second cycle compared to the first cycle. It confirms that also the bulk $Na_{0.67}Mn_{0.6}Fe_{0.25}Al_{0.15}O_2$ particles undergoes significant structural changes. Hence, we conclude that the capacity fading of $Na_{0.67}Mn_{0.6}Fe_{0.25}Al_{0.15}O_2$ is a complex phenomenon caused by both surface and bulk structural degradations, which require significant effort in terms of coating and doping respectively to mitigate the long-term fading.

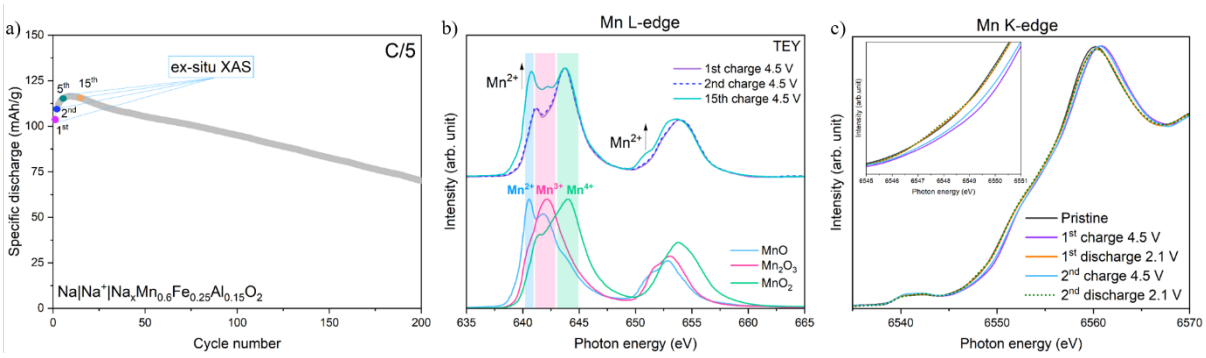

Figure 1. a) Cycling performance of $Na|Na^+|Na_xMn_{0.6}Fe_{0.25}Al_{0.15}O_2$ cell in a potential window of 2.1-4.5 V. b) XAS spectra in TEY mode of $Na_{0.67}Mn_{0.6}Fe_{0.25}Al_{0.15}O_2$ electrodes at different states of charge, acquired at the Mn L-edge. c) Mn K-edge XANES spectra upon first and second cycles.

References:

[1] M. Zarrabeitia, F.Nobili, O. Lakuntza, J. Carrasco, T. Rojo, M. Casas-Cabanas & M. Ángel Muñoz-Márquez, Chem. **2022**, 5, 11

Poster 4

The hydrotropic effect of ionic liquids in water-in-salt electrolytes

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[1]*Empa, Swiss Federal Laboratories of Materials Science and Technology, Switzerland*

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[1]. 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 extended by increasing the lithium salt solubility through the hydrotropic effect of ionic liquids[2]. 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-3-methylimidazolium 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 $Li_4Ti_5O_{12}$ (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 $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (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[3].

References:

(1) Suo, L.; Borodin, O.; Gao, T.; Olguin, M.; Ho, J.; Fan, X.; Luo, C.; Wang, C.; Xu, K. "Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science* **2015**, *350* (6263), 938-943. DOI: 10.1126/science.aab1595.

(2) Becker, M.; Rentsch, D.; Reber, D.; Aribia, A.; Battaglia, C.; Kühnel, R.-S. The Hydrotropic Effect of Ionic Liquids in Water-in-Salt Electrolytes**. *Angew. Chem. Int. Ed.* **2021**, *60* (25), 14100-14108. DOI: 10.1002/anie.202103375.

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Poster 5

Recycling of End-of-Life Li-Ion Batteries Including Material Quality Optimisation in order to Retain the Circularity of Key Battery Materials

Andrin Büchel[1], Nora Bartolome[1], Aurelio Brozi[2], Edouard Querel[3], Olivier Groux[4], Dawit Ayana[4], Rolf Widmer[1]

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Direct recycling of lithium-ion batteries (LIB) is a promising process because its several advantages over traditional methods. For instance with direct recycling, functional cathode particles can be recovered without its decomposition into its elements or the dissolution of the particles and later precipitation steps. This process is therefore more energy efficient. A direct recycling process for the cathode in aged lithium iron phosphate (LFP) LIB is here proposed with the ultimate goal to recover LFP active material to be reused in new battery manufacturing.

The process consist of two steps: (1) a water bath and (2) thermal healing. The thermal healing of the LFP active material is investigated at different atmospheres (e.g., He/H_2), temperatures, and exposure times. The final material is then characterized by several analytical techniques such as X-ray powder diffraction and scanning electron microscopy to determine the changes of the material (i.e., crystallographic information and particle imaging characterization) in comparison to the virgin material. Additionally, the LFP material is used in a "half-cell configuration" to characterize its electrochemical performance by galvanostatic cycling with potential limitation protocol. Results will be presented and discussed to see the feasibility of the process to be scaled up to industrial level.

Invited presentation

Autonomous Workflows for an Accelerated Design of Battery Electrodes

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The development of automated computational tools is required to accelerate the discovery of new functional materials, to speed up the transition to a sustainable future. Here, I address this topic by designing new battery electrodes for different intercalation battery chemistries. These workflows are implemented in the framework of Density Functional Theory, using MyQueue and the Atomistic Simulation Environment (ASE). In the first part, I describe a fully autonomous workflow, which identifies materials to be used as intercalation electrodes in batteries, based on thermodynamic and kinetic descriptors like adsorption energies and diffusion barriers.[1] A substantial acceleration for the calculations of the kinetic properties has been obtained due to a recent implementation of the Nudged Elastic Bands (NEB) method, which takes into consideration the symmetries of the system to reduce the number of images to calculate. Moreover, we have established a surrogate model to identify the transition states, which can further reduce the computational cost to at least one order of magnitude.[2,3] We have applied this workflow to discover new cathode materials for Mg batteries as well as solid state electrolytes for Li, Na, and Mg all-solid-state batteries.[1,3] In the second part of my talk, I discuss how nanostructured materials can positively impact the Li-ion battery solid/electrolyte interface, to adjust the change in volume during charge/discharge in Si-anodes.[4] In the last part of my talk, I will discuss the crucial importance of research data management for the acceleration of materials discovery. More in details, I will show the case of the the EU-H2020 BIG-MAP project – a cross-disciplinary project targeting disruptive battery-material discoveries. Essential for reaching the goals of the project is extensive sharing of research data across scales, disciplines, and stakeholders, not limited to BIG-MAP and the European BATTERY 2030+ initiative but within the entire battery community. The key challenges faced in developing the data management plan (DMP) for such a large and complex project were to generate an overview of the enormous amount of data that will be produced, to build an understanding of the data flow within the project and to agree on a roadmap for making all data FAIR (findable, accessible, interoperable, reusable). In this talk, I will describe the process we followed, how we structured the plan and how we make it operational by embedding ontology concepts.[5]

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Invited industry presentation

Automotive OEM views on Solid State Battery Technology

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The search for a next-generation solution is now a focus for many automakers, and solid-state batteries (SSB) are one of the more promising solutions. In order to be ready for the potential shift to this newer technology Mercedes has actively been involved in the research and development of SSB technology and its potential impact on the production and design of vehicles, as well as the production of the technology itself.

We are looking forward to welcoming you to the Swiss & Surrounding Battery Days at Empa Academy on August 26-28.

Horizon 2020 LC-BAT5 battery project cluster session

Innovative hybrid high voltage electrodes based on LMNO/LFP materials for lithium ion batteries

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Nowadays the markets of electric vehicles (EV) and energy storage devices are fast increasing pushing a constant increase in the demand for greener and more sustainable power sources. In particular, for EVs applications, batteries guaranteeing long cycle life combined with high specific energy and high power density are needed. To increase the specific energy, one solution is to increase the cell voltage and the capacity. For this reason, combine high voltage cathode, i.e. LMNO (Lithium Manganese Nickel Oxide), together with high capacity anodes, i.e silicon, can be an interesting solution. Unfortunately, LNMO suffers easy cation leaching during cycling, in particular at high Crate. The present abstract shows results achieved within HYDRA H2020 project based on the synthesis of new blended materials combining LMNO and LFP (Lithium Iron Phosphate) in order to combine their inherent positive characteristic to get better performing electrodes. LFP was chosen because of its outstanding thermal and electrochemical stability, as well as its Li-redox activity at a relatively high voltage. [1] Therefore, the presence of the LFP should increase the performances of the LMNO, especially at higher current rates.

In order to get a homogeneous coating of LFP particles on the LMNO surface, we used ball billing treatments modifying all parameters, such as frequency, time, and weight percent of LFP. The blended active materials were thus characterized from a morphological and structural point of view with FESEM and XRD analysis, and electrochemical characterization: galvanostatic cycling and cyclic voltammetry studies. The results obtained are showing that the mixing through ball milling does not significantly damage the structure of the two pristine materials but a homogeneous coating of LFP is actually hard to obtain through this method, However, the electrochemical data confirm that both materials actively contribute to the capacity of the blended electrodes.

Fast microwave synthesis of LFP, to trigger his growth on LMNO particles, was followed as an alternative approach to obtain the desired hybrid material. The characterization of these materials showed that this procedure could provide a more consistent layer of LFP around the LMNO particles.

Authors kindly acknowledge Hydra project (Horizon 2020 innovation programme under Grant agreement number: 875527) for funding.

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Poster 6

Ultrafast sintering and crystallization of $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ glass and its impact on ion conduction

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Abstract:

Lithium-ion batteries are a vital technology for the electrification of transportation and sustainable energy sectors. However, lithium-ion batteries currently suffer from serious safety risks due to the thermal instability and flammability of liquid electrolytes.[1] As solid-state electrolytes do not leak, are generally non-flammable, and have better thermal stability than liquid electrolytes, using them would alleviate the safety issues of conventional lithium-ion batteries. Li^+ conducting oxides with a NASICON-type structure are among the most promising solid electrolytes due to their ionic conductivity in the 10^{-4}-10^{-3} S/cm range. However, sintering such oxides is time- and energy-intensive, contributing to a significant portion of the solid-state battery preparation costs.[2] In this work, $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP), among the most promising solid electrolytes for lithium batteries, was sintered and crystallized in 180 seconds by ultrafast high-temperature sintering (UHS) from glassy powders under conditions attractive for continuous industrial processes (*i.e.,* ambient pressure and atmosphere). The fast heating rates characteristic of UHS significantly delay crystallization, potentially decoupling crystallization and sintering. Furthermore, EIS characterizations reveal that LAGP sintered and crystallized by UHS has an ionic conductivity of 1.15×10^{-4} S/cm, slightly lower than conventionally annealed samples (1.75×10^{-4} S/cm). The lower conductivity can be attributed to poorer inter-grain contact and grain boundary conductivity, likely due to the fast heating rates of UHS. To overcome this issue, additives such as B_2O_3 and Li_3BO_3 are used, resulting in ~2 and ~5 times higher grain boundary conductivity for LAGP+1%wt B_2O_3 and LAGP+1%wt Li_3BO_3, respectively, compared to LAGP.

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Horizon 2020 LC-BAT5 battery project cluster session

Graphite-based anodes with recycled silicon for lithium-ion batteries

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Silicon kerf is a byproduct generated in the diamond wire cutting of wafers in the photovoltaic (PV) industry. It amounts to more than 160000 tons/year and therefore it is crucial to recycle, this large source of high purity bulk silicon, back into PV or into other high value applications. One example is its combination with graphite to produce high-capacity negative electrodes for lithium-ion batteries.

The COBRA project has focused on Si waste sources from PV industry, development of processes for the silicon waste to adapt it to an anode material, its upscaling and processes to produce silicon-graphite electrodes with 10 wt% Si content. The silicon kerf is of flake-like morphology as visualized by SEM, samples featured different amounts of amorphous Si, up to 50%, evidenced by X-ray powder diffraction among other techniques. The slurry processing and post-processing methods for the electrode manufacturing have been optimized changing speed, mixing steps, etc. The viscosity of the slurry and morphology and mechanical properties of the dry electrodes after calendering have been investigated. In addition, silicon waste samples subjected to different processing were tested in half coin cell configuration (vs. Li foil) in order to screen the best performing recycled Si material.

Poster 7

Metal oxides/MXene heterostructure for Li-S batteries

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Lithium-sulfur (Li-S) batteries attract enormous attention due to their high theoretical capacities and energy densities. However, the Li-S system confronts great challenges including sluggish redox kinetics and the notorious "shuttle effect".[1] Herein, we propose a metal oxides/MXene heterostructure to confine polysulfide shuttle as well as catalyzing the Li-S redox reaction. In this contribution, we explain the working principle of our approach and show the first results of MXene synthesis.

Chemical adsorption is essential for polysulfide confinement as well as catalytic conversion. We thus classify the interaction as Li bond and S bond depending on the interacting atoms (Figure 1a). As widely studied two-dimensional metal carbides, the so-called MXenes, possess high conductivity and a layered structure. When combining MXene and semiconductive metal oxides to build a *p-n* heterostructure, the negatively and positively charged interfaces can strongly adsorb polysulfides via Li bonds and S bonds, respectively, at the built-in electric field (BIEF, Figure 1b).[2] The suspended nanosheets from our MXene synthesis are predominantly single-layered (Figure 1c).

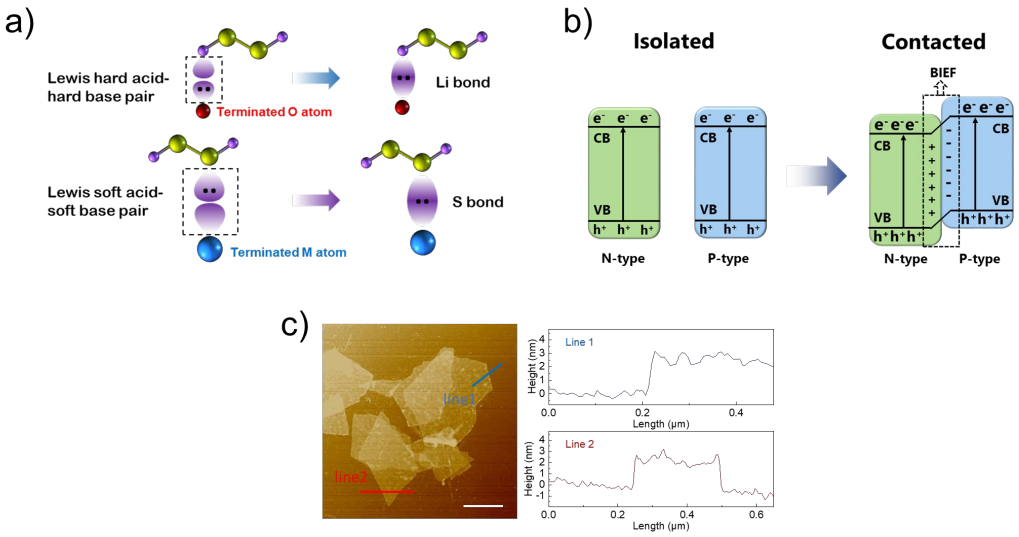

Figure 1: a) Formation of Li bonds and S bonds via Lewis acid-base pairs, with Li_2S_2 as example, b) The formed BIEF heterostructure; c) AFM image of delaminated MXene and the corresponding height profile along the lines, scalar bar is 0.5 μm..

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Poster 8

In-situ polymerization of PVEC polymer electrolyte provides superionic conductivity and tunable viscosity

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Polymer electrolytes (PEs) are an interesting alternative to traditional liquid electrolytes since they can be non-flammable (increasing safety), their viscosity is tunable (enabling new applications such as free-form batteries), their manufacturing is easily upscalable and they could integrate Li-metal as an anode (increasing energy density). Traditional solid PEs based on ethylene oxide such as PEO suffer from low ionic conductivity at room temperature, since Li^+ transport relies on interchain ion hopping based on segmental motion, a process that is highly temperature-dependent[1]. In this work, we investigate PEs containing sidechains of cyclic carbonates (such as vinyl ethylene carbonate – VEC) which present alternative ionic conductive pathways to ion hopping, hence being superionically conductive and providing a route towards high ionic conductivity at room temperature (> 0.1 mS/cm)[2]. The polymer electrolyte was synthesized in-situ: the monomer, initiator and Li salt were mixed and injected into the battery stack containing a scaffolding membrane; subsequently, the cells were cured at 80°C to initiate the free radical polymerization. Fig. 1(a) shows the dependency of conductivity versus radical initiator content, while Fig. 1(b) displays the resulting viscosity of the PE after doing in-situ polymerization inside coin cell batteries for a fixed polymerization procedure. By increasing the initiator content, ρ_{RT} decreases, while the viscosity of the PE is increased. Proof-of-concept full batteries based on PVEC PEs will be shown. Compatibility with Li-metal and cyclability of batteries built with PVEC and future routes for safe, stable Li-metal batteries based on PEs will be discussed.

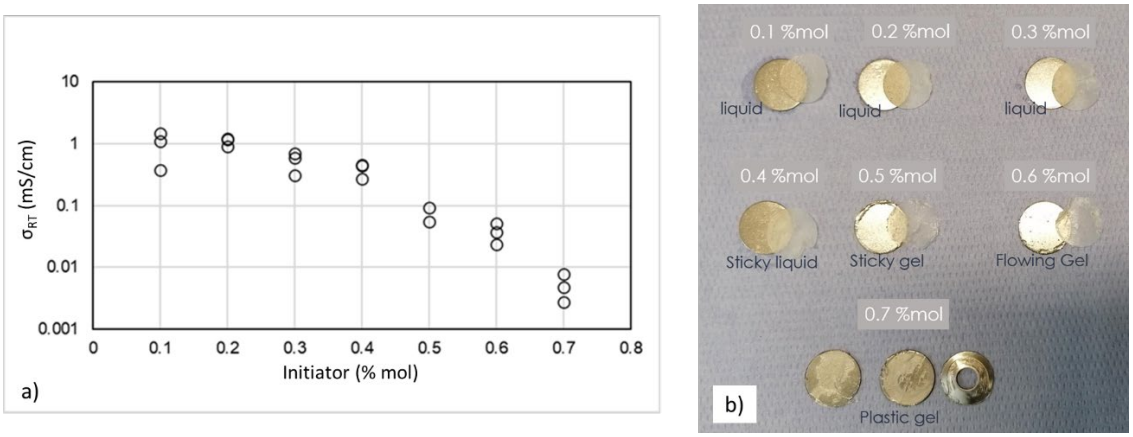

Figure 1: a) Room-temperature ionic conductivity versus initiator content of in-situ polymerized PVEC PEs in SS//SS configuration. b) Picture showing post-mortem analysis of the resulting separator/electrolyte composites, showing how only after 0.4 %mol the viscosity increases from liquid to a gel phase, in an opposite trend to its ionic conductivity.

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Poster 9

Exploring the Unique Lithium and Sodium Storage Pathways in $FeSbO_4$ Nanoparticles

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Abstract

The increasing energy demands have prompted research on conversion and alloying materials, offering high lithium and sodium storage capacities. In this study, we demonstrate a facile route to synthesize $FeSbO_4$ nanoparticles that possess high theoretical lithium and sodium storage capacity of 1220 mAh g^{-1}. We synthesized highly phase-pure $FeSbO_4$ nanoparticles by a slurry-mixing technique followed by calcination process. [1] Operando X-ray diffraction studies reveal the electrochemically induced amorphization of the nanoparticles upon alkali-ion storage. We achieved specific storage capacities of ~600 mAh g^{-1} for lithium-ion and ~300 mAh g^{-1} for sodium-ion batteries, respectively. The disparity in the lithium and sodium electrochemistry arises from the unique lithiation and sodiation pathways adopted by the $FeSbO_4$ nanocrystals. This study offers new insights into the chemistry and mechanism of conversion- and alloying-based energy storage materials that would greatly assist the development of next-generation active materials for energy storage.

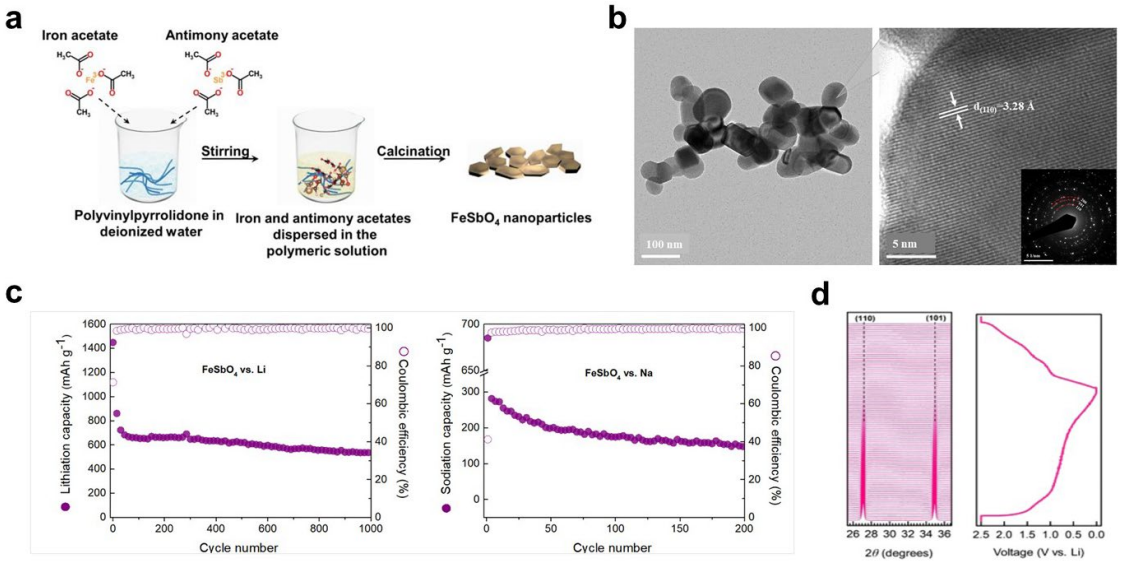

Figure 1: **a)** Synthesis Route of $FeSbO_4$ Nanoparticles, **b)** HR-TEM image of the synthesized $FeSbO_4$ nanoparticles, **c)** Galvanostatic cycling at 0.5 A g^{-1} versus Li and at 0.2 A g^{-1} versus Na, **d)** Operando XRD patterns collected during lithium storage in $FeSbO_4$ anode and the corresponding voltage profiles at a specific current of 30 mA g^{-1}.

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Poster 10

Driving battery experiments with robotics and software workflows

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The integration of automated simulation workflows with robotic experiments can enable rapid testing of scientific hypotheses and validation of physical models, improve reproducibility, and ultimately accelerate battery innovation.

In this contribution, we extend the AiiDA infrastructure[1] for computational science to interface with the Aurora autonomous battery development platform and orchestrate cell cycling experiments, with on-the-fly analysis of cell cycling data and a feedback loop to control cell cycling parameters. An AiiDAlab UI allows the user to set up a cycling protocol, launch and monitor the measurements, and analyze the data. Automated data provenance and cell history are stored in the AiiDA database. This, together with the automatic workflow management features of AiiDA, will allow the integration of experimental and computational capabilities into a unified infrastructure.

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Invited industry presentation

Printing of All Solid State Batteries

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Particular Hydroboranes and there combination not only exhibit high ioniq conductivity (1), but are also thermally, electrochemically and mechanically stable (2). Therefore this class of materials is a promising candidate for the use as solid state electrolyte.

This contribution gives an outlook on a possible fabrication of solid-state batteries based on hydroborane solid-state electrolytes by 3D printing

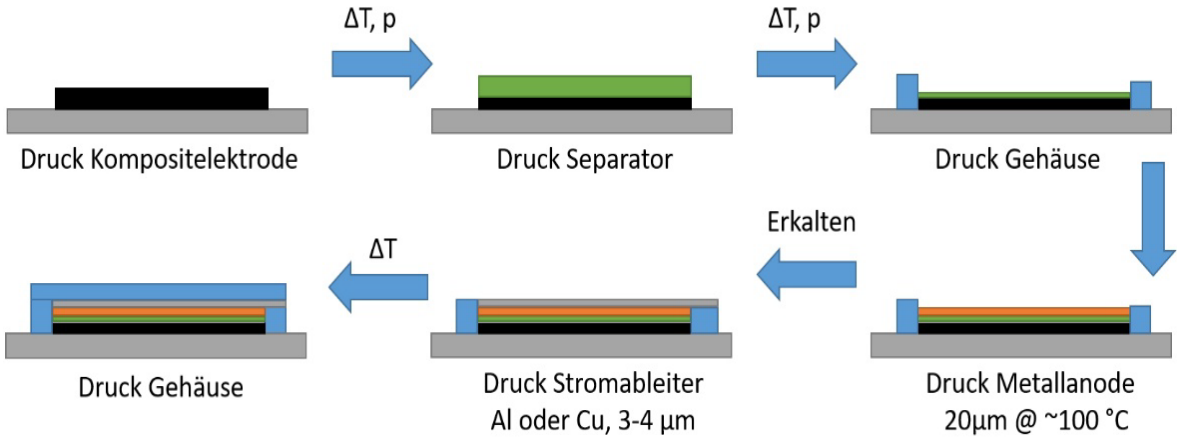

Figure 1: Schematic process of 3d printing a solid-state battery

The manufacturing of a solid-state battery is supposed to be a repetition of consecutive material deposition or printing steps. In return, with increased product size and complexity, i.e. capacity or voltage, the number of individual process steps increases and therefore the accumulated failure rate of the entire process. Therefore it is mandatory not only to find the right balance between quality assurance measures and production capacity, but to gain a deeper understanding of the criticality of different failure modes and ways to overcome them. In order to study these effects and consequences together with BFH a digital twin of a ASSB production line was created and simulations performed. The results are important for the next steps, incl. the planning of a prototype printing plant for ASSB.

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ACS Applied Materials & Interfaces **2021** *13* (46), 55319-55328

Poster 11

Strategies Towards Practical Implementation of Chemical Pre-lithiation of Si-based Anodes using Lithium Arene Complex Solutions

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Lithium ion batteries (LIBs) are state-of-the-art energy storage systems. For a successful market penetration of electric vehicles, there is an urgent need for further improvements in terms of gravimetric and volumetric energy density of LIBs. In this sense, the development of advanced negative electrode materials is considered one of the most appealing approaches.[1] The ~10-fold higher specific capacity and high abundancy make silicon (Si) one of the most promising candidates to replace state-of-the-art graphite negative electrodes.[2] However, Si undergoes severe volume changes up to 280% during (de-)lithiation, resulting in fast capacity fading and short cycle life due to the continuous re-formation of the solid electrolyte interphase (SEI), leading to active lithium losses (ALL).[3] To compensate for ALL, research on suitable pre-lithiation processes is of great interest. Among different pre-lithiation methods, chemical pre-lithiation by application of lithium arene complex (LAC) solutions is a fast, easy and cost-effective method to enable a sufficient lithium reservoir within the negative electrode to compensate for ALL.[4]

In this work, the stability of three different solvents to produce a 4,4'-dimethylbiphenyl (4,4'-DMBP) LAC is investigated *via* solid phase microextraction gas chromatography-mass spectrometry method (SPME-GC-MS). Further, the LAC is used to investigate the stability of different binder systems to choose the most stable binder system for optimized electrode manufacturing. Based on that, different parameters such as the reaction temperature and pre-lithiation time are systematically investigated to achieve suitable degrees of pre-lithiation (DOPL) of the negative electrode. DOPLs up to 55% can be reached by using 0.5 M 4,4'-DMBP in tetrahydrofuran (THF) as LAC solution. Results report that a higher temperature during the reaction reduces the pre-lithiation time to achieve a pre-lithiation plateau. Moreover, the impact of the DOPL to the Si-based LIB's full cell performance is investigated in detail. This pre-lithiation method significantly improves the cycle life of a silicon nanowire graphite (SiNW/Gr) composite negative electrode. Higher DOPLs can be achieved by variation of the arene concentration as well as using further tailored biphenyls. However, the use of 4,4'-DMBP leads to sufficiently low potentials *vs.* $Li|Li^+$ to pre-lithiate Si-based negative electrodes while being cost effective.

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Poster 12

Modeling Chemically Induced Stresses and Deformation in Li-Ion Batteries

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2COMSOL AB, Sweden

Batteries are subject to various chemically driven stress and deformation processes. In Lithium-ion batteries the intercalation of lithium in electrode materials, such as graphite, causes expansion and contraction of the lithium-ion battery electrode during charge and discharge cycles. These expansions and contractions lead to stresses and strains in the electrodes. Eventually, the stresses and strains may cause cracks in the electrode resulting in the deterioration of a battery's performance. Additional mechanical deformations arise during plating on lithium metal electrodes, due to metal deposition and dissolution. In our presentation we demonstrate new approaches to account for chemically-induced stress- and deformation processes in Multiphysics battery models of both heterogeneous and homogeneous type[1].

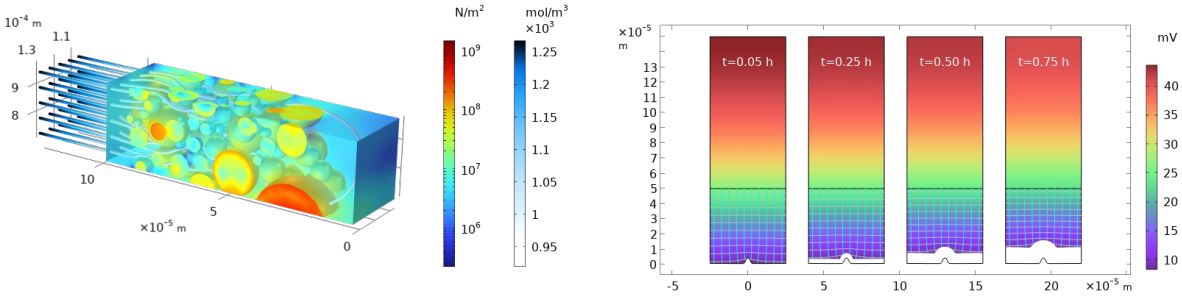

Figure 1: a) Heterogeneous battery model: surface: von Mises stress, streamline: cation flux colored for electrolyte salt concentration b) Homogeneous battery model, surface: potential in deformed geometry during plating on the negative electrode over a period of 45 min.

References:

[1] COMSOL Multiphysics® v. 6.0. www.comsol.com. COMSOL AB, Stockholm, Sweden.

Poster 13

The BATTMAN way of cooperation

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Innosuisse's Energy SCCER funding program (2013-2020) was designed to develop and implement solutions to the pressing issues related to the energy transition in Switzerland. over 1500 projects were launched during the entire funding program. Partners from business and society participated in around 900 projects.[i]

Within this framework, SCCER HAE Heat and Electricity Storage had focused on energy storage, including electrochemical storage of batteries. New and improved battery materials based on lithium ions and sodium ions have been developed, as well as scaling up the production of such batteries for future markets[ii].

A screening of the Swiss industry has shown that there is a specialized company for practically every manufacturing step. Even if Switzerland is not necessarily the right country for creating Giga Factories in battery production, there are still almost all suppliers for this topic.

Actually, the statement that there is no large battery production in Switzerland is not quite correct, because the company FZSoNick[iii] already produces large battery capacities in Ticino for some times.

To promote the topic of battery production in Switzerland, more precisely of lithium-ion batteries, an association has been founded that has taken up this specific topic.

In the start-up phase in the year 2019 one tried to reach the framework, however on Swiss level, like the ompetence center for lithium batteries KLib[iv] in Germany, also with the goal to co-operate. Unfortunately, due to lack of funding, this project had to be shelved and BATTMAN was founded, which is based on a different principle.

In order to achieve a maximum effect, the effort was greatly reduced compared to the KLib and the main focus was on networking. In this context, networking means meeting, exchanging ideas and not only ideas. An important part of the whole thing is also the exchange, the mutual availability of equipment, services and, if necessary, materials. This is done from one person to another without receiving anything in return directly from the same person. The original idea was to register the whole thing in a Favor Bank, so that the balance of given and received services is approximately kept. However, since the system has worked so well since its inception, the formal maintenance of this database has been abandoned for the main while.

It is important to note that this is an association primarily for Swiss industry. Of course, research partners active in Switzerland are also very welcome, even if they can only represent a minority in the management structure, in order to ensure the industrial character.

An additional note is that the focus is battery production including equipment, analysis techniques along the whole value chain of **Batt**ery **man**ufacturing, the design, production and recycling.

[i] www.innosuisse.ch/inno/de/home/ueber-uns/beendete-forderprogramme/foerderprogramm-energie1.html

[ii] www.psi.ch/en/ene/sccer-hae

[iii] www.fzsonick.com/

[iv] klib-org.de

Poster 14

Quantifying the density of mobile ions in LLZO solid electrolytes by transient current measurements

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One of the key properties of solid electrolytes is their ability to transport ions between anode and cathode. This ion migration is usually characterized by measuring the ionic conductivity by means of impedance spectroscopic measurements. However, the ionic conductivity is proportional to both the density and the mobility of mobile ions.

We show how measuring temperature-dependent current transient measurements can be used to quantify mobility and density of mobile ions in solid electrolytes. Using this method, we show how the amount of mobile lithium ions affects the ionic conductivity of amorphous $Li_7La_3Zr_2O_{12}$ (LLZO), and how doping crystalline LLZO with Al and Ga affects both the density and the mobility of mobile ions. Finally, we will show how different LLZO particle sizes and loadings affect the ionic conductivity in composite solid electrolytes of PEO and LLZO. The proposed approach of quantifying mobile ions can be extended to other mixed ionic-electronic conductors for a better understanding of ion migration and the influence on battery performance.

Horizon 2020 LC-BAT5 battery project cluster session

Plasmonic based fibre optic sensors as an in-situ battery diagnostic technique

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Improved battery diagnostics can significantly aid cell research and characterisation, battery design and use optimisation and enable early failure detection. In this study, plasmonic based fibre optic sensors are investigated as a diagnostic technique inside lithium-ion NMC vs graphite pouch cells. These sensors have the advantages of allowing data acquisition from directly inside the battery cell in real time and being minimally invasive, amongst other benefits. Here we demonstrate and discuss strong correlation of sensor optical signal and cell state, alongside other important characteristics such as the impact of the sensor presence on cell performance.

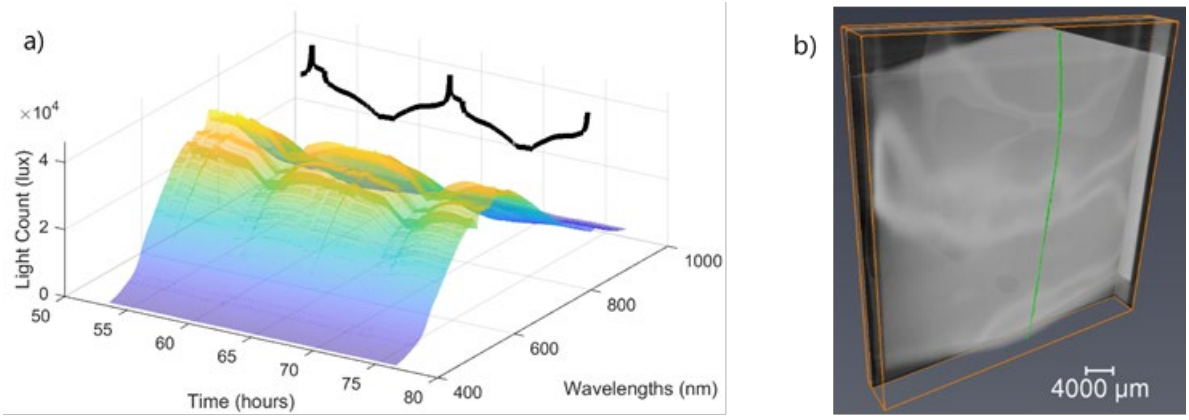

Figure 1- a) Optical data acquired during cell cycling (spectra), with indicative inverted cell voltage shown in background (black line), b) X-ray image of fibre sensor inside pouch cell. [1]

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Horizon 2020 LC-BAT5 battery project cluster session

Pre-lithiation additives for the positive electrode to compensate for active lithium losses in Si-based lithium ion battery cells

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Silicon is considered as the most promising high-capacity active material for the negative electrode for future high energy-density lithium ion batteries (LIBs). However, its commercialization is still hindered by several challenges, including massive volume changes upon (de-)lithiation resulting in continuous breakage and (re-)formation of the solid electrolyte interphase (SEI) and consumption of active lithium.[1] Pre-lithiation with the help of positive electrode additives has emerged as one of the most suitable scaling-up strategies to compensate for active lithium losses and could ease the practical application of silicon-based anodes in commercial LIB cells.[2] However, an evaluation of the impact of decomposition products such as releasing gases and remaining cathode porosity on cell performance after oxidation of the additive is still lacking.

In this work, lithium squarate ($Li_2C_4O_4$) is thoroughly evaluated as low-cost and air-stable pre-lithiation cathode additive in LIB cells with a Si-based negative electrode. Different amounts of $Li_2C_4O_4$ (0, 2.5, 5 and 10 wt.%) are added to a $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NMC622) cathode following standard electrode processing routes. The effect of additive oxidation on the electrode morphology and cell electrochemical properties is systematically investigated. The cycle life of NMC622+$Li_2C_4O_4$||Si/graphite LIB cells is linearly prolonged with the additive content within the cathode due to the excess of active lithium provided by the additive in the first charge that can compensate for SEI formation. However, this work not only reports the advantages of this pre-lithiation approach but also identifies considerable challenges for its practical application arising from the emerging porosity and gas development during decomposition of the pre-lithiation additive. The amount of additive must be carefully adjusted so as not to compromise the benefits provided in terms of cycle life. The dead volume created after the additive is decomposed can adversely impact the cell energy density. Furthermore, X-ray photoelectron spectroscopy investigations give some insights for the first time that the release of CO_2 during the decomposition of the additive results in an abrupt increase in cathode electrolyte interphase thickness and a high occurrence of carbonates and C-O species compared to the reference cathodes, slightly worsening the attainable capacity. Results reported herein can pave the way for further tailoring and optimization of the pre-lithiation process of Si-based negative electrodes using cathode additives.

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Poster 15

All-solid-state lithium-metal batteries with porous/dense/porous $Li_7La_3Zr_2O_{12}$ layers generated by chemical protonation followed by thermal deprotonation

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Abstract

Ceramic $Li_7La_3Zr_2O_{12}$ (LLZO) represents a promising candidate electrolyte for next-generation all-solid-state lithium-metal batteries. However, lithium-metal batteries are prone to dendrites formation upon fast charging. Porous/dense and porous/dense/porous LLZO structures were proposed as a solution to avoid or at least delay the formation of lithium-metal dendrites by increasing the electrode/electrolyte contact area and thus lowering the local current density at the interface[1,2,3]. In this work, we show the feasibility of producing porous/dense/porous LLZO by a new and scalable method. The technique consists in LLZO chemical deep protonation in a protic or acidic solvent[4], followed by thermal deprotonation at high temperature in order to create the porous structure by water and lithium oxide elimination[5]. We demonstrate that the produced structure extends lifetime of Li/LLZO/Li symmetric cells by a factor of 8 compared to a flat LLZO at a current density of 0.1 mA/cm^2 and with a capacity of 1 mAh/cm^2 per half cycle. We also show clear improvement of the Li/LLZO/$LiFePO_4$ full cell performance with a thermally deprotonated LLZO.

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Poster 16

Free standing thin flexible artificial polymer composite SEI to increase the performance of lithium-sulfur batteries

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To achieve high energy densities lithium (Li) metal is theoretically the optimal electrode material, as it is the lightest metal and possesses the most negative potential (- 3.04 V) vs. the standard hydrogen electrode.[1] In combination with a sulfur (S) electrode, high gravimetric energy densities are achievable which makes this battery type especially attractive for aviation. Yet the commercialization of Li-S batteries is strongly hindered by safety issues, as the dendritic growth of Li poses a risk of internal short circuits. Another challenge, the polysulfide shuttle mechanism, greatly reduces cycling performance.[2] To overcome these issues artificial solid electrolyte interphases (SEI) for electrode protection can be applied.

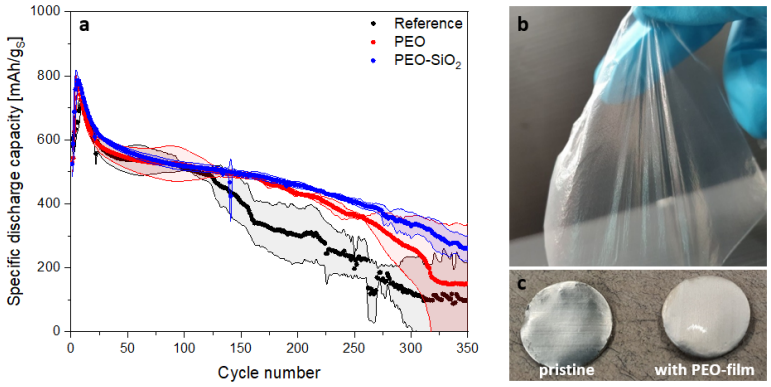

Figure 1: a) Long-term cycling at 0.1 C of three systems (Reference: without film, PEO film on Li, PEO-SiO_2 film on Li), b) free-standing PEO-film (thickness approximately 1.7 µm), c) film application.

In this work, an artificial SEI is applied directly to the Li-metal electrode to avoid undesired reactions. Particularly the implementation of flexible materials such as polymers proves to be a reasonable approach, since they can withstand the successive SEI breakage and building during cycling. Here, the artificial SEI is realized by a thin, free-standing flexible polymer layer based on polyethylene oxide (PEO) (see Figure 1 b), which can be applied to the surface of the Li-metal electrode in a solvent-free process (see Figure 1 c). The effectivity of the PEO-based protective layers was enhanced by the addition of SiO_2 particles, and the resulting composite layers were characterized via scanning electron microscopy (SEM). From the results, it was observed that the addition of an artificial SEI improves the cycling stability and cell repeatability in coin cells (see Figure 1 a).

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Poster 17

Stabilisation of Ni-rich layered oxide cathodes for high energy Lithium-ion batteries via Atomic Layer Deposition coating approach

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Despite huge improvements in the Lithium-ion battery technology over the past decades, there still needs to increase battery energy density to meet customers' demands and enable extensive market penetration of electric vehicles. In order to achieve high energy density, layered Lithium Nickel Cobalt Manganese Oxide (NCM) is considered as the most promising candidate for next generation cathode materials. Especially, state-of-art Ni-rich cathodes with Ni content higher than 60% and Co content lower than 20% exhibit outstanding specific capacity values and low material costs with the reduced usage of Co as the most expensive and critical raw material. However, by continuously increasing the Ni-content and reducing the Co-content in layered oxide cathode materials, several intrinsic (electro-)chemical challenges become aggravated and sacrifice cycle life and thermal stability. For example, upon cycling Ni-rich NCM batteries, Li^+/Ni^{2+} cation mixing disorder leads to crystal phase transformation from layered to inactive rock-salt phase yielding fast capacity fading and poor rate capability. In addition, the transition metals, Ni, Mn, and Co can be dissolved into the liquid electrolyte, causing transition metal deposition on the separator and the anode electrode surface [1,2].

Therefore, this work investigates a coating method to mitigate the aforementioned challenges of Ni-rich NCM cathode materials and improve cycle life. Among several stabilisation approaches reported so far, the coating method stands out for its ability to protect cathode active materials against direct contact with the liquid electrolyte preventing parasitic side reactions at the cathode/electrolyte interphase. Herein, a protective coating material, alumina (Al_2O_3) was applied on fabricated composite cathode electrodes using Atomic Layer Deposition (ALD) technique. By doing so, the coating could protect non-active as well as active materials and enhance electron transport pathways compared to the conventional cathode powder coating approach [3]. This work also thoroughly explores the impact of the ALD coating conditions on Ni-rich cathode sheets with varying coating thickness and the porosity of the cathode sheet with regard to electrochemical properties in lithium-ion cells.

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Poster 18

Swiss circular economy model for automotive lithium batteries (CircuBAT)

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Decarbonization of the transport sector is essential for achieving the Paris Climate Targets and Electric vehicles are considered as key technology for this, and their market share is increasing . There were 11 million electric vehicles worldwide in 2020, but by the end of the decade, that number could be 145 million . By 2040, it could be 530 million. With a market penetration of electric vehicles of 50%, when those vehicles reach their end of life, in the UK alone there will be around 200'000 metric tons of lithium-ion batteries that need to be disposed of, recycled, or reused . How that will be done in an economical and sustainable manner is still to be determined. Building a Swiss battery recycling indus-try will be challenging and will require coordination between economic, environmental, social, and regulatory requirements. The CircuBAT consortium, consisting of the seven affiliated research institutions listed above and a total of additional 24 industry partners along the battery value chain in Switzerland, aims to address above challenges in Switzerland and to elaborate a Swiss circular economy model for automotive lithium-ion batteries, which represents a notable economic, social, and ecological added value and targets the UN Sustainable Development Goals 12 (responsible consumption and production) and 13 (climate action). CircuBAT will forge a systemic innovation path towards a circular economy for automotive lithium-ion batteries in Switzerland by dealing with three main challenges along the complete battery value chain:

At first, extending the use in first life applications with better battery life prediction models and re-moving the barriers for a second life usage of EV batteries is addressed, as reuse can double the useful lifetime of the batteries, at which point, they can be recycled . Further, improving the economic and technical performance of battery recycling and remanufacturing technologies and enabling the upcycling of recycled materials to reintroduce them into the battery manufacturing process. A higher economical yield for recycling with lower energy cost and a more resilient raw material supply chain with lower cost, lower carbon footprint will also lower dependence from the market outside Switzer-land. Finally, addressing the social, environmental, and economic challenges for the introduction of a circular business model for automotive lithium-ion batteries through a continuous exchange and coor-dination among the project partners to understand drivers and hurdles for each actor across the value chain, and to use synergies within the consortium. The project is part of the newly launched Flagship Initiative of Innosuisse, the Swiss Innovation Agency, is funded by both Innosuisse and the 24 implementation partners and will be carried out within a four-year period ending in 2025. At the Swiss Battery Days conference, insights into the planned activities will be presented as the project just started in 2022.

References:

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an increase of 48.9% compared with the previous year. For plug-in hybrids (PHEV), the figure was as high as 237.2%.

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Poster 19

Impact of the primary particle morphology on the electrochemical performance of Ni-rich layered oxide cathode materials

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Cathode active materials (CAMs) are the most critical components of lithium ion batteries (LIBs) with regards to energy density and cost. Therefore, an enhanced mass-market penetration of LIBs in electric vehicles may strongly depend on the cathode of choice. State-of-the-art CAMs are Ni-rich NCM-type layered oxides, ***e.g.,*** $LiNi_{1-x-y}Co_xMn_yO_2$ (NCM). By increasing the Ni content, the discharge capacity and therefore the energy density on material level can be gradually increased. Simultaneously, the content of Co as the most critical raw material is reduced. However, the usage of NCMs with Ni contents between 80 and 100 atomic percent is accompanied by several challenges such as capacity fading, safety concerns and moisture sensitivity that need to be overcome before commercialization.[1]

Common approaches to tackle these challenges are the use of bulk substituents or surface coatings which, despite improving cycling stability, are in most cases electrochemically inactive and lead to lower energy densities on material level. Therefore, there is a growing interest to design NCMs particles with advanced morphology which can counteract these downsides while mitigating instability issues and particle cracking upon cycling. On the one hand, core-shell or concentration-gradient (CG) design within secondary particles can improve the electrochemical performance by stabilizing the electrode|electrolyte interface. On the other hand, advanced primary particles (***e.g.,*** rod-like or single crystal morphologies) can compensate the anisotropic lattice distortion during (de)-lithiation better than traditional grain-like primary particles, leading to an improved electrochemical performance.[2] However, CG particles or NCMs with rod-like primary particles are often synthesised using a discontinuous batch-type reactor, leading to dead-times, less efficiency and yield, which are important from an industrial point of view.

This work focuses on the modification of the primary particle morphology of Ni-rich NCMs. Therefore, the continuous co-precipitation route of the corresponding precursor is modified, leading to the synthesis of Ni-rich NCMs with rod-like primary particle morphology. The impact of the co-precipitation and calcination conditions on the primary particle morphology is herein thoroughly evaluated. Finally, the electrochemical performance of NCMs with advanced primary particle morphology is evaluated in NCM||Li metal and NCM||graphite full-cells.

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Poster 20

Rate-Limiting Processes in High-Temperature Sodium-Metal Chloride Batteries

Meike V. F. Heinz[1,*], Daniel Landmann[1,2], Gustav Graeber[1], Enea Svaluto-Ferro[1], Ronald Gutierrez[2], Louis Sieuw[1], Tu Lan[1], Sophia Haussener[2], Corsin Battaglia[1]

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Commercial sodium-metal chloride batteries are assembled from non-critical raw materials, mainly rock salt and nickel powder. Operated at temperatures > 250 °C, their hermetically sealed cells with ceramic electrolyte enable a long shelf and cycle life. Already now, sodium-metal chloride batteries provide a competitive cost of energy stored per cycle for niche market applications. However, large-scale deployment of this technology is currently hindered by high production costs, related to a complex tubular cell geometry, and by limited cycling rate capability, compared to lithium-ion batteries.

We have developed a planar high-temperature cell platform, which allows us to enhance the understanding of relevant transport processes, and to demonstrate the influence of electrode composition and microstructure. Here, we first discuss mechanisms and rate-capability of electrochemical nickel and iron chlorination, using disc-shaped model electrodes (Fig. 1a).[1] Then, we demonstrate cycling of porous, particle-based cathode granules, comprising both nickel and iron (Fig. 1b). At a high discharge rate of 1.6C (cathode loading 50 mAh/cm^2), we obtain a high average discharge energy of almost 280 Wh/kg over 50 cycles (cumulative capacity >2 Ah/cm^2), relative to the weight of granules.[2] In another project, we use these results to design zinc-based cathodes for sodium-zinc chloride batteries, which could provide a cost-efficient alternative to the current nickel-based compositions.[3]

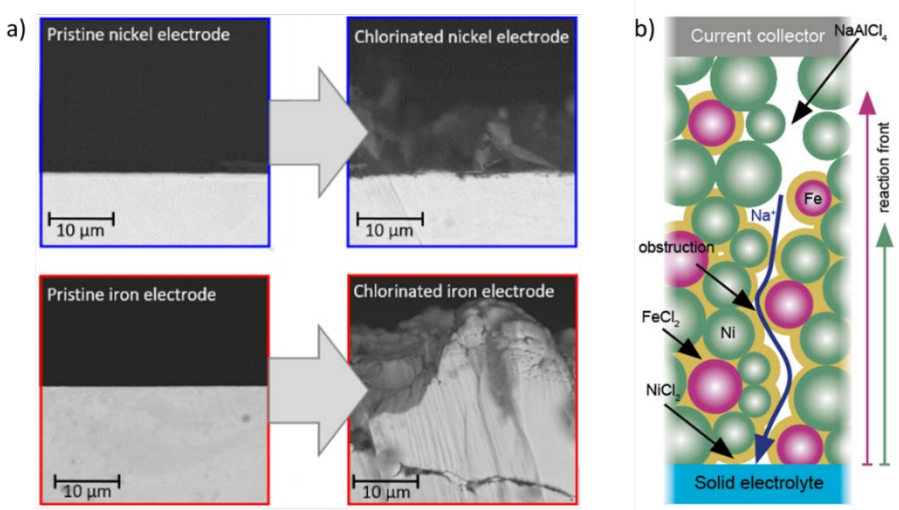

Figure 1: a) De-/chlorination of planar nickel and iron model electrodes.[1] b) De-/chlorination of porous, particle-based sodium-metal chloride electrode.[2]

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Invited industry presentation

Alternative Manufacturing Process For New Solid-State Electrolyte

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Solid-state batteries are considered a promising technology path for solving the safety risks of conventional Li-ion batteries and for achieving a significantly higher specific energy, among other things. The high variability of materials is also reflected in the diversity of concepts for solid-state batteries. There are now more than 2,900 patent families [1] dealing with solid-state electrolytes. They can be grouped into oxides, sulfides, polymers and others. However, every individual group is associated with challenges in manufacturing [2].

The production of almost all solid-state electrolytes takes place outside the battery cell and is therefore associated with challenges arising in particular from physics and process technology [2, 3]. In contrast, the manufacturing processes for batteries with liquid electrolytes are widely tested and mature. The production of the solid-state electrolyte developed by High Performance Battery takes place within the battery cell and allows the use of manufacturing processes for batteries with liquid electrolytes.

In order to characterize the solidification process of the High Performance Battery solid-state electrolyte in the cell [4] and to be able to investigate its properties, special 4x4x1cm^3 conductivity measurement cells were produced. X-ray tomography measurements were performed on these cells in collaboration with Empa's Laboratory Materials for Energy Conversion (voxel size: 31.4 µm). In Figure 1a, the solid/liquid phase boundary of the electrolyte is very clearly visible shortly after the chemical reaction has taken place in the cell. Figure 1b shows the measurement result of the same cell after one year without significant differences in the aggregate state.

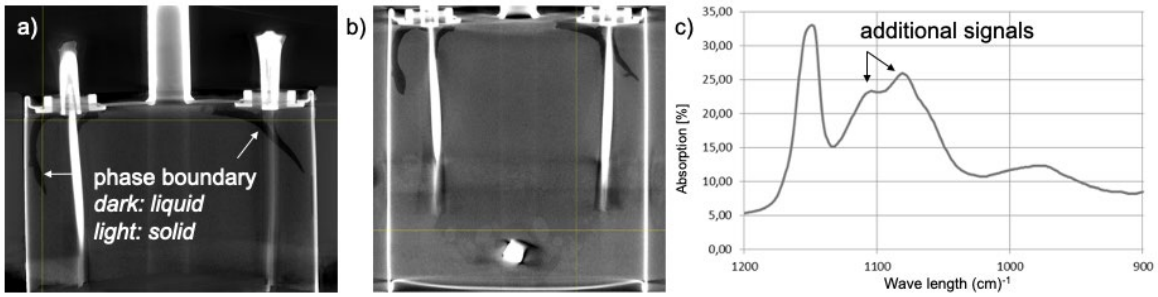

Figure 1: a) X-ray tomography scan of conductivity measurement cell right after the chemical reaction transforming the liquid electrolyte into a solid electrolyte, b) X-ray scan of conductivity measurement cell one year after the chemical reaction, c) Infrared spectrum of solid-state electrolyte developed by High Performance Battery.

The characterization of the solid ion conductor was carried out using Fourier transform infrared spectroscopy and compared with the spectrum of the liquid electrolyte [5]. The infrared spectrum shown in Figure 1c shows the additional signals in the wave range between 1200 and 900 cm^{-1} that are formed over time in a cycled cell with liquid electrolyte [5].

Ionic conductivity measurements performed at room temperature on the resulting solid ion conductor showed values in the range of 20-30 mS/cm, surpassing the conductivity of LPS [6], LGPS [7] and argyrodites [8] from the class of sulfide electrolytes [2] and comparable to liquid electrolytes [9].

The current challenge is now to optimize the production process with regard to the addition of the reactants in quantity and place for industrial production.

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Poster 21

Polymerized-Ionic-Liquid-Based Polymer Electrolytes for 4V and 5V Class Solid-State Lithium Metal Batteries

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Solid polymer electrolytes are a promising material class as enabler for lithium metal anodes in solid-state batteries, offering low material density and use of established processing technologies. The major challenges for the commercialization of polymer-based lithium metal batteries are the low ionic conductivity at room temperature, the suppression of lithium dendrite growth, and the electrochemical stability towards oxidative decomposition in combination with high voltage cathodes of the 4V and 5V class.

Herein, a polymer electrolyte based on a polymerized-ionic-liquid (PIL) poly(diallyldimethylammonium) bis(fluorosulfonyl)imide, room-temperature ionic liquid N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR13FSI) and Li conducting salt lithium bis(fluorosulfonyl)imide (LiFSI) is presented, providing good compatibility in contact with lithium metal and high oxidative stability >5.0 V versus Li|Li$^+$ under room-temperature operation [1]. The poly-cationic backbone of the PIL allows the uptake of large amounts of ionic liquid and conducting salt without leakage in freestanding polymer electrolyte films with an ionic conductivity of 0.8 mS cm^{-1} at 25 °C.

The PIL-based polymer electrolyte enables a stable lithium plating and stripping of 1.0 mAh cm^{-2} per half-cycle in symmetric Li||Li cells at a current density of 0.1 mA cm^{-2} for more than 1700 hours. The high oxidative stability was demonstrated in a high-voltage lithium metal battery using the spinel-type $LiNi_{0.5}Mn_{1.5}O_4$ as cathode material with an upper cut-off voltage of 5.0 V, where an initial specific capacity of 132 mAh g^{-1} and a capacity retention of 76% after 300 cycles was obtained at 25 °C. Additionally, galvanostatic long-term cycling experiments with uncoated high-energy $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ cathode material were conducted with an upper cut-off potential of 4.4 V, providing an initial specific capacity of 162 mAh g^{-1} and a capacity retention of 72% after 600 cycles at 25 °C. The overall performance at ambient temperature renders PIL-based polymer electrolytes a promising material class for the implementation in next generation lithium metal batteries.

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Poster 22

Pressure-induced phase segregation and conductivity correlation of highly conductive *closo*-hydroborate electrolyte for solid-state batteries

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Hydroborates are a yet underexplored class of solid electrolytes that combine very attractive material properties, including compatibility with lithium and sodium metal anodes, low gravimetric density (<1.2 g/cm^3), high thermal and chemical stability, low toxicity, solution processability, and mechanical properties that enable cold pressing. Mixing cage-like closo-hydroborate [B_nH_n] and/or closo-hydromonocarbaborate[$CB_{(n-1)}H_n$] ions, ionic conductivities above 1mS/cm were obtained and stable cycling of a 4V class solid-state battery has been demonstrated at room temperature.[1-4] Thereby the cathode composite can be assembled by cold pressing at pressures of typically 300 MPa.

Here we discuss the role of the applied pressure on the structure of mixed $Na_2B_{10}H_{10}$:$Na_2B_{12}H_{12}$ electrolytes and their conductivity. Two ratios of $Na_2B_{10}H_{10}$:$Na_2B_{12}H_{12}$ were investigated, 1:1 and 1:3. The as-synthesized powder of 1:1 ratio is phase pure and crystallize in a single, face-centered cubic (FCC) structure with cubic close packing of anions, while the 1:3 ratio results in a mixture of predominant room temperature monoclinic $NaB_{12}H_{12}$ phase and a body-centered cubic (BCC) phase. After applying pressure to densify the materials, the pellet shows a phase segregation into an FCC (for 1:1) or monoclinic (1:3) and a BCC phase, the latter being recently observed in the $NaCB_{11}H_{12}$ electrolyte.[5] The higher the pressure the higher the amount of BCC phase, which is the high temperature and high conductivity phase of $Na_2B_{12}H_{12}$. The BCC content saturates at about 300 MPa to the amount of $Na_2B_{12}H_{12}$ in the initial synthesized powder. The room temperature conductivity follows the same trend. For the 1:1 ratio, it increases from 0.2 mS/cm at 10% BCC content to about 1 mS/cm at 50% BCC content. Our results show that expensive $Na_2B_{10}H_{10}$ can in part be replaced by cheaper $Na_2B_{12}H_{12}$ and that pressing is a prerequisite to achieve the high conductivities by the introduction of a highly conductive bcc phase.

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Poster 23

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 (Fig. 1). Si NWs@SSFC anodes with different mass loadings are characterized before and after cycling by scanning and 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.

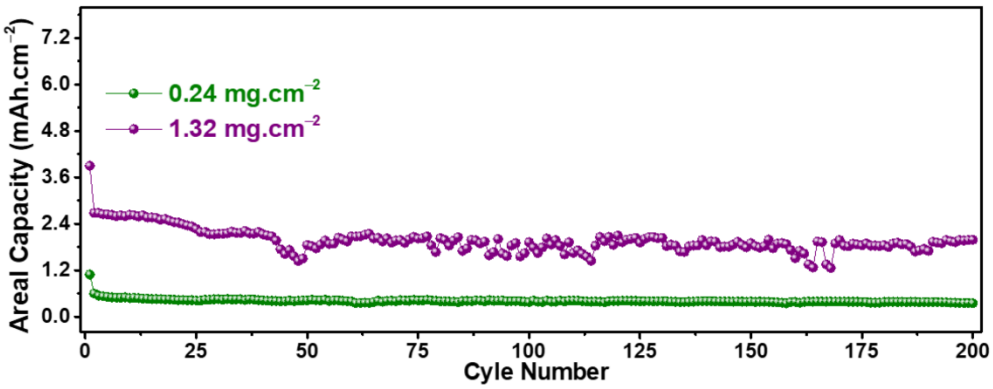

Figure 1. Areal capacity vs cycle number of Si NWs@SSFC with mass loadings 0.24 and 1.32mg.cm^{-2} at C/5

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Poster 24

Characterization of Lithium-ion cells degradation through deconvolution of Electrochemical Impedance Spectroscopy

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Li-ion cells aging is caused by complex physical and chemical degradation mechanisms which affect the different components inside the cell[1]. Cell measurements should be comprehensive and non-invasive, to embrace the complex interactions between these mechanisms and to be implemented in Battery Management Systems (BMSs) in order to improve battery state estimation[2].

This work introduces a methodology to characterize aging of commercial Li-ion cells through deconvolution of Electrochemical Impedance Spectroscopy (EIS) measurements[3] (Figure 1). Cylindrical commercial cells have been cycled with different protocols to simulate different aging paths. After cycling, the cells have been disassembled and half-cells have been made to detect the electrochemical and aging processes occurring at anode and/or the cathode sides. Moreover, lab-made full-cells have been exploited to verify the reproducibility and consistency when compared to cylindrical cells. Distribution of Relaxation Time (DRT) method has been applied to deconvolute EIS spectra in order to separate the polarization effects overlapped in the frequency domain by means of a peak-based representation[4]. The DRT profiles of lab-made and cylindrical cells have been compared evaluating the position (i.e. time constant), the magnitude and the variations of the peaks during lifetime. The results of an extensive analysis of around 500 EIS spectra returned an unambiguous attribution of different electrochemical processes to different time constants, and ultimately to different DRT peaks. These results were validated by means of imaging techniques: (i) digital imaging validated graphite degradation, mainly related to lithium plating and (ii) Scanning Electron Microscopy validated the degradation at the cathode, mainly attributed to particle cracking. It is concluded that DRT is a powerful tool to characterize Li-ion cell aging and DRT peaks' tracking can help to develop more reliable State of Health (SoH) estimators.

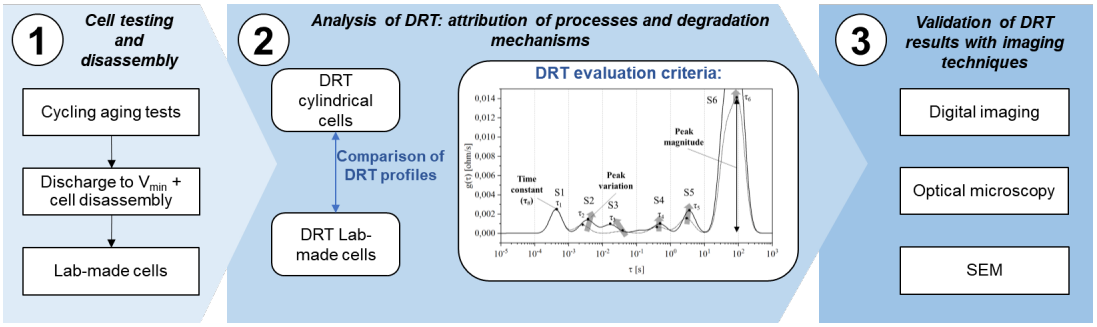

Figure 1: Methodology followed in this work: testing, analysis/attribution, and validation.

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Horizon 2020 LC-BAT5 battery project cluster session

Temperature-Driven Chemical Segregation and Doping in Co-Free Li-Rich Layered Oxides and Its Influence on Electrochemical Performance

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Co-free Li-rich layered oxides are gaining interest as feasible positive electrode materials in lithium-ion batteries (LIBs) regarding energy density, cost reduction, and alleviating safety concerns. Unfortunately, their commercialisation is hindered by severe structural degradation during electrochemical operation. This study demonstrates advanced structural engineering of a Li-rich Co-free oxide with composition $Li_{1.1}Ni_{0.35}Mn_{0.55}O_2$ by spray pyrolysis and subsequent calcination of an aqueous precursor, creating a segregated structure of two distinct layered phases with space groups $R\bar{3}m$ (rhombohedral) and *C2/m* (monoclinic). This particular structure was investigated with powder neutron diffraction, high-resolution analytical transmission electron microscopy imaging, and electron energy loss spectroscopic characterisation. This complex structure leads to high discharge capacity and good rate capability of 160 mAh/g at C/3 and 100 mAh/g at 1C. Additionally, doping with Al and Sn has been investigated, and cathodes show enhanced electrochemical stability for specific compositions. The overall doping strategy conducted at the COBRA project (H2020: 875568) for next-generation high energy density cathode materials will be discussed.

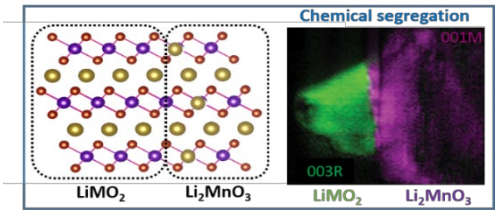

Figure 1 Structurally segregated particles enhance the electrochemical performance of $Li_{1.1}Ni_{0.35}Mn_{0.55}O_2$ cathode material.

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Invited presentation

Electrode Kinetics in Solid-State Batteries

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Solid-state batteries are considered as next technology step in the continuous development of improved electrochemical energy storage devices.[1-3] While lithium ion batteries with liquid electrolytes have been commercialized 30 years ago – with their development starting probably already 50 years ago – the development of solid-state batteries started only less than 10 years ago. Thus, the speed of development is very fast, and there is a gap between high-flying expectations and reliable and reproducible experimental information.

Against this background, this lecture aims to give a neutral and objective view into the current state-of-the-art of solid-state batteries. The focus will be laid on solid-state batteries with inorganic solid electrolytes. As both energy and power density are decisive for the future success of any cell concept, the kinetics of high-performance electrodes will be highlighted. Thus, the kinetics of the lithium (sodium) metal anode, as well as the kinetics of cathode composite electrodes will be discussed in depth.

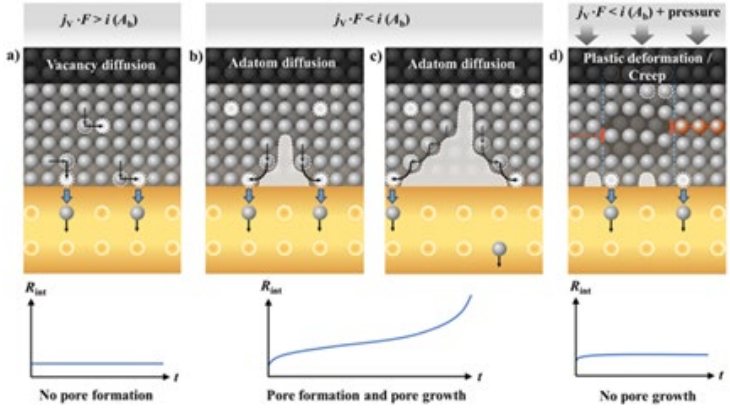

Figure 1: Pore formation at lithium metal/LLZO inter-face during anodic stripping.

The lithium metal anode provides a complex kinetics, due to the strong coupling between charge transfer and morphological instability. Recent results will be summarized. At the cathode, the optimization of ionic and electronic transport paths, as well as the chemo-mechanics of high-capacity cathode materials provide serious challenges.

Ultimately, the potential costs of SSB will also play a critical role, and will therefore be briefly analyzed.

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Invited industry presentation

Northvolt R&D Strategy and progress for next generation battery development

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Lithium-ion battery technology is one of key energy storage devices for a various range of applications such as portable electronics, power tools, electric vehicles, and stationary energy storage. Northvolt is a European supplier of sustainable, high-quality lithium-ion battery cells and systems. Founded to enable the European transition to a decarbonized future, the company has made swift progress on its mission to deliver the world's greenest lithium-ion battery. Positioning itself in response to the forecast in demand for lithium-ion batteries, Northvolt aims to establish 150 GWh of annual production capacity in Europe by 2030.

However, current Lithium-ion battery is facing challenges to meet ambitious market's needs such as high energy density over 400 wh/kg, high level of overall cell safety includes low risk of thermal propagation, and low production cost less than 70€/kwh. To deliver next generation batteries which can meet above targets, fundamental level of R&D activity is necessary from cell material level to cell design, as well as at the system level.

In this talk, Northvolt R&D strategy and its progress for next generation battery development will be presented.

Poster 25

Cross-Linked Copolymer-Based Hybrid Electrolyte for Room-Temperature Application in All-Solid-State Lithium-Sulfur Batteries

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The development of next-generation technologies for energy storage is crucial to reach net-zero carbon emission mobility. Current state-of-the-art Li-ion batteries have limited specific capacity and are fraught with safety concerns due to the use of liquid or gel electrolytes. Substituting liquid electrolytes with solid-state electrolytes is one of the most promising solutions to improve the safety of batteries. However, the development of solid-state electrolytes that exhibit all desired properties is challenging.

Polymer-based solid electrolytes are cheap, easy to process, flexible, and have better physical interfacial contact with electrodes compared to ceramic electrolytes. However, these polymer electrolytes, particularly polyethylene oxide (PEO)-based electrolytes, show high ionic conductivity only at elevated temperatures due to their semi-crystalline nature. As a result, there have been many attempts to enhance their performance, such as incorporating oxide particles into the polymer matrix to hinder crystallization of the polymer.

In this work, a novel cross-linked copolymer-based hybrid electrolyte, composed of pentaerythritol tetraacrylate (PETEA), tri(ethylene glycol) divinyl ether (TEG), lithium bis(trifluoromethanesulfonyl)-imide (LiTFSI), and functionalized $Li_7La_3Zr_2O_{12}$ (F-LLZO) particles, is introduced. The electrolyte shows exceptional ionic conductivity of 1.1×10^{-3} S cm^{-1} at 20 °C, which is 100× higher than that of PEO-based electrolyte (Figure 1(a)). The developed electrolyte was integrated into an all-solid-state lithium-sulfur battery, and its electrochemical performance was evaluated to demonstrate the suitability of the hybrid electrolyte. The cell containing hybrid electrolyte exhibits a higher initial capacity of 760 mA h g_s^{-1} than the cells with polymer and liquid electrolytes at room temperature, and shows comparable performance to the liquid electrolyte even for higher rates (Figure 1(b)).

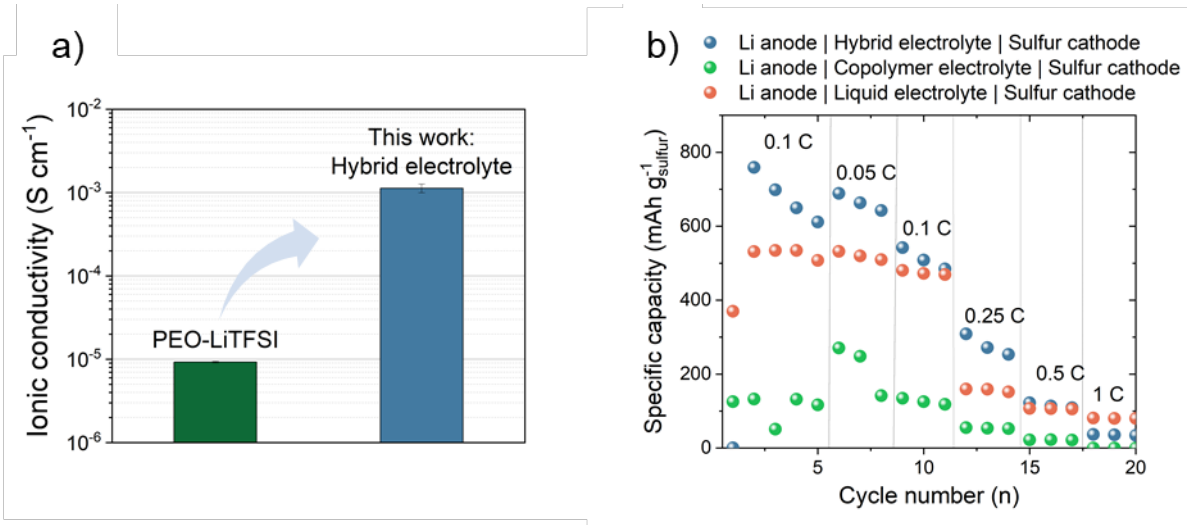

Figure 1. a) Comparison of ionic conductivities of PEO-based electrolyte and hybrid electrolyte composed of PETEA:TEG with F-LLZO at 20 °C, and b) cycling results of Li-S cells with hybrid electrolyte, copolymer electrolyte, and liquid electrolyte at 20 °C

Poster 26

Why potassium half cells fail to deliver reliable results

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Half cell experiments are an integral part of material evaluation in battery research. The performance of the working electrode is supposedly evaluated in the absence of influences by the metallic counter electrode. In practice, half cell experiments are often strongly dependent on properties of the counter electrode, like its thickness, storage conditions or pretreatments.

While the reactivity of lithium metal counter electrodes often has little influence on short-term experiments, we found this issue strongly amplified in sodium or potassium half cells. For instance, the build-up of electrolyte degradation products in electrolytes exposed to sodium or potassium metal proceeds rapidly. Electrode crosstalk leads to deposition of degradation products on the working electrode. Such crosstalk events impact the surface layer properties when analysed by surface sensitive techniques like photoelectron spectroscopy.

The focus of this presentation is placed on the difficulty of obtaining reliable results from half cell experiments when investigation post-Li battery systems using potassium-ion cells as a representative system. The presentation will focus on two main questions: What are the limitations of half cell experiments in post-Li systems? And how does the potassium electrode affect the results for the working electrode (independent of the electrode material you might look at).

The problems related to half cells will be discussed on two common analytical techniques, namely electrochemical impedance spectroscopy (EIS) and photoelectron spectroscopy (PES). The results obtained for the potassium system will be compared to corresponding lithium systems. In-house and synchrotron assisted PES studies on potassium-graphite half cells[1] (Figure 1), as well as graphite-$K_2Fe[Fe(CN)_6]$ full cells, were investigated to outline the significant differences between surface layers formed in half and full cells respectively. The results of this work outline that not every result is what it seems on first glance…

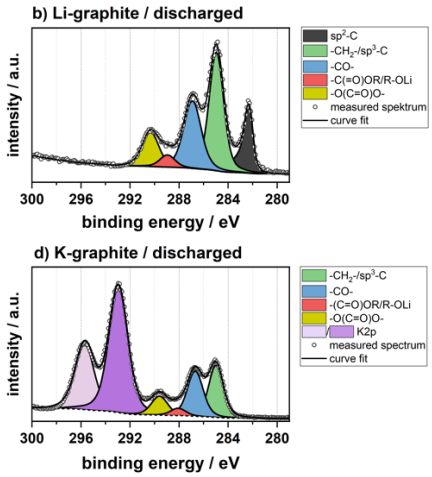

Figure 1: In-house PES spectra of a Li-graphite (top) and K-graphite (bottom) half cell in discharged state.

References:

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Poster 27

Thick NMC811 electrodes enabled by non-solvent induced phase inversion

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With the ever-increasing adoption of electric vehicles, higher energy density Li-ion batteries to enable longer driving ranges are desired. Increasing the thickness of electrodes and reducing the proportion of inactive components per cell is one way to achieve this. However, this comes with several challenges, namely poorer electronic and ionic conductivities, and mechanical failure (cracking, delamination etc.) induced by binder migration during the drying of such electrodes.

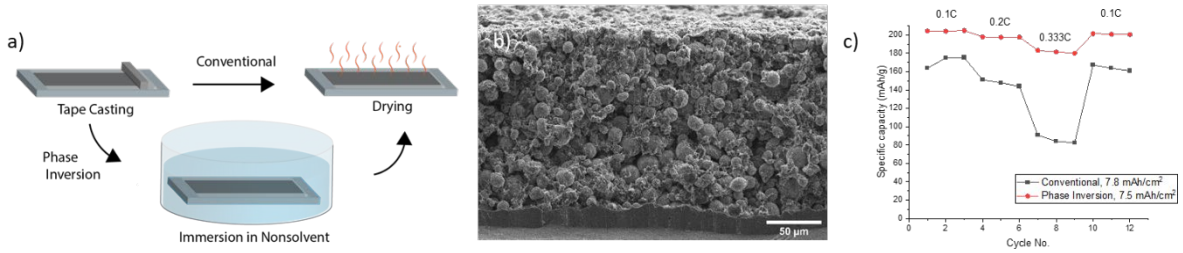

Figure 2: a) The phase inversion based scheme as compared to the conventional drying procedure, b) Cross sectional view of the 160 µm (~10 mAh/cm^2) NMC811 electrode manufactured using phase inversion c) Discharge capacities of NMC811 electrodes prepared using the conventional (black), and phase inversion based method (red) with 7.5-8 mAh/cm^2 mass loading at different c-rates

Here, we report Non-solvent induced phase inversion as a scalable, effective method to arrive at thick NMC811 electrodes, a method previously used to obtain thick LTO and LFP electrodes[1]. Commonly used in the membrane processing industry, the technique involves exchange of the binder-solvent with a suitable non-solvent (eg. Water, ethanol) in between the conventional tape casting and drying (Fig. 1a) used for battery electrodes. By tuning the non-solvent properties and other processing conditions to be compatible with Ni-rich electrodes, it was possible to obtain NMC811 electrodes with high mass loadings (upto 10 mAh/cm^2 , Fig. 1b), which were able to outperform their conventional counterparts in Li/NMC half cells (Fig. 1c). In addition, better adhesion to the Al current collector and less cracking are observed. These improvements could be attributed to the enhanced pore connectivity caused by the process, resulting in a lower electrode tortuosity, and the rapid solvent removal, thereby reducing the binder migration during drying. Further, the method also shows good compatibility with bilayered and double sided electrode configurations, making this a technique with high industrial feasibility towards making thicker NMC811 electrodes.

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Poster 28

3D printed Ta-LLZO solid electrode for high energy density Lithium batteries using Digital Light Processing (DLP)

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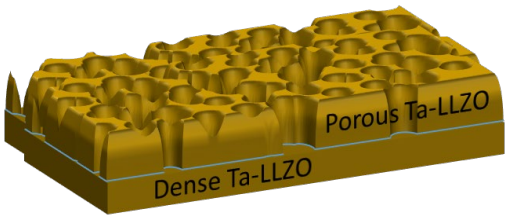
Nowadays, Garnet-based solid-state $Li_7La_3Zr_2O_{12}$ (LLZO) electrolytes have seen rapid interest because of their intrinsic characteristic allowing for safe, non-flammable, and temperature-tolerant energy storage batteries that improve energy densities and the cycle life of Li storage device compared to conventional liquid-electrolytes. In this work, we design 3D printed Ta-LLZO structures using the Digital Light Processing technique (DLP). DLP allows the production of dense and structured porosity in one component. Particular emphasis is given to discussing slurry preparation, optimized printing parameters, de-binding steps, and densification processing. Finally, we highlight challenges that must be addressed in the move toward the eventual commercial printing of LLZO structures for batteries.



Graphical abstract

Horizon 2020 LC-BAT5 battery project cluster session

A comparison of carbon materials as conductive additive for slurry formulations

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The energy storage industry is constantly looking for new materials to improve battery performance, e.g. to reach higher capacity, higher power or longer lifetime. Significant focus is on the advancement of new active materials. However, in order to enable the high performance of such active materials, the development of other battery components such as electrolytes, binders, and conductive additives becomes paramount to cell optimization.

In this presentation, we focus on the conductive additives. An overview on available carbon material families such as carbon black, carbon nanotubes, and graphene with their properties is provided. Especially for the latter two “wonder materials,” high expectations were often not met when mixed with other materials. The benefits as well as limitations of their use in different industries, especially their suitability for the battery industry, is discussed.

Results at the material and electrode level are presented for a range of conductive additives including a highlighted carbon material, which provides a suitable balance between required material/process design parameters such as electrical/thermal conductivity, mechanical, and rheological properties. This allows for more electrode formulation possibilities, where expected benefits on the cell and module level are outlined.

Poster 29

Influence of Li-substitution on Performance of Cobalt-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 of Na-ion batteries should be focused on the development of new electrode materials, offering higher specific charges and voltages, as well as longer cycle life-time than those of the-state-of-the-art Li-ion batteries.[1] One promising approach to achieve this goal is to modify existing active positive electrode materials, such as sodium-manganese-oxide by partially exchanging Mn by other metals, such as Fe or Al. The further substitution of one of the transition metals by lithium not only increases energy density due to its low molar mass, but also triggers anionic redox on oxygen. 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- and Fe-based oxides, $Na_{0.67}Mn_{0.6}Fe_{0.25}Al_{0.15-z}Li_zO_2$ (z = 0; 0.075 and 0.15). To achieve this goal, materials have been synthesized using sol-gel synthesis approach and characterized using electrochemical methods, online electrochemical mass spectrometry (OEMS) and X-ray absorption spectrometry (XAS).

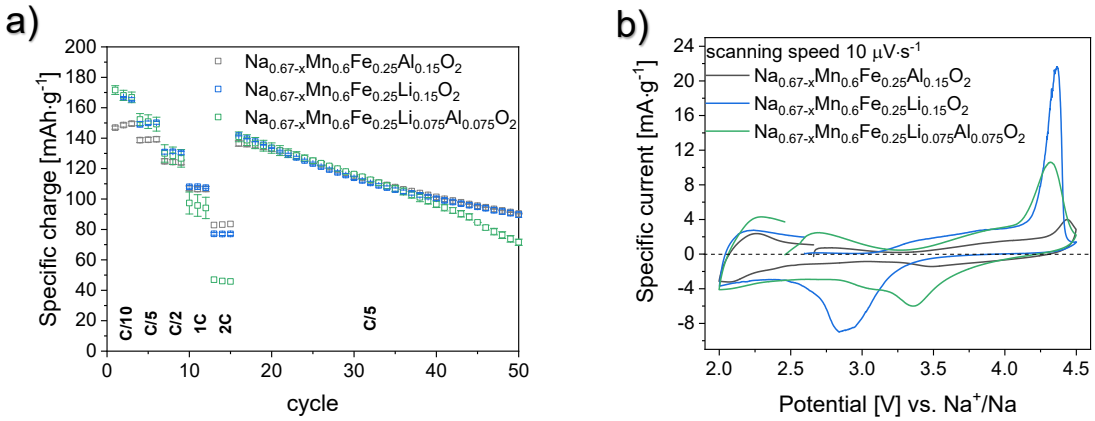

Figure 1: a) First cycle of cyclic voltammetry of $Na|Na^+||Na_xMn_{0.6}Fe_{0.25}Al_{0.15-z}Li_zO_2$, indicating different electrochemical activity on discharge, b) rate tests of $Na|Na^+||Na_xMn_{0.6}Fe_{0.25}Al_{0.15-z}Li_zO_2$.

The electrochemical performance showed excellent initial specific charge values of above 170 mAh/g for materials with lithium-substitution (Fig. 1a). The differences in potential profiles and cyclic voltammetry experiments (Fig. 1b) were observed, indicating the change of electrochemically activity, which has been confirmed by XAS, showing that iron redox is dependant on the degree of Li-substitution. Moreover, oxygen redox activity was observed in potential profiles above 4.2 V, however, no oxygen evolution was registered by OEMS for any of the examined materials, indicating the reversible anion redox process. The influence of different degrees of Li-substitution in $Na_{0.67}Mn_{0.6}Fe_{0.25}Al_{0.15-z}Li_zO_2$ on charge compensation mechanism and electrochemical performance will be discussed.

References:

[1] S. F. Schneider, C. Bauer, P. Novák, E.J. Berg, *Sustain. Energy Fuels* **2019**, 3, 3061

Poster 30

Next generation Na-β"-alumina electrolytes for battery application

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Sodium-nickel chloride batteries are an environmentally safer alternative to lithium-ion batteries and are based on a □"-alumina electrolyte which provides Na-ionic conductivity at 250-300°C. Currently, planar solid Na-□□ "-alumina (BASE) electrolytes with large diameters (> 100 mm) with thickness from 1.0 mm have been developed. To produce Na-β"-alumina membranes by an alternative promising production process we applied two methods: uniaxial pressing of sprayed granulated powder and tape casting using an additional warm pressing procedure. The composition of the obtained Na-β"-alumina electrolytes prepared by both the tape casting and uniaxial pressing methods corresponds to modern tubular electrolytes containing 9.7 ± 0.2 wt.% Na_2O. The mechanical integrity, flatness and reproducibility of the planar electrolytes were investigated. The conductivity and bending strength were measured on smaller Na-b"-alumina samples obtained by the same tape casting process followed by sintering and gave results consistent with BASE materials obtained by uniaxial powder pressing. The final product of Na-β"-alumina electrolyte obtained by both methods has a flexural strength of 226 ± 13 MPa, an ionic conductivity of 0.19 C/cm at 300 °C and a density of 97 %, which meets the requirements for the battery electrolyte. The integration of large, planar Na-β"-alumina electrolytes into the battery cells requires them to be sealed with insulating α-alumina rings to form a ceramic subsystem.

This was enabled by a glass sealing process. BASE flat membranes enable new cell designs that are predicted to have higher power densities and better stacking efficiencies than currently manufactured tubular cells.

Poster 31

Integration of an automated experimental battery platform with a computational workflow management software

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By integrating the automated robotic battery development platform (Aurora) with the computational workflow management software (AiiDA),[1] we can enable rapid testing of scientific hypotheses and validation of physical models, improve reproducibility in battery research, and ultimately accelerate battery innovation.

We present an open-source suite of software tools, developed within the Battery2030+ project BIG-MAP. [1] The suite includes an instrument automation tool, tomato, able to schedule, manage, and process coin cell cycling data from an array of multichannel potentiostats. Another key software is our FAIR data parser, yadg,[2] mapping instrument data in a standardized and timestamped format. On the hardware side, the Aurora battery development platform includes a cell assembly robot, capable of building batches of 32 coin cells, as well as a cell cycling station with 128 channels.

By incorporating the experimental features of Aurora into AiiDA-driven workflows, we are able to fully close the loop between simulations and experiment, and enable machine-driven materials discovery using a single workflow management system.

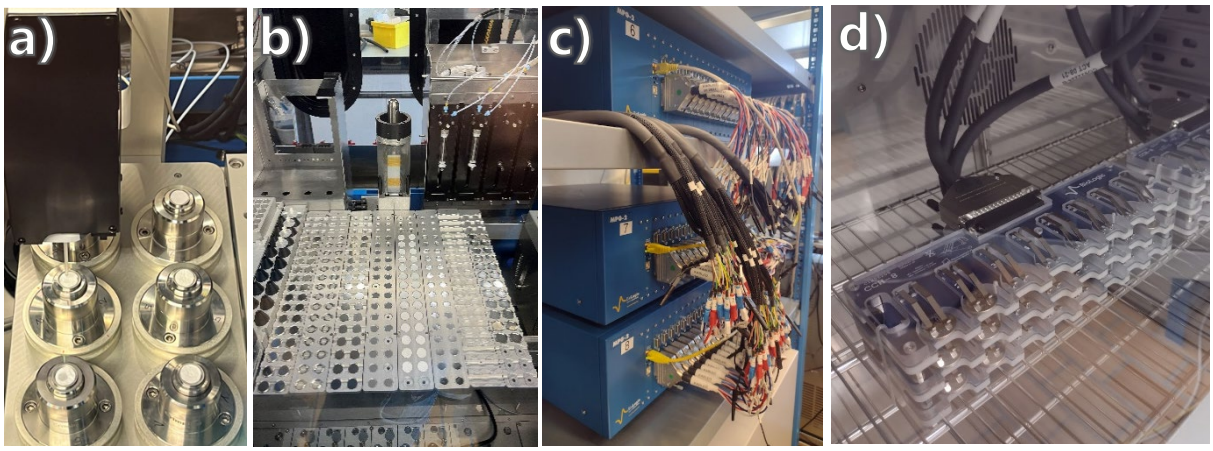

Figure 1: Aurora platform, including a) the crimping tool and b) the component racks of the cell assembly robot, and c) the array of multichannel potentiostats and d) the coin cell racks of the cell cycling station.

References:

[1] https://www.big-map.eu/

[2] S.P. Huber et al, Scientific Data **2020**, 7, 300.

[3] P. Kraus, M. Vetsch, C. Battaglia, Journal of Open Source Software **2022**, 7, 4166.

Poster 32

High loading cathodes: a critical path to high-energy solid-state batteries

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Nowadays, European economy in great extent depends on the import of fossil fuels which brings corresponding geopolitical risks. In this light, the electrification of road, water, and air transportation sectors is an essential step towards an energetically independent Europe. Advanced high-energy solid-state batteries (SSB) with enhanced safety and durability[1] will definitely play an important role in the electric revolution on transport. The development of SSB is often focused on the solid electrolyte and negative anode (mainly Li metal) components while attention to the cathode is marginal. Whereas the development of high loading solid state cathodes with effective ionic and electronic transport is a crucial milestone to achieve high energy SSB[2].

Figure 1a depicts the estimation of how SSB stack energy density depends on loading of a positive electrode based on a NMC chemistry. As it can be seen, to enter in the area of interest for high energy density SSB (>300 Wh/kg_{stack}, >700 Wh/L_{stack}) minimum positive electrode loading should be 2.5 mAh/cm^2. In this context, we have developed a composite NMC622 cathode with a loading of ≥2.5 mAh/cm^2 that achieved relevant discharge capacity in a SSB (**Figure 1b**). Noteworthy, special attention has been paid to the optimization of cathode preparation procedure to overcome technological issues related to the processing and upscale of slurries with high polymer content. The obtained experimental results and generated knowledge pave the way towards the development of high energy SSB.

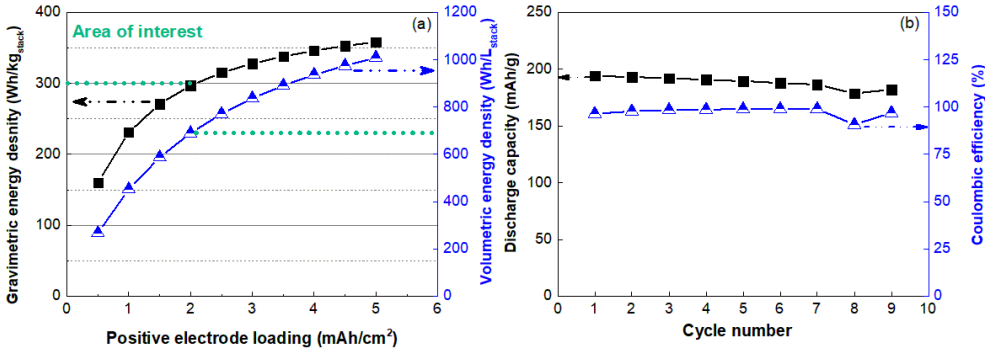

Figure 1: a) SSB stack (25 µm Li metal anode, 30 µm solid electrolyte) energy density as function of cathode loading (75 wt% of NMC, 180 mAh/g), b) Cycling behavior of a Li/NMC622 solid-state cell (cathode loading 2.5 mAh/cm^2, cycling conditions: 60ºC, 3.0-4.3 V, 0.1C).

More thoughts and experimental results about: (i) SSB cathode design and geometry optimization; (ii) the development on high loading LFP and NMC based cathodes via optimization of the formulation including electrochemically stable catholyte using plasticizer, Li salts and functional additives, and slurry preparation method; (iii) upscale of the developed cathodes; and (iv) the assessment of the electrochemical properties of the cathodes in different SSB configurations will be discussed further in detail.

References:

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Poster 33

Interface evolution of the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2/Li_6PS_5Cl$ solid-state battery cathodes during cycling

Barthélémy Lelotte*, Carlos A. F. Vaz[2], Camelia Borca[2], Thomas Huthwelker[2], Vincent Pelé[3], Christian Jordy[3], Lorenz Gubler[1], Mario El Kazzi[1]

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All-solid-state Li-ion batteries (ASSBs) are closer than ever to wide-scale applications. They bring improved safety and increased energy density if the compact solid electrolyte (SE) can prevent the Li metal dendrite growth and interface degradation at high operating voltage. For the past decades, research has focused on improving the ionic conductivity of the SEs, which led to the discovery of the thiophosphate family with an ionic conductivity similar or exceeding those of liquid electrolytes. However, due to their narrow electrochemical stability window, the current focus is to stabilize its interface with both cathode and anode materials. Understanding the degradation reaction mechanism taking place at these buried interfaces is extremely challenging: it requires the use of non-destructive surface sensitive techniques capable to provide chemical analysis with depth profile sensitivity combined with an excellent lateral resolution to discriminate signals originating from the surface and near surface of the different particles (active materials, SE and conductive carbon additive) composing the working electrode (WE).

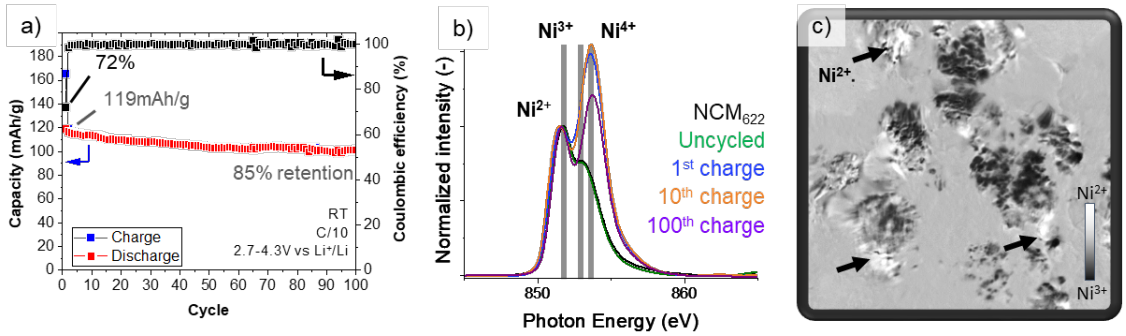

Figure 1: a) Galvanostatic extended cycling of the NCM_{622}/LPSCl/$InLi_x$ ASSB. b) XAS spectra of the Ni L-edge in TEY. c) XPEEM mapping of the Ni oxidation state at the Ni L-edge.

In this contribution, we present a detailed study of the interface in the NCM_{622}/LPSCl/C WE cycled up to 4.3 V vs. Li^+/Li. First, galvanostatic cycling (Figure 1.a) and impedance spectroscopy demonstrate a low coulombic efficiency of of 72% during the 1st cycle and a gradual increase of the impedance with the number of cycles, respectively. To explain the electrochemical performance, the chemical evolution of the interface is monitored *ex situ* by soft and tender-X-ray absorption spectroscopy (XAS) at the transition metals (TM) L-edges, P and S K-edges, as well as, at the C and O K-edges at the SIM and Phoenix beamlines of the Swiss Light Source. This technique provides informations on the oxidation states and local environment during cycling of both NCM_{622} and LPSCl (Figure 1.b,c). The XAS acquisition is performed by combining measurements with the (i) high lateral resolution and surface sensitivity of X-ray photoemission electron microscopy (XPEEM) and (ii) depth profile total electron yield (TEY) and total fluorescence yield (TFY). Our results demonstrate that the 1st irreversible charge is mainly associated with LPSCl oxidation but the gradual impedance increase is caused also by the surface degradation on the NCM_{622} leading to the formation of inactive layer rich in reduced TMs species and oxides (Figure 1.b,c).

Invited presentation

Electrolyte-electrode interphases in high voltage aqueous lithium-ion batteries

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The formation of electrode-electrolyte interphase in highly concentrated aqueous electrolyte, including both solid electrolyte interphase (SEI) on anode and cathode electrolyte interphase (CEI) on cathode, plays an important role in preventing electrolyte decomposition at potentials away from the electrochemical stability limits, thus broaden the electrolyte stability window of electrolyte. However, the formed electrode-electrolyte interphase faces many challenges, *e.g.*, dissolving again in the electrolyte, cracking and being eroded by the hydrogen evolution, *etc*.

Hence, achieving robust and protective electrode-electrolyte interphases in high voltage aqueous batteries is the aim of this work. Our strategies accordingly focused on two regards, *i.e.*, tailoring the particle surface of negative electrode materials (coating negative electrode material with a type of “Li-ion conductors” to simultaneously enhance its ionic conductivity and suppress the hydrogen evolution at the anode surface) and introducing the additive in the electrolytes (*i.e.*, adding polyacrylamide into 21m LiTFSI electrolyte to reduce the water content on the electrode surface and accelerate the SEI formation; or utilizing acrylamide monomer as an electrolyte additive to circumvent the high electrolyte viscosity resulting from the direct use of polyacrylamide and to realize the formation of dense SEI and CEI via in situ electropolymerization). The combination of these strategies results in stable cycling from an aqueous cell constructed with $LiMn_2O_4$ cathode and a modified TiO_2 anode. A high specific energy of 105 Wh kg-1 is obtained from it, and the capacity loss is only 0.45‰ per cycle (500 cycles at 5 C). In addition, the film forming mechanism, the function additives, the chemistry of both SEI and CEI layers were studied by both experimental characterizations and computational simulation, which will also be discussed in this talk.

We also proposed a new type of aqueous electrolyte, so called “Water-in-eutectogel” electrolyte, which displays a further broadened electrochemical stability window of 4.3 V, thus the use of $Li_4Ti_5O_{12}$ anode material that can further promote the specific energy of aqueous lithium-ion batteries can be realized. This electrolyte is also proved to be a promising candidate for flexible quasi-solid-state aqueous lithium-ion batteries.

Horizon 2020 LC-BAT5 battery project cluster session, poster 34

Multifunctional ethoxy(pentafluoro)cyclotriphosphazene additive enables safe carbonate electrolytes for silicon-graphite/nickel-rich NMC lithium-ion batteries

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The silicon (or silicon monoxide)-graphite/Ni-rich (≥80% Ni) NMC cell chemistry is currently regarded as a promising candidate to further improve the energy density of rechargeable lithium-ion batteries with the aim to enhance the driving range of electric vehicles beyond 500 km.[1] Meanwhile, battery safety is an increasingly important consideration for such energy-dense batteries.[2] Here, the compatibility of the flame retardant ethoxy(pentafluoro)cyclotriphosphazene (PFPN) as additive for carbonate electrolytes is studied, for the first time, for a SiO_x-graphite/NMC811 full cell system.[3] We find that 5 wt.% PFPN in combination with an increased lithium hexafluorophosphate ($LiPF_6$) concentration of 1.35 mol/L in ethylene carbonate/ethyl methyl carbonate reduces the self-extinguishing time (SET) of the electrolyte to a low value of 3 s g^{-1} while maintaining a high ionic conductivity of 8.4 mS cm^{-1} at 25 °C. Furthermore, PFPN improves the stability of the SiOx-graphite/electrolyte interface as well as the wetting properties of the electrolyte. As a result, SiO_x-graphite/NMC811 full coin cells display better capacity retention using the modified electrolyte during rate tests and long-term cycling. We study the evolution of the morphology of anode and cathode as well as the solid-electrolyte interphases, gaining important insights into the mechanism for the improved performance with PFPN. In addition, we confirm the enhanced cycling performance with the modified electrolyte for SiO_x-graphite/NMC811 pouch cells with a capacity of 1 Ah. Our research paves the way for safe and high-performance electrolytes for silicon-based lithium-ion batteries.

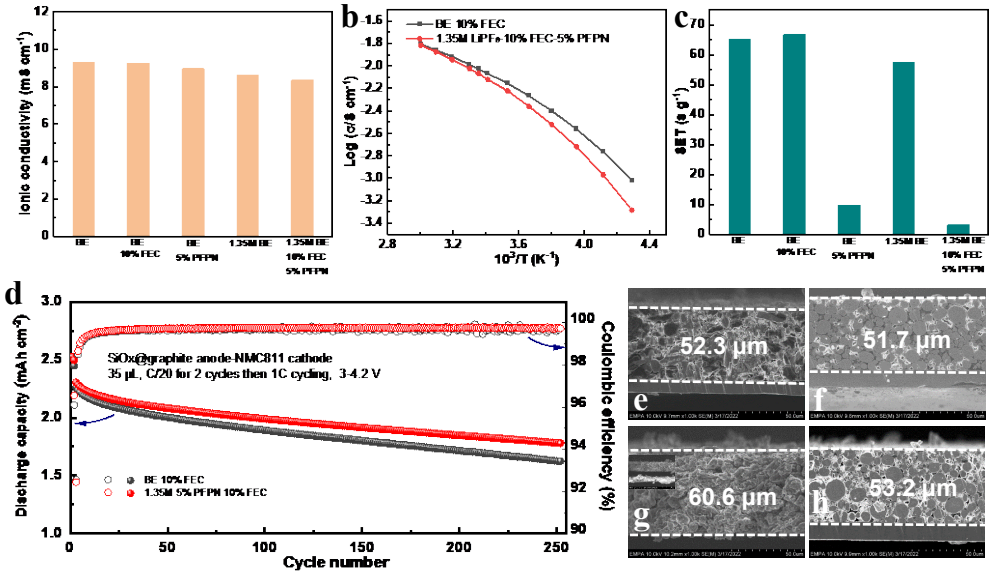

Figure 1: (a) Ionic conductivity at 25 °C, (b) ionic conductivity as a function of temperature, and (c) self-extinguishing time of various electrolytes. (d) Comparison of the cycling performance of SiOx@graphite/NMC811 full cells between the baseline electrolyte and the modified electrolyte. (e-h) Cross-sectional images of (e,g) SiO_x-graphite anodes and (f,h) NMC811 cathodes after the cycling test (e,f: modified electrolyte, g,h: baseline electrolyte). BE: 1M $LiPF_6$ in EC:EMC 3:7 (by volume).

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[3] S. Liu, G. Homann, R. Grissa, K. Egorov, Y. Huang, C. Battaglia, R.-S. Kühnel, in preparation

Poster 35

Regulating uniform Li plating/stripping via Li_2O/LiOH-rich passivation layer for long-life thin Li metal batteries

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Lithium metal is one of the most appealing anodes for high energy-density rechargeable batteries. However, the Li plating/stripping during long cycling suffers from morphological irreversibility and dendritic growth, causing a rapid fading of the cell. To address this issue, Li_2O/LiOH-rich passivation layer is introduced on top of 50 µm metallic lithium to uniformly regulate the Li plating/stripping process and to stabilize the electrolyte/Li metal interface. Both Li_2O and LiOH are considered as promising materials for minimizing electrolyte decomposition and mitigating dendrite formation.[1-2]

The experiments were carried out in an ultra-high-vacuum (UHV) surface preparation reactor connected directly to the X-ray photoelectron spectroscopy (XPS) system (Fig. 1a). The Li_2O/LiOH-rich layer is formed by exposing the thin metallic lithium to a Radio Frequency N_2 plasma using Li_3PO_4 as a target. The in-situ XPS at the C1s and O1s core levels demonstrate that the native Li_2CO_3 is converted to Li_2O/LiOH as major components on the surface due to the highly oxidative environment of the plasma (Fig. 1b). The formed ~700 nm Li_2O/LiOH-rich layer shows textured surface and particle agglomeration in the scanning electron microscopy (SEM) micrograph (Fig. 1c). From the ex-situ X-ray absorption spectroscopy (XAS) spectra at the O K-edge, Li_2O/LiOH is also detected in both total electron yield (TEY) (probing depth ~10 nm) and total fluorescence yield (TFY) (probing ~100s of nm) confirming that Li_2O/LiOH preserves its integrity underneath the surface (Fig. 1d). The Li_2O/LiOH-rich metallic Li symmetric cells cycled for about four times longer than the as received Li in ether-based electrolyte, reaching 1200h (400 cycles) with a current density of 1 mA/cm^2 and an area capacity of 1.5 mAh/cm^2 (Fig. 1e). At the end of Li plating after 20 cycles, much smaller and uniform plated Li clusters are observed indicating a regulated plating/stripping process thanks to the Li_2O/LiOH-rich passivation layer (Fig. 1f).

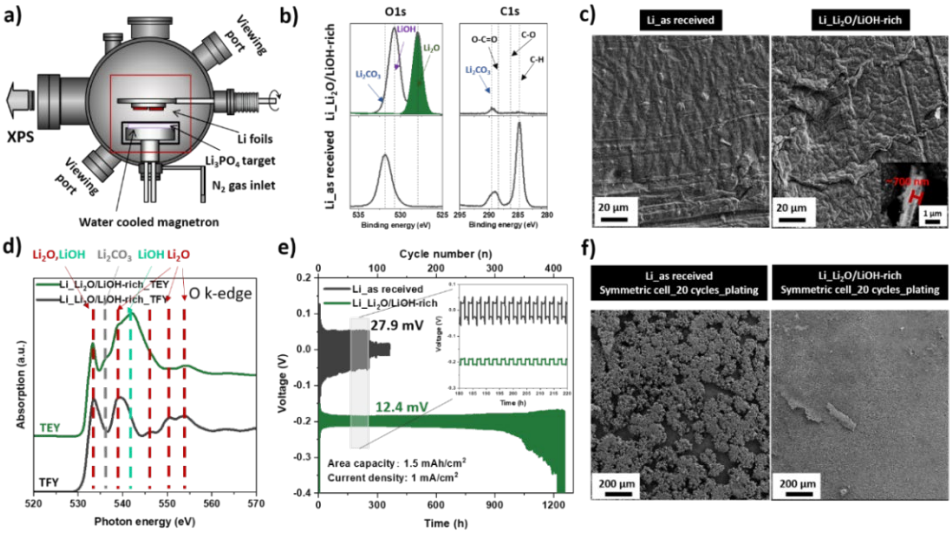

Figure 1. a) Schematic view of the UHV surface preparation reactor connected to the XPS system. As received and Li_2O/LiOH-rich Li metal investigated : (i) Before cycling b) in-situ XPS at the C1s and O1s core levels, c) SEM and d) ex-situ XAS at the O K-edge in TEY and TFY modes. (ii) After cycling e) galvanostatic charge-discharge symmetric cells at the current density of 1 mA/cm^2, area capacity of 1.5 mAh/cm^2 and f) SEM at the end of the Li plating after 20 cycles.

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Poster 36

‘Single-crystal’ Ni-rich layered oxide cathodes for lithium ion batteries – a fair performance comparison between different particle sizes

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Increasing the Ni-content in mixed transition metal layered oxide cathodes like $Li[Ni_xCo_yMn_z]O_2$ ($x + y + z = 1$, NCM*xyz*) has been a viable strategy to increase energy output and reduce cost of lithium ion batteries (LIBs).[1] However, the drawbacks of these Ni-rich formulations ($x \geq 0.8$) are a loss of cycling stability. In this regard, secondary particle cracking has been identified as a major failure mechanism as it allows surface-related degradation phenomena such as rock salt formation, transition metal dissolution and ongoing electrolyte decomposition to continue on newly formed, highly reactive surface cycle after cycle.[2] As opposed to their polycrystalline (PC) counterparts, ‘single-crystal’ (SC-)NCMs are comprised of well-separated micron-sized primary particles, so that during cycling the surface area of the active material remains constant, side reactions are reduced and thus, cycling stability is significantly improved.[3]

Particle cracking in layered oxide cathode materials is exacerbated with increasing Ni-content which qualifies the ‘single-crystal’ approach especially for Ni-rich NCMs, but there are two main challenges: (i) the synthesis is not straightforward as the conditions required for enhanced crystal growth are inherently damaging and (ii) the larger crystal size compared to PC-NCMs is believed to cause kinetic limitations impacting rate performance and material integrity.[4] In this work, we synthesized a series of ‘single-crystal’ $Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$ (SC-NCM811) with varying particle sizes. To deconvolute the effect of particle size from other influences, a molten salt-assisted synthesis was followed, so that bulk properties of SC-NCMs remained constant and PC-NCM reference samples could be synthesized from the same home-made precursors and with the same post-processing steps. The samples were thoroughly characterized in terms of physicochemical properties and their electrochemical performance was evaluated in NCM||Li and NCM||Graphite LIB coin cells. The objective of this research was to answer three questions:

(i) Can Ni-rich SC-NCMs outperform their comparable PC counterparts?
(ii) Can the optimization of particle size enhance the performance of SC-NCMs?
(iii) How exactly does the particle size affect performance?

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Horizon 2020 LC-BAT5 battery project cluster session

Environment Friendly Water-based Cathode Production from Co-free Li-rich Layered Oxides for Pouch Cells Testing

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Li-rich layered oxides have been intensively investigated as a promising candidate for the positive electrode for high energy lithium-ion batteries due to the large specific capacity.[1] However, these materials contain toxic Co in their structure and the electrochemical performances are restricted by the large first-cycle irreversible capacity loss and poor stability during long-term cycling. Inside Cobra Project an Al-doped Co-free Li-rich Layered Oxide materials ($Li_{1.26}Ni_{0.15}Mn_{0.60}Al_{0.05}O_2$, LNMA05) was produce. This material shows an improved coulombic efficiency in the initial cycle and a smaller voltage decay of the cathode material.[2] Up to now, most studies on Co-free Li-rich Layered Oxides based cathodes have involved PVdF-based binders that necessitate the use of toxic and expensive N-Methyl-2-pyrrolidone (NMP) as solvent. Water-based electrode processing of lithium-ion cathodes is one of the key steps towards environmentally friendly battery production.[3]

This study presents a water-based processing of homogeneous, and stable cathode coating with $Li_{1.26}Ni_{0.15}Mn_{0.60}Al_{0.05}O_2$ (LNMA05) as active material. The electrodes were processed directly on aluminum foil using water as solvent for slurry preparation and sodium carboxymethylcellulose was used as the only binder. Phosphoric acid was used to adjust the pH-value of the slurry to avoid the capacity loss due to the lithium-proton exchange in aqueous solution. The water-based approach leads to a good cycle stability and excellent coulombic efficiency of 99.08 % after 100 cycles (C/10) and a specific discharge capacity of about 199 mAh/g when Graphite was used as anode. Furthermore, Graphite -Silicon were also employed as the counter electrode for pouch cells testing. The cells indicated a good stability at a current density of C/10 after 50 cycles with high coulombic efficiency of about 99.86%. By further optimization of the initial formation cycle, these electrodes offer an electrochemical performance exceeding with promising stability for pouch cells testing, which are considered very promising for the realization of next-generation cobalt-free lithium-ion batteries with green process.

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Poster 37

Characterization and Ionic Conduction of Humidity-enhanced Halide Li_3InCl_6 Solid Electrolyte for Solid-state Li-ion Batteries

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Combusting fossil fuels for transportation significantly contributes to global CO_2 emissions and thus to global warming. Therefore, there is a need to transition from traditional automobiles to electric vehicles with higher energy-dense batteries[1]. Developing these sustainable technologies requires batteries that last longer, charge faster, and are safer and more sustainable[2]. Developing new sustainable technologies depends on battery materials development, explicitly investigating safer, low-cost, and higher energy density.[3] Halide solid-state electrolytes (HSEs) have gained attention recently due to their simple synthesis, high ionic conductivity, and processibility. Halide-based SEs were recently found to exhibit desirable characterization of sulfide, polymer, and oxide SE systems, including high ionic conductivity, deformability, and oxidative stability. Here, we investigate the synthesis of Li_3InCl_6 (LIC) HSEs by ball-milling followed by humidity-enhanced annealing. We analyzed the crystal structure, particle size, and ionic conductivity using a combination of X-ray diffraction, Scanning electron microscopy (SEM), and electrochemical impedance spectroscopy (Figure 1). Humidity-enhanced annealing increases the presence of impurities in the sample as well as the ionic conductivity. Benefitting from the highest Li^+ conductivity of 1.09 $mS.cm^{-1}$ for the LIC offers air stability and easy processibility to SSBs. Additional 1D and 2D pulsed-field gradient and NMR relaxation time measurements were used to understand the lithium diffusion mechanisms of ball-milled and annealed samples. 2D D-T_2 and T_2-T_2 measurements showed multiple unique Li atomic motion sites correlated to different rates of diffusive, micro-scale motion. This study sheds new light on humidity enhanced Li_3InCl_6 SEs, and provides a novel strategy for designing advanced materials, understanding the degradation mechanism, wet processing, and challenging the catholyte for solid-state battery applications.

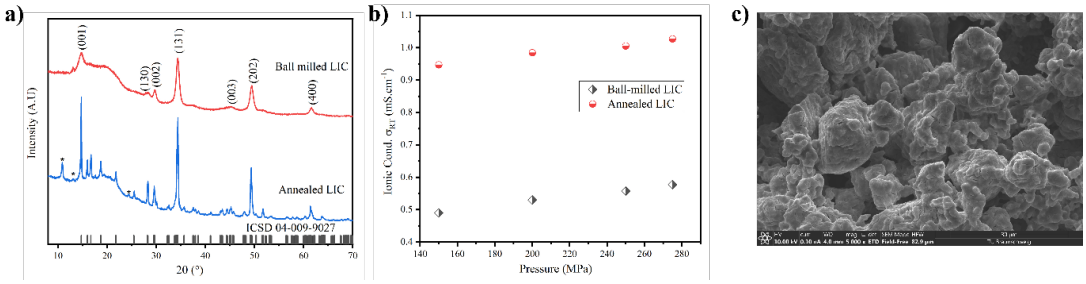

Figure 1: a) X-ray diffraction patterns of LIC. * Indicates InOCl impurities during heating under dry room conditions. b) The ionic conductivity of all-milled and annealed LIC sample with pressure-dependent ionic conductivities measured by EIS at room temperature. c) SEM image of ball-milled LIC.

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Invited presentation

Understanding imperfect battery materials

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Progress in energy storage materials requires an unprecedented ability to understand and control all levels of organization of matter, their coupling with function and their dynamic evolution. This includes 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 to design better materials.

In this talk we will discuss, through selected case studies, how progress in the characterization of disorder using X-ray scattering techniques[1] offers an accessible window for the observation and accurate parametrization of complex microstructural features.[2-4] Examples of dynamic evolution of stacking defects, determined from operando experiments will also be presented to illustrate how the application of such approaches with real-time data represent an incredibly powerful tool for the monitoring of internal processes upon battery cycling.[5] Nevertheless, obtaining high-quality, representative and exploitable data from operando measurements requires careful control of many experimental parameters (i.e. cell configuration, electrode preparation, etc.) as will also be shown.[6]

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Poster 38

Electron microscopy study of intragranular cracking mechanisms in Ni-rich transition metal oxide cathodes for Li-ion batteries.

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Ni-rich layered transition metal oxides such as $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) are promising cathode material candidates for Li-ion batteries thanks to their high specific capacity and lower cost compared to isostructural materials with lower nickel content. However, complex degradation pathways inhibit their use. The mechanisms of degradation discussed in the literature include bulk lattice changes, oxygen release at high states of charge, reduction and structural changes at the surfaces, inter- and intragranular cracking, side reactions with electrolyte, and transition metal dissolution. The problem is further complicated by the interactions of degradation mechanisms with each other. One of the least well-understood areas is the nanoscale origins of intragranular cracking in NMCs.[1–4]

In this work, we use carefully chosen NMC811 cathodes to investigate the influence of microstructure (polycrystalline, single crystal materials), calendering (calendered and not calendered electrodes), and cycling (pristine samples, samples after formation and after cycling) on the formation and nature of intragranular cracks. Samples were cycled in graphite/NMC811 full cells at C/20 rate for 3 cycles (formation). For extended cycling, 300 cycles at C/2 are employed. After cycling, cathodes were extracted and charged to 4.3 V vs Li/Li+ in a half cell. Using focused ion beam – scanning electron dual beam microscope (FIB-SEM) imaging we demonstrate that intragranular cracks are commonly present in all NMC811 samples in the charged state, but not the discharged state. Moreover, we show that intragranular cracks appear already after formation, regardless of material type (polycrystalline, single crystal) and calendering. Using high-resolution scanning transmission electron microscopy imaging (HR-STEM), electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDX) we probe the nanoscale structure and chemistry (oxidation states and composition) in the cracked areas. Briefly, on the intragranular crack surfaces, the material can be reduced (accompanied by a transformation of the structure to rock-salt). However, even after 300 cycles, some intragranular cracks remain in the original, unreduced layered structure. Furthermore, based on our results, we find that intragranular cracking is caused by local stress, which can have several origins such as Li and transition metal inhomogeneities (the latter cause for intragranular cracking was not reported previously). Lastly, we discuss the implications of our results to long-term battery performance.

In conclusion, using a carefully chosen sample set and comprehensive electron microscopy approach, we provide novel insights into the nanoscale nature of intragranular cracking in NMCs, the mechanisms of their formation and influence on macroscale battery performance.

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Poster 39

Understanding the influence of Li-Me-oxide coatings on the LLZO/LCO interface

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Among lithium-conducting solid electrolytes, LLZO has received much attention due to its high ionic conductivity (~10^{-4}-10^{-3} S cm^{-1}) and stability in contact with lithium metal over a wide voltage window (~0-5 V). [1] While the application of Li metal as anode has been intensively investigated [2], the integration of LLZO with high-energy cathodes such as layered mixed metal oxides is a challenge in the development of SSBs. [3] Chemical reactions occur during cell production, especially at high processing temperatures required to obtain conformal contact, and accelerate chemical reactions and diffusion processes, leading to high interface resistances.

In this study, the interface between LLZO pellets with LCO as cathode material is modified by applying different metal oxide interface coatings. The coatings are ternary Li-Me oxide interlayers (Me = Nb, Al, Ti) deposited on the pellets by magnetron RF sputtering and then coated with a thin film cathode. Co-sintering at high temperatures establishes uniform physical contact between the electrolyte and the cathode. To demonstrate the electrochemical functionality of the cells and to study the charge transport dynamics at the interface, all cells were first galvanostatically cycled. In the next step, electrochemical impedance spectroscopy was performed on the full cells (LCO|Li-Nb-O|LLZO|Li) to describe the impedance characteristics of the interfacial dynamics at the cathode interface. We systematically investigate the effect of different metal oxide interlayers by studying the interfacial dynamics between the thin film LCO cathode, an "artificial" solid electrolyte interface, and LLZO. The most promising interlayers will then be studied in the future by applying synchrotron-based characterization techniques such as X-ray absorption spectroscopy to model systems. In this way, we hope to gain deeper insights into the behavior of passivation layers under stress and the effects of concentration polarization phenomena on SSB lifetime.

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Poster 40

Building a Better Li-Garnet Solid Electrolyte/Metallic Li Interface with Antimony

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The quest for safe, non-flammable, and temperature-tolerant energy storage systems with high energy and power densities has caused a surge of research on batteries that consist solely of solid-state components.[1,2] In particular, solid-state batteries (SSBs) employing cubic $Li_7La_3Zr_2O_{12}$ (LLZO) garnet-type solid electrolytes are appealing as energy storage technology, owing to a superior set of properties, such as a high Li-ion conductivity of up to 1 mS cm^{-1} (RT), a low electronic conductivity of ≈10^{-8} S cm^{-1} (RT), a high thermal and mechanical stability and a wide electrochemical operation window of 0–6 V versus Li^+/Li.[3,4] LLZO-based SSBs, nevertheless, still face a number of obstacles before they can be practically deployed. One of the foremost issues is the poor LLZO wettability by lithium metal. In this work, we will present Sb as a compelling interfacial layer allowing superior wetting of Li onto an LLZO surface, resulting in a remarkably low Li/LLZO interfacial resistance of 4.1(1) Ω cm^2.[5] We determined that the Li/10-nm-Sb-LLZO/Li symmetrical cells exhibit a high critical current density of up to 0.64 mA cm^{-2} and low overpotentials of 40–50 mV at a current density of 0.2 mA cm^{-2} at room temperature and without the employment of external pressure. Using an advanced set of surface characterization methods such as XPS/HAXPES and TOF-SIMS, we revealed that the major factor governing an efficient plating/stripping of Li at the Sb-coated LLZO surface is the formation of a Li-Sb alloy, which enables an efficient Li-ion and electronic percolation at the Li/LLZO interface and effectively mitigates the formation of cavities and Li whiskers upon plating/stripping of Li. The electrochemical performance of Sb-coated LLZO solid-state electrolyte has also been assessed with an intercalation-type V_2O_5 cathode. Li/Sb-coated-LLZO/V_2O_5 full cells delivered stable areal capacities of around 0.45 mAh cm^{-2}, with a peak current density of 0.3 mA cm^{-2}.

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Poster 41

Polar Elastomers as Solid Electrolytes for Li-ion Batteries

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The flammable liquid electrolyte used in the battery of any portable device may be replaced one day by elastomers with high dielectric permittivity. Unfortunately, common elastomers have a low dielectric permittivity, and attempts to increase it detrimentally affect the elasticity. The solution is to chemically modify the elastic network with permanent dipoles, such as nitrile.[1] However, to achieve a significant increase in the dielectric permittivity, the density of dipoles in the network has to be as high as possible, which, due to the dipolar interaction, will reduce the mobility of the polymer chains and thus will increase the glass transition of the polymer. Using the highly flexible polymer backbone of a polysiloxane and chemically modifying it with polar nitrile groups, the glass transition temperature of the modified polymer is still sufficiently low to allow the formation of polar elastomers at room temperature. Additionally, nitrile groups facilitate the dissolution of Li ions needed for increasing the Li-ion conductivity. Thus, the low glass transition polymer allows for ion movement and the elastic network prevents hysteresis due to volumetric changes in the battery during charging-discharging.[2]

This presentation will introduce a new class of polymer electrolytes that can potentially replace the currently most explored polymer electrolyte, polyethylene oxide.

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Poster 42

PVD of lithium rich oxychloride antiperovskite

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Dense thin-film solid–state electrolyte separator are interesting to offer (a) a model system to investigate interfaces, and more importantly, (b) a promising pathway to increase the energy density of solid-state cells. The reference of thin-film solid-state electrolyte, for a while, is the lithium phosphate oxynitride LiPON, due to its easy way of deposition/synthesis via reactive RF-Magnetron sputtering. However, LiPON has a ceiling ionic conductivity of ~10^{-6} S.cm^{-1}.[1]

For a decade, the new family of Lithium Rich Antiperovskite (LiRAP) $Li_{3-x}OH_xHal$ (Hal = Br,Cl) has been investigated and exhibits low raw material costs, low temperature of synthesis and a bulk ionic conductivity of ~10^{-3} S.cm^{-1}.[2,3] In addition, previous studies report the possibility to use PVD method to obtain thin layers of the Li3OCl composition with an acceptable Li^+, and electronic conductivity.[4,5]

Here, we explore a different way to synthesize thin layers of the Li3OCl solid-state electrolyte by using RF-Magnetron Sputtering with a post annealing treatment. We will presents the structural, chemical and physical characterization, for LiRAP films prepared on glass and platinum coated sapphire substrates, via grazing incident x-ray diffraction, Fourier-transform infrared spectroscopy, impedance spectroscopy and chronoamperometry. These findings might accelerate the development of thin film electrolyte as a potential pathway to further increase the energy density of a solid-state cell.

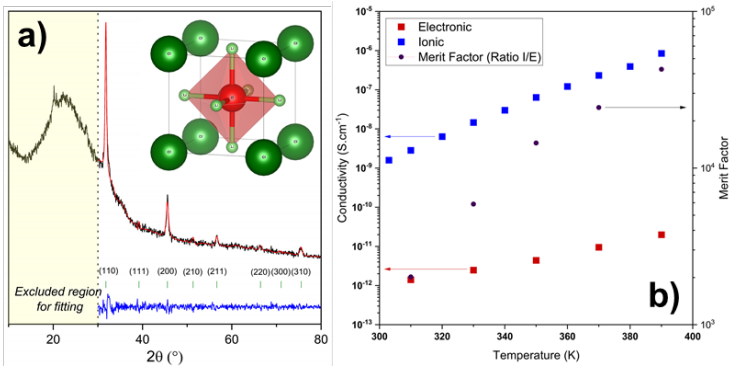

Figure 1: Characterization of a LiRAP thin film layer obtained by RF-Magnetron Sputtering with a post-annealing treatment a) Crystallographic structure refinement via GI-XRD and Le Bail method b) Evolution of the ionic and electronic conductivity with the temperature (and their ratio).

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Poster 43

Differences in performance of solvent mixtures and additives in half and full cells potassium-ion batteries

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Potassium-ion batteries (KIBs) have the same working principle and setup as sodium-ion batteries and lithium-ion batteries (LIBs). They offer some advantages compared to LIBs: The use of aluminum as an anode current collector, cheaper, abundant, and evenly distributed potassium reserves. Moreover, based on the low standard potential of K/K^+ vs. the standard hydrogen electrode (−3.04 V for Li/Li^+, −2.93 V for K/K)[1]. It shows that KIBs could be as attractive as NIBs

For K-ion batteries providing a stable full cell configuration is essential. Cut K-metal as an ion source would increase safety and application variation for K-ion batteries in general. One of the biggest problems is that the full configurations currently lack reliable electrolytes.

The most common electrode materials for KIBs so far are graphite as a negative electrode and the class of Prussian blue analogs (PBAs), e.g. $K_2Fe[Fe(CN)_6]$ (KFF), as a positive electrode. However, cycle life is still a major issue and although improvements have been demonstrated in many half-cell configurations, the compatibility in full-cell configurations is still a matter of debate. For example, EC: DEC based electrolyte has good performance in graphite‖K cell[1] but poor performance at high voltage.

A common solution is to use electrolyte additives, such as the sulfate ester 1,3,2-dioxathiolane 2,2-dioxide (DTD) that was reported recently by the Komaba group for $K‖K_2Mn[Fe(CN)_6]$ half cells[2]. Electrolytes with DTD exhibited larger reversible capacity and suppressed irreversible reactions (Figure 1).

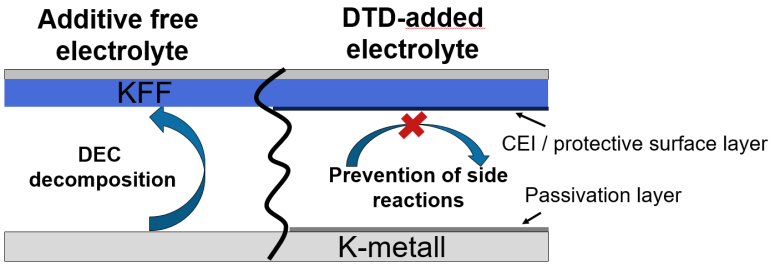

Figure 1: Schematic DTD-electrolyte behavior

In this context, focusing only on half-cell configuration could lead to optimization of the potassium counter electrode, rather than actual improvements on a full cell level. Therefore, the scientific questions of this presentation: to what extent can currently use additives that are effective in half cells increase the performance of full cells?

The main line of this work is to examine a series of additives and electrolyte combinations that have been deemed effective, particularly the DTD additive in a graphite-$K_2Fe[Fe(CN)_6]$ full cell setup. This extends to the challenge related to matching and optimizing KIBs full cell setups.

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Invited presentation

Electrochemo-mechanics of metallic lithium anodes

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Batteries with energy densities that go beyond the commercial Li-ion chemistry are required to fuel the electric revolution. Metallic lithium is the ultimate high-energy anode, but its successful implementation is dependent on increasing plating and stripping efficiency and preventing dendrite formation. In my talk, I will discuss how the interplay between the unique mechanical properties of lithium, the transport and thermodynamic properties of the electrolyte and the physicochemical properties of the solid electrolyte interphase affects lithium's cycling behaviour [1–7].

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Poster 44

Synthesis of piezoelectric separator for self-healing Li-metal batteries

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Li-metal batteries are considered the next generation of the Li-ion technology, but they will only be enabled if Li loss is avoided at the anode/electrolyte interface. One strategy to be explored is the use of piezoelectric materials to mitigate dendritic growth. In this study, we use a polar polymer to prepare piezoelectric porous separators by non-solvent induced phase separation (NIPS) [1]. This method takes advantage of the polymer's difference in solubility in two different solvents to trigger a phase separation from liquid to solid. This process is visually summarized in Fig. 1(a). The phase separation mechanism yields a microscopic architecture of interconnected pores, see Fig. 1(b). The polar polymer, here polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE), is selected because upon phase inversion from the liquid phase, it spontaneously crystallizes in the polar phase of PVDF, called β-phase, instead of the non-polar α-phase in which PVDF crystallizes. The crystalline domains solidify with a random orientation of the structure, yielding polar domains in the polymer matrix that are randomly oriented. Hence, the polymer is piezoelectric at a microscopic level but does not display a macroscopic direct piezoelectric response. To obtain the latter, a poling process is necessary to align the polar domains with an electric field. Liu et al. in 2019[2] demonstrated that polarized, and hence piezoelectric, PVDF separators, are more resistant to dendrite penetration. Their finding motivated us to use PVDF-TrFE in lithium metal batteries as potential self-healing material to mitigate lithium dendrite growth. Optimization and validation of the NIPS process by a combination of SEM imaging and by structural characterizations such as FTIR, DSC, and NMR will be shown, discussing our findings on the poling process and its challenges. The produced membranes are then compared in full battery configurations as displayed in Fig. 1(c), demonstrating the potential of piezoelectric polymers in mitigating the build-up of dead lithium. This work was performed in the framework of the Battery 2030+ initiative and the affiliated project HIDDEN.

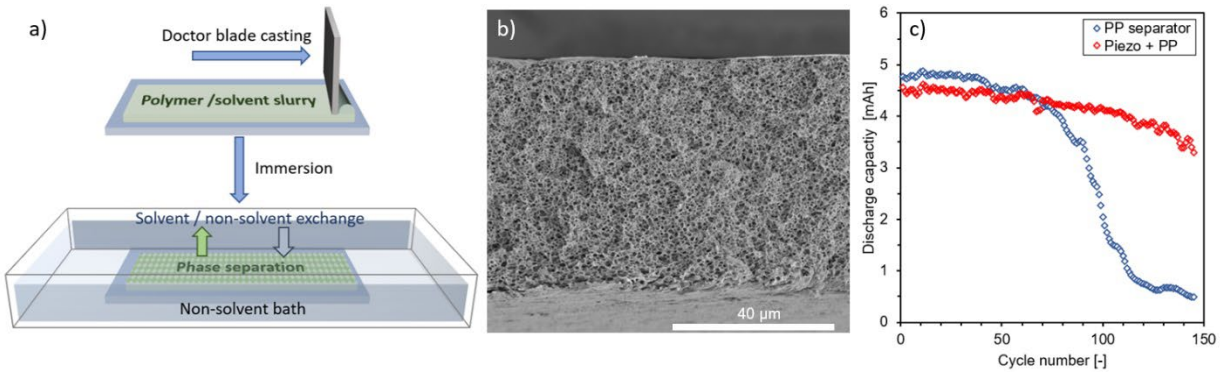

Figure 1: a) Diagram of the NIPS process, b) Cross-section SEM image of the NIPS-produced PVDF-TrFE separator showing the resulting porous structure, c) Li metal/PP/NMC full battery cycling with and without PVDF-TrFE separator (Piezo).

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Poster 45

Enhancing the conductivity in block copolymer electrolytes by controlling the electrode-electrolyte interface

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Conventional lithium-ion batteries use a liquid electrolyte, which is flammable and therefore poses risks of fire. Using a non-flammable material to replace liquid electrolytes such as a solid polymer electrolyte (SPE) not only leads to safer batteries. It also allows for higher-energy density batteries as the mechanical strength of polymers enables replacing the conventional graphite anodes with lithium[1]. Among the different classes of polymers that can be used as SPEs, block copolymer (BCP) electrolytes comprise stiff non-conducting domains and soft conducting domains for lithium-ion transport. While this allows for independent tuning of the mechanical properties and ion conductivities, the conductivity performance of BCP electrolytes often lies much below the expected morphology-driven value, which limits their utility[2]. However, we recently uncovered that the wetting behavior of the BCP on the electrode has a very strong effect on the overall conductivity[3].

Here we show that the conductivity in lamellar polystyrene–block–poly(ethylene oxide) (PS-*b*-PEO, SEO) doped with lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) salt can be significantly increased by engineering the electrode-electrolyte interface. This is remarkable as lamellar SEO has been the most-studied BCP electrolyte for decades. To demonstrate the strong effect of the electrode–electrolyte interface on the bulk conductivity, we grafted different types of polymer brushes to the electrode surfaces of symmetrical stainless steel cells. Whereas a PEG brush makes the surface more hydrophilic, a random PS-P2VP copolymer brush renders the surface approximately neutral for the BCP. Remarkably, the bulk conductivity increases by two orders of magnitude comparing neutral and hydrophilic surfaces (**Figure 1**). These results show that engineering the electrode-electrolyte interface provides an effective means to improve the conductivity in BCP electrolytes, which is key to developing SPEs for higher-energy density batteries.

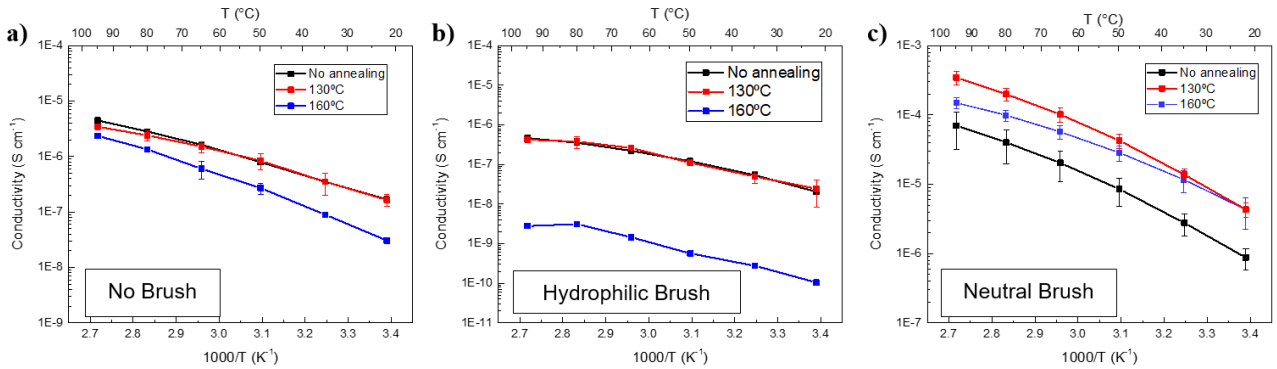

Figure 1. **Ionic conductivity of SEO 40-31 with r [Li]/[EO]=0.08 a)** Surface without any treatment (hydrophobic) **b)** Surface with PEG brush treatment (hydrophilic) **c)** Surface with PS-P2VP brush treatment (neutral).

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Poster 46

Mechanism of Li_2S formation and dissolution in Lithium-Sulfur batteries

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Beyond intercalation-type batteries, such as Li-sulfur (Li-S) batteries could be game-changers in many respects: a theoretical specific capacity amongst the highest of all batteries paired with low cost and sustainability of sulfur. However, insufficient understanding of the mechanism that reversibly converts sulfur into lithium sulfide (Li_2S) via soluble polysulfides hampers the realization of high-performance Li-S cells. Typically Li_2S formation is explained by direct electroreduction of a PS to Li_2S; however, this is not consistent with the size and shape of the insulating Li_2S deposits.

Here, we present operando small and wide angle X-ray scattering (SAXS/WAXS) and operando small angle neutron scattering (SANS) to track the growth and dissolution of solid deposits from atomic to sub-micron scales during charge and discharge[1]. Stochastic modelling based on the SANS data[2, 3] allows quantification of the chemical phase evolution during discharge and charge. Combined with complementary data from electron microscopy and Raman spectroscopy, we show that the deposit is comprised of nanocrystalline Li_2S and smaller, solid short-chain PS particles, which we argue are likely Li_2S_2 (Figure 1). Our data are consistent with solid Li_2S_2 precipitating from solution and then being partially converted in the solid-state to Li_2S, probably via direct electroreduction and chemical diffusion through the Li_2S_2 particle network. Discharge capacity and rate capability in Li-S battery cathodes are therefore limited by mass transport rather than electron transport through a thin passivating surface film. The found mechanism also explains why in practice not all S is converted to Li_2S; a certain amount of Li_2S_2 remains as a second solid discharge product.

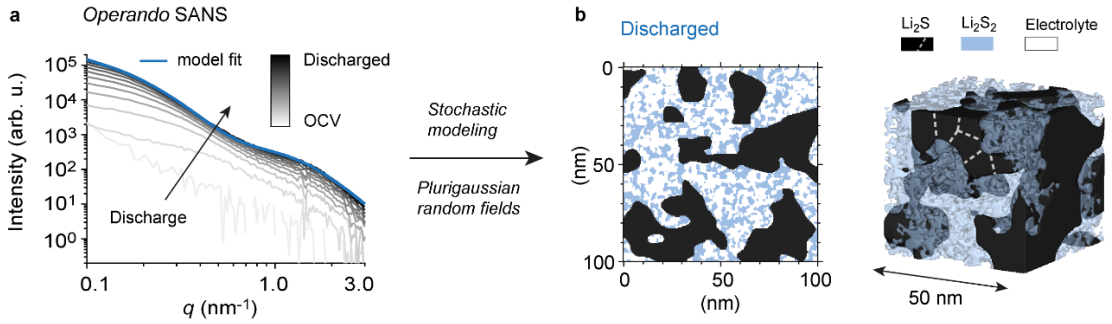

Figure 1: a) *Operando* SANS data of a Li-S battery cathode during potentiostatic discharge. b) 3D visualization of the solid Li_2S/Li_2S_2 deposits obtained from the model fit in a) using stochastic modeling[1, 3].

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Poster 47

Effect of morphology of C-rich silicon carbonitride ceramic on electrochemical properties of sulfur cathode for Li-S battery

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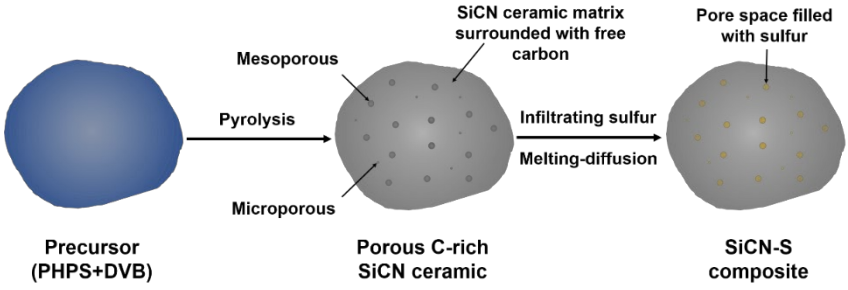
Porous conducting materials represent a promising support for the immobilization of sulfur in the cathode of lithium–sulfur (Li-S) batteries. Herein, we provide an easy and scalable procedure for the prepa- ration of such cathodes. This strategy consists of an infiltration of sulfur under solvothermal conditions at 155 °C into pores of carbon-rich silicon carbonitride (C-rich SiCN). Porous polymer-derived SiCN ce- ramics possess a unique combination of high electronic conductivity and robust, stress accommodating mechanical properties. The impact of the initial porosity and elemental composition of SiCN ceramics on the electrochemical performance of SiCN-S composites is addressed in this work. It is shown that the SiCN precursor pyrolyzed at 1000 °C reveals a mesoporous character in line with the presence of a free carbon phase dispersed in SiCN and demonstrates the best electrochemical stability and the highest capacity (more than 310 mAh/g over 40 cycles) at a high sulfur content of 66 wt.%.[1, 2]



Scheme: Fabrication of porous C-rich SiCN-S composite by polymer-derived ceramic method.[2]

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Poster 48

Cellulose Based Fungal Battery

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Using cellulose as a material for 3D-printing, inks with living fungal cells present a novel way to harness the metabolic activity of fungi for potential use in electrochemical devices. Previously, we showed the metabolic activity of white-rot fungi in the presence of nanocellulose[1]. Here, we describe the electrochemical properties of 3D-printed TEMPO (2,2,6,6-tetramethylpiperdine-1-oxyl radical) oxidized cellulose nanofibrils and sulfuric acid hydrolyzed cellulose nanocrystals (CNC) inks, containing *Saccharomyces cerevisiae*, the chemical mediators thionine or methylene blue, carbon black and graphite flakes. Cyclic voltammetry (CV) was used to screen the optimum composition of the active 3D-printed fungal gels, deposited directly on a previously developed printable current collector[2]. Based on the results from CV, we demonstrate full device data acquired using a customized electrochemical cell. The electrochemical cell can be tailored for use with different device components, volumes of nutrients, and electrolyte for testing the redox properties of *S. cerevisiae*. To our knowledge, this is the first study that reports on applying the use of a 3D-printed cellulose based fungal electrode in a battery system.

Acknowledgements: This study was financed by the Gebert Rüf Stiftung, Switzerland (Project num. GRS-08/19).

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Poster 49

The synergistic role of functional electrolyte additives containing phospholane-based derivative in NMC811II Si-graphite cells

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Lithium-ion batteries (LIBs) are considered one of the most efficient and reliable energy storage candidates to satisfy the future energy storage demands. Over the last years, intensive research has been devoted to the transition from conventional to next-generation LIBs by developing alternative anode and cathode materials with higher theoretical specific capacities. In this regard, nickel-rich cathodes and silicon-based anodes are regarded as two promising examples of next-generation electrode materials for LIBs. However, the aforementioned chemistries suffer from structural failure leading to rapid capacity fades due to interfacial instabilities. These failures originate from irreversible phase transition, transition metal dissolution, and oxygen evolution during charge/discharge cycling on the cathode side, as well as from large volume expansion of Si-based anodes during the lithiation, which results in structure cracking at the surface and renewed formation of the interphase in each cycle[1-2].

Here we report on a novel multifunctional phospholane-based electrolyte additive, 2-phenoxy-1,3,2-dioxaphospholane (PhEPi), designed and synthesized by our group [3-4]. The addition of optimum concentration of PhEPi to the EC:EMC 3:7, 1 M $LiPF_6$, taken as the baseline electrolyte, simultaneously improves the solid-electrolyte interphase (SEI) and cathode electrolyte interphase (CEI) properties of NMC811||Si-graphite (20% Si) cell chemistry, thus leading to enhanced overall performance. The two well-known film-forming additives, namely vinylene carbonate (VC) and fluoroethylene carbonate (FEC), as co-additives with PhEPi at optimum concentrations, were implemented in the above-mentioned cell chemistry. Obtained results indicate that the VC additive outperforms the FEC at optimum concentrations in terms of overall performance in the NMC811||Si-graphite cell. In addition, t the performance and cycle life of the considered cells are significantly improved when PhEPi is implemented into the VC-containing electrolytes. To understand the underlying mechanisms for the observed synergistic effect of VC and PhEPi in the considered cell chemistry, we performed *post-mortem* analysis by combining selected complementary structural and spectroscopic techniques.

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Poster 50

Capacity-limiting factors of solid-state S/Li_2S conversion in microporous carbon-based Lithium-sulfur batteries

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Lithium-sulfur (Li-S) batteries promise extraordinary theoretical capacities, low cost and sustainability due to the abundance of sulfur [1]. The solid-liquid-solid conversion from sulfur (S) to Lithium sulfide (Li_2S) in common ether-based electrolytes results in problems caused by the soluble polysulfides: active material loss, poor cycle life and self-discharge. Solid-state S/Li_2S conversion using carbonate electrolytes and microporous carbons (pores < 2 nm) could circumvent these issues [2]. A cathode-electrolyte interface (CEI) layer prevents polysulfide dissolution and ensures solid-state conversion with high cycle life. However, major progress in understanding the capacity and rate-limiting processes is necessary to improve S loadings, S utilization and rate capabilities.

In this work we investigate the physicochemical mechanism of S/Li_2S solid-state conversion in microporous carbon-sulfur cathodes using a variety of electrochemical/materials characterization methods with a focus on electrochemical impedance spectroscopy (EIS). We systematically vary parameters such as the carbon pore size, the temperature, the sulfur loading in the cathodes and the charging rate. In-situ EIS with the galvanostatic intermittent titration technique (GITT) monitors CEI formation, Li ion transport and interface charge transfer during galvanostatic cycling. The study demonstrates that next to Li ion diffusion into the porous carbon particles, charge transfer across the S/Li_2S-C interface, is the rate/capacity limiting factor. Our results indicate that solid-state S/Li_2S conversion with carbonate electrolytes is also possible in carbons with pores beyond 2 nm, a strategy that could significantly increase S loadings in the future.

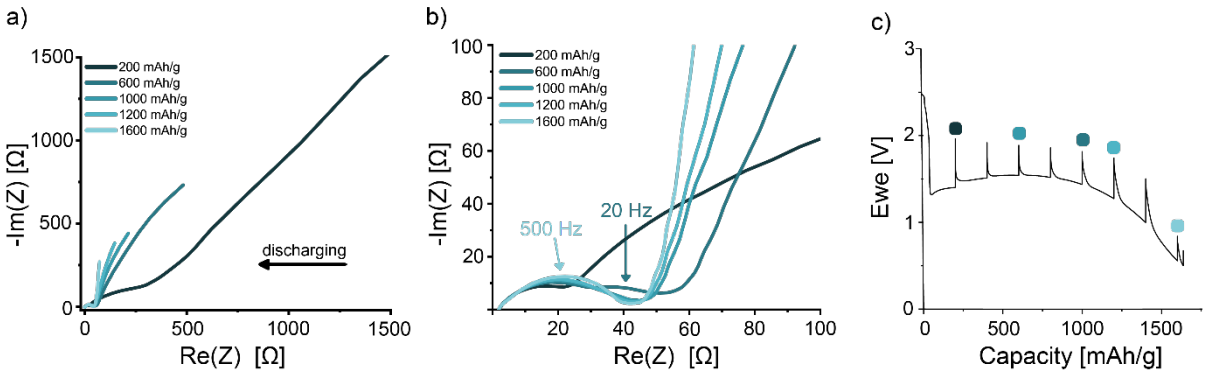

Figure 1: a) EIS spectra during the first discharge, b) magnification of the high and middle frequency region of EIS spectra, c) GITT curve during the first discharge, dots represent the EIS measurement points with their colors matching the spectra.

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Poster 51

Towards Solid-State Magnesium Batteries: Ligand-Assisted Superionic Conductivity in Complex Hydrides

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Functional electrolytes is a major challenge for the development of magnesium batteries, as good and compatible electrolytes in both liquids and solids have been absent.[1] Recently, a high Mg^{2+} conductivity was achieved for solid electrolytes, where the addition of a neutral ligand to $Mg(BH_4)_2$ enhanced the conductivity by several orders of magnitude.[2,3] However, a rechargeable solid-state magnesium battery has not yet been reported.

Here we present an investigation in two parts. The first part is the discovery of a new superionic solid electrolyte based on magnesium borohydride tetrahydrofuran composites.[4] The composite, $Mg(BH_4)_2{\cdot}1.5THF{-}MgO$(75 wt%), displayed the highest conductivity, $\sigma(Mg^{2+})$ ~10^{-4} S cm^{-1} at 70 °C. The electrolyte displayed an ionic transport number of t_{ion} = 0.99, and an oxidative stability of ~1.2 V vs. Mg/Mg^{2+}. In addition, the electrolyte displayed stable magnesium plating/stripping for at least 100 cycles at 55 °C with a current density of 0.1 mA cm^{-2}.

The second part is the utilization of these electrolytes in all-solid-state batteries. $Mg(BH_4)_2{\cdot}1.5THF{-}MgO$(75 wt%) was used in a battery with a magnesium metal anode and a layered TiS_2 cathode. A maximum discharge capacity of 94.2 mAh g^{-1} was displayed, which corresponds to y = 0.2 in Mg_yTiS_2.[4] For another electrolyte, $Mg(BH_4)_2{\cdot}1.6NH_3{-}MgO$(75 wt%), the intercalation mechanism of Mg^{2+} into TiS_2 was investigated using a similar cell.[5] The performance of the cell chemistry was evaluated by utilizing different cut-off voltages in constant current constant voltage charging, effectively leading to a better battery performance.

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Horizon 2020 LC-BAT5 battery project cluster session

High areal capacity Ni-rich NMC water-based electrodes with excellent long-term cycling stability

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Research efforts in the last three decades have resulted in a steady increase in the energy density of Li-ion batteries (LIBs), leading to their integration into electric vehicles (EVs). Therefore, car manufacturers have increased the number of EVs into their fleet and decided to move towards their introduction into the mass market, with 200M of EVs expected to be sold by 2025. In such a fast-growing market, the cost and the environmental impact of LIB production play major roles. A crucial step in battery manufacturing is the processing of anode and cathode active materials to produce electrode coatings. While commercial anode electrodes (i.e. graphite, silicon-graphite) are already water-based, cathode electrodes (i.e. $LiNi_xMn_xCo_xO_2$ (NMC), $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) etc.) are still largely processed using organic solvents, specifically N-methyl-2-pyrrolidone (NMP), with poly(vinylidene difluoride) (PVDF) as a binder. However, the NMP-PVDF combination has many disadvantages[1]. Firstly, the binder is considerably more expensive than water-soluble binders and not easy to dispose at the end of the battery life. Secondly, NMP is also costly, toxic, and being a volatile organic compound (VOC), needs solvent recovery at commercial scale. On the other hand, water-soluble binders such as Na-carboxymethylcellulose (Na-CMC) and styrene butadiene rubber (SBR) are not only cheaper but also easier-to-recycle [2]. Additionally, the use of water as a solvent would remove the need for solvent recovery. It is then clear that switching to water-based processing also for cathode materials would decrease the cost and improve the environmental sustainability of LIB production. Nevertheless, aqueous cathode processing has many challenges [1], the major one being the instability of the active material in water. The leaching of Li^+ ions gives rise to very high pH (~ 12) values and, in turn, to the corrosion of current collector (aluminium) and bubble evolution during coating. Consequently, electrodes usually show cracks, pinholes and poor flexibility. These issues are even more enhanced for thick coatings, which are needed to achieve high energy density cells. Therefore, the electrochemical performance of water-based cathode electrodes is generally poorer than that for NMP-based electrodes.

In this work, Ni-rich NMC electrodes with commercially relevant areal capacity (~ 4 mAh cm^{-2}), high active material contents (> 90%) and low binder amounts (3 wt.%) were produced by aqueous processing and coating roll-to-roll on a pilot line. Our goal was to study the influence of different amounts of phosphoric acid (H_3PO_4) on the slurry rheology, electrode adhesion and morphology, electrochemical performance as well as to perform a feasibility study of acid-addition to control the pH at pilot scale. A fast-mixing procedure was developed to minimize the contact time between NMC and water and, at the same time, phosphoric acid was added in amounts between 1.5 and 3 wt.%. The pH evolution over time showed that the aluminium corrosion pH threshold (pH=8.5-9.0) was reached after 1h, 12h and 48h for 1.5, 2.25 and 3 wt.% H_3PO_4, respectively. All slurries showed a shear thinning behaviour with a viscosity that increased with the amount of acid. Conversely, the adhesion to the current collector decreased by increasing the amount of acid, e.g. electrodes with 3 wt.% acid even showed cracks at the edges of the coating. The electrochemical performance was studied in full-cell configuration vs graphite. NMC electrodes prepared with 1.5 wt.% acid in the slurry formulation showed a specific capacity of around 180 mAh g^{-1} at C/10 and 165 mAh g^{-1} at C/3 and an excellent cycling stability reaching a capacity retention above 90% after 500 cycles, which is comparable to NMP-based electrodes. However, a slight decrease in specific capacity and cycling stability was observed by increasing the acid content.

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Poster 52

A facile strategy for reclaiming discarded graphite and enhancing the rate capabilities of recovered graphite anodes

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Graphite negative electrodes are unbeaten hitherto in lithium-ion batteries (LiBs) due to its unique chemical and physical properties. The increasing scarcity of graphite resources makes smart recycling or repurposing of discarded graphite particularly imperative, in order to fully close the waste loop and makes it sustainably critical[1]. Waste graphite streams recycling has considerable value embedded in manufactured LiBs for new rounds, particularly for those countries that rely heavily on graphite imports[2].

In this work we propose a facile recycling perspective to transform waste graphite originating from two different state of health (SOH) spent LiB batteries into a high-performing regenerated graphite. The regenerated graphite provides superior electrochemical performance due to 2-order-of-magnitude increase in the average diffusion coefficient of lithium ions. We performed an assessment of the aging characteristics of the internal resistance in combination with commercial LCO cathode by means of hybrid pulse power characterization (HPPC) experiments with a 10 % change in SOC from each set of current pulses tested. The results show that LCO|RG2 has area lower specific impedance. Although the performance of re-established graphite is comparable to that of commercial graphite in all respects, the low first coulombic efficiency (RG1 79.81 %, RG2 80.06 %) restricts its widespread use to some extent, which might lead to a necessity of a prelithiation which we will address in our future research.

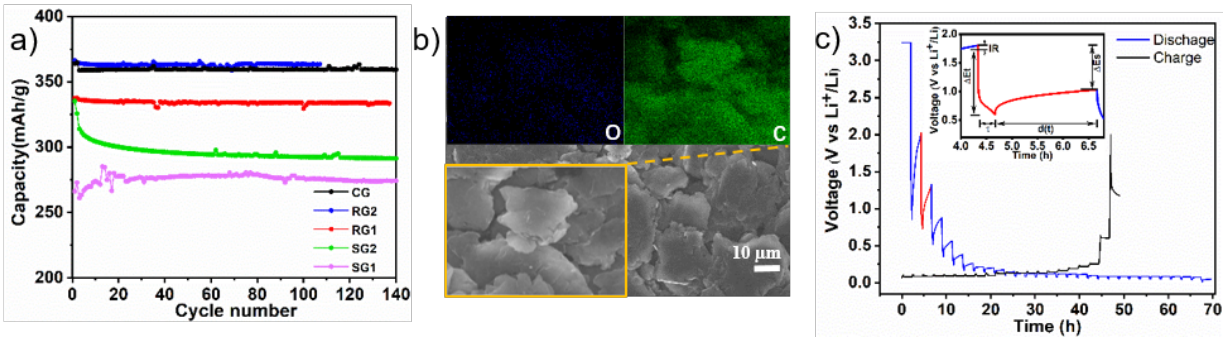

Figure 1: a) Galvanostatic charge/discharge curves, b) SEM images and mapping of RG2, c) the current pulse vs. voltage profile of RG2 at first cycle with a schematic representation at a single step (inset shows the ‘‘pulse + galvanostatic + relaxation’’ process during discharging).

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Invited industry presentation

Perspectives on automotive all solid state batteries

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The electrification of the automotive transportation sector creates an ever-increasing demand for high-performance, low-cost and safe batteries. Steady progress in the standard Li-ion battery technology is predicted to reach a plateau with limitations based on its physico-chemical properties. Especially improvements in energy density will aid further adoption of electric vehicles in the transportation sector.

Solid state batteries, represent a promising future technology for electric vehicles, by fully or partly replacing liquid electrolyte-soaked separators. In addition to potentially enabling lithium-metal anodes, employing non-flammable, intrinsically safe electrolytes materials would translate to significant system level safety related simplifications. The combined benefits would in turn enable improved energy densities and with that a larger driving range or lighter/smaller battery packs.

In practice, however, there are multiple hurdles to overcome: Cycle-life, operating temperature window, required mechanical pressure, coulombic efficiency and material stability issues are just some characteristics that need fundamental understanding and further efforts both from academia and industry.

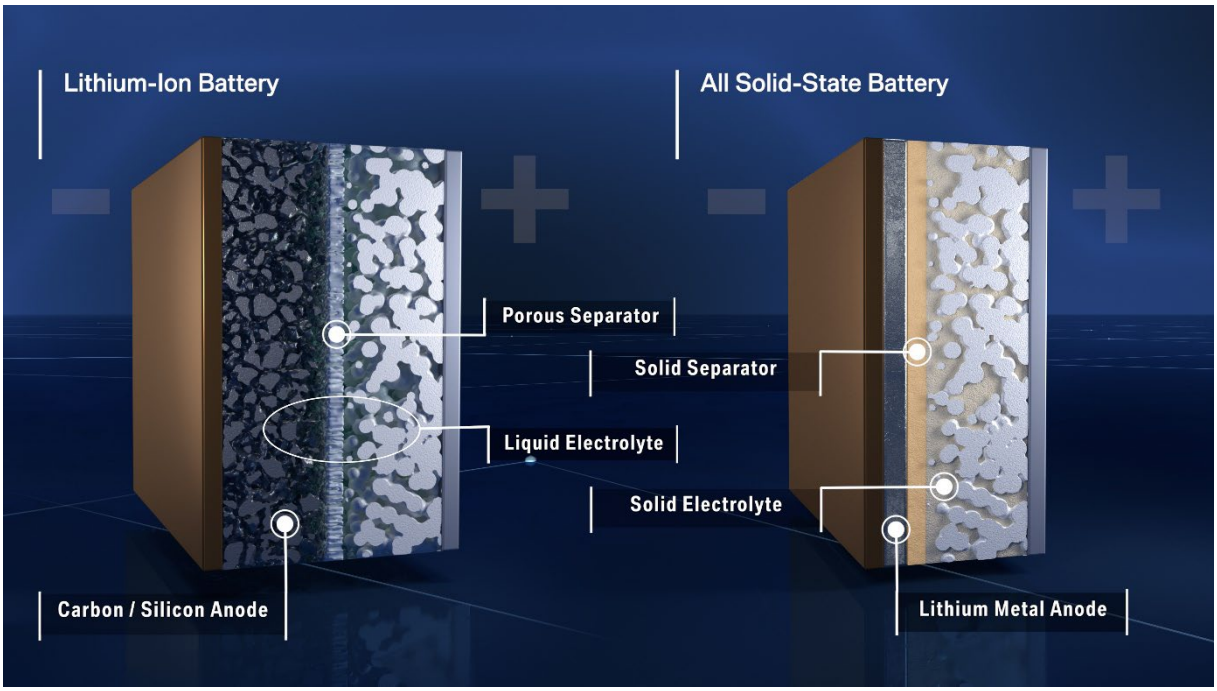

Figure 1: Li-ion battery compared to all-solid-state battery

Poster 53

Linking the performance of lithium-sulfur batteries to electrode composition and electrolyte formulation through mixture-process design of experiments

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Lithium-sulfur batteries (LSBs) are among the most promising candidates to replace state-of-the-art lithium-ion chemistry[1]. Indeed, traditional insertion-type compounds reveal a limited specific capacity[2] due to their intrinsic nature, and they usually contain cobalt, which belongs to the family of critical raw materials[3]. Sulfur-based batteries exploit elemental sulfur as the active material, an abundant and cheap[4] element. Furthermore, sulfur shows a theoretical specific capacity surpassing that of state-of-the-art materials by an order of magnitude (1675 mAh g^{-1})[5]. Nevertheless, these systems are not ready for the market. LSBs suffer from fast capacity fading and low material utilization due to the high resistivity of sulfur, the well-known shuttle effect, and cracking during cycling[6]. Two common strategies to overcome these drawbacks are sulfur encapsulation in high-surface-area carbons[7] and electrolyte optimization[8]. Encapsulation allows for efficient electrical conduction and sulfur utilization[9], while a designed electrolyte formulation is critical to limit the shuttle effect and develop a stable SEI[10]. In spite of the plethora of literature concerning these topics, research on the simultaneous optimization of the electrode composition and electrolyte formulation is lacking. To fill this gap, we decided to use a D-optimal[11] mixture-process Design of Experiments[12] to derive an empirical model linking the performance of lithium-sulfur cells to a specific electrode-electrolyte combination. The aim of this modeling, together with an in-depth physicochemical characterization of the electrodes, is to improve the understanding of the relationship between electrode composition, electrolyte formulation, and cell performance for the lithium-sulfur chemistry. In order to achieve this goal, we employed electrodes with a sulfur-carbon nanohorns (S-CNH) composite as the active material, while using solutions of lithium bis(trifluoromethanesulfonyl)imide and lithium nitrate in 1,2-dimethoxyethane and 1,3-dioxolane of varying composition as electrolytes. This study provides a solid base for further optimization of this system through more complex models and, at the same time, an example of an effective work plan for researchers willing to study new electrode-electrolyte systems.

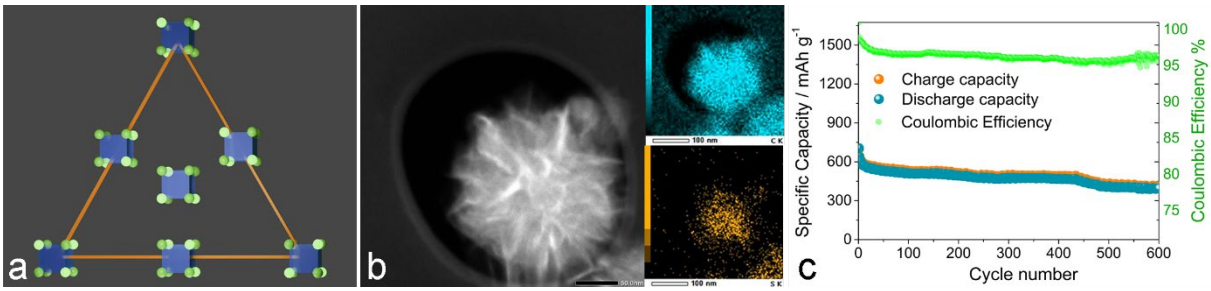

Figure 1: a) Process in mixture representation of an experimental design with a three-component mixture and three process variables, b) STEM-EDS map of the sulfur-carbon nanohorns composite, c) Specific capacity of a representative S-CNH electrode during galvanostatic cycling.

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Poster 54

Operando X-Ray Diffraction and Tomography to track Morphological Changes in LiNi0.8Mn0.1Co0.1O2 (NMC 811) Cathode Particles

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High nickel content Li(Ni,Mn,Co)O2 cathode materials allow energy density to be increased while reducing the use of cobalt. However, these materials often have lifetime issues, which are partly due to mechanical changes in the material that occur during cycling, particularly during deep delithiation (i.e., high voltage operation). Direct observation of these morphological changes is challenging. Here, we demonstrate that it is possible to gain quantitative insight into the morphological changes occurring during cycling and their electrochemical origins by comparing the volume change of the unit cells measured using operando XRD to the volume change of the secondary particle measured using operando x-ray tomography. Specifically, we show that while the primary particles reversibly expand and contract, the secondary particles do not reversibly contract following the expansion of the primary particles along the c-axis.

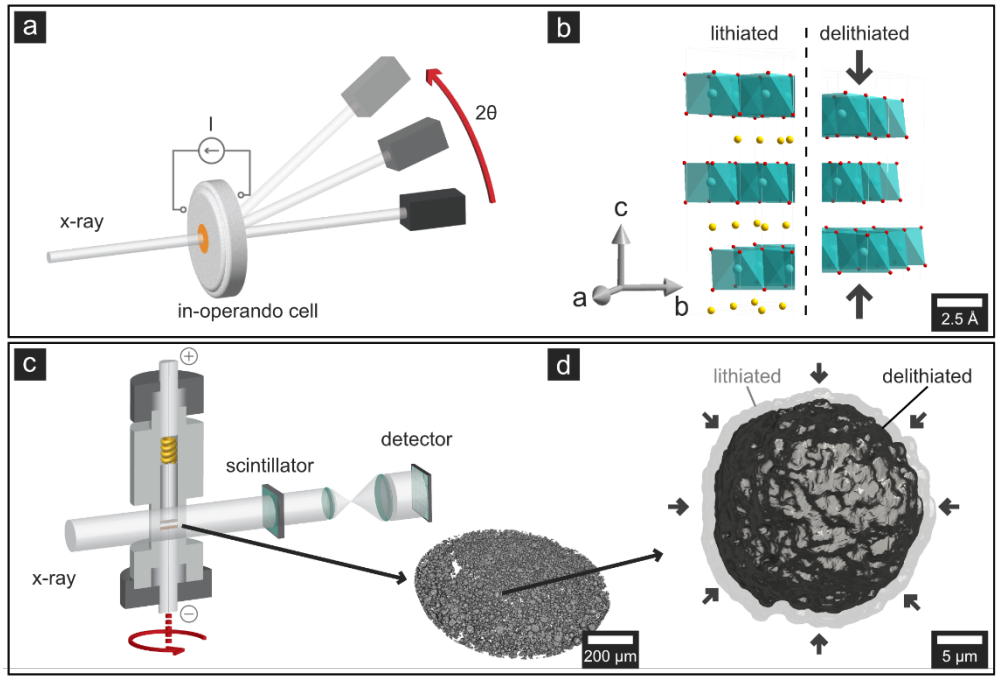

Figure 1 We studied the volume dynamics of NMC811 cathodes during the first cycle on two different length scales. Using in-operando x-ray diffraction spectroscopy (a) we measured the dynamics of the lattice (b) and used this to calculate the evolution of the unit cell volume. High resolution in-operando x-ray tomography (c) allowed us to track the volume dynamics of individual secondary particles, which consist of densely packed primary particles (d). Comparing the two we found that the secondary particle likely undergoes morphological changes and that its volume evolution is a complicated function of the crystal lattice change and mechanical interactions of the primary particles.

Poster 55

Impact of interface properties and structure on charge transport and distribution in composite solid electrolytes

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To decarbonize the transport sector, a widespread switch to battery electric vehicles is needed. To tackle this challenge, the energy density of LIBs needs to be increased.[1] 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.[2] 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.[3] 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 solid electrolytes (CSEs). Ceramic electrolytes offer the highest ionic conductivities and stability; however, they are brittle, challenging to manufacture and cannot adapt to volume changes during battery operation.[3] Polymer electrolytes are easy to manufacture, cheap and sufficiently flexible to ensure good interfacial contacts during battery operation.[3,4] Combining polymer and ceramic in a CSE, 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.[3-5] Also, CSEs allow cost effective, slurry-based manufacturing on large scales.[6]

In CSEs, Li-ion transport through and along the polymer-ceramic interface is a key factor in ionic transport;[5,7] however, detailed understanding of the relative importance of bulk and interface transport is missing. To understand this, we use x-ray tomography to quantify the structure of CSEs made of 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 different assumptions of specific interfacial resistivity and temperature. The simulations allow us to study the relative contributions of LLZO, PEO, and their interfaces to the transport as a function of structure and different operating conditions and the resulting distribution of current density within the CSEs. These findings guide the selection of materials and interface treatments for CSEs. For example, we find that surface treatments decreasing interfacial resistivity[6] are critical above 15 vol% LLZO, particularly in the case of smaller LLZO particles, to enable uniform and higher current densities throughout the SE.

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Poster 56

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 contact.

Here, we schematically investigate how commonly used battery electrolyte solvents and carbonate-based electrolytes affect the surface of Li, Na, and K. The SEI layers formed under these conditions are studied using X-ray photoelectron spectroscopy (XPS)[1,2]. 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 electrochemical performance can be obtained.

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Poster 57

Unravelling Lithium Nucleation and Dissolution in Lithium-Metal Batteries

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Metallic lithium is considered the 'holy grail' of rechargeable lithium-based batteries, as its incorporation into the battery would double the available energy density. In post-Li-ion-batteries, such as Li–S, the projected gain is twice as compared to graphite, while with current Li-ion battery positive electrodes it would be about 30 %. [1] Metallic lithium as a negative electrode material has been under investigation since the early 1970s, but declined with the invention of graphite intercalation technology, which was considered a safer alternative. [2] However, recently, interest in the metallic lithium as a negative electrode has spiked again. The majority of research is focused on battling the obvious shortcomings of metallic lithium instead of trying to understand fundamental laws governing electrochemical lithium nucleation and dissolution, which often result in dendrite growth, electrolyte consumption and hence safety concerns.[3] Instead of studying correlations between various parameters and final long-term performance, which depends on many experimental factors working together, it is often chosen to focus on a single experimental setup and finding a remedy for that particular set of parameters at given conditions. In contrast, we are seeking a fundamental understanding of metallic Li behaviour upon deposition and stripping.
A first study covering long-term cycling of Li in different types of electrolytes hereby served as our experimental baseline.[4] Using asymmetric (Cu||Li) cells as a good model system to study lithium nucleation on bare copper electrodes, we have supplemented our previous findings with a set of both *post-mortem* and *operando* characterization methodologies. We present a potentiostatic 'Li pumping' method in combination with scanning electron microscopy to evaluate how electrolyte properties affect Li nucleation, where a connection between measured flow of current and observed electrode morphology is established. Further, we move to operando visualization of these processes via novel high-resolution neutron imaging that provides valuable insights into lithium nucleation and film growth during cycling. Finally, we are going to shed light on the role of electrolyte additives in the formation of 'dead' lithium and cycling reversibility, which can be clarified using nano-dilatometry. By putting all puzzle pieces together we will discuss what key steps will be needed on the way to safe Li metal negative electrodes.

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Poster 58

Accurate voltage measurement in all-solid-state batteries enabled by the design of three-electrode cells

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All-solid-state batteries (ASSBs), through the use of solid electrolytes (SEs), offer improved safety and increased energy density compared to conventional liquid-based batteries. This can be achieved by combining high voltage cathode active materials (CAM) and thin (10 to 20 µm) metallic lithium foils as anode. Nonetheless, the electrochemical instability of SE/CAM and SE/Li interfaces as well as the limited Li-ions kinetics at high cycling rates require reliable diagnostic electrochemical measurements to assess the various failure mechanisms.

In this contribution, we report on the design and experimental results of bulk-type ASSB three-electrode cells with an integrated pressure sensor dedicated for (i) an accurate deconvolution and diagnosis of the voltages applied between the cathode and the anode during cycling and (ii) precise real time monitoring of the manufactured and cycled stack pressure respectively. Figure 1.a shows the configuration of the custom made three electrode cells where the reference electrode (RE) is located on top of the working electrode (WE) separated by the SE as well as the integrated pressure sensor located underneath the counter electrode (CE). [1] The cell design was inspired by the work of Jin Nam *et al.* using similar three-electrode cells design. [2] Figure 1.b presents the galvanostatic cycling performance at different C-rates (C/20, C/10 and C/5) of $InLi_x$|LiPSCl|$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$|LiPSCl|Li stack where $InLi_x$, $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622) and Li are used as CE, WE and RE respectively, and Li_6PS_5Cl (LPSCl) as SE. The voltage deconvolution demonstrates that the potential between the $InLi_x$ and RE stay considerably stable along the different C-rates, with only small variation, around 1 mV measured at C/10, attributed to change in the lithiation extent in the indium. The validation of the cell design and the consistency of the obtained result with the theoretical values acknowledge that much complex cathode and anode materials can be evaluated to monitor the voltage, adjust the balancing and even to deconvolute the impedance originate from the different electrodes.

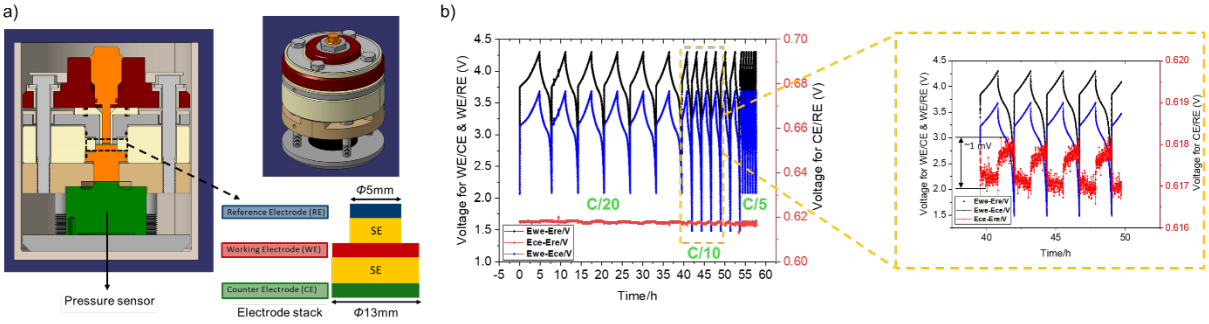

Figure 3: a) Three-electrode cells design with integrated pressure sensor. b) Voltage deconvolution at different cycling rates during galvanostatic cycling of $InLi_x$|LiPSCl|NCM622 cell using Li, as RE.

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Poster 59

The impacts of cell physical parameters on the cycling performance of thin metallic lithium in sulfide-based all-solid-state batteries

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For all-solid-state batteries, the use of thin (10 to 20 µm thick) metallic lithium as anode holds the promise to enable batteries with high energy density above 400 Wh/Kg. In order to achieve stable cycling performance and long lifetime at high current density (> 3 mA/cm^2), a variety of challenges still need to be addressed. Among them, the propagation of lithium dendrite and the formation of dead lithium cause the rapid failure of the cell. In this work, we report on the physical parameters applied during the cell assembly process and cycling and their direct impacts on the cell short circuit. Systematic investigation is carried out by varying (i) the solid electrolyte thickness and densification, (ii) the applied pressure during cycling, (iii) the protection of the edge and (iv) the current density and area capacity. The electrochemical measurement is performed on symmetric cells using argyrodite Li_6PS_5Cl solid electrolyte pellet sandwiched between two 50 µm metallic lithium coated on Cu foil.

With low stack pressure from 10 MPa to 20 MPa, the symmetric cells using 500 µm thick Li_6PS_5Cl and a disk protective edge of HDPE with 7 mm outer and 5 mm inner diameter exhibit reliable plating and stripping behavior at 0.1 mA/cm^2 and 0.1 mAh/cm^2 over 1000 hours (500 cycles) (Figure 1.a). However, the higher stack pressure (> 20 MPa) results in cells shorting after 23 hours (12 cycles). At increased current density e.g. 0.2 mA/cm^2 (Figure 1.b) and 0.4 mA/cm^2 (Figure 1.c) with the same area capacity of 0.1 mAh/cm^2, the cells short much earlier. For the fabrication pressure of the solid electrolyte pellet, a compromise between the thickness and porosity needs to be considered because of their opposite effect. The contribution of edge protection for metallic lithium electrode will be presented. These results serve as baseline to form a guideline toward cell configuration, assembly process and cycling conditions. Finally, our study will contribute to improve the cycling reproducibility and provide guidance to further improve the cycling performance of metallic lithium in all-solid-state batteries.

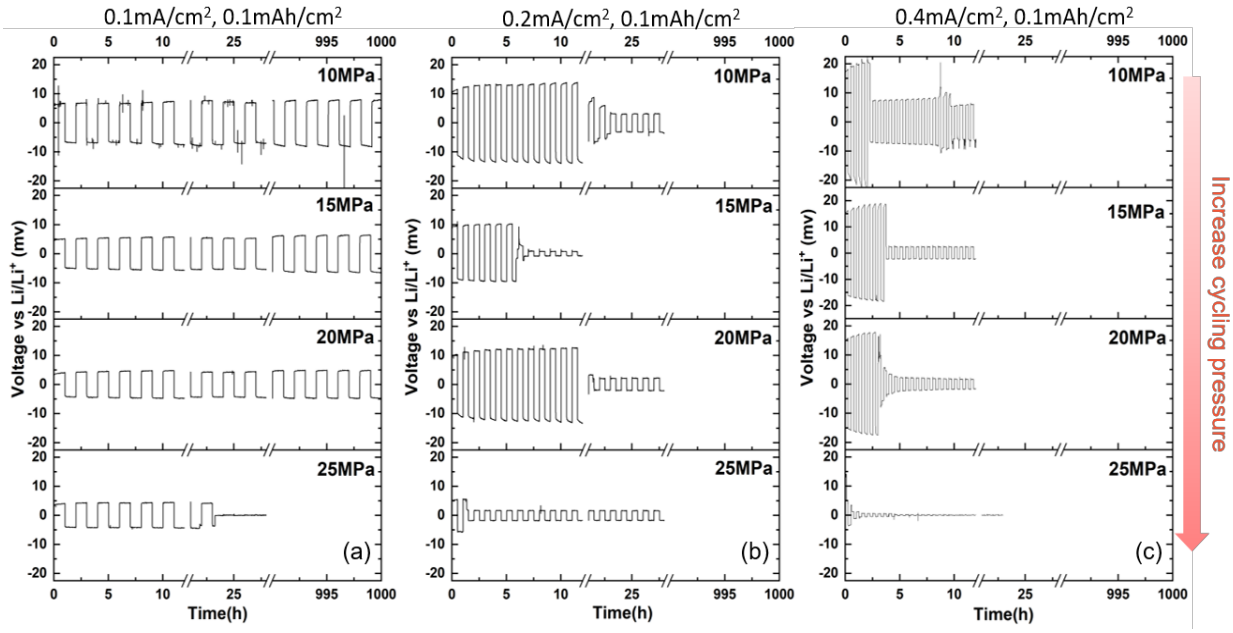

Figure 4: Galvanostatic cycling of Li symmetric cells using Li_6PS_5Cl solid electrolyte pellet. Li plating and stripping performed at different stack pressure and different current densities a) 0.1 mA/cm^2, b) 0.2 mA/cm^2, c) 0.4 mA/cm^2 with an area capacity of 0.1 mAh/cm^2.