SOLID-STATE BATTERIES VI
FROM FUNDAMENTALS TO APPLICATION

An International Bunsen Discussion Meeting (IBDM)

NOVEMBER 13-15, 2024
House of Logistics & Mobility (HOLM)
FRANKFURT/MAIN

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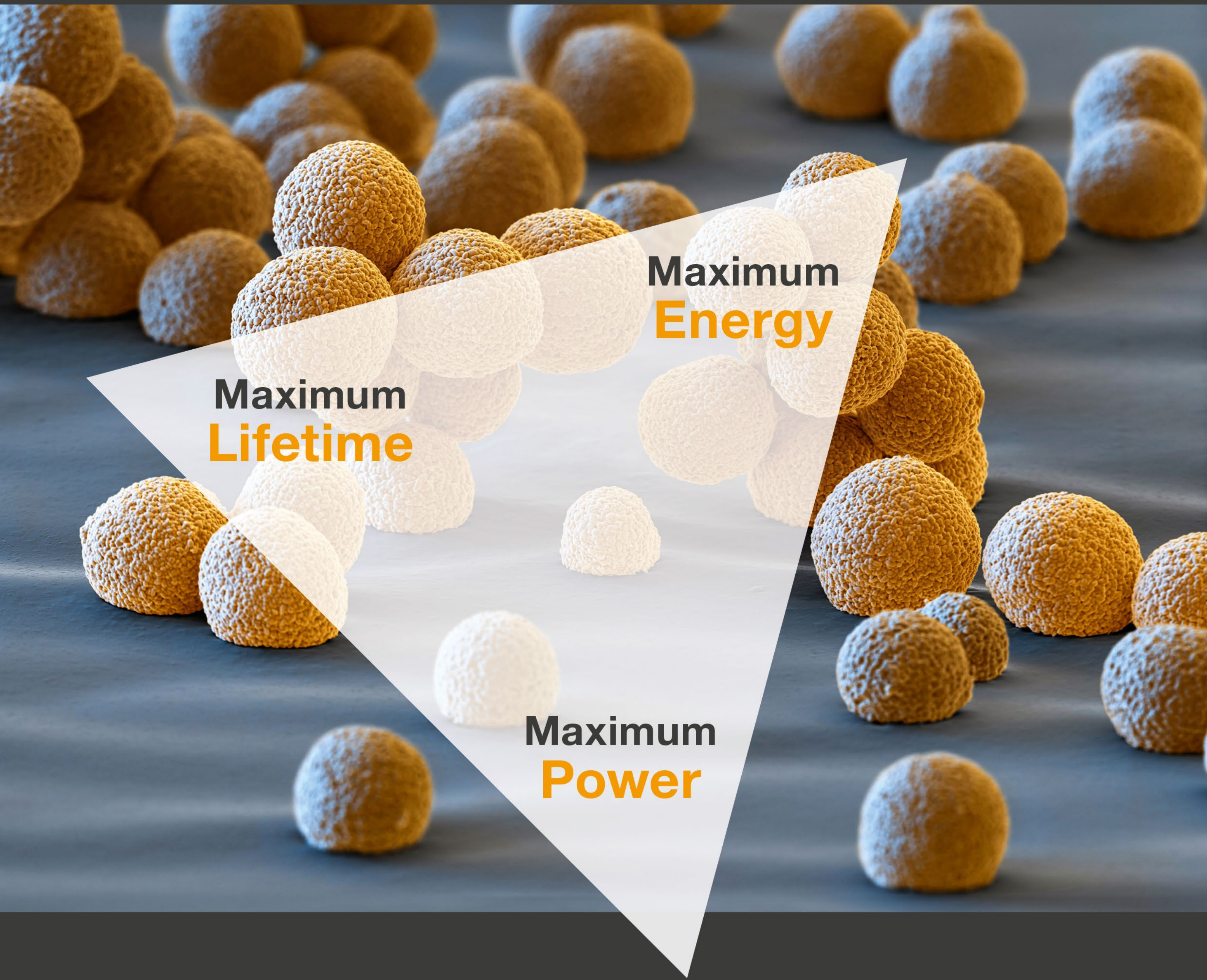

BASF Battery Materials

CONFERENCE PROGRAMME

Wednesday, Nov 13, 2024

11:30	Registration		
12:00	Lunch		
13:00	Opening Remarks		
	Session I: Cell Concepts		
13:15	KEYNOTE LECTURE Efforts from Semi-Solid to All Solid Lithium Batteries Via in situ Solidification Technologies	Q. Li (Beijing/CN), JM. Li (Beijing/CN), JL. Qiu (Beijing/CN), Q. Yang (Beijing/CN), WJ. Li (Beijing/CN), BN. Liu (Liyang/CN), F. Luo (Liyang/CN), HG. Yu (Beijing/CN), XQ. Yu (Beijing/CN), LQ. Chen (Beijing/CN), **Hong Li** (Beijing/CN)	O 01
14:00	INVITED LECTURE Columnar Si Anodes for Sulfide-Based All-Solid-State-Batteries	**Holger Althues** (Dresden/DE), S. Dörfler (Dresden/DE), F. Hippauf (Dresden/DE), S. Cangaz (Dresden/DE), A. Dupuy (Dresden/DE), T. Abendroth (Dresden/DE), B. Schumm (Dresden/DE), S. Kaskel (Dresden/DE)	O 02
14:30	INVITED LECTURE Cutting Edge Research: An Introduction to CATL 21C Lab	**Ulderico Ulissi** (Ningde/CN)	O 03
15:00	Printed All-Solid-State Na-Ion Batteries Based on Hydroborates	**Ingo Bardenhagen** (Bremen/DE), J. Thomas (Bremen/DE), J. Schwenzel (Bremen/DE)	O 04
15:20	Polymer Electrolytes at Interfaces in Hybrid Systems: Impact on Ion Transport	**Andreas Heuer** (Münster/DE), A. Thum (Münster/DE), L. Hölzer (Münster/DE), G. Shukla (Münster/DE), D. Diddens (Münster/DE), M. Kozdra (Uppsala/SE), D. Brandell (Uppsala/SE)	O 05
15:40	Coffee Break		
16:10	Operando FIB-SEM Revealing the Dynamics of Morphological Changes Occurring in Positive Electrode Composite in Solid-State Battery	**Patrice Perrenot** (Grenoble/FR), P.-H. Jouneau (Grenoble/FR), A. Boulineau (Grenoble/FR), P. Bayle-Guillemaud (Grenoble/FR), C. Villevieille (Grenoble/FR)	O 06
16:30	Understanding the Morphological, Structural, and Redox Behavior of Metal Sulfides as Cathode Active Materials in Solid-State Batteries	**Katherine A. Mazzio** (Berlin/DE), C. Bai (Berlin/DE), Z. Zhang (Berlin/DE), P. Adelhelm (Berlin/DE)	O 07
16:50	Hydroborate Solid-State Lithium Battery With High-Voltage NMC811-Cathode	**Hugo Braun** (Duebendorf/CH), R. Asakura (Duebendorf/CH), A. Remhof (Duebendorf/CH), C. Battaglia (Duebendorf/CH)	O 08
17:10	Expanding the Practical Stability Window of Halide Solid Electrolytes via Beneficial Redox Activities	**Zhu Cheng** (Delft/NL), W. Zhao (Delft/NL), M. Wagemaker (Delft/NL)	O 09
17:30	Role of Grain-Level Chemo-Mechanics in Composite Cathode Degradation of Solid-State Lithium Batteries	**Chuanlai Liu** (Düsseldorf/DE), F. Roters (Düsseldorf/DE), D. Raabe (Düsseldorf/DE)	O 10
17:50	Poster Speed Talks I		
18:20	Poster Session I - "Dinner@Poster"		

Thursday, Nov. 14, 2024

Session II: Electrode Interfaces and Characterization

08:30	KEYNOTE LECTURE Ductile Super-Ionic Conductors for All-Solid-State Lithium Batteries	**Linda F. Nazar** (Waterloo/CA)	O 11
09:15	INVITED LECTURE Understanding the Evolution of Anode Materials and Interfaces in Solid-State Batteries	**Matthew T. McDowell** (Atlanta/US)	O 12
09:45	INVITED LECTURE Impact of Particle Size Distribution and Densification on the Development of Solid-State Pouch Cells	**Daniel Rettenwander** (Trondheim/NO)	O 13
10:15	Coffee Break		
10:45	In situ Characterization of Alkali Metal Battery Interfaces Using Advanced Analytical Methods	**Anja Henss** (Gießen/DE), T. Meyer (Gießen/DE), A. Weiss (Gießen/DE), T. Weintraut (Gießen/DE), B. Aktekin (Gießen/DE)	O 14
11:05	Operando X-Ray Computed Tomography of Lithium Plating and Stripping in Zero-Excess Lithium Metal Solid-State Batteries	**Linfeng Xu** (Villingen/CH), J. Zhang (Villingen/CH), J. Le Houx (Didcot/UK), V. Kachkanov (Didcot/UK), T. J. Schmidt (Villingen/CH), M. El Kazzi (Villingen/CH)	O 15
11:25	Microstructure of Lithium Metal Electrodeposited at the Steel|Li_6PS_5Cl Interface in Solid-State Batteries	**Juri Becker** (Gießen/DE), T. Fuchs (Gießen/DE), T. Ortmann (Gießen/DE), S. Kremer (Gießen/DE), F. H. Richter (Gießen/DE) and J. Janek (Gießen/DE)	O 16
11:45	Pressure-Dependent Mechano-Electrochemical Failure Mechanisms of Anode-Free Solid-State Batteries	**Jianneng Liang** (Ulm/DE), A. Varzi (Ulm/DE)	O 17
12:05	Lithium-Rich Alloy Electrodes for Solid State Batteries.	**Jack Aspinall** (Oxford/UK), M. Pasta (Oxford/UK)	O 18
12:25	Lunch		

Session III: Cell Concepts and Characterization

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14:10	INVITED LECTURE Chloride Electrolytes: A Perspective on Structure, Ion Conduction, Reactivity, and Cell Performance	**Raphaële Clément** (Santa Barbara/US), E. Sebti (Santa Barbara/US), T. Pennebaker (Santa Barbara/US), P. Richardson (Santa Barbara/US), E. Wu (Chicago/US), P. Ridley (Chicago/US), Y. S. Meng (Chicago/US), S. Banerjee (San Diego/US), J. Qi (San Diego/US), S. P. Ong (San Diego/US), H. Evans (Gaithersburg/US), C. Brown (Gaithersburg/US), A. Mondal, H. Chen (Singapore/SG), P. Canepa (Singapore/SG), T. Cheetham (Santa Barbara/US), K. P. Koirala (Richland/US), Y. Xu (Richland/US), C. Wang (Richland/US)	O 20
14:40	INVITED LECTURE Challenges of All-Solid-State Battery for EV Application	**Koichiro Aotani** (Yosuka/JP)	O 21
15:10	Operando Characterisation of Dendrites in Single-Crystal LLZO	**Diana Avadanii** (Karlsruhe/DE), S. Lang (Karlsruhe/DE), S. Ganschow (Berlin/DE), D. Kramer (Karlsruhe/DE), R. Moenig (Karlsruhe/DE), C. Kirchlechner (Karlsruhe/DE)	O 22
15:30	Using Resistor Network Models To Predict the Transport Properties of Solid-State Battery Composite Electrodes	**Lukas Ketter** (Münster/DE), W. G. Zeier (Münster/DE)	O 23
15:50	Coffee Break		
16:20	Deciphering the Influence of Pressure, Heat Treatment, and Coating on the Electronic Conductivity of Active Materials for All-Solid-State Batteries	**Vanessa Miß** (Marburg/DE), S. Seus (Marburg/DE), E. D. Steyer (Marburg/DE), A. Marx (Marburg/DE), B. Roling (Marburg/DE)	O 24

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16:40	KEYNOTE LECTURE Insights Into Performance and Durability of Garnet Solid Electrolytes From Multiscale Simulations	**Brandon C. Wood** (Livermore/US)	O 25
17:25	INVITED LECTURE Lithium, Speed & Interfaces - Designing Next Solid Battery Materials Real Fast With High Control of Chemistry	**Jennifer L. M. Rupp** (München/DE)	O 26
17:55	Drawing the Landscape for Ion Diffusion in Solid-State Electrolytes	**Amber Mace** (Uppsala/SE)	O 27
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18:45	Poster Session II - "Dinner@Poster"		

Friday, Nov. 15, 2024

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09:15	INVITED LECTURE Solid Electrolytes: From Mine to Cell	**Christoph Hartnig** (Frankfurt/DE), Vera Nickel (Frankfurt/DE)	**O 29**
09:45	Perspective on Warm Isostatic Pressing for Mass Production of Solid-State Batteries	**Timo Rabe** (Västerås/SE), M. Dixit (Oak Ridge/US), C. Beamer (Columbus/US), J. Shipley (Västerås/SE), J. Fischer (Västerås/SE), I. Belharouak (Oak Ridge/US)	**O 30**
10:05	Insights on Electrochemical Sodium Storage in Sodium/Sodium-Ion Batteries by Advanced in situ and ex situ Solid-State NMR	**Torsten Gutmann** (Darmstadt/DE), E. Šić (Darmstadt/DE), M. Melzi d'Eril (Darmstadt/DE), K. Schutjajew (Jena/DE), M. J. Graczyk-Zajac (Darmstadt/DE), H. Breitzke (Darmstadt/DE, M. Oschatz (Jena/DE), G. Buntkowsky (Darmstadt/DE)	**O 31**
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10:50	A Mechanistic Insight Into the Cascade Dissolution and Coprecipitation Process in the Wet Synthesis of Argyrodite Li_6PS_5Cl	Seunggu Kim (Daejeon/KR), Mukarram Ali (Changwon/KR), Yoon-Cheol Ha (Changwon/KR), **Hye Ryung Byon** (Daejeon/KR)	**O 32**
11:10	Scalable Mechanochemical Synthesis of Sulfide-Based Solid Electrolytes	**Michael Grube** (Braunschweig/DE), M. Witt (Münster/DE), J. Schubert (Gießen/DE), S. Zellmer (Braunschweig/DE), A. Kwade (Braunschweig/DE)	**O 33**
11:30	Functional Magnesium and Calcium Electrolytes for Solid-State Batteries	**Torben R. Jensen** (Aarhus/DE), T. Kjær (Aarhus/DE), J. Grinderslev (Aarhus/DE), M. Amdisen (Aarhus/DE), P. Dansirima (Aarhus/DE), L. Kristensen (Aarhus/DE)	**O 34**
11:50	Solid Electrolyte Design Through Anion Sublattice Engineering: A Case Study of Oxyhalides	**Saneyuki Ohno** (Sendai/JP), Z. Huang (Sendai/JP), N. Yadav (Golden/US), P. Gorai (Golden/US)	**O 35**
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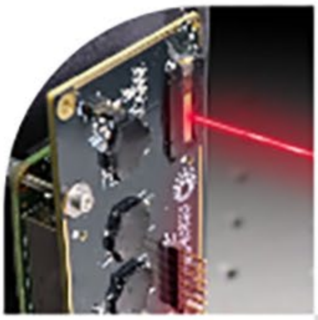
12:50	Concluding Remarks		
13:00	Lunch and Departure		



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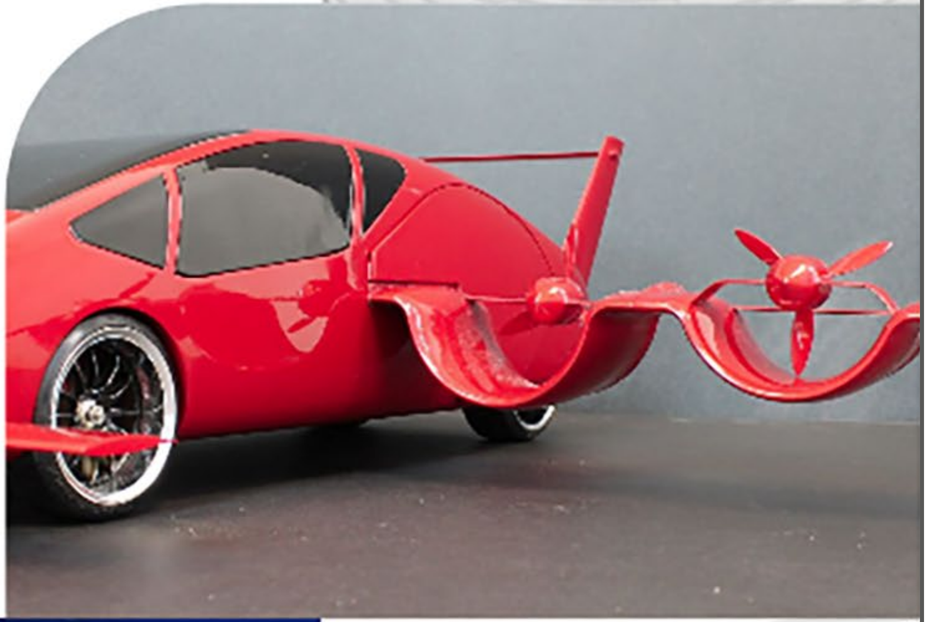

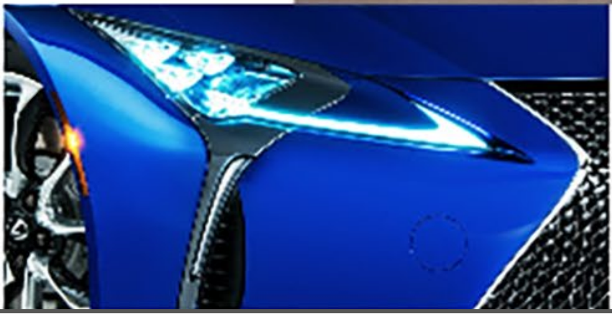

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Christoffer Karlsson (Darmstadt/DE), M. Schöll (Darmstadt/DE), M. Drüschler (Darmstadt/DE), M. Soans (Ulm/DE); D. Bresser (Ulm/DE), A. Varzi (Ulm/DE), B. Huber (Darmstadt/DE)

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Hao Guo (Bayreuth/DE), M. Häfner (Bayreuth/DE), H. Grüninger (Bayreuth/DE), M. Bianchini (Bayreuth/DE)

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T. Kolesnikov (Karlsruhe/DE), D. Voll (Karlsruhe/DE), F. Jeschull (Eggenstein-Leopoldshafen/DE), P. Theato (Karlsruhe/DE)

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Nina Hoinkis (Mainz/DE), J. Schuhmacher (Mainz/DE), S. Leukel (Mainz/DE), C. Loho (Mainz/DE), A. Roters (Mainz/DE), F. H. Richter (Gießen/DE), J. Janek (Gießen/DE)

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Johannes Hartel (Münster/DE), W. G. Zeier (Münster/DE)

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Ulf-Christian Rauska (Eggenstein-Leopoldshafen/DE), C. Röder (Eggenstein-Leopoldshafen/DE), T. Kolesnikov (Eggenstein-Leopoldshafen/DE), F. Jeschull (Eggenstein-Leopoldshafen/DE)

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Cerun Alex Varkey (Braunschweig/DE), C. Gavagnin (Braunschweig/DE), S. Melzig (Braunschweig/DE), C. Schilde (Braunschweig/DE), S. Zellmer (Braunschweig/DE)

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Thomas Demuth (Marburg/DE), S. Ahmed (Marburg/DE), P. Kurzhals (Gießen/DE), J. Haust (Marburg/DE), A. Beyer (Marburg/DE), J. Janek (Gießen/DE), K. Volz (Marburg/DE)

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Franziska Hüppe (Marburg/DE), J. Becker (Gießen/DE), J. Belz (Marburg/DE), S. Ahmed (Marburg/DE), T. Fuchs (Gießen/DE), B. Aktekin (Gieße/DE), J. Janek (Gießen/DE), K. Volz (Marburg/DE)

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Sabrina Lang (Eggenstein-Leopoldshafen/DE), D. Avadanii (Eggenstein-Leopoldshafen/DE), D. Kramer (Eggenstein-Leopoldshafen/DE), L. Hennerici (Bayreuth/DE), M. Linz (Bayreuth/DE), J. Kita (Bayreuth/DE), R. Moos (Bayreuth/DE), Reiner Mönig (Eggenstein-Leopoldshafen/DE)

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Andre Borchers (Forchheim/DE), R. Tripathi (Oberkochen/DE), B. Linn (Oberkochen/DE) E. Reisacher (Aalen/DE), P. Kaya (Aalen/DE), S. Christiansen (Forchheim/DE), R. Zarnetta (Oberkochen/DE)

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Mervyn Soans (Ulm/DE), C. Karlsson (Darmstadt/DE), M. Schöll (Darmstadt/DE), B. Huber (Darmstadt/DE), D. Steinle (Ulm/DE), D. Bresser (Ulm/DE), A. Varzi (Ulm/DE)

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Valerie Siller (Villigen/CH), R. Wullich (Villigen/CH,) B. Lelotte (Villigen/CH), C. A. F. Vaz (Villigen/CH), C. Jordy (Levallois-Perret/FR), V. Pelé (Levallois-Perret/FR), M. El Kazzi (Villigen/CH)

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Tommi Aalto (Stuttgart/DE), O. Clemens (Stuttgart/DE)

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Priya Ganesan (Ulm/DE), M. Soans (Ulm/DE), M. A. Cambaz (Ulm/DE), R. Zimmermanns (Karlsruhe/DE), R. Gond (Uppsala/SE), S. Fuchs (Karlsruhe/DE), Y. Hu (Ulm/DE), S. Baumgart (Ulm/DE), M. Sotoudeh (Ulm/DE), D. Stepien (Ulm/DE), H. Stein (Karlsruhe/DE), A. Gross (Ulm/DE), D. Bresser (Ulm/DE), A. Varzi (Ulm/DE), M. Fichtner (Ulm/DE)

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Naohiro Horiuchi (Ageo/JP), T. Koketsu (Ageo/JP), T. Ito (Ageo/JP), N. Miyashita (Ageo/JP)

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Shiori Kawasaki (Sendai/JP), I. Honma (Sendai/JP), S. Ohno (Sendai/JP)

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Feng Jin (Trondheim/NO), I. Ellingsen (Trondheim/NO), H. Rotvær Bratlie (Trondheim/NO), D. Rettenwander (Trondheim/NO)

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Jaedong Kim (Daejon/KR), H. R. Byon (Daejon/KR)

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E. Sánchez Ahijón (Madrid/ES), A. Pendashteh (Madrid/ES), Juan Vilatela (Madrid/ES)

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Kiran Romaus (Gründau/DE), F. Hartmann (Gießen/DE), A. Lorenzoni (Böblingen/DE)

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A. Dupuy (Dresden/DE), B. Schumm (Dresden/DE), Felix Hippauf (Dresden/DE), T. Abendroth (Dresden/DE), H. Althues, S. Kaskel (Dresden/DE)

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Maria Rosner (Dresden/DE), A. Dupuy (Dresden/DE), F. Hippauf (Dresden/DE), S. Dörfler (Dresden/DE), H. Althues (Dresden/DE), S. Kaskel (Dresden/DE)

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Johannes Schachtl (Munich/DE), L. Wach (Munich/DE), E. Jaimez-Farnham (Munich/DE), R. Daub (Munich/DE)

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Andriy Kvasha (Donostia-San Sebastián/DE), M. Álvarez (Donostia-San Sebastián/DE), O. Garcia-Calvo (Donostia-San Sebastián/DE), M. Cobos (Donostia-San Sebastián/DE), I. Combarro (Donostia-San Sebastián/DE), I. Landa-Medrano (Donostia-San Sebastián/DE), L. Ganborena (Donostia-San Sebastián/DE), I. Urdampilleta (Donostia-San Sebastián/DE)

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David Laughman (Waltham/UK), M. Su (Hangzhou/CN), H. Van Benschoten (Waltham/UK)

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Yannic Collette (Jülich/DE), M. Finsterbusch (Jülich/DE), O. Guillon (Jülich/DE), D. Fattakhova-Rohlfing (Jülich/DE)

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Christoph Alt (Giessen/DE), N. Mueller (Giessen/DE), L. M. Riegger (Giessen/DE), B. Aktekin (Giessen/DE), P. Minnmann (Giessen/DE), K. Peppler (Giessen/DE), J. Janek (Giessen/DE)

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Asvitha Ramanayagam (Marburg/DE), V. Miß (Marburg/DE), B. Roling (Marburg/DE)

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Niklas Abke (Münster/DE), A. T. Strohschein (Münster/DE), K. Kuratani (Osaka/JP), T. Takeuchi (Osaka/JP), Y. Ito (Osaka/JP), M. Winter (Münster/DE), S. Nowak (Münster/DE), S. Wiemers-Meyer (Münster/DE)

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Arndt Strohschein (Münster/DE), N.M. Abke (Münster/DE), U. Rodehorst (Münster/DE), M. Winter (Münster/DE), S. Wiemers-Meyer (Münster/DE)

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Kotaro Yoshida (Kanagawa/JP), A. Ikezawa (Kanagawa/JP), T. Okajima (Kanagawa/JP), Hajime Arai (Kanagawa/JP)

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Ajay Gautam (Delft/NL), V. Kannan (Delft/NL), M.Wagemaker (Delft/NL)

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Pranav Karanth (Delft/NL), J. H. Prins (Delft/NL), A. Gautam (Delft/NL), Z. Cheng (Delft/NL), S. Ganapathy (Delft/NL), M. Wagemaker (Delft/NL), F. M. Mulder (Delft/NL)

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Cristina Garcia (Madrid/ES), Ricardo Jiménez (Madrid/ES), J.A. Alonso (Madrid/ES), J. Kilner (London/UK), R. Chater (London/UK), A. Panagiotopoulos (London/UK), A. Aguadero (Madrid/ES)

P 238 **Interfacial Stabilization by Prelithiated Trithiocyanuric Acid as an Organic Additive in Sulfide-Based All-Solid-State Lithium Metal Batteries**
Leonie Braks (Fribourg/CH), J. Zhang (Villigen/CH), Ali Coskun (Fribourg/CH)

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Matthias Klimpel (Zürich/CH), H. Zhang (Zürich/CH), K. Wieczerzak (Thun/CH), R. Dubey (Zürich/CH), F. Okur (Zürich/CH), J. Michler (Thun/CH), L.P.H. Jeurgens (Dübendorf/CH), D. Chernyshov (Grenoble/FR), W. van Beek (Grenoble/FR), K. V. Kravchyk (Zürich/CH), M. V. Kovalenko (Zürich/CH)

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Matthew Burton (Oxford/UK), Y. Lang (Oxford/UK), J. Aspinall (Oxford/UK), B. Jagger (Oxford/UK), M. Pasta (Oxford/UK)

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Lars Pateras Pescara (Darmstadt/DE), M. Drüschler (Darmstadt/DE), F. Kalyk (Jülich/DE), N. M. Vargas Barbosa (Bayreuth/DE), W. Zeier (Jülich/DE)

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Soutam Panja (Ulm/DE), Anantha Gopikuttan (Ulm/DE), Amr Radwan (Ulm/DE), Maximillian Fichtner (Ulm/DE)

P 243 **The Riddle of Succinonitrile Based Polymer Electrolytes: An NMR Perspective**
Meera Mohankumar (Delft/NL), P. Karanth (Delft/NL), F. Ooms (Delft/NL), S. Ganapathy (Delft/NL), M. Wagemaker (Delft/NL)

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V. Landgraf (Delft/NL), M. Tu (Delft/NL), Z. Cheng (Delft/NL), J. de Leeuw (Delft/NL), S. Ganapathy (Delft/NL), T. Famprikis (Delft/NL), Marnix Wagemaker (Delft/NL)

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Wenxuan Zhao (Delft/NL), E. van der Maas (Delft/NL), S. Ganapathy (Delft/NL), M. Wagemaker (Delft/NL)

P 246 **Degradation Mechanisms in $LiFePO_4$-Based All-Solid-State Batteries Containing a Hybrid Electrolyte With Garnet $Li_7La_3Zr_2O_{12}$ Designed for Maritime Applications**
Jeyhun Abbasov (Enschede/NL), Q. Qiu (Enschede/NL), M. Huijben (Enschede/NL), A. ten Elshof (Enschede/NL)

P 247 **Tape Casting Li_6PS_5Cl: Effect of Particle Size Distribution and Densification Pressure**
Meenal Agrawal (Trondheim/NO), Q.A. Tran (Trondheim/NO), M. Hausler (Leoben/AT), I.S. Ellingsen (Trondheim/NO), J. Todt (Leoben/AT), L. Fadillah (Trondheim/NO), P.E. Vullum (Trondheim/NO), M.M.U. Din (Trondheim/NO), R. Zettl (Graz/AT), V. Henninge (Graz/AT), J. Keckes (Leoben/AT), R. Brunner (Leoben/AT), D. Rettenwander (Trondheim/NO)

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Seunggu Kim (Daejeon/KR), M. Ali (Changwon/KR), S. Kim (Daejeon/KR), Y. Choi (Pohang/KR), Y.-C. Ha (Changwon/KR), H. R. Byon (Daejeon/KR)

P 249 **Potassium-Ion Conducting Chloride Solid Electrolyte with High Voltage Stability**
Changhoon Kim (Seoul/KR), J. Park (Seoul/KR), H. Kwak (Seoul/KR), J.-S. Kim (Daejeon/KR), S. Jun (Seoul/KR), B. Jang (Seoul/KR), J. Jeon (Seoul/KR), S. Bong (Seoul/KR), D.-H. Seo (Daejeon/KR), Y. S. Jung (Seoul/KR)

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Raul Artal (Madrid/ES), H.L. Andersen (Madrid/ES), J.A. Alonso (Madrid/ES), R. Jiménez (Madrid/ES), A. Aguadero (Madrid/ES)

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Maica Morant-Miñana (Vitoria-Gasteiz/ES), E. Sasieta-Barrutia (Vitoria-Gasteiz/ES), J. Blanco (Vitoria-Gasteiz/ES), M. Armand (Vitoria-Gasteiz/ES), L. Otaegui (Vitoria-Gasteiz/ES), A. Villaverde (Vitoria-Gasteiz/ES)

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R. Asakura (Dübendorf/CH), Z. Lodziana (Krakow/PL), D. Rentsch (Dübendorf/CH), C. Battaglia (Dübendorf/CH), Arndt Remhof (Dübendorf/CH)

P 253 **Reducing Overpotential in Quasi-Solid-State Lithium Sulfur Batteries by Integrating Solid-State Electrolyte into the Cathode Slurry**
Boyi Pang (London/UK), H. Li (London/UK), J.B. Robinson (London/UK)

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Yaoguang Song (London/UK), A. Rettie (London/UK)

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Jemma L. Cox (Newcastle upon Tyne/UK)

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P 257 **A High-Throughput Technique for Unidirectional Critical Current Density Testing of Solid Electrolyte Materials**
Alireza Torabi (San Jose/US), D. M. Gendron (San Jose/US), M. Wanees (San Jose/US), M. Savio Dsouza (San Jose/US), B. Feddersen (Hamburg/DE), T. Holme (San Jose/US)

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Ali Mohammad Bazzoun (Stuttgart/DE), J. Piruzjam (Stuttgart/DE), S. Hink (Stuttgart/DE), L. Rubaceck (Stuttgart/DE), A. Fill (Stuttgart/DE), P. Birke (Stuttgart/DE)

P 259 **Influence of Layered Electrode Designs on the Performance of All-Solid-State Batteries**
J. Drews (Ulm/DE), E. Schlautmann (Münster/DE), M. Clausnitzer (Ulm/DE), T. Danner (Ulm/DE), W. Zeier (Münster/DE), Arnulf Latz (Ulm/DE)

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Anastasia. K. Lavrinenko (Delft/NL), T. Famprikis (Delft/NL), J. A. Quirk (Berlin/DE), V. Landgraf (Delft/NL), P. B. Groszewicz (Delft/NL), J. R. Heringa (Delft/NL), J. A. Dawson (Berlin/DE), M. Wagemaker (Delft/NL), A. Vasileiadis (Delft/NL)

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Ana Carolina Coutinho Dutra (Newcastle/UK), J. Quirk (Newcastle/UK), Y. Zhou (Newcastle/UK), J. Dawson (Newcastle/UK)

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Jingxuan Zhang (Muenster/ DE), J. Huang (Muenster/ DE), W. Zeier (Muenster/DE)

P 263 **Impact of Cathode Design on All-Solid-State Sodium-Sulfur Battery Performance**
Stefano Tagliaferri (Berlin/DE), R. Healy Corominas (Berlin/DE), F. Piccolo (Berlin/DE), P. Adelhelm (Berlin/DE)

P 264 **The Role of Nanoporous Carbon Materials for Thiophosphate-Based All-Solid-State Lithium Sulfur Battery Performance**
Magdalena Fiedler (Dresden/DE), F. Hippauf (Dresden/DE), S. Dörfler (Dresden/DE), H. Althues (Dresden/DE), S. Kaskel (Dresden/DE)

P 265 **Identification and Quantification of Kinetic Limitations of Thiophosphate-Based Solid-State Cathodes by Chronoamperometry**
S. Yanev (Dresden/DE), Markus Pöthe (Dresden/DE), K. Nikolowski (Dresden/DE), M. Partsch (Dresden/DE), A. Michaelis (Dresden/DE)

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ABSTRACTS (ORAL)

Efforts From Semi-Solid to All Solid Lithium Batteries Via *in situ* Solidification Technologies

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Developing lithium ion batteries with high energy density, high power density, high safety, long cycle life, wide operation temperature, low cost and large production ability is an important target for various emerging applications. ASSB is regarding as the most promising direction. There are several possible technological solutions. The commercialization time of ASSB have been claimed from 2026-2030 by several famous manufacturers. We had purposed to scale up in-situ solidification technology for LIB since 2016. Semi-solid or ASSB cell have been developed based on this technology. The main advantage is to solve the solid/solid contact and form continuous ion paths in the cell during the whole operation life. In order to improve the safety, rate performance and energy density of LIB, the layered cathode coated by solid electrolyte or mixed ionic conductor, solid electrolyte coated separator, low expansion nano-Si/C anode with high capacity, anode prelithiation, in situ solidification have been developed and demonstrated. Consequently, LIB for 3C, drone, EV and energy storage have been developed. In this report, we will update related progresses on LIB using in situ solidification technology, from semi-solid to ASSB.

Columnar Si Anodes for Sulfide-Based All-Solid-State-Batteries

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While sulfide solid electrolytes provide outstanding properties including high ionic conductivity exceeding 3 mS/cm, there is still a need for innovations in processing and design of electrodes and cells for the development of stable high energy all-solid-state batteries.

We report on 100 % silicon anodes with a columnar film morphology being deposited via physical gas phase deposition. Si films with a thickness of several µm were applied as stable high energy anode concept in single- and multi-layer pouch cells with NMC / LPSCl composite cathodes and LPSCl solid electrolyte membranes [1]. The cycling performance was studied in dependence of temperature and external pressure revealing high rate capability up to 4 C and cycle life up to 1.000 cycles even at reduced external pressure as low as 5 MPa. Further, the columnar silicon anode concept has been successfully transferred to Li_2S / Si all-solid-state full (pouch) cells revealing reversible cycling and promising energy density.
Another key process innovation is the solvent free manufacturing of all solid state composite cathodes (both NCM-, as well as Li_2S based) based on fibrillated binder [2]. Here, we demonstrate the scalability of the dryfilm concept by roll-to-roll experiments using the DRYtraec® process.

Literature:

[1] S. Cangaz et al. Adv. Energy Mater. 2020, 10, 2001320
[2] F. Hippauf et al. Energy Storage Materials 21 (2019) 390 – 398

CATL R&D - Insights into high-energy chemistries

Ulderico ULISSI, Ningde/CH

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21st Century (21C) innovation laboratory is the world-class crucible of innovation for the energy transition operated by market leader Contemporary Amperex Technology Co., Limited (CATL). 21C is a crossroad for academic research and industrial development. A key focus is commercializing battery cells with specific energies of 400-550 Wh/kg and uncompromised safety and cost. Achieving this will likely require using lithium metal negative electrodes integrated into battery cells manufactured at the industrial scale (TRL9+). This is both an open challenge in our field and a potential game changer for society, as it could enable electrification of notoriously hard-to-abate sectors, such as electric aviation. This presentation will offer insights into the CATL R&D system and highlight some of the latest research while providing an industrial perspective on the development of lithium metal batteries.

Literature:

[1] Rate-Dependent Failure Mechanisms and Mitigating Strategies of Anode-Free Lithium Metal Batteries, H. Wang, et al., ACS Applied Materials & Interfaces, (2023) 15 (10), 12967-12975, DOI: 10.1021/acsami.2c20422

[2] Quantifying Interfacial Reactions in Lithium Metal Batteries for a New Paradigm of Long-Cycling Electrolyte Designs, H. Wang, et al., (2024) 10.21203/rs.3.rs-3855314/v1.

Printed all-solid-state Na-ion batteries based on hydroborates

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In the search of new electric storage technologies, sodium-ion batteries (SIBs) have attracted huge interest due to the possibility to create high performance batteries without scarce elements. However, the theoretical energy density of the liquid electrolyte system is only around half of that of a lithium-ion battery. One way to bypass/tackle this issue can be the application of a sodium metal anode. Similar to the lithium system this seems to be possible only with a solid electrolyte.

Beside the, for the lithium system commonly investigated, classes of oxides, sulfides and polymers another class of electrolytes have been identified. The hydroborate $Na_2(B_{10}H_{10})_{0.5}(B_{12}H_{12})_{0.5}$ has shown excellent ionic conductivities over 1 mS/cm at room temperature with an electrochemical stability window of 0 – 3 V vs Na/Na^+ thus, making them perfect for the usage of metallic sodium [1].

In this contribution, we are going to show the processing of all-solid-state SIBs based on hydrobrates via screen-printing. This technique is especially suited for producing customized cell sizes, while manufacturing the cells layer-by-layer. It is important to understand the necessary pressure steps for achieving working components in between the subsequent printing steps to achieve the best possible ionic conductivity [2]. Different routes either dissolving the electrolyte or processing the electrolyte as solid particles will be shown and electrochemically compared. Finally, a fully printed battery cell will be presented.

[1] L. Duchêne, A. Remhof, H. Hagemann, C. Battaglia, Energy Storage Materials, 25, 2020, 782-794

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Polymer electrolytes at interfaces in hybrid systems: impact on ion transport

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Ion transport in polymer electrolytes near interfaces is generally very different from that in bulk systems. Since interfaces play an essential role in batteries, a thorough understanding of the underlying mechanisms is of utmost importance. In this talk we discuss three different scenarios for which we unravel the relevant mechanisms via extensive molecular dynamics simulations.

(1) For polymeric systems the presence of interfaces determines the free energy landscape and thus the dynamics of lithium ions close to the interface [1]. By changing the length of the polymers one can clearly identify polymer specific effects on the free energy landscape and the consequences for the lithium dynamics.

(2) Recently, in collaboration with the groups of Brunklaus and Latz, it was observed that the ionic conductivity of the polymer electrolyte PCL increases when Al2O3 particles with polymers grafted on their surface are added. Here we discuss the ion transport near the oxide-polymer interface and rationalize that experimental observation.

(3) Even more complex is the situation when additional cation transport is possible between the oxide and the polymer electrolyte [2]. Here we show for the model system of LLZO-PEO how the two components of that hybrid system have an impact on each other in terms of structure and ion transport.

Literature:
[1] A. Thum, A. Heuer, D. Diddens, J. Phys. Chem. C 2021, 125, 25392.
[2] M. Kozdra, D. Brandell, C. Moyses Araujo, A. Mace, Phys. Chem. Chem. Phys. 2024, 26, 6216.

Operando FIB-SEM revealing the dynamics of morphological changes occurring in positive electrode composite in solid-state battery

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Thiophosphates have emerged as a promising solid electrolyte for solid-state battery technology, provided that both electronic and ionic transport properties within the composite electrode can be effectively controlled [1]. However, the cycling process induces various chemo-mechanical degradations that impede the transport properties [2]. In order to track the dynamics of such degradation processes, the development of a specific *operando* FIB-SEM approach enables imaging during cycling, facilitating the dynamic morphological investigation of a composite electrode comprising $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) coupled with amorphous Li_3PS_4. This methodology allows for the identification of mechanical stress experienced by both the electroactive materials and the electrolyte during cycling. Moreover, we monitored the microstructural evolution of polycrystalline NMC622 during charge and discharge, revealing its poor adaptability to solid-state batteries and emphasising the importance of better controlling interface adhesion to enhance electrochemical performance.

Literature:

[1] Janek, J. & Zeier, W. G. Challenges in speeding up solid-state battery development. Nat. Energy 8, 230–240 (2023).
[2] Perrenot, P., Bayle-Guillemaud, P. & Villevieille, C. Composite Electrode (LiNi0.6Mn0.2Co0.2O2) Engineering for Thiophosphate Solid-State Batteries: Morphological Evolution and Electrochemical Properties. ACS Energy Lett. 4957–4965 (2023) doi:10.1021/acsenergylett.3c01975.

Understanding the Morphological, Structural, and Redox Behavior of Metal Sulfides as Cathode Active Materials in Solid-State Batteries

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One bottleneck in the development of solid-state battery (SSB) technologies is the cathode active material (CAM). Layered oxide materials commonly utilized in other lithium-ion battery technologies are quickly approaching their limits in terms of capacity. It is also clear that realizing the benefits of lithium metal anodes in SSBs necessitates the use of high-capacity conversion-type cathodes. Sulfides offer an intriguing direction for further research because they can reversibly contribute to charge storage through stable anion redox ($2S^{2-} \rightarrow (S_2)^{2-} + 2e^-$), which can help boost capacity despite their low operating voltage windows. Understanding the charge storage process and material changes in SSBs under realistic operating conditions is challenging, due to the high stacking pressures applied during cycling when evaluating new materials. We have recently been developing a variety of incisive tools that enable us to evaluate the morphological, structural, and redox behavior of our CAMs under operating conditions in SSBs through computed X-Ray tomography, X-Ray diffraction, and X-Ray absorption and photoemission spectroscopies. In this talk I will discuss our recent work on understanding charge storage and structural changes in metal sulfide-based CAMs for SSBs through a combination of ex-situ and in-situ analysis. I will detail our findings on CuS, which undergoes a macroscopic displacement reaction during lithiation, whereby micron-sized Cu networks form, which we were able to follow by in-situ synchrotron-based X-Ray tomography.[1] Despite the large volume expansion of 75% and unique displacement mechanism, CuS-based cells show surprisingly stable cycling behavior, maintaining a capacity of 305 mAh/g over 100 cycles.[2] We investigate further structural stabilization through implementation of ternary compositions such as Cu_3PS_4 and $CuFeS_2$ and find that in both cases we are able to promote stable cycling behavior (maintaining a capacity of 508 mAh/g over 60 cycles for Cu_3PS_4 and

Hydroborate Solid-State Lithium Battery with High-Voltage NMC811 Cathode

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Hydroborate solid electrolytes offer high ionic conductivity and are stable in contact with alkali metal anodes but are challenging to integrate into batteries with high-voltage cathodes. Here, we demonstrate stable dis-/charge cycling of solid-state Li batteries combining a $Li_3(CB_{11}H_{12})_2(CB_9H_{10})$ hydroborate electrolyte with a 4 V-class $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) cathode, exploiting the enhanced kinetic stability of the $LiCB_{11}H_{12}$-rich and $LiCB_9H_{10}$-poor electrolyte composition. Cells with Li metal and InLi anodes achieve a discharge capacity at C/10 of ~145 mAh g^{-1} at room temperature and ~175 mAh g^{-1} at 60 °C (Figure 1). InLi cells retain 98% of their initial discharge capacity after 100 cycles at C/5 and 70% after 1000 cycles at C/2. Capacity retentions of 97% after 100 cycles at C/5 and 75% after 350 cycles at C/2 are also achieved with a graphite anode without any excess Li. The energy density per cathode composite weight of 460 Wh kg^{-1} is on par with the best solid-state batteries reported to date. [1]

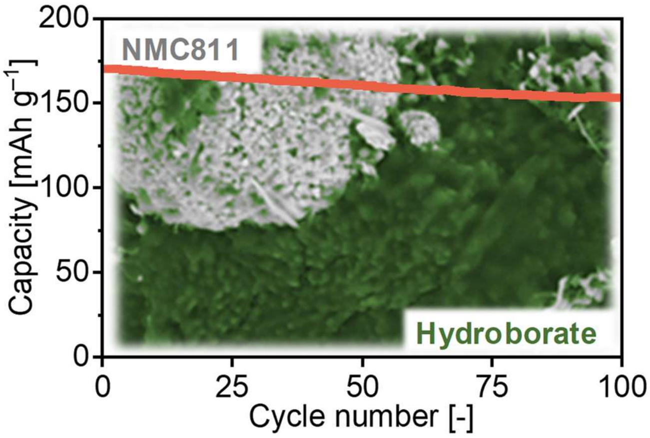

Figure 1. Discharge capacity over 100 cycles of the solid-state battery at 60 °C; SEM image of the NMC811 particles (grey) embedded in $Li_3(CB_{11}H_{12})_2(CB_9H_{10})$ electrolyte (green).[1]

Literature:

[1] Braun et al., ACS Energy Lett. 2024, 9, 707−714

Expanding the practical stability window of halide solid electrolytes via beneficial redox activities

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Solid electrolytes (SEs) exhibiting high ionic conductivity and wide electrochemical stability windows are crucial for the development of high-performance all-solid-state batteries (ASSBs). However, currently highly conductive SEs show unsatisfactory electrochemical stabilities. For example, sulfide SEs have a narrow stability window of 1.7~2.5 V; halide SSEs have excellent high-voltage stability but decompose at low voltages. Recently sulfide SEs are reported to show a decomposition behavior via an indirect way, first undergoing lithiation/delithiation process followed by decomposition into stable products [1-2]. Although this can lead to a slightly wide practical stability window, the poor conductivity of the decomposition products severely impedes the efficient ionic transport at the anode/SE interface, leading to poor performance of the ASSBs.

Unlike the decomposition of sulfide SEs, we demonstrate that halide SEs, such as monoclinic $Li_3YCl_3Br_3$ and trigonal Li_2ZrCl_6, exhibit redox activity beyond their thermodynamic stability window, through structurally reversible lithiation/delithiation behavior. This offers three key benefits: 1) an expanded practical stability window, allowing compatibility with low-voltage anodes, 2) additional capacity from their redox activity, and 3) enhanced ionic conductivity for the halide SEs after lithiation. These findings deepen our understanding of the intricate relationship between redox activity and electrochemical stability in SEs, paving the way for designing SEs that enable high-performance electrode/SE interfaces [3].

Literature:

[1] Schwietert, T. K. et al. Nat. Mater. 19, 428–435 (2020). [2] Schwietert, T. K., Vasileiadis, A. & Wagemaker, M. JACS Au 1, 1488–1496 (2021). [3] Cheng Z, et al ChemRxiv. (2024); doi:10.26434/chemrxiv-2024-x2rld

Role of grain-level chemo-mechanics in composite cathode degradation of solid-state lithium batteries

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Solid-state Li-ion batteries, based on Ni-rich oxide cathodes and Li-metal anodes, can theoretically reach a high specific energy of 393 Wh kg^{-1} and hold promise for electrochemical storage. However, Li intercalation-induced dimensional changes can lead to crystal defect formation in these cathodes, and contact mechanics problems between cathode and solid electrolyte. Understanding the interplay between cathode microstructure, operating conditions, micromechanics of battery materials, and capacity decay remains a challenge.

In this talk, we will present a microstructure-sensitive chemo-mechanical model to study the impact of grain-level chemo-mechanics on the degradation of composite cathodes [1]. We reveal that crystalline anisotropy, state-of-charge-dependent Li diffusion rates, and lattice dimension changes drive dislocation formation in cathodes and contact loss at the cathode/electrolyte interface. These dislocations induce large lattice strain and trigger oxygen loss and structural degradation preferentially near the surface area of cathode particles. Moreover, contact loss is caused by the micromechanics resulting from the crystalline anisotropy of cathodes and the mechanical properties of solid electrolytes, not just operating conditions. These findings highlight the significance of grain-level cathode microstructures in causing cracking, formation of crystal defects, and chemo-mechanical degradation of solid-state batteries.

Literature:
[1] Liu C, Roters F, Raabe D. Role of grain-level chemo-mechanics in composite cathode degradation of solid-state lithium batteries. ChemRxiv. 2024; doi:10.26434/chemrxiv-2024-2h7kn-v2

Ductile super-ionic conductors for all-solid state lithium batteries

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All-solid-state Li-ion batteries (ASSBs) have emerged as attractive alternatives to conventional liquid electrolyte cells for e-mobility, owing to their enhanced safety and higher energy densities. ASSBs are founded on high performance fast-ion conducting electrolytes, where halides and oxyhalides are particularly promising classes of materials owing to their unsurpassed interface stability with high voltage NMC-type cathodes. Oxyhalides show particular advantage owing to their excellent mechanical properties. The talk will focus on our recent understanding of superionic conductivity in new Li and Na-ion electrolytes in this class of materials using a combination of structural elucidation via X-ray/powder neutron diffraction, pair distribution function analysis, and *ab initio* molecular dynamics simulations. The talk will particularly highlight a new their application in solid state batteries and factors that govern the cathode-electrolyte interface.

Understanding the Evolution of Anode Materials and Interfaces in Solid-State Batteries

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ABSTRACT: Solid-state batteries offer the promise of improved energy density and safety compared to lithium-ion batteries. However, the electro-chemo-mechanical evolution of materials at solid-solid electrochemical interfaces is different than at solid/liquid interfaces, and contact evolution in particular plays a critical role in determining the behavior of solid-state batteries. Using X-ray tomography, cryo-FIB, and finite-element modeling, we show that anode-free solid-state lithium metal batteries are intrinsically limited by current concentrations at the end of stripping due to localized lithium depletion. This causes accelerated short circuiting compared to lithium-excess cells. Based on these results, the beneficial influence of metallic interfacial layers on controlling lithium evolution and mitigating contact loss from localized lithium depletion will be discussed. The second part of the talk focuses on alloy anodes. Alloy anodes typically exhibit fast capacity decay in lithium-ion batteries because of excessive solid-electrolyte interphase growth. We show that alloy anodes in solid-state batteries can exhibit improved interfacial stability and enhanced cyclability, but a comprehensive study on 12 alloy materials shows that lithium trapping is a key limitation for most materials. Further characterization of alloy anodes reveals the dynamic nature of interfacial fracture during reaction processes. Based on these insights, we present a new design for dense foil alloy anodes that uses multiple alloy phases to prevent trapping and improve performance. Taken together, these findings show the importance of controlling chemo-mechanics and interfaces in solid-state batteries for improved energy storage capabilities.

Impact of Particle Size Distribution and Densification on the Development of Solid-State Pouch Cells

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Solid-state batteries are widely regarded as a promising next-generation technology, addressing critical limitations of conventional Li-ion batteries, particularly safety concerns related to the flammable liquid electrolyte. Moreover, they offer the potential for higher volumetric and gravimetric energy densities compared to Li-ion systems.[1] Despite substantial progress in the development of solid-state batteries, scaling up from successful lab-scale cells to commercially viable pouch cells remain a significant challenge, especially when utilizing inorganic solid electrolytes.[2,3] For example, recent studies have demonstrated that the particle size ratio between the cathode material and the solid electrolyte plays a critical role in achieving low tortuosity, thereby enhancing power density.[4] However, commercially available materials often exhibit broad particle size distributions, with large particles that even exceed the thickness of the composite cathode, posing challenges for densification and leading to poor electrochemical performance.

In this talk, I will discuss our recent advances in optimizing the particle size distribution of Li_6PS_5Cl (LPSCl) electrolytes while maintaining their superior transport properties. Further, I will explore how particle size distribution affects the densification of slurry-cast LPSCl tapes and their corresponding Li-ion conductivities. Finally, I will share our progress in fabricating solid-state pouch cells with various cathodes (e.g., Si, LiIn), emphasizing the influence of LPSCl particle size distribution, pre-pressing conditions, and formation pressure on cell performance.

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In-Situ Characterization of Alkali Metal Battery Interfaces Using Advanced Analytical Methods

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Battery performance is strongly influenced by interfacial processes, particularly the formation of interphases, which affect ion transport and contribute to impedance growth and degradation. Understanding these interphases is critical to improving cell performance and requires advanced characterization techniques with high sensitivity and resolution. This is particularly important in solid-state batteries (SSBs) with alkali metal anodes such as lithium (Li) and sodium (Na), where the stability of solid electrolytes (SEs) against these reactive metals is challenged by interphase formation. A comprehensive understanding of the chemical composition, formation mechanisms, and evolution of these interphases is critical for improving battery efficiency.

Our research investigates the interphases between alkali metal anodes and flexible solid polymer electrolytes (SPEs), which offer advantages such as improved electrode contact and easier processability. However, the interfacial behavior, especially with Na, is still underexplored. To address this, we use a multi-analytical approach combining *in-situ* secondary ion mass spectrometry (SIMS), *in-situ* X-ray photoelectron spectroscopy (XPS) and coulometric titration time analysis (CTTA).[1] SIMS provides detailed insights into buried metal-SPE interfaces at the nanometer scale, while in-situ XPS reveals chemical degradation pathways, especially in ether-based SPEs, improving our understanding of their stability and failure mechanisms.

This multi-analytical framework using advanced in-situ techniques allows detailed temporal and spatial characterization of Li|SPE and Na|SPE interphases, providing deeper insights into their formation and degradation. These findings are critical for improving the stability and longevity of alkali metal-based batteries.

Literature

[1] Aktekin, Burak, et al. *Nature Communications* 14.1 (2023): 6946.

Operando X-ray Computed Tomography of Lithium Plating and Stripping in Zero-Excess Lithium Metal Solid-State Batteries

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Zero-excess Li metal solid-state batteries (ZELMSSBs) are often considered a promising route to further improve the energy density of all-solid-state batteries. Adding a nucleation layer like Ag on the current collector has been found to be helpful to regulate Li plating/stripping and mitigate the dendrites [1]. However, the underlying (electro)chemo-mechanical mechanisms still require deeper understanding. In this contribution, operando X-ray computed tomography (XCT), as a non-destructive technique, has been applied to visualize and quantify in real time the Li plating/stripping at the interface between the current collector and the solid electrolyte. The Li|LPSCl|Cu and Li|LPSCl|Ag/Cu asymmetric cells illustrated in Figure 1a) were cycled during the operando XCT measurements, with consecutive Li plating and stripping on/from from bare Cu (or 40 nm Ag on Cu) current collectors at various current densities.

An image-analyzing process based on image subtraction method (ISM) has been developed to visualize and quantify the plated/stripped Li. Unlike conventional segmentation method, ISM provides accurate Li quantification, validated by comparing the average Li thickness evolution between calculation from the XCT data and theoretical equivalence from the electrochemical data (Figure 1b). By analyzing the subtracted images, we revealed different Li plating/stripping morphology between bare Cu and Ag. For instance, at 1.2 mA/cm^2, the heterogeneous plating on Cu has induced spallation which is correlated with the cell failure, whereas the plating on Ag forms a dense Li layer with higher homogeneity (Figure 1c), allowing the plating current density to reach 1.8 mA/cm^2 without the formation of any visible cracks in the solid electrolyte. Nevertheless, the irreversible Li amount after stripping is 120% higher on Ag than on bare Cu, also consistent with the coulombic efficiency calculated from the electrochemical data.

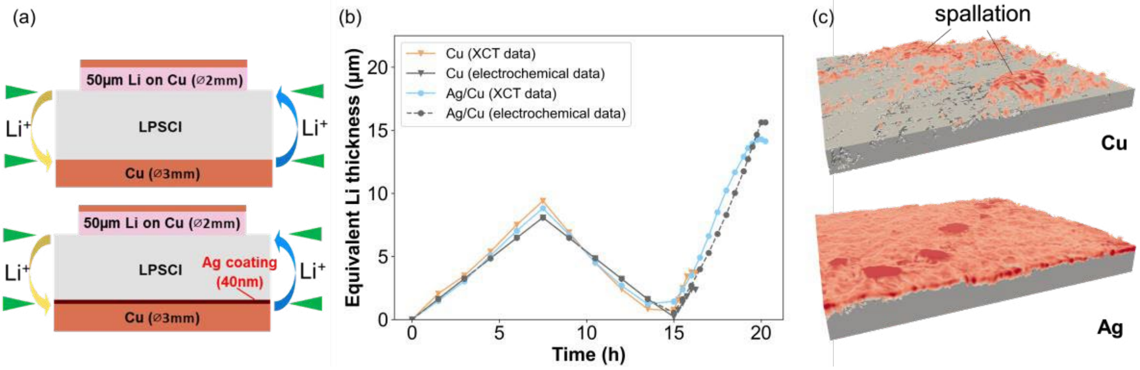

Figure 1 a) Schematics of the two cells measured in operando XCT experiments; b) equivalent Li thickness evolution of both cells by XCT and theoretical calculation; c) different Li-plating morphology on Cu (top) and 40 nm Ag (bottom)

Reference: [1] Choi, Hong Jun, et al. Advanced Science 9.1 (2022): 2103826.

Microstructure of Lithium Metal Electrodeposited at the Steel|Li_6PS_5Cl Interface in Solid-State Batteries

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Enhancing the energy density of state-of-the-art batteries could be achieved by utilizing lithium metal anodes.[1] However, due to the high reactivity of lithium, the fabrication process must be carefully controlled. To prevent degradation during storage and simplify handling, reservoir-free cells (RFCs) are explored.[2,3] In these cells, lithium metal is formed during the first charging cycle, using lithium stored within lithiated cathode materials. The electrochemical performance of the electrodeposited lithium film is closely linked to its microstructure, which can affect the amount of lithium that can be redissolved during subsequent cycles.[4,5] Despite its importance, the microstructure of electrodeposited lithium and methods to control it remain poorly understood.

To shine light on this aspect, we investigate the microstructure of electrodeposited lithium at the steel|Li_6PS_5Cl interface, focusing on the effects of applied current density and lithium layer thickness. The microstructure is characterized using a combination of cryogenic ion beam milling, scanning electron microscopy (SEM), and electron backscatter diffraction (EBSD). Making use of this reliable workflow[6], we reveal that the microstructure of electrodeposited lithium layers substantially differs from commercially available lithium foils. Instead of being randomly oriented, the electrodeposited films comprise a columnar structure with grains spanning the whole film thickness in all cases. Furthermore, our findings indicate that the microstructure of electrodeposited lithium layers with relevant thicknesses is not governed by nucleation, showing no clear dependency of applied electrodeposition current density and resulting grain size or density. Instead, a substantially larger grain size is observed for thicker electrodeposited lithium layers, revealing a lateral grain growth mechanism, which is discussed and described using a Monte-Carlo Potts model.

Our research provides deeper understanding of electrodeposited lithium films in reservoir-free cell setups. We think that having knowledge of the lithium microstructure will trigger further research on this topic, making it possible to pursue more advanced scientific research in this field.

Pressure-dependent Mechano-Electrochemical Failure Mechanisms of Anode-free Solid-State Batteries

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Anode-free solid-state lithium batteries (AFSSLB) have advantages of enhanced energy density, improved safety, and extended calendar life. The absence of anode active material also dramatically reduce costs. However, many problems arise as well. Without the hosting material, lithium(Li) deposits as metal directly on current collector (CC) surface with high nucleation energy and poor uniformity, resulting in Li dendrites and dead Li. Side reactions between Li metal and the electrolyte lead to further irreversible loss of lithium. The uneven Li deposition behaviour will also cause the formation of gaps/voids at the interface, resulting in a locally high current density. This further exacerbates the formation of Li dendrites. Li dendrites will penetrate SSE layer, making cracks, and undermining the electrochemical performance.[1]

In this work, we examined how stacking pressure influences Li deposition behaviour in AFSSLB. The stacking pressure is provided in a dynamically compensated manner, where the applied pressure will change with the change of cell pressure to keep stacking pressure a constant value. Our results show that stacking pressure is necessary for maintaining good interface contact, which is the premise for uniform Li deposition. Using focused ion beam, SEM, TEM and EDX studies, we found that the failure of AFSSLB is highly replated to the problems of (i) Li deposition on the porous SSE grain boundary, (ii) island-like Li deposition resulting in the formation of big gaps between Li islands, (iii) exposed Li reacting with the atmosphere of the interface spaces, resulting in the irreversible loss of active Li, and (iv) loss of CC/SSE contact due to the formation of solid electrolyte interphase.

Literature:
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Lithium-rich alloy electrodes for solid state batteries.

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Lithium alloys have the potential to overcome anode-side challenges in solid state batteries such as contact loss on discharge and current focusing on charge. This talk explores a range of lithium alloy anode chemistries including magnesium [1] and indium [2], to identify design criteria for high performance, high energy density lithium alloy electrodes. Magnesium solid-solution alloying is shown to affect the surface chemistry, mechanics and diffusion of lithium electrodes, which all contribute to the observed electrochemical behaviour. The addition of just 1% magnesium significantly enhances contact retention, without meaningfully slowing lithium transport, leading to enhanced performance over pure lithium in realistic low stack pressure operating conditions.

Indium alloys, specifically the two-phase InLi/In region, is shown to be an excellent counter/reference electrode. The microstructural evolution as a function of charge, quantified using x-ray tomography and electrochemical impedance spectroscopy, is tied to the observed electrochemical performance.

Insights from both indium and magnesium alloying are considered in designing lithium-rich two-phase alloy electrodes.

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Hybrid Material Concepts and Benchmarking Solid-State Battery Performance

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The renewed interest in further developing solid-state batteries (SSBs) is mostly due to the high room temperature conductivities (> 1 mS/cm) of sulfide- and halide-based solid electrolytes. However, such materials tend to have limited (electro)chemical stabilities against state-of-the-art electroactive materials. Moreover, when the solid electrolytes are incorporated in composite electrodes dynamic electro-chemo-mechanical and tortuous charge transport challenges arise due to volumetric changes of electroactive materials and residual porosity in the composite electrodes. The first part of this talk shows how the combination of such solid electrolytes with other materials (polymers and liquid electrolytes) can be exploited to tackle some of these challenges.[1,2] Our approach is strongly focused on attaining a good understanding of the transport bottlenecks in these hybrid materials, as well as inter-facial (in)stabilities and monitoring the formation of new interphases via impedance spectroscopy. The second part of this talk will show results on a recent international interlaboratory (Round Robin) study on the reproducibility of solid-state battery cell performance.[3] In general, there a lot of room for improvement,[4] but the study allowed us to identify various sample processing, cell assembly and cell parameters not typically reported that can help improve comparability and reproducibility of solid-state battery cell performance across groups.

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Chloride Electrolytes : A Perspective on Structure, Ion Conduction, Reactivity, and Cell Performance

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Chloride solid electrolytes have spurred significant research interest over the past few years due to their high ionic conductivities and good stability against high voltage cathodes. While their bulk properties depend sensitively on the synthesis conditions, these materials often constitute a challenge for characterization. Using solid-state NMR, X-ray diffraction, computational simulations, and other complementary tools, we obtain atomic-level insights into the links between structure and ion transport. In particular, we show that materials prepared by mechanochemical synthesis comprise a significant concentration of planar defects, which can reduce ion transport barriers. [1] We also show that cation disorder and the polymorphic makeup of chloride electrolyte samples can be tuned through synthesis and processing, with significant impacts of ion transport. [2, 3] While more disordered or even amorphous chloride phases tend to enhance the ionic conductivity, those materials are inherently unstable even under mild heating (< 100°C), limiting practical applications. [4] Finally, I will present our recent work examining the reactivity of chloride electrolytes against sulfide electrolytes for dual electrolyte solid-state batteries. [5]

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Challenges of All Sloid State Battery for EV Application

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In 2010, the Nissan Leaf became the first mass produced, fully electric vehicle in the world to utilize the now ubiquitous lithium-ion battery. More than a decade later, the demand for xEV has dramatically increased due accelerating pressure to mitigate global climate change. The current market demands significant improvements in energy density and quick chargeability, without compromising safety.

All-solid-state batteries (ASSBs) are one of the most promising candidates for next-generation energy storage, owing to their advantageous balance of safety, high capacity, and high power. It is generally said that the use of solid electrolytes (SE) improves battery safety by reducing the flammability and increasing thermal stability compare to conventional liquid electrolyte systems. However, in order to achieve much higher energy densities, solid electrolytes must be used in conjunction with higher energy active materials such as metallic lithium and high-nickel oxide cathodes. The safety of such systems requires a more detailed and rigorous investigation.

Herein, we present an analysis of the reactions and products of high-energy active materials with solid electrolytes at high temperatures. We further detail the impact of these reactions on the safety design of all-solid-state batteries for automotive use.

Operando characterisation of dendrites in single-crystal LLZO

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Batteries with solid electrolytes are expected to have increased energy densities and improved safety. These improvements are achieved by using a high-energy density anode (e.g., lithium-metal anode with a theoretical capacity 3860 mA h/g) and non-flammable, solid-state electrolyte materials such as $Li_6La_3ZrTaO_{12}$ (LLZO). Despite significant research and commercial progress over the past decade, the key challenge in the implementation of solid-state electrolytes is the initiation and propagation of cracks filled with Li metal, i.e. dendrites.

In this study, we quantify the driving forces required for dendrite propagation in a single-crystal LLZO sample. We use an annealed single crystal to assembly a symmetrical Li|LLZO|Li cell. We apply a wide range of current densities (0.001–10 mA/cm^2) and observe the propagation of dendrites using a high-resolution optical microscope. We note that the morphology of the dendrites changes with applied current density and the rate of growth is proportional to the applied current, similar with previous studies. However, once Li is depleted from a dendrite, the Li redeposition in an empty crack is much faster compared to the initial propagation. We attribute the difference in energies to the energy required for crack opening and propagation.

Our study probes the fundamental processes related to dendrite propagation in solid-state electrolytes by investigating a single crystal as a case example. Thus, our results have implications for the limiting factors behind the successful development of all solid-state batteries.

Using Resistor Network Models to Predict the Transport Properties of Solid-State Battery Composite Electrodes

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In solid-state batteries, composite materials consisting of active materials and solid ion conductors are often employed as electrodes. To tailor the performance of such electrodes, profound knowledge about their effective ion, electron and heat transport properties is paramount. As these parameters strongly depend on composition and microstructure however, effective transport must be reevaluated every time the system is slightly altered. To help streamlining this often-tedious process of optimizing effective transport in composite electrodes, a resistor network model is presented and benchmarked against experimentally assessed effective ion, electron and heat transport of $LiNi_{0.83}Co_{0.11}Mn_{0.06}O_2$ (NCM83)-Li_6PS_5Cl (LPSCl) composites.[1] The resistor network modelling approach succeeds in describing the experimental data measured in this work. To test the broadness of the application space, also literature case studies are examined using this model.[2-4] Despite its simplicity, general trends of the conductivity dependence on volumetric ratio and particle size are well reflected for electrode composites with well-defined microstructures. Since the model can easily be adapted to other systems and extended to tackle further research questions it can provide guidance for experimentalists, helping to accelerate research on transport properties of solid-state electrode composites.

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Deciphering the Influence of Pressure, Heat Treatment, and Coating on the Electronic Conductivity of Active Materials for All-Solid-State Batteries

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Lithium-ion batteries are increasingly used in electric vehicles and for renewable energy storage. For these fields of application, improvements in gravimetric and volumetric energy density as well as in battery safety are important issues. [1] Such improvement should be achievable by the further development of all-solid-state batteries (ASSBs). A major challenge in ASSB research is the establishment of good interfacial contacts between the solid particles inside the battery, in particular inside the composite cathode consisting of cathode active material (CAM) particles and solid electrolyte (SE) particles. [2] For modelling the electrochemical processes in ASSBs, accurate values of the ionic and electronic conductivities of all materials used in the battery are of utmost importance [3]. While the ionic conductivity of many SEs was measured with rather high accuracy [4], experimental studies on the electronic conductivity of CAMs are scarce, and values reported for the electronic conductivity of a specific CAM vary often by several orders of magnitudes. Overall, the existing literature values do not allow for clearly deciphering the influence of pressure, heat treatment and coating on the electronic conductivity of CAMs.

Here, we have carried out a systematic study on the influence of these parameters on the electronic conductivity of fully lithiated LCO particles and of NMC particles. The CAM particles are either uncoated or coated with thin $LiNbO_3$ layers using two different techniques. The particles are either taken without any heat treatment or after being subjected to different types of heat treatment. Pressure-dependent impedance spectra of CAM pellets sandwiched between metal electrodes are taken and analyzed. The results reveal high bulk electronic conductivities of LCO and NMC already in the fully lithiated state.

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Insights into performance and durability of garnet solid electrolytes from multiscale simulations

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Garnet-type $Li_{7-x}La_3Zr_2O_{12}$ (LLZO) solid electrolytes and cathode-electrolyte composites can exhibit cyclability and performance issues when incorporated into real components and solid-state cells. In many cases, these limitations are associated with chemomechanical changes at buried solid-solid interfaces, including grain boundaries, phase boundaries, and interphase regions. These interfaces introduce structural disorder, strain, and compositional variations that can affect transport, mechanical response, and chemical reactivity. In this talk, I will illustrate how our team is using multiscale computational simulations to better understand the underlying physics at evolving interfaces in garnet solid electrolytes. Results from atomic-scale simulations, machine learning tools, and mesoscale microstructural continuum models will be presented, along with simulation-derived insights into charge transport limitations and mechanical failure under practical operation. The role of interfacial structural and chemical disorder on the desired transport of Li through and across interfaces will be highlighted, as well as impacts of interfaces on the undesired transport of other cationic species that can lead to chemical changes and degradation. I will also show how our simulations can predict the chemomechanical response of LLZO during cycling, including evolving stress distributions that can give rise to fracture, delamination, and local phase changes with important performance implications. Finally, I will discuss the interplay among atomic-scale interactions, mesoscale microstructural effects, and operating conditions, with general applicability to understanding performance and degradation of ceramic solid electrolyte materials. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Lithium, Speed & Interfaces -
Designing Next Solid Battery Materials Real Fast with High Control of Chemistry

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Next generation of energy storage devices may largely benefit from fast and solid Li^+ ceramic electrolyte conductors to allow for safe and efficient batteries. For those applications, the ability of Li-oxides to engineer their interfaces and be processed as thin film and bulk structures and with high control over Lithiation and phases at low temperature is of essence to control performance. The role of dopants and stability strategies for interfaces requires attention. With climate change on the rise and translating more shares to storing renewable energy in batteries and using sustainable materials, we have to reconsider the ways we select elements, synthesize at low CO_2 footprints and shorten time-spans in translation of new materials to reach highest performances. Through this presentation we provide perspective on how high throughput synthesis and ML enables fast sceening of properties and optimizing synthesis of solid battery material compounds at best performance characteristics. Also, we discuss options of performance engineering at interfaces towards critical current densities.

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Drawing the landscape for ion diffusion in solid-state electrolytes

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

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

In my talk I will present my work on the Ionic-TuTraSt methodology, developed to this end. Based on a topological analysis of the potential energy landscape felt by the mobile ion, it constructs a lattice model that predicts the ionic diffusivity of a crystalline material at an accuracy comparable to molecular dynamics, yet at only a fraction of the computational cost, even at the DFT level of theory. I will also discuss how I am working towards extending this framework to non-crystalline solid-state electrolytes (i.e., polymer-based) as well as composites consisting of several phases.

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Cathode and anode interfaces in a lithium-anode ceramic-electrolyte battery

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Of the challenges facing realisation of the all solid-state battery, solid/solid interfaces rank high. At the lithium metal / ceramic electrolyte interface, the formation of dendrites on charging can lead to short circuit and cell failure. Typically, for relatively dense ceramics, this occurs above a critical charging current (CCD) and therefore depends on the local current density at the Li/ceramic electrolyte interface. Contouring the interface increases the interfacial area, which naively might seem helpful. The influence of the interfacial topography on CCD will be considered. It has often been posited that densification of the ceramic electrolyte should benefit charging. However, not all changes in microstructure on densification are predicted to lead to an increase in CCD, some changes are positive while others are negative. The relationship between the ceramic microstructure, densification and the CCD will be considered with particular reference to the Argyrodite solid electrolyte, Li_6PS_5Cl. The composite cathode, composed of a cathode active material, the solid electrolyte and carbon, presents a different yet equally challenging set of problems. Sulphide based solid electrolytes such as Argyrodite, possess the high conductivities necessary in the composite cathode and are relatively compliant compared with, for example, oxides. However, they suffer from a low oxidative stability. Coated cathode active particles are generally required to suppress degradation reactions, which adds cost and complexity to manufacture. The separate and combined effects of the cathode active material and the carbon on the degradation reactions will be considered.

Solid electrolytes: from mine to cell

Christoph Hartnig, Vera Nickel, AMG Lithium, Frankfurt, Germany

Sulfidic solid electrolytes (SSE) are considered the most promising class of materials for All-Solid-State Batteries (ASSBs). The availability and, in parallel, high quality of base materials are key for performance and stability of SSEs.

In this presentation, we share some insights in the product creation pathway based on a completely backward integrated supply chain. AMG Lithium starts the production of Lithium containing compounds in their fully owned spodumene mine Mibra in Minas Gerais, Brazil. Lithium salts are refined to battery grade in the recently inaugurated first European Lithium Hydroxide plant in Bitterfeld, Germany. Relying on the qualified supply chain, Lithium Sulfide is produced in a subsequent step based on the in-house sourced lithium precursor. In further downstream development activities, Lithium Sulfide is optimized for the application in sulfidic solid electrolytes.

Since both Lithium Sulfide and sulfidic solid electrolytes are new products with a so far unique application in all-solid-state batteries, new markets and new production capacities have to be established on a global perspective. We will share insights into our point of view on this evolving market and the need for secured raw material sources which allow for complete control over quality along the entire value chain.

Perspective on Warm Isostatic Pressing for Mass Production of Solid-State Batteries

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In recent years, there have been serious commercial advancements with regards to solid-state batteries (SSBs), in which liquid electrolyte is replaced by a solid-state electrolyte (SSE).[1,2,3] Cell concepts with functional layers realizing zero-excess lithium metal anodes were developed, combining overall reduced weight and lithium metal anodes, achieving superior energy density (>1000 Wh/l).[4,5] The need for external pressure, also called “stack pressure”, of SSBs due to cell volume change in operation and subsequent particle contact loss was reduced to a minimum (~2 MPa) with cells based on highly conductive sulfide SSEs densified by warm isostatic pressing (WIP).[5,6] Considering mass production, it seems that the common, uniaxial methods for calendering lead to insufficient composite density and lower electrochemical performance.[7] Most individuals working in battery production are critical towards WIP, because of its batch process characteristic. Ironically, the knowledge about WIPs scaling potential is unknown to the community.[8] Vessel volumes for presses which are already employed in mass production have reached 2000 l and above. With this presentation Quintus Technologies will give the audience at “SSB VI” a summarizing perspective of basics for (warm) isostatic pressing and the status for industrial production of SSBs from an equipment suppliers view.

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Insights on electrochemical sodium storage in sodium/sodium-ion batteries by advanced *in-situ* and *ex-situ* solid-state NMR

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The expanding global demands of the energy sector have raised great attention on development of solutions for more sustainable, cost-efficient, and environmentally friendly energy storage technology. Significant progress has been made in the research field of sodium/sodium-ion batteries (SIBs), as potential alternative for lithium/lithium-ion batteries (LIBs). [1] Although, at first glance sodium and lithium are similar, there are differences in their physico-chemical properties, necessitating different materials i.e. electrodes and electrolytes. For development of commercial high-performance SIBs with high energy-density, knowledge of the electrochemical behavior is essential. This goes in hand with a deeper understanding of the sodium storage as well as of reactions which occur in SIBs. These can be analyzed under *in-situ* conditions employing solid-state NMR. [2] The presentation will give an overview on recent advances in *in-situ* ^{23}Na NMR of sodium-based batteries, and how it can be employed in combination with *ex-situ* NMR to investigate the sodium storage properties. As examples, results obtained on polymer-derived silicon carbonitride ceramic (SiCN) electrodes, and hard carbon powder electrodes are presented including developments of cell designs and improvements of cell assemblies for *in-situ* NMR investigations. [3, 4]

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A Mechanistic Insight into the Cascade Dissolution and Coprecipitation Process in the Wet Synthesis of Argyrodite Li_6PS_5Cl

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I present a Li_2S-free and cost-effective wet chemistry method for the preparation of sulfide solid electrolytes (SSEs), which addresses a major challenge in the commercialization of all-solid-state batteries (ASSBs). Our method universally synthesizes various electrolytes, including Li_xMS_4 (M = P, Sb, Si) and Li_6PS_5X (X = Cl, Br, I). It particularly produces Li_6PS_5Cl of high quality (5.7 mS cm^{-1} of ionic conductivity at 25°C) at a material cost of one-tenth of previously reported methods. The synthesis process, featuring a cascade-dissolution-coprecipitation mechanism, is investigated using analytical techniques for soluble intermediates and sediment products. The mechanism study revealed the structural evolution from long-chain to short-chain thiophosphates in Li-naphthalene (NAP)-containing tetrahydrofuran (THF) solution. After starting Li_3PS_4 precipitation, depleting thiophosphates and the formation of aggregated ion pairs involving sulfides and LiCl lead to Li_3PS_4-Li_2S-LiCl co-sediments. This phenomenon has not been observed in previous Li_2S-based syntheses in THF. The Li_6PS_5Cl-based pellet ASSBs with a $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ cathode and a Li-In anode provide high initial capacity (190 mAh g^{-1} at a 0.1C rate, 55 ^{o}C) and hold a capacity retention of >80% after 1,000 cycles at a 2.0C rate. Additionally, a 0.7 Ah pouch cell with a silver/carbon anode exhibits a remarkable energy density (352.8 Wh kg^{-1} at 45 ^{o}C). This solvent-based, and Li_2S-free synthetic process proposes a cost-effective pathway toward sustainable mass production for synthesizing sulfide solid electrolytes.

Scalable mechanochemical synthesis of sulfide-based solid electrolytes

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Sulfide-based solid-state batteries (SSB) or hybrid concepts involving sulfides represent a promising technology for future high-performance energy storage. Nevertheless, there are still several challenges, such as the development of high-quality and more sustainable, resource-efficient production processes of solid electrolytes (SE) [1-3]. Therefore, sulfide-based SSB have been just established at the laboratory and pilot scale. Aiming at the availability of these highly demanded materials, the focus of this work was to develop and establish a scalable mechanochemical synthesis process for sulfide-based SE, like Li_3PS_4, Li_6PS_5Cl or Cl-rich argyrodites, without the use of solvents to increase material purity and performance compared to the more established solvent-based syntheses. In a first step, the mechanochemical synthesis was investigated and highly optimized in lab scale via high energy ball milling and accompanying DEM simulations. In a subsequent upscaling step in scalable mill types, the process conditions and handling strategies were further investigated up to the kg-scale. Based on the conducted experiments in a larger scale, the solvent-free production of sulfide-based solid electrolytes was successfully demonstrated with high product purity and performance, which will thus support the further industrialization of sulfide-based SSB.

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Functional magnesium and calcium electrolytes for solid-state batteries

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Solid-state batteries made from abundant and cheap elements may pave the way towards a more sustainable future [1-3]. Recently, we prepared series of new magnesium and calcium borohydrides with very high Mg^{2+} or Ca^{2+} cationic conductivity at moderate temperatures (see Fig. 1). Density functional theory (DFT) calculations of $Mg(BH_4)_2{\cdot}NH_3$ reveal that the neutral molecule (NH_3) is exchanged between the lattice and interstitial Mg^{2+}, facilitated by a highly flexible structure, mainly owing to a network of di-hydrogen bonds, $N–H^{\delta+}\cdots{}^{-\delta}H–B$, and the versatile coordination of the BH_4^- ligand. Here we present the best known Mg^{2+} and Ca^{2+} electrolytes (fig. 1) with very high ionic transport numbers, t_{ion} ~ 1, and also a new mechanism for cationic conductivity in the solid state [4].

The electrolytes are stable towards magnesium or calcium metallic electrodes and in some cases Mg plating/stripping for at least 100 cycles can occur. Finally, proof-of-concept rechargeable solid-state magnesium battery cells were assembled with these new electrolytes using magnesium metal anodes and a TiS_2 cathode [7,8]. We conclude that the chemistry of metal borohydrides is very diverse and allows for rational design of functional electrolytes for solid-state batteries.

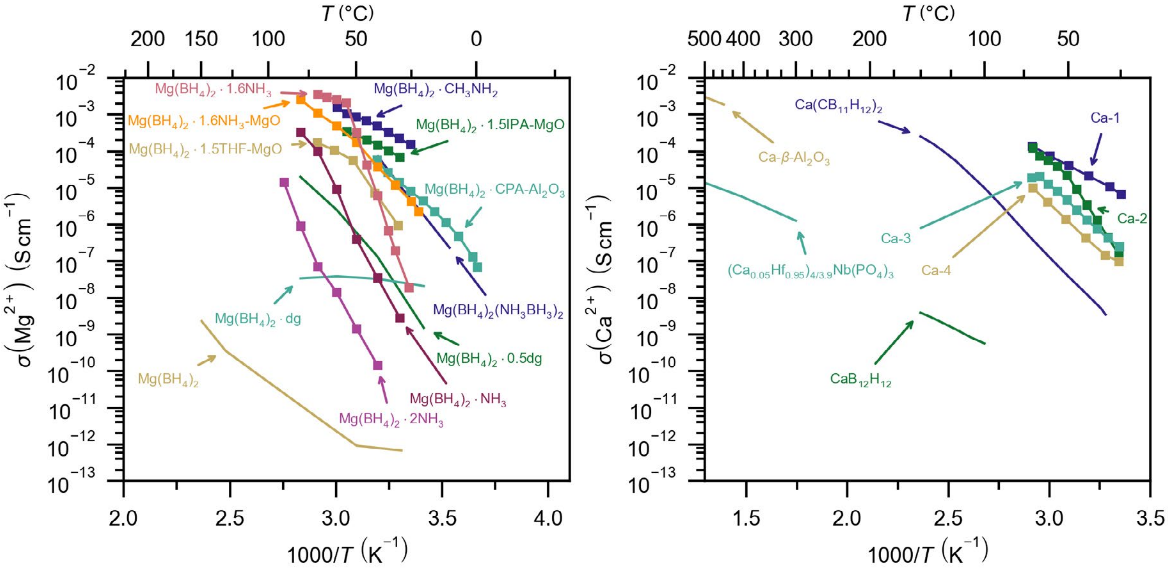

Fig. 1. The best Mg^{2+} and Ca^{2+} electrolytes are metal borohydrides. Data points (squares) are measured of new materials under investigation.

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Solid electrolyte design through anion sublattice engineering: a case study of oxyhalides

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All-solid-state batteries represent a compelling alternative to conventional lithium-ion batteries, owing to their enhanced safety and superior energy density, enabled by ion-conducting solids. In addition to oxides and sulfides, halide-based analogues have recently emerged as a new category of solid electrolytes. The exploration of halides as a novel class of ion-conducting materials has advanced considerably, solidifying their position as a new "single-anion" compound group comparable to oxides and sulfides.

Our research, however, has particularly focused on the high chemical affinity of halides with both oxides and sulfides, stemming from the intermediate nature of halogens. This unique characteristic has led us to pursue the design of complex anion sublattices through the combination of multiple anions. This approach aims to leverage the synergistic properties of different anion types, potentially overcoming the limitations of single-anion systems. Indeed, some oxyhalide systems possessing fast ion conduction have recently been reported, e.g., $LiTaOCl_4$, $LiNbOCl_4$, and $NaAlOCl_2$.

Nevertheless, the underlying mechanisms of high ionic conductivity in oxyhalides and their design principles remain elusive. In this presentation, we employ Na_2O-$TaCl_5$ oxychloride glasses as a model complex-anion system with fast ion transport (over 3 mS cm^{-1} at RT) and discuss the origin of its exceptional ionic conductivity by comparing it with the recently reported Na-ion conducting halide $NaTaCl_6$[1]. Given that the material space encompassed by multi-anion compounds is substantially more expansive than that of single-anion systems, a mechanistic understanding could provide guidelines for exploring a rich landscape of materials, potentially opening up new avenues to discover various new solid electrolytes.

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Enhancing the Ionic Conductivity and Dendrite-Tolerance of NaSICONs by Grain-Boundary Engineering

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Sodium-based batteries are gaining increasing attention due to their comparable physicochemical properties, abundant resources as well as the lower costs of raw materials. Similar to their lithium-counterparts, sodium-based batteries with solid-state design (SSNBs) are considered as the next-generation batteries, offering improvements in long-term stability, safety, and energy density compared to conventional liquid electrolyte-based batteries. Developing highly conductive and reliable solid electrolytes is still an important step for the advancement of SSNBs. NaSICON-type $Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$ (NZSP) exhibits extraordinary bulk conductivity (σ_{bulk}) of 15 mS cm^{-1} at 25 °C [1]. The total ionic conductivity (σ_{total}) remains outstanding among state-of-the-art solid electrolytes (SEs), but it decreases to 5 mS cm^{-1} at 25 °C [1]. This indicates the dominance of grain-boundary resistance (R_{gb}) to the total resistance (R_{total}) in the polycrystalline NZSP, which is mainly due to the thermal expansion anisotropy of NZSP lattices. In the present study, we modified the grain boundaries of NZSP by adding 2.5 mol% $Na_3LaP_2O_8$ to counteract the effect of thermal expansion anisotropy. The σ_{total} of modified NZSP increased to 7.1 mS cm^{-1} at 25 °C [2], surpassing other reported polycrystalline oxide SEs. The critical current density of Na | modified NZSP | Na symmetric cells increased to 20 mA cm^{-2}. Galvanostatic cycling of the cells with 2 mA cm^{-2} / 2 mAh cm^{-2}, 5 mA cm^{-2} / 5 mAh cm^{-2} and 10 mA cm^{-2} / 2.5 mAh cm^{-2} (per half cycle) were demonstrated for 800 h, 90 h, and 16 h [2], respectively, which is not only much better than the results of pristine NZSP [3], but also indicating the unprecedented dendrite tolerance. Remarkably, the main failure mode in these cells shifts from Na-dendrite short-circuiting to substantial polarization of the Na electrodes, and even after a short-circuit a polarization occurs again.

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Large-Scale Manufacturing Superionic Lithium Argyrodite Solid Electrolytes Enabling Stable All-Solid-State Battery

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All-solid-state batteries (ASSBs) with non-flammable solid electrolytes offer enhanced safety features, and show the potential for achieving higher energy density by using lithium metal as the anode. [1] Among various solid electrolytes, halogen-rich lithium argyrodites solid electrolyte are favored due to their high room-temperature ionic conductivity and ease of processing. [2] However, the low production quantity due to complex preparation process, and capacity degradation arising from side reactions at the electrode/solid electrolyte interface hinder their large-scale application in all-solid-state batteries (ASSBs). [3]

In this work, we successfully prepared $Li_{5.5}PS_{4.5}Cl_{0.75}Br_{0.75}$ (LPSCB) electrolytes with ultra-high room temperature ionic conductivity (13 mS cm^{-1} for cold-pressed pellet and 25 mS cm^{-1} for sintering pellet) and low activation energy (0.24 eV). Using fast dry mixing followed by annealing, a large production scale of over 300 g per batch is achieved for the first time. Combining neutron diffraction and ^{6}Li-^{7}Li tracer exchange NMR tests, it has been revealed that the LPSCB electrolyte shows a higher Li+ occupancy at the interstitial 16e site compared with $Li_{5.5}PS_{4.5}Cl_{1.5}$, which will lower the activation energy barrier and promote the ion transport between the lithium cages. Combining LPSCB with the coated crystal $LiNi_{0.83}Co_{0.11}Mn_{0.06}O_2$, the assembled ASSBs show stable cycling for over 2500 cycles at 0.5C and 1800 cycles at 2C without any capacity degradation, respectively. All the results indicate that LPSCB is a promising solid electrolyte candidate used for ASSBs.

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ABSTRACTS (POSTER)

New Sample Environment for *in Operando* Characterization of Solid-State Batteries

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As the field of battery research moves towards solid-state batteries (SSBs), it is crucial that *in operando* characterization methods are available. During battery cycling, complex processes take place. Powder X-ray diffraction (PXRD) is commonly used to shed light on structural changes within the cell for batteries with a liquid electrolyte [1-3]. However, SSBs often cycle at elevated temperatures and with an applied mechanical pressure [4,5]. Therefore, in order to obtain *in operando* PXRD data for SSBs, the electrochemical cell must accommodate these conditions.

We present a new sample environment, the Aarhus Pressure Temperature *in Operando* X-ray cell (APTIOX), developed for powder X-ray diffraction measurements during operation. The APTIOX cell can be used both with in-house X-ray sources and at synchrotron facilities. We present a versatile cell that offers temperature control and monitoring of mechanical stack pressure. Furthermore, we have investigated a wide variety of X-ray window materials, including metals, polymers, and glasses.

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Advanced Characterization of Sulfidic All-Solid-State Batteries: A multi-scale and *Operando* Microscopic Work Flow Approach

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All-solid-state batteries (ASSBs) have emerged as a promising technology to address the current limitations in conventional liquid electrolyte based Li (and potentially Na) ion batteries [1,2]. However, even though considerable progress has been made in recent years there are still many challenges on materials, electrode, and cell level that need to be tackled [3]. For instance, insufficient interface contacts as well as electrochemical instability between the cathode active material (CAM) and the solid electrolyte (SE) in composite cathode (CC) have to be improved [4,5]. Last but not least, inadequate ionic and electronic charge transport paths must also be overcome [6,7]. To tackle abovementioned challenges and also to generate a deeper understanding of performance and processability, it is crucial to investigate the relationship between microstructural and electrochemical properties at the particle, interface and electrode level. In this study, an inert gas workflow combining high-resolution X-ray microscopy (XRM) with correlative fs-Laser/FIB preparation and FIB-SEM tomography will be presented. Additionally, we will show operando/In-situ FIB-SEM analyses of sulfidic Li- and Na-ion ASSBs to provide new insights in microstructural changes during cycling.

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Sodium Solid-State Batteries (Na-SSBs): The Tale of Layered Oxides and Sulphides – Will They Ever Get Along?

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Abstract:

Since the pioneering demonstration of a solid-state battery with a layered oxide cathode by Takada and colleagues in the early 1990s[1], sodium-layered oxides in solid-state batteries (Na-SSBs)[2] have attracted attention as a promising alternative to traditional lithium-ion batteries due to their cost-effectiveness, enhanced safety, and the abundance of sodium resources. Sodium-based systems are also easier to recycle than lithium-solid state batteries[3] because they rely on more readily available elements for the cathode. In our current study, we examined a Na-SSB configuration comprising a P2-type layered oxide cathode (either $\mathrm{Na_{.67}Mn_{0.5}Fe_{0.4}Mg_{0.1}O_2}$ (FMMg) $\mathrm{Na_{.67}Mn_{0.5}Fe_{0.4}Ti_{0.1}O_2}$ (FMT) synthesized by ball milling), a sodium sulfide-based solid electrolyte (either Na_3PS_4 or Na_3SbS_4), and a $Na_{15}Sn_4$ (sodium-tin) alloy anode. Additionally, an oxy-halide-based solid electrolyte ($NaTaOCl_4$) was included in the catholyte to enhance stability. Electrochemical testing was carried out using Galvanostatic Cycling with Potential Limitation (GCPL) and Electrochemical Impedance Spectroscopy (EIS) to explore the interfacial transport properties.

Our preliminary findings suggest that cathode materials screening for Na-SSBs may need to be reconsidered in the context of solid-state configurations. What performs well in liquid electrolyte systems may not necessarily translate to solid-state systems due to significant differences in interfacial stability and ionic transport properties. In particular, the stability of the electrode-electrolyte interface is critical to battery performance and warrants further investigation.

Interestingly, our results regarding anodic stability deviate from established literature[4], highlighting the complex interactions at the interface. This interaction results in a substantial increase in interfacial impedance over cycling, as evidenced by EIS data, suggesting that transport isues remain key challenges for Na-SSBs.

Our findings underscore the importance of careful material selection and interface engineering in developing efficient sodium solid-state batteries. Prioritizing material composition and chemical compatibility is essential, with fine-tuning of microstructure coming at a later stage. With dedicated material science advancements, sodium-layered oxides paired with sulfide-based solid electrolytes could indeed achieve stable cycling, though significant interface engineering will be crucial to overcome the current limitations.

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Non-Destructive Investigation of Provoked Electrode Delamination in Solid-State Batteries Using Ultrasonic Techniques

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The manufacturing process of solid-state batteries poses unique challenges. Unwanted issues during the processing, including the potential for defects such as voids, delamination, and cracks within the solid electrolyte and between the active material layers and current collector, might emerge. All can significantly impact the performance, reliability, and safety of the batteries. [1] To ensure the production of reliable solid-state batteries, ultrasonic testing has emerged as a key monitoring tool, using high-frequency sound waves to inspect battery materials and reveal their internal structure without causing damage. This non-destructive evaluation technique can be used for detecting and characterizing defects, supporting quality control, and aiding in the research and development of new materials and manufacturing processes. [2] In this work, we investigate the application of ultrasonic testing methods to identify and characterize defects such as delamination and cracks which were introduced intentionally during the manufacturing process. By employing this technique, the method is able to detect voids, cracks, and delamination in both solid-state electrolytes and electrodes. Additionally, we examine the correlation between the state of charge (SOC) and the presence of defects. The findings highlight ultrasonic inspection's role in improving solid-state battery reliability and safety, crucial for advancing next-generation energy storage systems.

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A three-electrode setup for all-solid-state battery research

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A reference electrode makes three-electrode measurements possible, enabling differentiation between cathode and anode processes that otherwise overlap in two-electrode measurements. Implementing a reference electrode in a solid-state electrolyte system however poses several challenges. In addition to finding a suitable redox couple that can provide a known reference potential, it needs to be chemically stable with the electrolyte of choice, in order to avoid long-term potential drift as well as high surface resistance [1]. Complicating the matter further, the geometry is very restricted in the thin cells that typically constitute solid-state batteries. A non-symmetric reference electrode can lead to measurement artifacts, especially in electrochemical impedance spectroscopy [2].

Within the REFA project, funded by the Federal Ministry for Economic Affairs and Climate Action, a system for three-electrode measurements in solid-state electrolytes has been developed. This entails a pressure application frame, several options for reference electrode chemistries, as well as a high-precision measurement cell designed for easy assembly of multilayer cell stacks with a variety of well-defined reference electrode geometries. The results of this three-year project will be presented, including showcase experiments of all-solid-state full cell batteries characterized in three-electrode mode.

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Cryo-workflow for the investigation of $Li_7La_3Zr_2O_{12}$ at sub-nanometric resolution

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Abstract

Lithium Lanthanum Zirconium Oxide (LLZO) is a garnet-type oxide material that has gained significant attention as a solid-state electrolyte, owing to its high ionic conductivity, excellent chemical stability with lithium metal, and wide electrochemical stability.

However, understanding the influence of dopants and grain boundaries on the electrochemical performance of LLZO remains still challenging. The limited capability of conventional preparation/characterization techniques to further reveal key structural and chemical properties is a significant barrier to optimising its performance.

In this work, we introduce a cryo-workflow that enables the preparation of LLZO specimens at cryogenic temperatures for further characterization including atom probe tomography (APT), transmission electron microscopy (TEM), etc. This approach addresses the limitations of traditional FIB preparation methods by preventing unwanted diffusion and beam-induced damage in beam-sensitive materials.

Operando SEM observations of lithium-metal anodes during dissolution and deposition through LLZO

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Solid-state batteries (SSB) with lithium metal promise higher energy densities compared to conventional lithium-ion batteries. To bring forward this technology, efficient ways to produce electrode stacks need to be developed and stable interfaces between lithium metal and inorganic solid electrolytes have to be established.

Here, we focus on the observation of interface processes during cell operation. Our electrolyte layers are fabricated using powder-aerosol-deposition (PAD) at RT [1]. To produce reservoir-free cells, LLZO layers with thicknesses of 30 µm are deposited on copper substrates. We then pressed small lithium electrodes with diameters as small as 200 µm on the LLZO and performed galvanostatic experiments inside the SEM with very small currents (~ 6 nA, 20 µA/cm^2). The operating Li|LLZO|Cu stack was imaged in top view to observe the morphology of the lithium in detail.

Our *operando* SEM images show that the dissolution and deposition of lithium-metal electrodes are not necessarily reversible processes. Observations of electrode stacks with varying heat treatments show clear differences in the evolution of the lithium metal and indicate the importance of the Li|LLZO interface and the microstructure of lithium.

The fundamental mechanisms of lithium metal dissolution and deposition are expected to be crucial for the reliability of SSBs. Further *operando* SEM investigations will be needed in order to better characterize, understand, and eventually minimize the degradation of metallic electrodes in SSB.

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Microstructural Analysis of Deposited Alkali Metal in "Anode-free" Solid-State Batteries using EBSD

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Lithium metal, when used as an anode material, can significantly enhance the energy and power density of solid-state batteries.[1] However, issues such as local contact loss and dendrite formation restrict the applicable current density. Previous studies have demonstrated that the lithium metal microstructure plays a crucial role in determining the electrochemical performance, particularly in terms of stripping capacity before pore formation occurs.[2]

Solid-state batteries (SSBs) without an alkali metal reservoir are being extensively studied for their potential to achieve unparalleled energy densities while eliminating the need to handle reactive and inherently hazardous alkali metal foils. Despite its anticipated impact on electrochemical performance, the microstructure of freshly deposited lithium has not yet been thoroughly analyzed.

In this study, we reveal with a combination of focused-ion-bream preparation and electron backscatter diffraction that the grain size of plated alkali metal films is independent of the current collector's microstructure and generally consists of very large grains, though not as large as those found in commercially purchased foils. More intriguingly, each deposited film exclusively comprises columnar grains with grain boundaries oriented perpendicular to the solid electrolyte interface, highlighting a distinct difference from using an alkali metal foil as the anode. We believe that our research on metal anodes will pave the way for addressing more advanced scientific questions that were previously difficult to explore.

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Thermal Stability of Li_6PS_5Cl Argyrodite

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Sulfide electrolytes exhibit the highest ionic conductivities (10^{-3} – 10^{-2} S cm^{-1}) among other solid electrolytes (SE) and are on par with liquid electrolytes.[1] The compatibility with lithium metal anode and the decent cost efficiency make Li_6PS_5Cl one of the most promising SEs.[1] However, the thermal stability of solid-state batteries is a concern due to possible thermal runaway reactions and the potential formation of harmful gases.[2] Therefore, knowledge on thermal stabilities, reaction temperatures and enthalpies as well as thermophysical properties of such materials and materials composites is essential for commercialising solid state batteries.

Reported thermal properties of Li_6PS_5Cl are scarce and inconsistent in literature. Some articles report the stability of this argyrodite as high as 900 °C, investigated by the optical analysis of the sulfur formation inside the ampule upon heating.[3] In other investigations, the thermal decomposition occurs already in the range of 200-400 °C, indicated by the mass loss in the thermogravimetric (TG) signal.[4]

We investigated the thermal stability of Li_6PS_5Cl from various sources using simultaneous thermogravimetry and differential thermal analysis coupled with mass-spectrometry (TG-DTA-MS). We confirmed that in argon, Li_6PS_5Cl is stable up to 800 °C, while in air it starts to oxidize at 255 °C. Commercially acquired Li_6PS_5Cl is less stable, with the release of volatile species beginning in the worst-case scenario already at 120 °C.

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$CuFeS_2$ as a Cathode Active Material in All Solid-State Batteries

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One bottleneck in the development of solid-state battery (SSB) technologies is the cathode active material (CAM). Layered oxide materials commonly utilized in other lithium-ion battery technologies are quickly approaching their limits in terms of capacity. It is also clear that realizing the benefits of lithium metal anodes in SSBs necessitates the use of high-capacity conversion-type cathodes. Sulfides offer an intriguing direction for further research because they can reversibly contribute to charge storage through stable anion redox ($2S^{2-} \rightarrow (S_2)^{2-} + 2e^-$). I will discuss our recent work on copper iron disulfide (Chalcopyrite, $CuFeS_2$) as a conversion-type CAM for SSBs ($CuFeS_2 + 4Li^+ + 4e^- \rightarrow Cu + Fe + 2Li_2S$). $CuFeS_2$ has a theoretical capacity of 587 mAh g^{-1} and it is further attractive because it is a naturally occurring mineral that is mechanically soft and has high electronic and ionic conductivities. These properties enable stable electrochemical cycling without conductive additive and despite a large volume expansion during discharge of ~63 %. Our group previously reported on a macroscopic displacement mechanism that occurs during lithiation of CuS in SSBs, whereby micron-sized Cu networks were observed with lithiation, the process of which was also followed by in-situ synchrotron-based X-ray tomography.[1,2] We hypothesize that the inclusion of a second metal center (e.g. Fe in combination with Cu) in the CAM will help to promote increased stability by hindering the macroscopic displacement mechanism. I will discuss our recent work applying $CuFeS_2$ as CAM in Li-SSBs. Through a combination of X-Ray diffraction, X-Ray absorption spectroscopy, resonant inelastic X-ray scattering, constant pressure experiments, and electrochemical characterization we are able to identify the complete reaction mechanism and better understand the roles of anion redox for boosting capacity and metastable states in improving stability in $CuFeS_2$-based Li-SSBs.

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Sulfur spillover on carbon materials and its relevance for metal-sulfur solid-state batteries

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Lithium-sulfur batteries have gained a lot of interest in the past years due to their high theoretical capacity and energy density. However, among other factors, its insulating nature as well as the formation of polysulfides in liquid medium have halted its progress to reach commercialization. On one side, to overcome the formation of polysulfide intermediates, moving to a solid-state configuration has been gaining popularity over the last years. On the other side, the approach to deal with its low electronic conductivity, carbon/sulfur composites have been widely studied and shown to improve the overall cell performance as well as increase the sulfur utilization[1].The most common techniques to develop these have been through intensive ball milling or melt infiltration. Despite the widespread use of these methods, the characterization of such sulfur/carbon nanocomposites can be easily misleading[2]. Our past research showed a room temperature transport phenomenon in which sulfur covers the surface of the porous carbon, resulting in total amorphization and loss of crystalline properties of sulfur[3]. The process was given the name "sulfur spillover". We believe such a behavior can be of great advantage for metal-sulfur batteries, both in liquid and solid media, considering that the effect has been proven for both. Here, we present more characterization results that are leading towards a better understanding of this phenomenon.

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Development of lithium and silicon anodes for sulfide-based solid-state batteries produced via physical vapor deposition

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Solid-state batteries (SSBs) are a promising innovation in energy storage technology, providing improved safety and higher energy density compared to traditional liquid electrolyte batteries. Lithium, known for its high theoretical capacity (3860 mAh/g) and low electrochemical potential, remains a favored anode material. However, challenges such as dendrite formation, limited cycle life, and safety issues require innovative strategies to optimize its performance in SSBs. In contrast, silicon, with an even higher theoretical capacity (4200 mAh/g), offers a compelling alternative due to its abundance and superior energy storage potential. Nevertheless, silicon anodes encounter significant obstacles, including substantial volume expansion during lithiation, leading to mechanical degradation and rapid capacity fade. This work focuses on the analysis of magnetron-sputtered lithium and silicon anodes in SSBs, aiming to highlight their respective advantages and challenges. Magnetron sputtering allows the creation of uniform, high-purity thin films essential for next-generation anodes. This comparative study utilizes electrochemical testing with sulfide solid electrolytes. Key performance indicators of this, such as cycling stability, rate capability and interfacial resistance are analyzed to evaluate the viability of the anode materials. The findings emphasize the need for advanced material engineering to reach the full potential of lithium and silicon anodes in SSB applications. In summary, this study offers valuable insights into performance metrics that can inform future research and development aimed at commercializing high-performance SSBs with optimized anode configurations.

Densification of Sulfide-Based Separators for Solid-State Batteries

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The densification of separators for solid-state batteries is significant to achieve high energy density, improved ionic conductivity, and a defined microstructure. In this study, fundamental investigations for the densification of Li_6PS_5Cl- and Li_3PS_4-based separators by uniaxial pressing and calendering were conducted. Separator slurries based on p-xylene as solvent and a hydrogenated nitrile butadiene rubber type as binder were produced using a dissolver and coated on a substrate foil by doctor blading. Amongst others, the ionic conductivity was analyzed for different line loads, as well as fabrication and stack pressures. The microstructure, for example, was investigated by scanning electron microscopy and synchrotron tomography. [1]

Calendering reduced the porosity of Li_6PS_5Cl-layers from 38 % to 11 %. However, no improvement in ionic conductivity was found with increasing line load or uniaxial pressure for both Li_6PS_5Cl and Li_3PS_4. In this context, impacts such as reduced contact with the current collector at low stack pressures [2,3] or elastic deformation predominantly caused by the binder are discussed. Moreover, the role of particle breakage and binder migration induced by compaction are considered. Overall, this work addresses arising challenges and opportunities related to the densification of sulfide-based electrolytes for solid-state batteries.

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3D-Printed hydroborate based all-solid-state sodium-ion battery

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In the search of new electric storage technologies, sodium-ion batteries (SIBs) have attracted huge interest due to the possibility to create high performance batteries without scarce elements. However, the theoretical energy density of the liquid electrolyte system is only around half of that of a lithium-ion battery. One way to tackle this issue can be the application of a sodium metal anode. Similar to the lithium system this seems to be possible only with a solid electrolyte.

Beside the, for the lithium system commonly investigated, classes of oxides, sulfides and polymers hydroborates have been identified as another class of solid electrolytes. Hydroborates have shown excellent ionic conductivities over 1 mS/cm at room temperature with an electrochemical stability window of 0 – 3 V vs Na/Na^+, thus making them perfect for the usage of metallic sodium [1]. Moreover, they can easily be processed by dissolution and precipitation, which allows for processing techniques like screen-printing.

In this contribution, we are going to present the processing of all-solid-state SIBs based on hydrobrates via screen-printing. This technique is especially suited for producing customized cell sizes, while manufacturing the cells layer-by-layer. A glovebox system consisting of three interconnected boxes for paste preparation, material printing and cell assembly will be used to simulate an encapsulated process chain. We will show the printing process of electrodes as well as separators and first morphological and electrochemical results for these components.

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A metallic lithium anode for solid-state batteries with low volume change by utilizing a porous carbon host

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Lithium metal is a promising negative electrode material for solid-state batteries (SSBs) to achieve high energy densities. However, uncontrolled lithium deposition and stripping cause several issues during cycling. Herein, the microporous carbon YP-50F and its modifications obtained by chemical vapor deposition (CVD) are investigated as 3D host to accommodate and control the deposition of metallic lithium. The structure of the carbons was analyzed by SEM and TEM, physisorption measurements, SAXS as well as helium pycnometry. The results showed the (partial) closure of the micropores by CVD indicating inner porosity. In half-cells vs. lithium, the CVD-YP composite electrode with Li_6PS_5Cl electrolyte shows significantly higher initial coulombic efficiency (79.5 %) than the pristine carbon (55.3 %) due to the succesful reduction of side reactions. The metallic character of the deposited lithium is evidenced by ^{7}Li Nuclear Magnetic Resonance spectroscopy. Full cells with nickel-rich NCM ($LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$) positive electrode and CVD-YP composite negative electrode achieve promising performance over 50 cycles without occurrence of (micro-) short-circuits (in contrast to 2D reference electrodes). In addition, small prototype pouch cells are investigated and the thickness change during (dis)charging is less than one third compared to a bare lithium metal electrode. This demonstrates low breathing behavior of the CVD-YP electrode and confirms the reversible storage of metallic lithium within the 3D carbon-based composite electrode. The adaption of carbonaceous frameworks for the reversible storage of a significant amount of lithium is an important step to make lithium-based electrodes viable for solid-state batteries at all, and is crucial for the final application of high energy solid-state cells in electric vehicles.

Tribochemistry of Metalsulfides (TiS_4/VS_4) with Sulfidic Solid-State Electrolytes for High Energy Applications

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Abstract: This study examined how milling energy and solid electrolyte content affected the microstructural and electrochemical properties of TiS_4 and VS_4 composites, comparing high-energy ball milling (HBM) and low-energy ball milling (LBM). Scanning electron microscopy (SEM) showed that HBM produced homogeneous mixtures, while LBM preserved distinct particle structures, impacting electrochemical performance. FIB-SEM and ToF-SIMS analyses revealed that LBM-prepared TiS_4 and VS_4 dry films exhibited distinct particle visibility and compositional overlays indicating lithiation patterns. In contrast, HBM-prepared films displayed uniform particle distributions, suggesting successful formation of triple-phase boundaries. Raman spectroscopy and X-ray diffraction (XRD) indicated that HBM induced greater amorphization of TiS_4 and VS_4, while LBM maintained crystalline structures. Electrochemical tests showed LBM-prepared TiS_4 composites had significant capacity drops at higher C-rates, whereas VS_4 composites, particularly VS_4-LBM$_{50}$, demonstrated stable discharge capacities. HBM-prepared composites exhibited superior electrochemical performance, with VS_4-HBM$_{50}$ outperforming TiS_4-HBM$_{50}$ across all C-rates. Dry-film composites mirrored these results, with HBM films showing better cycle stability and higher initial capacities. VS_4-HBM$_{50}$ displayed remarkable capacity retention over 85 cycles, indicating its potential for high-energy applications. This research provided valuable insights into optimizing TiS_4 and VS_4 composites for solid-state batteries.

Polymer protective coatings on lithium metal anodes for application in solid-state batteries

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The use of lithium metal in solid-state batteries (SSBs) is of big importance for increasing the energy density in comparison to lithium-ion batteries. However, many challenges towards this goal remain to be solved, like the stabilization of the interface between lithium metal and the solid electrolyte (SE) to ensure a long cycling life of the battery. A promising approach to solve this issue is the incorporation of a flexible polymer interlayer with a sufficient mechanical stability, which can provide protection against dendrite growth and compensate for pore formation during cycling. In this work, differently substituted polyphosphazenes are used as a protective layer between lithium and Li_6PS_5Cl (LPSCl) as SE. Different coating methods (e.g. dip coating, spin coating) are used to deposit the dissolved polyphosphazenes directly on lithium. The homogeneity and thickness of these polymer-coated lithium discs are analyzed via confocal microscopy and SEM (cross sectional analysis). The electrochemical characterization is performed via impedance spectroscopy as symmetrical lithium-SE-lithium cells in a pouch cell format.

Evaluating of the Pressure Dependence of Charge Transport in Composite Cathodes for Solid State Batteries

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Solid-state batteries (SSBs) have gained attention as a promising alternative to conventional liquid electrolyte-based lithium-ion batteries (LIBs) due to their potential for higher energy density and improved safety.[1] One of the critical challenges preventing the widespread adoption of SSBs in practical applications is their reliance on operating at higher stack pressures than LIBs. Recent studies demonstrated the importance of an optimized design of the cathode microstructure to decrease the stack pressure requirements of SSBs.[2,3] This indicates a strong correlation between charge transport in the cathode and SSB performance at low stack pressures. However, despite the strong influence of stack pressure on the cathode microstructure, the relationship between stack pressure and partial electronic and ionic charge transport has not been systematically investigated. We have evaluated electronic and ionic charge transport properties of composite cathodes as a function of stack pressure. By using Li_6PS_5Cl powders with different particle size distributions as catholyte materials we investigated how changing the composite microstructure influences the pressure dependence of charge transport. Our findings indicate that the partial electronic conductivity is highly sensitive to pressure. Although the partial ionic conductivity is less pressure sensitive at more application-oriented stack pressures it diminishes as well. Reducing the SE particle size results in higher ionic conductivities, but it does not affect the pressure dependence of the conductivity. Given the pronounced pressure dependence of electronic conduction, we found that addition of conductive carbon results in a particularly pronounced improvement of SSB performance at lower stack pressures.

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All-solid-state Li batteries with co-sintered NCM-LLZO based composite cathodes

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All-solid-state batteries featuring a Li-metal anode, a garnet type separator, and a thick composite cathode, composed of a solid-state electrolyte and a high-capacity active material (CAM), are promising candidates for the next generation energy storage systems. They address several challenges of conventional lithium-ion batteries (LIBs) by offering higher energy densities and intrinsic safety. However, the fabrication of such ceramic, fully inorganic batteries is challenging due to the necessary high temperature processing leading to material compatibility issues. Especially, the high capacity CAMs, like $LiNi_xCo_yMn_{1-x-y}O_2$ (NCM), which are absolutely necessary to obtain high energy densities comparable to current LIBs, show insufficient thermodynamic stability towards the solid electrolyte $Li_7La_3Zr_2O_{12}$ (LLZO) during co-sintering.

In our work, we comprehensively and systematically studied both, the impact of different NCM and LLZO compositions on the secondary phase formation during co-sintering by combining multiple experimental approaches, such as XRD, SEM, TEM, EDS, and Raman spectroscopy, in combination with simulation studies. The reaction onset temperature as well as the nature and amount of the formed secondary phases were determined and so far not reported secondary phases were identified. It was found that the chemical composition of the CAM as well as of the LLZO strongly affect the onset temperature of the decomposition reaction, the nature, and amount of formed secondary phases. In order to overcome the thermodynamic stability limits, innovative manufacturing processes for ceramic cell components, reducing sintering time and temperature, were investigated.

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Systematic optimization of slurry-cast all-solid-state battery cathodes and characterization of critical components

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Sulfide-based solid electrolytes (SEs), such as Li_6PS_5Cl, are extensively studied and chosen as the standard for testing all-solid-state batteries (ASSBs) due to their superior ionic conductivity and mechanical ductility. To facilitate industrial-scale production of ASSBs, it is essential to consider and adapt the sheet-type electrode structure commonly used in conventional liquid electrolyte-based lithium-ion batteries (LIBs). Aside from that, electro-chemo-mechanical degradation within the cathode composite poses significant challenges to the practical implementation of ASSBs. A systematic optimization is required, focusing on critical components, including the layered Ni-rich oxide cathode active material [CAM; here, $LiNi_{0.85}Co_{0.10}Mn_{0.05}O_2$ (NCM85)], SE, and anode material, such as indium-lithium alloy (In/InLi) or $Li_4Ti_5O_{12}$.
In our recent research, we studied the slurry casting of ASSB cathodes. For the latter, sol-gel and advanced nanoparticle coatings were applied to reduce side reactions at the CAM|SE interface. Additionally, a strategy to mitigate mechanical degradation, due to electrode breathing, was successfully implemented by properly balancing anode and cathode. Our results highlight the trade-off between attainable capacity and capacity retention in sulfide-based ASSBs, striving to approach the energy density of LIBs. Furthermore, we developed a reliable three-electrode setup for ASSBs to better understanding the kinetics and limitations of widely used cathode and anode materials.

Impact of Si content in Si/graphite composites on electrochemical and chemo-mechanical properties of solid-state batteries

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Silicon-graphite composites are among the most widely used anode materials in conventional lithium-ion batteries. Each component helps buffer the drawbacks of the other: the vast volume expansion of silicon and low capacity of graphite.[1] With such success, silicon-graphite composites have been considered as promising candidates in lithium-ion solid-state batteries (SSBs).[2,3] Herein, we investigate the influence of silicon content on the electrochemical and chemo-mechanical behaviors of different Si/graphite composites in Li-ion SSBs. All anode composites show excellent cycling performance in half-cells. An increase of Si presence in the composites enhances the cyclability at high current density. Using DC polarization and temperature-dependent electrochemical impedance spectroscopy, we observe no significant differences in either electronic or ionic conductivity of the composites, and both values are sufficient for battery performance. *Operando* stress measurement demonstrated how internal pressure varies as a function of Si content. At 20 wt% of Si in the composite, the stress induced from the anode shows a significant increase compared with low-Si ones. This study emphasizes the importance of optimizing Silicon/graphite ratio in the anode composites to build Li-ion SSBs that can offer high battery performance and stable chemo-mechanical properties.

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Graded NCM-cathodes for uniform reaction in solid-state batteries

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Solid-state-batteries are promising, as they are expected to offer increased energy density over conventional lithium-ion batteries by using lithium metal or silicon as anode material. To achieve these high energy densities a cathode with the highest possible loading is required. [1] Due to kinetic limitations of the charge transport the high loadings lead to reaction regions and with that to an incomplete utilization of the active material. [2] One possible solution could be an optimized charge transport trough a graded structure of the cathode, in which the content of active material in the composite is varied over the thickness of the cathode. [3] Therefore, an investigation of these graded cathodes is essential.

In this work, the cathodes consist of three layers with varying content of $LiNi_{0.83}Co_{0.11}Mn_{0.06}O_2$ and Li_6PS_5Cl. The gradient is built once with increasing active material content from the separator towards the current collector and reversed. Rate performance tests and long-term cycling were performed on half cells to investigate the electrochemical cell performance. The effective charge transport properties were determined by impedance spectroscopy using a transmission line model.

This work underlines the importance to adjust the structure of the electrode to design an optimized charge transport in solid-state battery composites. An increasing content of the active material from separator to current collector side can improve the charge transport and with that the active material utilization.

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Challenges and Opportunities in Calendering Composite Cathode of Polymer-Based Solid-State Batteries

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The established lithium-ion battery will reach its physical limits in the future [1]; therefore, it is important to research new types of batteries. A promising next-generation battery is the solid-state battery, which is expected to have a significantly higher energy density compared to the established lithium-ion battery [1, 2]. The polymer-based solid-state battery is characterized by its high flexibility and machinability in production [3]. Another notable feature is the low production cost compared to other types of solid-state batteries [4].

The polymer-based composite cathode presents exceptional challenges regarding individual processes and the design [3]. In production, calendering is a critical process that can affect the mechanical and electrochemical properties of the polymer-based composite cathode. Currently in calendering, there is a lack of accessible information on transferring the laboratory scale to a pilot scale. Therefore, a scalable concept for calendering on a pilot scale is presented. Material, product, and process-specific requirements are considered. Based on these requirements, a concept is developed to implement the calendering of the polymer-based composite cathode at the pilot scale.

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Investigation of the comminution of Li_6PS_5Cl and its influence on the improvement of the performance of composite cathodes

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For the performance of solid-state batteries (SSB), small-sized particles of the electrolyte are beneficial for the interconnection between the corresponding materials and therefore is crucial to achieve a high lithium-ion movability in order to realise a reduction of the internal lithium-ion flow resistances [1]. For the comminution of the particles, ball milling is a widely used method for the reduction of particle sizes [2] but needs to be investigated systematically.

In this study, the comminution of commercial Li_6PS_5Cl argyrodite electrolyte was investigated under wet conditions in xylene in the dual centrifuge DeltaVita 1. Different variations were investigated, such as the influence of the solid content and the use of different concentrations of polyisobutylene to prevent the re-agglomeration of the ground particles. As a result, the stabilization of the particles was demonstrated in the xylene-binder-solution, reaching a particle size median of $x_{50,3} = 4$ µm at a binder content of 2 wt.-%. Nevertheless, the XRD investigations show additional reflexes, indicating the formation of small quantities of decomposition products, such as Li_2S. However, the measured ionic conductivity of the obtained material is maintained at a level of $\sigma_{\text{ion}} = 0.7$ mS/cm within the process.

Subsequently, the improved comminution process for a successful particle size reduction was applied at varying comminution times within the production of solid-state cathodes using NCM811. The carried out cyclization tests show an improvement in the cyclization performance. Overall, this study aims to provide concrete recommendations for a successful comminution of sulfide-based electrolyte and its usage in cathode composite electrodes.

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Systematic investigation of stressing cathode composites for sulfide-based solid-state batteries in a planetary ball mill

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Investigating and improving the electrode's microstructure in sulfide solid-state batteries (SSBs) is crucial to achieve favourable electronic and ionic contact of the composite particles. [1, 2] One key aspect here is the solid electrolyte and active material particle size ratio. In this context, reduction of the electrolyte particle size can result in optimized charge transport and higher interface area to the active material particles. [2]

In this study, the stressing of cathode composites by a planetary ball mill for different rotational speeds was investigated systematically. Therefore, $LiNi_{0.83}Mn_{0.06}Co_{0.11}O_2$ (NMC83) was used as active material and Li_6PS_5Cl (LPSCl) as electrolyte. The influence of mixing time and rotational speed was investigated by particle size analysis, imaging by scanning electron microscopy, porosity of the pressed pellets, and X-ray diffraction analysis. Electrochemical cyclization tests of pellet-type cells were carried out. Excessive rotational speeds were found to result in strong caking of the materials and further degradation mechanisms. Moreover, building on these milling process first tests with polytetrafluoroethylene as binder were conducted. This study reveals important recommendations for the stressing of sulfide-based composite cathode, as well as important hints for further scale-up research for SSB production.

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Process Optimization of Sulfur-Carbon Black Cathodes for Enhanced Performance in PEO-based Solid-State Lithium-Sulfur Batteries

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Solid-state lithium-sulfur batteries have been considered as a potentially remarkable development in energy storage technology, especially for portable electronics and electric vehicles [1]. By combining the potential high specific capacity of sulfur-based cathodes with the stability and safety of solid-state electrolytes, these batteries promise enhanced performance, including longer cycle life and a more compact form factor. However, the challenges caused by sulfur's low electrical conductivity and the polysulfide shuttle effect result in capacity fading and lower efficiency [2]. This study involves the design and production of a sulfur-carbon black cathode material with a polymer electrolyte composed of poly(ethylene oxide) (PEO) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI). The ratio of sulfur to carbon black in the cathode plays a crucial role, as excess of carbon is often used to improve the electrical conductivity in Li-S batteries. Furthermore, determining the size of the carbon black particles in electrode slurries is a crucial step in the manufacturing of cathode using a solvent-based method [3]. The final particle structure of CB and its distribution within the slurry is highly variable depending on the energy input and the dispersion device. This research investigates the effects of varying sulfur-to-CB ratios as well as the impact of two different dry mixing methods and process parameters such as different tip speeds, dissolver disks and dispersing time. These results lead to a recommended set of parameters that enhance the battery's cycle performance and product characteristics (slurry, viscosity), potentially paving the way for more efficient and durable energy storage solutions.

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Impact of HNBR-Based Binders on the Electrochemical and Mechanical Stability of Solvent-Based Argyrodite Solid-State Separators

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The fabrication of solvent-based argyrodite solid-state separators depends on polymeric binders to ensure mechanical integrity during cell assembly. These binders must also maintain high electrochemical stability during battery operation to prevent degradation and extend battery life. Hydrogenated nitrile butadiene rubber (HNBR)-based binders are particularly advantageous due to their solubility in low-polarity solvents and their ability to provide mechanical stability to separators. However, linear sweep voltammetry measurements indicate that HNBR binders may contribute to electrochemical deterioration in solid-state separators. This study examines the impact of HNBR binders on the electrochemical and mechanical stability of separators and explores strategies to optimize binder composition for enhanced battery performance and longevity.

Exploring the Humidity-Induced Reactivity of Li_3PS_4 Solid Electrolyte: An In-Depth Analysis Using Advanced Characterisations Techniques

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The massive growth of the electric vehicle market has led to a surge in demand for safer and more energy-dense lithium-ion batteries. Sulfide solid electrolytes (SSEs) are a promising alternative to traditional liquid electrolytes, offering high ionic conductivity and suitable mechanical properties for processing [1]. However, they have a major drawback: extreme sensitivity to air and moisture with release of toxic H_2S gas. In the present study, a combination of advanced characterization methods is applied to investigate the reaction between pelletized SSE and humidity:

- H_2S evolution was quantified upon a SSE pellet exposure to humid atmosphere using a home-made flow-through setup [2],
- Surface and bulk morphology of the exposed pellets observed using SEM-EDX and X-ray holotomography (nano-resolution scale, ID16b beamline ESRF),
- Structural changes in the degradation front in the bulk were studied by X-ray diffraction-computed tomography (XRD-CT, ID15a ESRF Beamline),
- Ionic conductivities of pristine and degraded pellets compared using EIS.

An exposure of SSE pellet to humid air creates a 50-90µm deep degradation front where structural strains for SSE crystalline phase are followed by formation of new phases (S, Li_2S, Li_2O, $P_2S_2O_3$, P_2O_5) ending in massive SSE cracking and loss of ionic conductivity. To the best of our knowledge, this is the first comprehensive study of reaction between SSE and humidity.

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Microstructural Design and Analysis of Transport Properties of Li_6PS_5Cl-based Composite Cathodes in All-Solid-State Batteries

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Next to the reliable use of elemental Lithium as an anode material, overcoming the complexity of the composite cathode (CC) microstructure is one of the major challenges to achieve ASSBs with sufficient performance [1,2]. The microstructural design becomes more relevant when thick CCs [3] are combined with passivation coated cathode active materials (CAM) for high energy density and long cycle life, as conducting pathways (CP) become longer and the electronic conductivity of the CAM is reduced due to the passivation coating [4,5]. It is therefore necessary to design the ion. and elec. pathways and reduce their tortuosity through microstructural parameters like phase fractions, particle size distribution (PSD) and the porosity. In a previous work, we showed that the electronic conductivity of the solid electrolyte (SE) can be improved by adding conductive additive forming a conductive matrix (CM) – and that the amount needed can be determined and adjusted by a percolation study [6].

In this study, we fabricated CCs comprising passivation-coated single crystal NMC and the optimized CM via a dry and slurry-coating process. We analysed the effect of the PSD of the SE, the densification technique (UP, CIP, calender) and the phase fraction on the CC. The electrochemical performance was measured via galvanostatic cycling and EIS in blocking conditions to analyse the ion./elec. conductivity. Additionally, FIB-SEM tomography and machine learning based phase-segmentation was used to analyse the connected ion./elec. CPs within the CC. We found that the formation of coherent elec. CPs is crucial for thick CCs. Additionally, we show effective processing strategies to avoid big SE particles in the CC microstructure and thus increase its ion. conductivity.

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Microstructure Evolution and Transport Properties of Na_3PS_4-Based Composite Cathodes for Sodium-Solid-State Batteries

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Sodium solid-state batteries are promising candidates for future energy storage, combining the safety and stability of solid-state technology with the advantages of sodium, such as higher abundance and sustainability [1-3]. However, several challenges must be addressed, particularly the limited ionic transport capabilities of current solid electrolytes (SE) and the critical design of composite cathodes (CC) [4]. A well-designed CC should establish a percolating network of ions and electrons while ensuring electrochemical compatibility of SE and cathode active material (CAM) [4-5]. To achieve these requirements, the microstructural design of CCs, including phase fractions, particle properties, and phase distributions, must be carefully adjusted.

In this work, our motivation is to gain a deeper understanding of the interplay between the microstructure and the transport properties of the Na_3PS_4-based CC by applying the conductive matrix (CM) approach [6]. Within this aim, the CM mixtures (Na_3PS_4 + VGCF), with varied percentages (wt.% 2–12 VGCF in CM), were fabricated and analyzed for determining the percolation threshold of CCs. The CCs with different percentages (wt.% 40–70) of $NaCrO_2$ were investigated. Our findings revealed that the percolation zone for the CM is found to be VGCF content between 4-6 wt.% in the CM. Additionally, both ionic and electronic conductivity values increase with reducing the $NaCrO_2$ content.

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Development of Sodium Metal Anodes for Ceramic Solid-State Batteries

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As global electrification advances, the importance of electrochemical energy storage technologies is increasing rapidly. While significant strides have been made in the field, such as the commercialization of sodium-based batteries that rely on more abundant resources, the development of rechargeable batteries without liquid components remains an elusive goal. A critical challenge in this domain is the safe and reversible cycling of both lithium and sodium metal electrodes in conjunction with solid electrolytes at current densities which are comparable to today's lithium-ion battery technology. However, achieving metal/solid-electrolyte interfaces that can meet these demands remains largely unresolved.

This presentation provides new insights into the development of the anodic interface in model cells with sodium metal electrodes and ceramic $Na_5SmSi_4O_{12}$ solid-electrolytes. Here, particular focus is set on in-situ-formed, zero-excess sodium metal electrodes with sputter deposited metallic seed layers. The effect of the seed layers on the homogeneity of the initial sodium deposition is characterized in electrochemical nucleation experiments.

The failure modes of these sodium metal electrodes are examined with respect to sodium penetration (dendrite formation) through the ceramic separator during sodium plating, as well as interfacial void formation during sodium stripping. By measuring the critical current densities associated with these failure modes in DC-stripping/plating experiments at varying cell-stack pressure across a large number of test cells with identically assembled $Na_5SmSi_4O_{12}$ separators, the statistical impact of property variability intrinsic to polycrystalline sintered ceramics on their electrochemical behavior is evaluated.

Microstructural Impact on Filament Growth in All Solid-state Sodium Batteries via In-situ TEM Observation

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Solid electrolytes (SEs) serving for all solid-state batteries (ASSBs) are projected to overcome the performance and the safety limitations of liquid counterparts. However, they bring numerous microstructural features which can hint the performance as well. For instance, grain boundaries (GBs) of the inorganic SEs and the interface between SEs and electrodes are non-negligible factors that decrease the overall ionic conductivity and are supposed to be the weak area for filament growth and penetration. This topic is quite investigated in all solid-state lithium batteries, however, less pronounced in all solid-state sodium batteries.

Differing from most Li oxide SEs, Na-β’’-alumina solid electrolyte (BASE) possessed 2D Na-ion transport path due to its layer structure. Therefore, by the microstructural impact on the Na-ion transport and potentially Na-filament growth within electrolyte, the GBs should not be the only considered factor, but also the orientations of the grains play an essential role on the local current density. To investigate their influence on the ion transport and filament growth, a direct correlation between the microstructure and the Na deposition behavior through in-situ biasing TEM measurement. During the biasing, Na segregation around certain GB was visualized in real-time. Through 4D-STEM and automated crystal orientation map (ACOM) analysis, the orientations and the GBs information were obtained. It was found that Na filament always start growing at the GB of the two adjacent grains with special orientation relationship, which is in good agreement with the anisotropic 2D pathways for ion migration in Na-beta’’-alumina. The simulation of the current within the experimental sample can also support it.

In addition to intrinsic microstructure of the SE, this characterization was furtherly applied to investigate the behavior of the Au interlayer between the SE and the current collector, which is one solution for Na-ion batteries to minimize the filament growth at the interface. The microstructural evolution of this interlayer during operation was discussed. It was found that the microstructure of Au interlayer and the operation condition decide the effective protection of the Au interlayer.

Coating Copper Current Collectors on Ceramic Solid Electrolytes with Atmospheric Plasma Spraying for Zero-Excess Solid-State Batteries

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Smooth interface contact between a current-collector (CC) and the solid electrolyte is essential for plating a dense layer of sodium at the anode in a zero-excess solid-state battery. Atmospheric plasma spraying (APS) offers a novel approach for producing copper coatings on ceramic solid electrolytes (SE) for anode-free solid-state batteries (AFSSBs). This study investigates the feasibility of APS for the fabrication of pure Cu current collectors with enhanced interfacial contact without the use of additional layers for sodium nucleation with a high material deposition rate in comparison to physical or chemical vapor deposition of Cu. The qualitative results suggest that APS can produce dense and thin Cu coatings (3 µm) with high interfacial contact without crack formation in the thin and brittle solid electrolyte substrates (down to 300 µm). 10 µm of metallic sodium with a density greater than 80% was plated at such an interface of 10 µm thick sprayed Cu and Beta-alumina solid electrolyte.

Understanding and Quantifying Multiphase SEI Growth in Sulfide Solid Electrolytes

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The application of lithium metal anodes in solid-state batteries (SSBs) is prevented at the device level by the insufficient reduction stability of sulfide solid electrolytes, which necessitates the development of electrolyte materials with optimized properties [1]. Due to its thermodynamic instability, Li_6PS_5Cl is reduced upon contact with highly reactive lithium metal, forming a multiphase solid electrolyte interphase (SEI). This comprises a mixture of compounds, including Li_2S, Li_3P, and LiCl. The growth mode and microstructure of a few model-type SEIs are slowly being unveiled. Consequently, the electronically insulating nature of the evolving SEI is believed to restrict further formation and cause a significant slowdown in growth [2].

In this work, the direct reaction of Li_6PS_5Cl with lithium metal powder is employed to gain insight into typical multiphase SEIs with respect to their conduction properties. In order to estimate the SEI growth rate using a Wagner-type diffusion model, both the partial ionic and electronic conductivity of the SEI-type material are measured using dc polarization (*i.e.*, Wagner-Hebb configurations). These kinetic predictions enhance our understanding of SEI growth (specifically for Li_6PS_5Cl), leading to more accurate modelling of SEI transport parameters. Consequently, this improves predictions of SEI growth and kinetics in SSB cells, and highlight the importance of stabilizing the Li|SE interface through proper control of the partial conductivities of the SEI. [3]

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Unveiling the Decomposition Mechanism of $Na_{2.9}Sb_{0.9}W_{0.1}S_4$ with Na metal via In-situ XPS Analysis

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Sulfide-based sodium solid electrolytes (SE) are known for their outstandingly high ionic conductivity and their easy processability at room temperature due to their inherent softness, rendering them promising candidates for application in Na-based solid-state batteries (SSBs) [1]. The ionic conductivity of sulfide-based SEs depends on the crystal structure that can be altered by doping and substituting elements. While the undoped Na_3SbS_4 with its tetragonal structure has an ionic conductivity of 1.1 mS cm^{-1}, the cubic $Na_{2.9}Sb_{0.9}W_{0.1}S_4$ has an exceptionally high ionic conductivity of 41 mS cm^{-1} at room temperature [2]. However, these SEs react with sodium metal upon contact and form less conductive interphases, which would increase the overall resistance in SSBs, consume the anode reservoir, and ultimately can lead to short-circuiting of full cells, thus significantly decreasing battery performance [3].

This study investigated symmetric cells of $Na|Na_3SbS_4|Na$ and $Na|Na_{2.9}Sb_{0.9}W_{0.1}S_4|Na$. The chemical reaction rate between Na metal and SE was compared by time-dependent EIS analysis. The results showed that the interface resistance of $Na_{2.9}Sb_{0.9}W_{0.1}S_4$ increased much faster compared to Na_3SbS_4. To better understand the decomposition and the differences between these two SEs, in-situ XPS was applied to detect decomposition products during the Na deposition on the SE. For that purpose, pure Na metal was deposited onto $Na_{2.9}Sb_{0.9}W_{0.1}S_4$ inside the XPS chamber. The changes of the Na 1s, S 2p, O 1s, W 4d, and W 4f spectra were tracked for different amounts of deposited Na, revealing that elemental W formed that increased electron conductivity of the forming interphase and may explain the high decomposition rates.

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Quantification of Side Reactions and SEI Growth on Lithium Metal Anodes with Coulometric Titration Time Analysis

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All-solid-state batteries (ASSBs) with lithium-metal negative electrodes are promising candidates for advanced battery applications. However, most solid electrolytes are not thermodynamically stable with lithium metal. This results in undesired side reactions at the SE|Li interface, and thereby formation of solid electrolyte interphase (SEI) or mixed conducting interphase (MCI). Formation of such interphases leads to lithium inventory losses, increases the cell resistance, and eventually results in cell failure. Therefore, it is crucial to understand the quantitative nature of such reactions (and their kinetics).

We have recently proposed a new electrochemical approach[1] to quantify the side reactions occurring at the SE|Li interface. This new method, named as coulometric titration time analysis 'CTTA', [1] enables an accurate determination of electrolyte side reactions occurring on active metal electrode surfaces. The cell setup is in 'so-called' anode-free cell configuration with a noble current collector used as the working electrode' and an electrode active material with fixed potential and excess lithium used as the counter/reference electrode. A typical experiment consists of a series of lithium titration and subsequently applied open circuit voltage (OCV) resting steps. A full consumption of titrated lithium in each OCV step causes an abrupt voltage change enabling an indirect quantification of side reactions. We demonstrate that the method can be used to study the compatibility of different solid electrolytes and current collectors with lithium metal, and it can be useful in investigations of dendritic lithium growth.

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Heteroionic interfaces of thiophophate solid electrolytes

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From the various solid-electrolyte (SE) materials, thiophosphate-based SEs such as undoped and doped members of the xLi_2S-yP_2S_5 class are promising candidates for large scale production due to superior conductivity and good processability. Especially the high conductivity of materials like Li_6PS_5Cl (LPSCl), or $Li_{12}GeP_2S_{10}$ (LGPS) may enable fast charging of thicker cathodes, which are usually limited by ionic transport due to the desired minimized volume fraction of solid electrolyte.[1]

However, highly conductive SEs doped with cations such as Ge- or Si often exhibit poor anodic stability, leading to the use of dual hybrid batteries in which different SE materials are used for the separator and the catholyte, respectively. This introduces a new SE-SE-interface with a heteroionic interfacial resistance originating from an impeded ion transfer between the two SE materials. One example is a high interfacial resistance of up to 10 kΩ cm^2 in the case of $Li_7La_3Zr_2O_{12}$/polyethylene oxide-based systems.[2]

We also found interface-attributed signals in the impedance data of symmetric multilayer setups of crystalline LGPS and glass-ceramic $1.5Li_2S$-$0.5P_2S_5$-LiI against LPSCl. Nevertheless, using an in-depth investigation with scanning electron microscopy, we can demonstrate that these resistances originate from microscopic contact imperfections of the model system. Therefore, different thiophosphate SEs can be assumed to be fully compatible and exhibit a negligible heteroionic interface resistance in optimized contact conditions.

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Dilatometric Measurement of Pore Volume During Stripping of Lithium Metal Electrodes in Solid State Batteries

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Solid-state batteries (SSBs) have the potential to significantly increase energy density by enabling the use of a lithium metal anode (LMA). However, one of the key challenges is the formation of pores at the LMA|solid electrolyte (SE) interface during discharge, leading to contact loss and battery failure. Pore formation occurs when the local current density exceeds the vacancy diffusion rate within the LMA, leading to vacancy accumulation [1,2]. To better understand and address the limitations caused by pore formation, it is essential to gain operando insight into the total pore volume.

In this study, we present a novel dilatometric measurement setup with nanometer precision to track the height changes of the stripping electrode under constant pressure and isothermal conditions. This approach allows direct calculation of the operando pore volume. The power of this method is demonstrated by a case study on a $Li|Li_{6.25}Al_{0.25}La_3Zr_2O_{12}|Li$ model system subjected to different stripping current densities. The combination of the dilatometric data with electrochemical impedance spectroscopy data and microscopic image analysis provides a comprehensive understanding of the pore formation dynamics at LMA|SE interfaces in SSBs.

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Modifying the interface between solid electrolytes and Fe-Mn based oxide cathode active material for sodium solid-state batteries

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Sodium solid-state batteries (NaSSBs) have attracted great attention due to the promise of improving energy density, power density, safety, and abundance over traditional lithium-ion batteries. In this work, we have chosen P2-layered sodium transition metal oxides (Fe and Mn-based) due to their high theoretical capacity (170 mAh g^{-1}), and sulfide electrolyte (Na_3SbS_4) due to its fair ionic conductivity (0.5 mS cm^{-1}) and ease of processability.[1] However, there is significant capacity fade, which is due to mechanical contact loss between solid electrolyte and cathode active material.[2] Contact loss is caused by degradation reactions at the interface and volume change of the cathode active material during cycling. Interfacial degradation reactions may be mitigated by polymer coatings prepared by a spray drying process on the cathode active material particles as has hitherto proven an effective strategy for LiSSB.[3] However, the volume changes due to Na^+ and Jahn-teller distortion associated with Fe^{3+} and Mn^{3+} make it difficult to sustain the polymer coating.[4][5] Therefore, optimization of pressure with polymer-coated cathode and NaSICON ($Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$) electrolyte demonstrate improved interfacial performance. Thus, the optimization of cathodic interface with solid electrolyte, and pressure conditions cumulatively can help attain high-performance solid-state batteries.

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Carbon/Solid electrolyte hybrid materials for SSB

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Several challenges, comprising low ionic conductivity of solid electrolytes (SEs) as well as the poor electrochemical and chemical stability of most SEs remain, before realizing any practical application using Sodium-ion all-solid state batteries (Na-SSBs). [1] The chemical stability of the anode/SE interface is the key to reduce interfacial resistances to achieve high Coulombic efficiencies (CE) and a long cycle life. A promising class of negative electrode materials are hard carbons (HC) which enable the incorporation of Na^+-ions and are considered as being capable of bypassing interfacial constraints. In HC´s pores that are inaccessible for gas molecules (“closed pores”) enable the formation of quasi-metallic sodium within their bulk volume, thus delivering comparable capacities as the bare sodium metal and therefore offer high plateau capacities. [2,3] In this contribution, HC material is synergistically hybridized with Na_3SbS_4 (σ_s= 0,1-1 mS/cm). These hybrids were synthesized to optimize the interfacial contact between electrode and SE, which is considered crucial for the performance and efficiency of SSBs. To this end, different pore structures in the HC were introduced and then filled with SE via a liquid phase infiltration technique. A thorough structural and electrochemical characterization of a series of carbon/Na_3SbS_4 nanohybrid materials and their analogous physical mixtures as reference was conducted. The infiltrated composite materials display lower interfacial resistances compared to the reference. The influence of pore structure and filling degree of SE will be evaluated in the future to examine the optimal ratio of active material and SE. Furthermore, the reversible capacity, CE and cycling stability will be investigated based on half-cell measurements.

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“Cubic LLZO in Solid-State Batteries: Correlating Doping, Nanostructure and Electrolyte Performance”

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Abstract

The garnet-type solid electrolyte $Li_7La_3Zr_2O_{12}$ (LLZO) has attracted attention since its discovery due to its high ionic conductivity (~10^{-4} S cm^{-1}), stability with lithium, and wide voltage window (>5 V vs. Li/Li+), making it ideal for high-voltage, Ni-rich cathodes [1]. Cubic LLZO (cLLZO, space group Ia-3d) offers superior ionic conductivity, initially stabilized by Al^{3+} doping and later by Ta^{5+} substitution [2]. While extensive work has been conducted on bulk LLZO, often synthesized via coprecipitation, nanostructured LLZO is still under development [3]. This study investigates the electrochemical performance of PEO-LLZO composite electrolytes using various LLZO particles, including Ta- and Al-doped LLZO and particles obtained by electrospinning [4]. The reported values represent the specific discharge capacities measured at 4.1 V for NMC811 composite cathodes. Notably, the particles obtained by electrospinning achieved superior electrochemical performance, even though Ta-LLZO exhibited the highest ionic conductivity across all temperatures. This discrepancy was attributed to particle size and microstructure differences. The narrower particle size distribution enhances its homogeneity with the polymer phase, improving the structural uniformity and likely facilitating efficient ionic pathways, leading to higher discharge capacities.

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Rational design of cathode formulation with halide electrolyte for solid-state battery assembly via dry process chemistry

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All-solid-state lithium-ion batteries (SSBs) with halide solid electrolytes (SEs) have been developed to gain a high conductivity of 1 mS cm^{-1} through studies aiming at fast ionic conductivity of SEs. However, no matter how high the ionic conductivity of SE is, the design of cathode and electrolyte formulations is favourable for the improvement of contact between active material and SE for reaching the fully high ionic conductivity of SE compared to powder and achieving stable electrochemical performance. Therefore, the effective methods for preparing the composite electrode and SE should have better compatibility to be able to improve electro-chemomechanical aspects for manufacturing SSBs to develop scalable production technologies [1]. Here, this work, it was investigated the NMC cathode and halide SE formulation via the dry process chemistry for SSB assembly. It was considered the key parameter of optimization of the preparation of composite cathode and SE layer. It was shown the improvement of SSB strategy with NMC cathode and halide SE by modifying the mixing methods, their surface morphology, compatibility, processability, and electrochemical performance are compared. This project has received funding from the European Union's Horizon Europe programme for research and innovation under grant agreement No. 101069681 (HELENA project).

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Exploring the Structure-Property Nexus in Solid-State Electrolytes

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Advancing solid-state electrolytes (SSEs) is pivotal in developing all solid-state energy-storage systems, which expand across various classes of materials such as inorganic solid electrolytes, organic polymer solid electrolytes, and hybrid composite solid electrolytes. [1] They offer significant improvements over traditional liquid electrolytes in terms of enhanced safety, improved stability and longevity, higher energy density and minimized dendrite formation. [2]

This work focuses on the current research on chalcogenide-based SSEs for all-solid-state sodium-ion batteries, highlighting the structure-property relationships utilizing advanced techniques, including powder X-ray diffraction, solid-state nuclear magnetic resonance spectroscopy and electrochemical impedance spectroscopy. [3] The key topic includes innovations in chalcogenide material design for superionic conductivity by tuning the elemental composition with the assistance of tungsten substitution.

This presentation aims to comprehensively describe how SSEs can reshape the energy-storage landscape and contribute to developing safer, more efficient, and higher-performing battery technologies from foundational chemical science principles. This work concludes with an outlook of ongoing research directions aimed at optimizing SSE performance and promising scalability for commercial use, instilling optimism about the practical applications of these materials.

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Nanocellulose-templated Preparation of $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ (NZSP) NASICON Electrolytes

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Solid-state electrolytes (SSEs) can address the issues of safety, longevity, and energy density limitations in batteries, but an up-scaling challenge remains from high-risk processing parring with good ionic conductivity and interfacial contact. [1] Meanwhile, NASICON-type SSEs for sodium-ion batteries have been investigated widely for achieving a decent balance of stability for performance. Their progress nonetheless is still hampered by non-uniform structural design and impurity apparitions which reduces the Na^+ ion transport efficiency. [2]

Our group introduces cellulose nanofibers (CNF) as a biotemplate [3] for the arrangement of $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \leq x \leq 3$) electrolytes. The CNF's 3D fibre network permits the passage of NZSP sol, creating a systematic alignment of NASICON grains. Preliminary X-ray diffraction (XRD) and scanning electron microscopy (SEM) results reveal a reduction of the amount of ZrO_2 impurities and more uniform NZSP grains from the CNF-NZSP provided density improvements upon sintering, rendering better feasibility as templated framework for developing composite NASICON electrolytes.

This work aims to determine the magnitude of ionic conductivity improvement and reduction of interfacial resistance with biotemplated NASICON SSEs. Alongside, this work has the potential to increase the valorisation of biomass components in energy storage application, speeding up the realisation of solid-state, sodium-ion batteries.

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Development of a sulfidic electrolyte: industrial perspective from modelling to mass production

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All solid state electrolytes as critical enablers of denser, safer and cost effective batteries, are one of the critical components for future batteries. Among them sulfidic electrolytes possess the uniqueness of being compatible with throughput requirements of battery industry while being able to ensure room temperature operation combined with advanced cathode and anode materials.

Syensqo (formerly Solvay) will present the some of the key highlights of their recent years of research which allowed the construction of the first European pilot facility for sulfide manufacturing located in La Rochelle, France.

The presentation will show how, starting from the design of material done by modeling, the combined understanding of chemical synthesis routes and surface chemistry allowed us to design a proper sulfide electrolyte. The presentation will then focus on the application properties of this sulfide in electrochemical cells and on the exploration of its integration in wet and dry processes.

Experimental and Computational Investigation of Structure and Ionic Conductivity in the Halide Solid Electrolyte $Na_{1+x}Zn_xAl_{1-x}Cl_4$

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Sodium solid-state batteries (SSBs) are promising alternatives for lithium-ion batteries, offering improved safety and reduced cost. The key component of sodium SSBs is the sodium ion conductor. Metal halides have emerged as materials combining excellent mechanical processibility and compatibility with the electrodes.[1] However, the low ionic conductivity problem remains unsolved (10^{-6}~10^{-5} S/cm). Work on the subject has proliferated in recent years. The introduction of vacancies via aliovalent substitution is widely employed to improve the ionic conductivity of the ion conductor.[2]

In this work, we synthesized and studied the influence of Zn^{2+} substitution in $NaAlCl_4$ ($Na_{1+x}Zn_xAl_{1-x}Cl_4$ formula unit).[1] Since the second end member Na_2ZnCl_4 belongs to a different structural type as compared to $NaAlCl_4$, a solid solution is not guaranteed. We find phase separation does occur to some extent, indicating a 2-phase system can be formed to a limited degree. Hence, we are also simultaneously investigating the introduction of Al (and Na vacancies) in Na_2ZnCl_4. The stability of a 2-phase system with enhanced ionic conductivity will be discussed based on ab initio (DFT) calculations and the structures observed experimentally by XRD.

Furthermore, the system is investigated by EIS and variable temperature NMR to clarify the Na conductivity and the origin of its improvement. Overall, we shed light on a promising electrolyte system for Na-based SSBs, especially for the catholyte part.

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Polymer Ceramic Electrolyte (PCE) for Medium Temperature All-solid-state Sodium Batteries

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All-solid-state sodium batteries (ASSBs) offer a safer alternative to conventional sodium-ion batteries by replacing liquid electrolytes with solid polymer and inorganic electrolytes. This design mitigates safety risks like dendrite growth and short circuits, enhancing battery performance and stability. [1] These inorganic fillers in polymer electrolytes are either passive or active. Passive fillers enhance ion transport by reducing crystallinity in the polymer matrix, while active fillers also provide direct pathways for ion movement due to their inherent conductivity. Both types improve the performance of composite electrolytes in solid-state batteries. [2,3] The incorporation of inorganic fillers into polymer electrolytes enhances mechanical strength and electrochemical properties, unlocking the full potential of these batteries. The recent advancements, also highlights the development of an ultra-thin single-particle-layer composite polymer electrolyte membrane combined with a sodium beta-alumina ceramic electrolyte, which offers the flexibility of a polymer membrane alongside efficient sodium-ion transfer pathways, ensuring compatibility with anode components. [4] Herein, the dispersion of Na-ß-aluminate systems into a solvent-free UV cross-linkable PEO matrix will be presented. Secondly integration these PCEs with cathodes will be another challenging step in this direction. The systematic studies to understand the engineering aspects of the polymer cathode composite (PCE) formation by varying the different contents of active material NVP, conductive additives, ion conducting components in order to elucidate the ideal ion as well as electron conduction morphology in the cathode composite, will be explained in detail.

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Laser Sintering of Ceramic Solid Electrolytes

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The success of commercializing solid-state batteries depends on the properties of the materials, their costs and their processing, regardless of the material class. In particular, two areas of research have been identified for the processing of ceramic solid-state electrolytes - synthesis and sintering of the material.

NASCION-type lithium aluminum titanium phosphate (LATP) is considered to be a promising solid electrolyte due to its chemical and thermal stability and low cost. However, the powdery material requires sintering to compact the loose particles and reduce the interfacial resistance. Various sintering techniques can be used, including conventional furnace sintering and field-assisted sintering technologies (FAST). Nevertheless, long process times, discontinuous process management and complex systems with costly vacuum systems make their suitability for large-scale production questionable. In addition, the resulting material properties, such as lithium loss or intensive post-processing to remove unwanted reaction products, also limit the progress.

Accordingly, new sintering techniques are needed to reduce these disadvantages and shorten the development time. An innovative approach to sinter LATP is the use of laser radiation as a heat source, as this process benefits from a fast processing time. It also eliminates the need for vacuum systems and allows the realization of complex sample geometries.

In this work, the laser-material interactions are analyzed and the effects of infrared radiation on the solid electrolyte LATP are determined. For this purpose, different laser parameters (average output power, scanning speed, etc.) are varied and their influence on the material is evaluated. The results show that higher processing intensities lead to greater sintering depths, although this is accompanied by the formation of secondary phases.

2-Adamantanone as potential solid-state electrolyte for post-lithium batteries

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In contrast to the conventional liquid electrolytes used in lithium-ion batteries, solid-state electrolytes offer several advantages, including greater safety, improved stability, and the potential to enable higher energy densities and faster charging speeds. The focus of solid-state electrolyte research is on oxide ceramics, sulfides, and polymers, with each material class having different advantages and disadvantages. In recent years, plastic crystals have gained attention as another class of materials for solid-state electrolytes. Like polymer-based solid electrolytes, plastic crystals can serve as a matrix to dissolve the conducting salts, leading to good ionic conductivities.

Bardenhagen et al. [1] showed that using 2-Adamantanone, which belongs to the plastic crystal class, in combination with lithium bis(trifluoromethanesulfonyl)imide, results in a high ionic conductivity of 0.1 mS/cm and good thermal and electrochemical stability.

In this study, 2-Adamantanone was utilized in combination with either lithium bis(trifluoromethanesulfonyl)imide or sodium bis(trifluoromethanesulfonyl)imide to investigate the influence of residual solvent on ionic conductivity. The primary objective was to identify an optimal composition for enhancing ionic conductivity. This investigation was carried out using Design of Experiments methodology, allowing for a systematic and efficient exploration of the experimental space. The findings provide valuable insights into the role of residual solvents in the ionic conductivity of these systems and aid in the identification of suitable compositions for potential applications.

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Standardization and automation of the ionic conductivity measurements of solid electrolytes

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The rapid advancement of technologies increased energy production and the development of battery technologies. Research has concentrated on innovating and investigating electrolytes in Li-ion batteries, particularly seeking safer alternatives to the toxic and flammable liquid electrolytes currently in use. Solid electrolytes (SEs), which can be polymeric or inorganic, have emerged as a promising option. However, challenges such as limited commercial and large-scale availability of SEs and the lack of standardized methodologies for their characterization hinder their full implementation in battery systems. A recent Round Robin study highlighted significant variability (up to ±50% of the average ionic conductivity) in ionic conductivity measurements of superionic lithium thiophosphate solid electrolytes, even among nominally identical samples. This variability underscores the need for a systematic approach to establish standardized protocols for SE characterization. Our research focuses on examining the effects of sample processing conditions and the parameters for collecting impedance data, which is used to determine conductivity values.

The influence of the pelletizing pressure and the measurement set-up on the reproducibility and accuracy of conductivity measurements were investigated. Furthermore, we explore the parameters for impedance data collection, such as frequency range, electrode material, and contact quality, which are crucial for reliable conductivity extraction. The expansive dataset generated through our experiments will serve multiple purposes. Firstly, it will provide a robust foundation for developing a standardized protocol for SE characterization. Secondly, the dataset will be instrumental in training machine learning algorithms to automate the evaluation of impedance spectra, enhancing the precision and efficiency of conductivity measurements. Our efforts aim not only to advance scientific understanding but also to facilitate the practical application of SEs in battery technologies. By ensuring consistent and reliable SE characterization, we can accelerate the development and deployment of safer, more efficient batteries, ultimately supporting the growth of smart technology and electric vehicles. This research represents a step toward the future of energy storage, emphasizing the importance of standardization and automation in material science.

Chemo-Mechanics of Solid Electrolytes: Investigating Fundamental Mechanisms of Lithium Metal Nucleation

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Pairing lithium metal with non-flammable solid electrolytes promises to enhance the safety of Li-metal batteries. Over the past decades, significant progress has been made in producing solid electrolytes with high ionic conductivity. However, metallic lithium can nucleate and grow within inorganic solid electrolytes at current densities between 1-2 mA/cm^2, leading to short circuits. The exact mechanism of Li metal nucleation and penetration through inorganic solid electrolytes remains unclear. This lack of knowledge prevents the development of strategies to mitigate lithium-induced short circuit failures in batteries. In this work, we unveil the nucleation mechanism of Li metal in solid electrolytes, using LLZTO as case study, aiming to mitigate the chemo-mechanical degradation of solid electrolytes. In addition to visualizing the feature of Li filament using advanced cryo-electron microscopy coupled with insert air transfer suitcase, we explore the in-situ stress response in solid electrolytes (LLZTO) in macro-and micro-scale during electroplating, which can be used to diagnose the chemo-mechanical degradation of solid electrolytes.

Polyimide-PEO Copolymers as Novel Thermally Stable Solid Polymer Electrolytes for Lithium-Metal Batteries

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Polymer electrolytes (PE) consisting of lithium salt dissolved in polymer matrix are widely recognized as attractive electrolyte materials for the next generation of solid-state energy storage devices. They offer several benefits in comparison with traditional liquid electrolytes, including flexibility, enhanced safety, ease of membrane formation, and excellent electrochemical stability. Over the past five decades, poly(ethylene oxide) (PEO) has become a preferred option for PE application due to low glass transition temperature, chain flexibility, remarkable electrochemical stability against lithium metal, and great solubility for conductive lithium salts. Polyetherimides (PEI) are widely recognized high-performance polymers widely used in areas such as membrane separation, adhesive, electrical insulation, gas transport, oil storage and composite matrices, due to their excellent thermal and chemical resistance in combination with good mechanical properties.

The goal of this study was to synthesise PEI-PEO copolymers with the aim to combine the benign properties of both polymer classes. Herein we synthesized novel polymer with flexible ether linkage and bulky fluorinated substituent in the backbone. The polymer properties were varied by studying different monomer concentrations, resulting in copolymers with different PEI-to-PEO block ratios (from x = 0.05; 0.15; 0.3). The structures of copolymers were confirmed via ^{1}H NMR and FT-IR spectroscopy. By tweaking the PEO content, the glass transition temperature can be adjusted in the range from 24 to 195 °C enhancing mechanical properties. Our results show that the polymers with high concentration of PEO block are able to dissolve high amounts of Li-salts (up to 70%$_{wt}$) to form “polymer in salt compositions” with intriguing electrochemical properties such as a wide electrochemical stability window and excellent flame stability.

SCHOTT's LLZO and LATP Materials: Pioneering the Future of Solid-State Batteries

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At the forefront of solid-state battery technology, SCHOTT presents its latest advancements in lithium solid-state ion conductor materials: lithium lanthanum zirconia (LLZO) and lithium aluminum phosphate (LATP). These materials are pivotal in the development of post-lithium-ion batteries, offering a promising leap towards more efficient, durable, and safer energy storage solutions. Leveraging its profound expertise in glass and glass-ceramic manufacturing, SCHOTT has honed a unique production process that integrates a minor amorphous phase within the functional crystalline matrix. This distinctive approach not only enhances the material's overall performance but also allows for precise customization to meet the diverse requirements of various cell designs, including both inorganic sintered ceramics and hybrid electrolytes. SCHOTT's poster will delve into the empirical findings on the aging behavior of LLZTO, providing valuable insights into its stability under different atmospheric conditions [1]. The main issue addressed is the reaction of LLZO with water and carbon dioxide, leading to the formation of lithium carbonate, which hinders its manufacturing and processing. The study focuses on Ta-doped LLZO powders, examining the kinetics of their hydration and carbonation. It was found that degradation occurs in a two-step process, influenced by particle size, with larger surface areas accelerating the reaction. The hydration step is crucial before carbonation can occur, and the rate of both reactions is directly proportional to the particle size. These findings are significant for improving the handling and processing of LLZO powders for better surface quality in battery applications.

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Investigating the formation of $Li_{6-x}PS_{5+x}Cl_{1+x}$ based on precursor pre-treatment

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Contemporary research in the realm of solid-state batteries shows one common basis: high ionic conductivities of the applied solid electrolytes.[1] $Li_{6-x}PS_{5+x}Cl_{1+x}$ (LPSCl) shows promise for application in actual commercial cell systems.[2] Understanding preparation-structure property relationships is critical, especially as depending on the preparation method a wide spread of ionic conductivities is accessible for formally the same product. Limited efforts have been devoted to scrutinize the specific impact of processes such as ball milling on the reaction mechanism, aside from acknowledging potential pre-coordination effects and reduction of particle sizes/increase of contact areas that notably reduce reaction times.[3] From ball milling to intensive mixing in a blade grinder, substantial endeavors have been undertaken to manipulate reaction temperatures and pre-treatment methods, expanding the boundaries of conductivity and commercial feasibility, e.g. scalability.[4] To achieve this, in-depth knowledge on the exact reaction pathway and observable intermediate phases is needed. Existing literature sheds limited light on the occurring reaction mechanism of the unsubstituted LPSCl.[5] Here we present a study which monitors the occurring phases and formation of LPSCl during heating of differently treated starting mixtures via in-situ neutron and ex-situ X-Ray diffraction. These observations were subsequently used to test the scalability of the respective synthesis in regards to the mixing method of the starting materials by comparing blade ground as well as ball milled mixtures to achieve a working and very reproduceable lab synthesis protocol in the multi-gram scale.

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Sodium metal oxychlorides as superionic solid electrolytes

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Na-ion solid electrolytes are currently being investigated as promising candidates for solid state batteries. Due to the scarcity of the Li metal in the current Li-ion technology and the safety issues of liquid batteries, the scientific interest has been shifted to alternative ways with the desire to meet the demands for high energy density capabilities in solid state batteries. [1,2] *Sulfides*, *oxides* and *halides* have been the different classes of materials thoroughly studied as potential solid electrolytes. Although all the families show a reasonable transport performance, they lack electrochemical stability, mechanical stability and/or easy processing. In this context, the use of *mixed-anion* chemistries could be a reliable tool to design novel solid electrolytes since they could combine different properties of each class of material. Recently, some sodium metal oxychlorides with nominal composition $NaMOCl_4$ (M^{5+} = Nb^{5+} or Ta^{5+}) have been experimentally found. [3] The fact that those materials combine chlorine and oxygen anions can improve their deformability and their electrochemical oxidation stability and make them promising candidates as solid electrolytes.

Here we present an extensive investigation of the structure, transport properties and electrochemical stability of $NaMOCl_4$ (M^{5+} = Nb^{5+} or Ta^{5+}) by the combination of scanning electron microscopy–energy dispersive X-ray spectroscopy, X-ray diffraction, pair distribution function analysis, Raman spectroscopy, nuclear magnetic resonance spectroscopy and impedance spectroscopy. By fully analysing those materials, we hope to offer a reliable guidance to design novel *mixed-anion* solid electrolytes.

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Investigating the influence of transition metal substitution in lithium argyrodites on structure, transport and solid-state battery performance

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Lithium argyrodite solid electrolytes are promising candidates for solid-state batteries mainly due to their superior ionic conductivities. However, during charging oxidative decomposition reactions at the interface between solid electrolyte and cathode active material impede cell performance.

In this study, transition metal substitutions of lithium argyrodites are investigated with the intention to tune the composition of the cathode electrolyte interphase (CEI) and thereby improve the cycling performance. Since a ZnO additive has shown the capability to mitigate oxidative decomposition of Li_6PS_5Cl[1], Zn^{2+} substitutions in the $Li_{5.5-2x}Zn_xPS_{4.5}Cl_{1.5}$ ($0 \leq x \leq 0.15$) and $Li_{6-2x}Zn_xPS_5Br$ ($0 \leq x \leq 0.15$) substitution series are investigated with regard to structure, Li^+ transport and their performance as catholytes in solid-state batteries. Co-refinement of the neutron and X-ray powder diffraction data unveils the occupation of Li^+ positions by Zn^{2+}, which leads to blocking of Li^+ transport pathways, causing a minor decrease of ionic conductivities. By using a combination of cycling experiments, impedance spectroscopy and X-ray photoelectron spectroscopy, the composition of the CEI and the state-of-charge dependence of the CEI growth when using $Li_{5.5-2x}Zn_xPS_{4.5}Cl_{1.5}$|NCM-83 composites was investigated in half-cells.

The results show, that Zn^{2+} substitution of argyrodites does indeed affect the composition of the CEI and the kinetics of its formation, highlighting the potential of transition metal substitutions to tune CEI composition and thereby cell performance.

Literature:

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Pre-Passivation Strategy for More Reversible Ca-Plating and Stripping from Poly(ethylene oxide)-Based Solid Polymer Electrolytes

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A major roadblock in the field of multivalent ion transport in solid polymer electrolytes (SPEs) is related to the surface chemistry at the highly reactive metallic negative electrodes (e.g. Mg or Ca) towards electrolyte salt and polymer host.[1] As a result, reversible plating and stripping of multivalent ions tends to proceed with low Coulombic Efficiencies. A promising strategy to address this challenge is to activate the electrode surface through the formation of an artificial SEI layer.

Here we present how more efficient and reversible metal deposition can be achieved in $Ca(TFSI)_2$-based polymer electrolytes through a pre-passivation approach. The modified Ca-metal electrodes were examined with a PEO-based solid electrolyte in a symmetrical cell setup and displayed significantly reduced overpotentials compared to pristine electrodes. The results represent an encouraging step towards more efficient SPE-based calcium metal batteries.

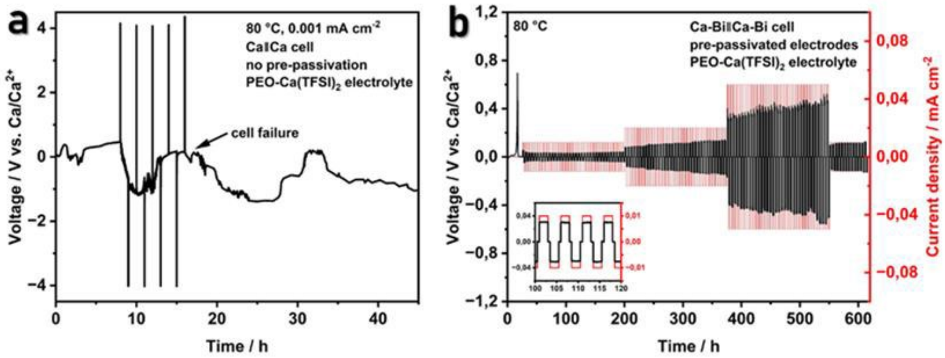

Fig. 1: Voltage profiles of symmetrical Ca-Ca cells with PEO-$Ca(TFSI)_2$ solid electrolyte, a) pristine Ca/Ca and b) surface modified Ca/Ca electrodes.

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Effect of Processing Conditions on Transport and Cycling Properties of All-Solid-State Battery Cathodes

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All-solid-state batteries (ASSBs) are promising next-generation batteries offering improved safety properties and high energy densities.[1] Among the solid electrolytes (SEs), thiophosphate-based SEs are an attractive class due to their high room temperature ionic conductivity (>1 mS/cm). While most of the thiophosphate-based ASSB cells in the literature have been tested in custom-made press cells, more application-oriented ASSB cathode sheet processing has recently become more important.[2,3] However, their processing procedures differ significantly from those of press cells, with many additional steps affecting the system. For example, the use of solvents, drying temperatures and polymer binder is required.

Here, we investigate the effect of processing conditions on an argyrodite (Li_6PS_5Cl)-NMC-based composite cathode, comparing electrochemical characteristics such as partial transport and cycling properties, with those of an untreated reference. The processing conditions investigated include (I) the effect of two different solvents, acetonitrile and *o*-xylene; (II) the influence of heating (drying) steps and (III) the impact of incorporating a polycaprolactone (PCL)-based polymer.

The present work shows that all three factors, mild heat-treatment, solvent treatment and polymer addition, decrease the partial electronic or ionic conductivity, or both. This is also reflected in the cycling properties, where lower capacities and worse cycling performance are observed as a consequence. These results indicate that all processing parameters must be carefully selected, separately tested and optimized.

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New Li-rich niobate and tantalate phases: A combined structural investigation using diffraction and spectroscopic methods

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In Li metal-based batteries, the Li-rich materials are of interest for application as Li-ion conducting solid electrolytes as well as artificial interphase/coating layers [1,2]. Due to sparse reports on electronically insulating Li-rich materials containing Group V d^0 metal oxides, we explored the Li-rich side of Li-M-O phase diagrams (M= Ta and Nb).

In the solid-state route by tuning the Li/M ratio we have successfully synthesised two new phases, $Li_8M_2O_9$ and $Li_{10}M_2O_{10}$. A combined synchrotron X-ray diffraction (SXRD) and neutron diffraction (ND) analysis revealed a layered structure with a complex superstructure. To get complete structural insights, local M-O distances and symmetries were assessed by extended X-ray absorption fine structure (EXAFS) analysis. We conducted in-depth Nb ssNMR measurements on the known Nb compositions to develop a structural assignment of the different Nb sites in the Li-based oxides. Following this we recorded Nb ssNMR spectra on the two new Nb phases. We will summarise the synthesis optimisation and in-depth structural characterisation of the new phases using long-range (diffraction) and short-range (EXAFS and ssNMR) characterisation techniques.

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Discrete Element Method for determining the contact properties of Halide based ASSBs

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Halide is prominently recognized as a promising electrolyte for all-solid-state batteries (ASSB) due to their advantageous combination of properties derived from both oxides and sulfides. They exhibit moderately high ionic conductivity at room temperature (>2 mS/cm) and safe processibility. Understanding the microstructural behavior of these particles is crucial for comprehending their mechanical properties during cycling, as well as their ionic and electronic transport characteristics. This understanding is best achieved through the application of the Discrete Element Method (DEM). In this context, we introduce a contact model that computes normal forces by taking into account the elastic-plastic behavior and simultaneously addressing all contacts of a halide particle [1,2]. We assess how the volume changes of the active material (AM) particles during charge and discharge cycles affect contact parameters such as contact area and reaction force. The contact properties obtained are utilized to estimate grain boundary conductivity, a property that is often challenging to measure experimentally. This study offers a realistic approach for calculating contact forces and estimating important material properties that are difficult to evaluate through experimental means.

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Model-Based Cathode Optimization: Maximizing the Energy Density in High-Performance Solid-State Batteries

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The development of solid-state batteries depends significantly on the optimization of the cathode's microstructure and composition. The microstructure governs the transport of ions and electrons. Key parameters, such as mass loading and porosity, can be fine-tuned to improve ionic and electrical conductivity, thereby maximizing the energy density [1, 2].

This study focuses on the relation of cathode microstructure, material composition, and discharge performance. We study nickel-rich cathode materials ($Li[Ni_xCo_yMn_z]O_2$, where x ≥ 0.8), which promise high theoretical specific capacities (≥ 200 $mAhg^{-1}$). This makes them ideal for solid-state batteries, especially when combined with sulfide-based solid electrolytes, known for their high ionic conductivity at room temperature [3].

However, challenges such as tailoring the cathode's structure and composition during fabrication for specific applications remain. Addressing these issues requires a comprehensive approach to fine-tuning cathode parameters.

To advance this optimization, we utilized a Doyle-Fuller-Newman (DFN) model for single-ion conductors [4], parameterized with experimental data from cells featuring a composite cathode of NMC82 (Li[Ni0.82Mn0.07Co0.11]O2) and lithium phosphorus sulphur chloride (LPSCl) solid electrolyte. Through sensitivity analysis, we evaluated the impact of active material weight fraction and cathode thickness on achievable energy density and areal capacity. Subsequently, numerical optimization identified the most effective parameters to maximize both energy density and areal capacity, establishing a clear relationship between cathode design and battery performance.

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Investigating self-heating of all-solid-state batteries via 3D modelling

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All-solid-state batteries (ASSBs) as one of the most promising candidates for next generation energy storage systems are usually assumed to be safer than conventional lithium-ion batteries with organic liquid electrolyte. However, studies have shown that solid-state batteries are not ultimately safe and they can undergo thermal runaway when exposed to high temperatures [1,2]. One common method of safety investigation for battery cells is applying a thermal ramp on the cell, increasing their temperature from room temperature to around 600^{o}C with a rate of 5-10 ^{o}C/min and investigation of self-heating due to the heat flow from chemical reactions occurring in high temperatures. By using mathematical modelling and with the help of differential scanning calorimetry (DSC) test data [3] it is possible to predict self-heating in ASSBs as a result of heat flows inside the cell in high temperatures. In this contribution, we analyse the temperature profile within ASSB cells during overheating. We analyse the case for which exothermic reactions could occur inside the cell, and the temperature of the cell starts to increase due to the heat flow from those reactions (self-heating). Results for ASSBs with several different materials, including sulphide and oxide solid electrolytes, will be presented and compared. These results are obtained via a 3D modelling approach implemented in COMSOL Multiphysics. The modelling results provide insights for safer operation and better designing of ASSB cells in the first step and will need to be validated using experimental data in the future.

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Enhancing Stability of Li_6PS_5Cl Solid Electrolyte through NMP Treatment

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The stability of Li_6PS_5Cl, a promising solid electrolyte for lithium-ion batteries, has been a significant challenge due to its reactivity with lithium metal. Recent experimental studies have demonstrated that N-Methyl-2-pyrrolidone (NMP) treatment can enhance the stability of Li_6PS_5Cl by serving as a non-passivating layer. In this study, we explore the underlying mechanism of this stability through Density Functional Theory (DFT) calculations.

Our results reveal a strong interaction between NMP's oxygen atom and the lithium ions on the argyrodite surface, with an adsorption energy of 1.03 eV. This interaction leads to a significant elongation of the C=O bond and a red shift in its vibrational frequency. The average adsorption energy decreases with increased NMP coverage, indicating a saturation effect.

Furthermore, static energy calculations suggest that the partial oxidation of Li_6PS_5Cl via the S-O exchange reaction between NMP and PS_4^{3-} units is thermodynamically feasible, with a slightly negative reaction enthalpy (-0.07 eV). However, preliminary calculations suggest a high reaction barrier or a complex mechanism.

These insights provide a potential pathway for improving the stability of Li_6PS_5Cl in battery environments and suggest that future research should focus on targeted surface modifications to further enhance the performance of solid-state batteries.

Keywords: Li_6PS_5Cl, NMP, Solid Electrolytes, DFT, Battery Stability.

Li diffusion in the argyrodite-type Li6PS5Br: Effects beyond Br/S anion disorder

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Several sulfide solid electrolytes (SEs) convince with high ioinic conductivity, which is an important condition to realize solid-state batteries with high performance. In particular, argyrodite-type materials derived from the model composition Li_6PS_5X (X=Cl, Br) have attracted a lot of attention in the recent years. We will first recap our approaches by using atomistic simulations focusing on Li_6PS_5Br, showing that Li diffusion critically depends on an important structural feature of the material: anion disorder among the Br and S sublattices. At low degrees of disorder, Li ions are only able to diffuse locally, but miss convenient long-range pathways. Such pathways are installed as soon as sufficient Br/S disorder is introduced, which can be controlled experimentally by quenching the material from high temperatures.

Similarly to the case of Li_6PS_5Br, bulk properties of many other SEs have been analyzed and sufficiently understood. Microstructural aspects, on the other hand, still remain uncertain in the realm of sulfide SEs. For this reason, we recently investigated the effects of grain boundaries (GBs). To this end, two symmetrical GB models have been generated with varying Br/S disorder and Li diffusion has been analyzed. Interestingly, GBs are found to have an ambivalent character: Whereas GBs improve Li diffusion in the fully ordered Li_6PS_5Br, they reduce the overall Li diffusivity at high degrees of Br/S disorder. In the first case, the improved diffusivity stems from structural disturbances induced by the GB, enabling long-range pathways for Li diffusion in the GB's vicinity. In the second case, however, efficient pathways are already accessible in the bulk and the presence of the GB partially disrupts these paths. This can be seen in a reduced density of tetrahedral sites near the GB and highlights the importance of microstructural engineering in sulfide SE. [1]

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Investigating fracture formation of solid-state batteries at the microscale

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Solid-state batteries, renowned for their superior safety and energy density, pose distinctive difficulties concerning the structural integrity of their solid electrolytes. When subjected to mechanical stress, the fracture characteristics of these materials become crucial, affecting both their performance and lifespan. Ionic crystals, such as cathode materials and ceramic electrolytes, possess inherent brittleness caused by significant energy barriers for dislocation nucleation. Consequently, their fracture toughness is relatively low. Crack propagation in battery systems primarily occurs at interfaces and within solid components. The key points include the transgranular fractures within cathode active particles and cracking in the solid electrolyte. Crack growth, void formation from the anode side, and intergranular fractures induced by Li-dendrites are crucial factors in the solid electrolyte where microcracks frequently initiate at the edges of the electrolyte, ultimately resulting in failure. [1]

This study employs crystal plasticity and phase-field damage methods to capture fracture events in the intricate polycrystalline electrodes of solid-state batteries. The double-phase-field approach is used to track the formation and propagation of shear cracks with Coulombic characteristics and tensile cracks driven exclusively by tensile stresses. The proposed framework is sufficiently flexible to capture the brittle behavior of constituent materials in batteries under operando conditions.

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Benchmarking Data-driven Anomaly Detection in Battery Cycling Protocols

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With increasing adoption of batteries for various applications spanning from consumer electronics to electric vehicles and aircraft, large amount of battery datasets are being curated and collected for different purposes. During battery cycling across hundreds of cycles, anomalies could happen inevitably due to reasons such as equipment breakdown, batteries manufacturing flaw, measurement errors or even cell failure. As a result, collected dataset is often contaminated with different outliers, which could cause performance deterioration over an extended cycling period. While removing a few anomalous data points manually by visual inspection during one cycle is trivial, handling outliers across multiple cycles for hundreds of cells is time-consuming and cumbersome.

In this study, we present combined statistical methods with machine learning models for high-throughout outliers detection across thousands of cycles for different cell chemistries, including solid-state cell chemistry. We create labelled dataset for algorithms benchmarking purposes and make the dataset publicly available using state-of-the-art database. Here, we show that statistical methods combined with machine learning models could shorten the time required to detect outliers in battery cycling protocols. By tracking outliers during battery cycling processes systemically, possible reasons causing outliers can be identified to improve the long-term battery performance and reliability.

Speeding up solid state battery development - benefits of high-throughput concepts for battery materials research

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Increased demand for affordable, safe and performant energy storage has led to extensive efforts in R&D for new battery materials among which solid state electrolytes show great potential. Cell performance of this new class of batteries is largely governed by the properties of the employed materials and for further development, control of interdependent parameters in the various process steps is necessary. This includes i.e. optimization of compositions, coatings, particle sizes and morphologies as well as rapid exploration and benchmarking of novel concepts and material systems. To stay competitive in a volatile, fast-developing field means that numerous material systems have to be investigated in parallel. Optimizing not only material properties, but also process conditions results in a high number of optimization steps and experiments that need to be performed simultaneously.

Most of these experiments cannot be conducted on a pilot scale due to limitations in available materials, capacity, space and cost, and lab scale approaches promise much faster results. However, even on a lab scale the number of experiments and amount of relevant data that must be handled requires innovative approaches such as miniaturization, parallelization, automatization and digitalization. Each of these approaches has its specific challenges that need to be addressed.

We will present guidelines for a solid-state battery materials R&D workflow that improves sample preparation quality and parameter optimization, while retaining the necessary information for scaling up. Here it is important to detect and address bottlenecks during sample preparation since these will affect the quality and throughput for all following steps. Additionally, we summarize common error sources and demonstrate how a classification of these can enable the implementation of fast troubleshooting approaches. We show, how sample output can be maximized with high-throughput methods while data quality is maintained and demonstrate, how automatization and standardization can accelerate battery materials research along the whole process chain from materials synthesis to full cell testing.

STEM, PED, and EELS: A powerful combination for the investigation of cathode-active-materials for batteries

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The Cathode Active Material (CAM) is the main component contributing to a battery's specific energy as well as its cost. State-of-the-art CAMs are transition metal oxides of the form $Li(Ni_{1-x-y}Co_xMn_y)O_2$. To increase the specific energy and simultaneously decrease the cost of the CAM, high Ni contents well above 80% are desired. [1] In this study, we investigate the influence of a two-step temperature swing synthesis on the structure, morphology, and performance of coarse-grained $LiNiO_2$ CAM particles. [2] In this process, we demonstrate the effectiveness of combining direct imaging, diffraction, and spectroscopy for investigating LNO secondary particles across various length scales. High Angle Annular Darkfield Scanning Transmission Electron Microscopy (HAADF STEM) can provide high-resolution images at atomic resolution. However, the data acquisition is locally confined to an area of a few hundred nanometers and the differentiation between similar structures of different phases may not always be unambiguous. Complementary, Precession Electron Diffraction (PED) offers detailed information about the phase and orientation of entire CAM particles with a local resolution in the nanometer range, but this information relies on previous knowledge about the expected phases as input. Thus, unknown inter- and mixed phases cannot be identified, which necessitates validation by other measuring techniques. Electron Energy Loss Spectroscopy (EELS) provides insight into the elements present in the CAM and their bonding environment, which effectively complements PED and STEM measurements.

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PFIB-Preparation and STEM-Characterization of Electrochemically Plated Lithium at the Interface to the Solid Electrolyte Li_6PS_5Cl

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Solid-state batteries are of particular interest when it comes to safe high-energy storage as they potentially enable the usage of lithium anodes. But, industrial production of highly reactive lithium metal anodes is challenging. One approach is to electrochemically deposit lithium in a so-called *anode-free* cell. In the half-cell assembly investigated throughout this study, the current collector consists of stainless steel and the solid electrolyte of argyrodite-type Li_6PS_5Cl. The latter comes along with a solid electrolyte interphase (SEI) formation when in contact with lithium metal [1]. Therefore, the characterization of interfacial side reactions at the micro- and nanoscale is crucial.

Scanning transmission electron microscopy (STEM) offers structural insights at atomic resolution. Still, it comes with a challenging sample preparation that is further complicated by moisture and ion beam sensitivity of the battery materials. The plasma focused ion beam (PFIB) system is capable of an inert-gas transfer from and to the glove box as well as sample thinning at temperatures around -190 °C. The electron-transparent sample is transferred to the glove box and mounted in a sealed transfer holder. Low-dose electron STEM-imaging and STEM-EDX (energy dispersive X-ray spectroscopy) at cryogenic temperatures are performed. An approximately 200 nm thick chlorine-rich layer between plated lithium and argyrodite-type Li_6PS_5Cl is already observed. Further measurements like STEM-EELS (electron energy loss spectroscopy) to detect lithium and TEM-PED (precession electron diffraction) for structural information need to be carried out.

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Investigating *operando* behavior of solid-state batteries with rapid, non-equilibrium impedance spectroscopy

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A better understanding of the intricately linked transport and interfacial processes in solid-state battery (SSB) electrodes is needed to clarify limiting factors and potential optimization routes. Since *ex-situ* characterization cannot capture these processes in action, *in-situ* impedance measurements are ubiquitously employed to gain insight into electrochemical phenomena. However, conventional impedance spectroscopy (EIS) requires cell stability on the order of minutes to hours, which hinders the observation of transient changes during cell cycling. Here, we apply rapid impedance measurements to examine the *operando* electrochemical evolution of SSB during cycling. Half-cells comprising a composite Li(Ni,Co,Mn)O_2-Li_6PS_5Cl (NCM-LPSCl) cathode and alloyed In/LiIn anode are examined at different rates of charge/discharge. Impedance spectra are extracted by combining frequency- and time-domain data using the distribution of relaxation times (DRT), allowing collection 20-fold faster than conventional EIS[1]. The short duration of these measurements ensures that each spectrum presents a snapshot of a pseudo-steady state, even during fast cycling. Cell impedance can then be monitored during charge and discharge, as a function of state of charge and C rate. The data is used to construct a detailed picture of SSB electrochemical impedance, which can be linked to changes in the NCM-LPSCl composite and the In/LiIn counter electrode.

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Structure and Ion-Dynamics in Inorganic Solid Electrolytes using Solid-state NMR

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Inorganic solid electrolyte (SE) with desired transport properties and electrochemical performances is a crucial component of all-solid-state batteries. A detailed understanding of the structural complexity of SEs and its influence on ion-dynamics is necessary for such development – a task that can be efficiently explored using solid-state nuclear magnetic resonance (NMR) spectroscopy. Here, we present some of the recent works from our group involving structural investigation and observing cation dynamics in SEs using several solid-state NMR techniques to showcase its utility in solid-state battery research.

Important structural information, *e.g.* experimental distinction of tetrahedral *vs.* octahedral Li^+-coordination [1], phase evolution in lithium halide-based substitution series [2], observing different crystallographic sites in sodium metal halides *etc* can be obtained using magic angle spinning (MAS) NMR experiments. Cation dynamics in a wide frequency range (several kHz to MHz) can be observed using static variable-temperature single-pulse experiments and spin-lattice (T_1) relaxation measurements, which provides activation barriers of corresponding jump processes. Furthermore, exchange of cation between different crystallographic sites can be experimentally observed using two-dimensional exchange spectroscopy (EXSY). Thus, solid-state NMR can be utilized to efficiently unravel the complex interplay between structural diversity and resulting ion dynamics in SEs, facilitating the quest towards developing improved SEs for future battery technologies. [3]

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Visualizing Diverse Lithium Growth and Stripping Behavior in Anode-Free Solid-State Batteries

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Lithium metal exhibits complex growth and stripping behavior in solid-state batteries, manifesting as dendrite formation, void generation, and varied lithium growth patterns depending on electrochemical conditions and solid-state electrolyte properties. Previous studies utilizing optical microscopy, *in situ* TEM, cryogenic focused ion beam and X-ray computed tomography have contributed substantially to understanding lithium growth mechanisms.[1-4] However, many investigations concentrate on singular instances or restricted regions. In this work, we leverage *operando* X-ray computed tomography to comprehensively track and quantify lithium evolution across 2 mm interfaces under diverse deposition and stripping conditions. Specifically, three distinct scenarios were examined in half cells featuring varying solid-state electrolyte (SSE) characteristics: uniform deposition and stripping in a low-impedance cell, extensive dendritic growth in a high-impedance cell, and uniform deposition followed by dendrite growth triggered by higher current densities. The low impedance cell enabled favorable conditions for uniform deposition and stripping across three half cycles. Segmentation revealed expected volume evolution in the working and counter electrode. In stark contrast to uniform lithium growth, the high-impedance cell featured highly dendritic growth dispersed throughout the SSE. This cell utilized a coarse-grained SSE that resulted in poor interfacial contact at the solid-solid interface and in a porous SSE pellet. Throughout deposition, dendritic lithium was observed to grow around pre-existing cracks/pores, often closing them as deposition continued. Segmentation methods were used to track and quantify the evolution of lithium throughout the first cycle, finding that ~20% of the mechanical damage was irreversible after the first cycle. Finally, we also observed that dendritic networks grow near the edges of another cell at higher current densities after initially growing uniformly, indicating different chemo-mechanics at the cell boundary. Collectively, the lithium growth behavior captured and reported here enhance our understanding of the diversity of evolution of lithium in SSBs.

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Development of *Operando* Solid State Battery Testing Technique for Scanning Electron Microscopy

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The underlying issue associated with all-solid-state batteries (ASSBs) is the poor interfacial contact between its components. Operating ASSBs at higher pressure and enables good contact and maintaining higher temperature facilitate better charge transfer kinetics, however, this is possible only by placing the cell in a hard casing making it impossible to probe their material characteristics and degradation behavior.

Addressing these issues, we present a novel in-situ solid-state battery testing technique for scanning electron microscope. It facilitates the cycling and impedance spectroscopy measurements of the ASSBs at the controlled and desired pressure and temperature (±100°C) while observing the cross-section directly under the electron beam. To enable a seamless workflow, a battery cycler, a focused-ion-beam (FIB) for accessing the deeper areas and interfaces and an energy dispersive X-ray spectroscopy (EDS) to assess the chemical composition is integrated in the microscope.

The data obtained from the in-situ testing module has been used to study the interface and its evolution during the working of the ASSB, its charge transfer kinetics, aging behavior, and associated failure mechanism. Overall, the present work combines an important and powerful battery testing techniques in a single, user-friendly and automated workflow that can aid the battery researchers and manufacturers alike in achieving their targets faster for breakthroughs in commercialization of ASSBs.

Development of Reference Electrodes and Three-Electrode Cell Set-Ups for Lithium-Ion and Lithium-Metal Solid-State Batteries

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Understanding the electrode performance and aging of upcoming solid-state battery chemistries requires precise and reliable reference electrodes (REs) with highly stable reference potentials to aid the investigation of the electrode kinetics by enabling the deconvolution of the impedance spectra and voltage profiles [1,2]. For lithium batteries, lithium metal, metallic pseudo-reference electrodes (e.g., Au, Ag, Pt), two-phase materials such as lithium alloys (e.g., Li_xAu, Li_xSn, Li_xAl), and insertion-type materials such as $LiFePO_4$ and $Li_4Ti_5O_{12}$ have been proposed as REs in combination with liquid electrolytes [1,2]. However, there is still a lack of understanding about the stability of such REs with different solid-state electrolytes.

In this work, we have comprehensively studied the properties of several pseudo-REs and two-phase materials in solid-state cells, with both polymer and inorganic solid-state electrolytes, following an initial screening based on their open-circuit potential stability vs lithium metal. Subsequently, a few selected REs were validated in advanced cell set-ups, which facilitate simple and intuitive cell assembly and, additionally, allow for an accurate pressure and temperature control with the objective of obtaining artefact-free impedance measurements and stable cycling.

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Disclosing the NCM surface degradation and the coating benefit in sulfide-based ASSBs by operando XAS and XPEEM spectroscopies

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The high energy density of Ni-rich layered oxide cathodes is limited by the instability of the (electro-)chemical interface with the solid electrolyte (SE) and the formation of highly resistive species, which arise from (i) the limited thermodynamic stability of the SE and (ii) structural degradation of the cathode surface at high voltages. To date, standard post-mortem studies could not disclose the accurate interface reaction byproducts, particularly those related to cathode surface degradation. Further, the reason for the beneficial role of cathode surface coatings in mitigating the impedance rise is not fully understood.

By combining surface sensitive and non-destructive *operando* X-ray absorption spectroscopy (XAS) [1] and X-ray photoemission electron microscopy (XPEEM) [2], we performed highly surface sensitive elemental mapping with lateral resolution better than 70 nm at different depth analysis to disclose the $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NCM_{622}) surface degradation and the effect of a $LiNbO_3$ protective layer on the interface evolution in contact with SE Li_6PS_5Cl (LPSCl). Oxidizing to high cut-off potentials of 4.6 V, *operando* XAS and XPEEM reveal the formation of a highly reduced NCM_{622} surface, rich in inactive reduced transition metals (TMs), which contribute strongly to the impedance rise. Chemical mapping across the cathode and SE particles interface corroborated the presence of chemical instabilities that lead to the formation of the reduced TMs. Finally, we demonstrate that $LiNbO_3$ coating mitigates the chemical reactivity and alleviates the reduced TMs formation, in line with a drop in impedance. Our work highlights the advantage of combining *operando* XAS and XPEEM to probing the degradation mechanisms of ASSB interfaces at multiple length scales in obtaining insights into battery degradation processes and more generally, in optimizing the interface stability.

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Conductive oxides as a substitute for carbon black: deconvoluting side reactions and the importance of volume changes in fluoride-ion batteries

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This study demonstrates the substitution of conductive carbon additives with conductive oxide nanoparticles in all solid-state fluoride-ion batteries (ASS-FIBs). In earlier publications [1, 2], the rapid capacity fading of intercalation-based ASS-FIBs has been attributed to the electrochemical fluorination of carbon. This reaction was assumed to reduce the electronic conductivity of the carbon additive, leading to a significant deterioration in the battery's performance.

In the present study, we investigate the validity of this assumption. By replacing conductive carbon with more oxidatively stable conductive oxide nanoparticles, limited improvement of the battery’s performance was observed. This observation suggests that carbon fluorination might not be the primary factor undermining the performance of ASS-FIBs, but that the small but non-negligible volume change of the intercalation-based active material had a more significant impact. The application of 180MPa stack pressure enabled the cells with both types of additive to operate with high coulombic efficiency and cyclic stability, regardless of the type of conductive additive used. While the oxidative fluorination of carbon additives has certainly been experimentally demonstrated [1, 2], a direct causality might thus be questionable. On the contrary, this study shows that the ASS-FIBS can perform with excellent cyclic stability and high capacities of 133 $mAhg^{-1}$ for intercalation based materials. This discovery encourages further research into mechanical optimization to realize the full potential of all solid-state fluoride-ion batteries.

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Fluorine-substituted halide solid electrolyte with enhanced stability towards lithium metal

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Abstract:

Halide based solid electrolytes have gained tremendous attention owing to its better ionic conductivity, mechanical and chemical stability in comparison with oxides and sulphide based electrolytes. However, their oxidation stability and reaction with Li metal anode at the interface is one of the major drawbacks that needs to be addressed. Recent reports have shown that halide solid electrolytes are outstanding candidates with higher ionic conductivity and oxidative stability[1] with the disadvantage of anodic instability with Li metal. Although, a buffer layer or additives present at the interface helps in solving the problem of SE/Li reaction, the cost of the overall cell fabrication increases significantly. Dual halogen doping is a recent strategy that had been employed in $Li_3YBr_{5.7}F_{0.3}$ and $Li_3InCl_{4.8}F_{1.2}$ to improve the stability and to suppress dendrite growth. Herein, $Li_2ZrCl_{6-x}F_x$, a low cost and earth abundant compound with good ionic conductivity and better electrochemical stability is reported compared to its parent counterpart (Li_2ZrCl_6). Fluorine rich SEI layer helps to suppress dendrite growth and improve the critical current density (CCD) from 0.5mA/Cm^2 to 1mA/cm^2. Stable stripping/plating over 1000 h at 38.4 μA/cm^2 is achieved. The interface analysis by XPS has shown the presence of LiF that attributes to the formation of stable SEI with Li metal. The presence of metallic zirconium in Li_2ZrCl_6 further confirms the mixed conducting interface mechanism for this class of systems. Linear Sweep Voltammetry (LSV) measurements further confirm that anion doping strategy (fluoride doping) could not only improve the reduction stability but also the oxidative stability by 0.2 V.

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Thin film composite electrolyte with small amount liquid for quasi-solid-state batteries

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Solid-state batteries (SSBs) promise high energy density and exceptional safety, and are considered to be the next generation of energy storage devices, replacing traditional lithium-ion batteries. Garnet-type oxide electrolytes, such as $Li_7La_3Zr_2O_{12}$ (LLZO) are promising candidates for lithium-metal solid-state batteries due to the high ionic conductivity (~1 mS cm^{-1}) at room temperature and chemical stability. However, manufacturing ultrathin and freestanding solid electrolyte membranes for practical all-solid-state pouch cells remains very challenging.[1]

In this work, Al doped LLZO (LLZAO) self-supported films as thin as 8 μm were produced via a simple dry processing method, with 1 wt.% polytetrafluoroethylene (PTFE) as binder. Given the lack of a sintering step, in order to improve the interfacial contact between the LLZAO particles, as well as between the separator and the electrodes, 15 wt.% self-polymerized 1 3-dioxolane (DOL) polymer electrolyte was added to the LLZAO thin film to form a composite electrolyte, where the initial liquid content is less than 7.5 wt.%. After setting, the membrane becomes a quasi-solid-state electrolyte. The room-temperature electronic conductivity of the composite electrolyte is higher than 0.5 mS cm^{-1}. In addition, the discharge specific capacity of $LiFePO_4$|Li battery is around 130 mA h g^{-1} at 0.2C. The solvent-free dry film technology provides a viable and promising approach for quasi-solid-state batteries.

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A High-performing Argyrodite-based Cathode Material for All-Solid-State Lithium-Sulfur Batteries

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Solid-state Lithium–Sulfur (Li–S) batteries have been attracted attention as the next-generation batteries. They are freed from the polysulfides dissolution issues unavoidably observed in the liquid electrolyte system, improving the cyclability of the batteries. Their intrinsically non-flammable feature largely enhances the safety of the batteries. At present, Sulfur, lithium sulfide, and carbon composites with sulfur-based solid electrolytes including LGPS and Li_3PS_4 have been reported as the cathode materials [1, 2].

In this paper, we present the use of the composite of Argyrodite-based compounds and conductive carbon for a cathode active material of all-solid-state Li–S batteries [3]. We synthesized the composite from conductive carbon and Argyrodite solid electrolytes. The synthesized powders were characterized using all-solid-state battery cells made by compressing the powders under uniaxial pressure molding. In the cathode layers, additional Argyrodite solid electrolytes were incorporated to enhance the lithium-ion conductivity. The weight ratio of the active material to solid electrolyte was at 60:40 wt%. In-Li foil was used as the anode materials.

Figure 1 shows the charge-discharge curves for the cell using the Argyrodite-derived cathode active material at the current density of 0.1C. The reversible capacity reached ~1000 mA h g^{-1}. and the areal capacity was 10 mA h cm^{-2}. Specific energy density was calculated based on the cathode electrode configuration of this experiment, in reference to the methodology proposed by Hakari et al. [4] It exceeded 500 Wh kg^{-1}, suggesting that our developed Argyrodite-derived cathode active material has the potential to significantly enhance the energy density of all-solid-state Li–S batteries.

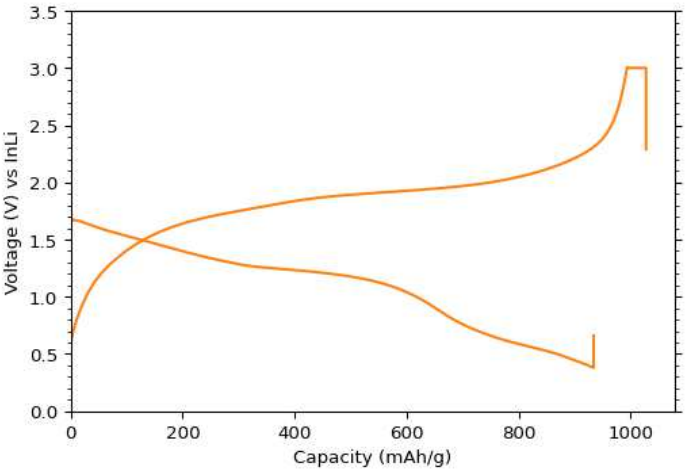

Fig 1. Charge-discharge curves for the cell employing the active material composite derived from the Argyrodite solid electrolyte.

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Effects of Metal Halides on Sulfide-Based Cathode Composite of All-Solid-State Lithium-Sulfur Batteries

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All-solid-state lithium-sulfur batteries have attracted attention due to the high theoretical energy density, abundance, and inexpensiveness of sulfur. The active material sulfur is electronically and ionically insulating and needs to be composited with an electrolyte and conductivity aid for use in the battery cathode. However, the sluggish ion transport in the composite, which is particularly prominent with a very high interfacial area density, has been hindering further improvement [1].

In this study, we successfully improved the cycling performance and ion transport by adding metal-halide additives to sulfide-based cathode composites, Li_3PS_4-S-C-MCl_x (M: V, Nb, Ta). In comparison to the composite of Li_3PS_4-S-C with no additives, the discharge capacity increased in the order with $TaCl_5<NbCl_5<VCl_3$. In particular, the composite with 2.5 wt% of the VCl_3 additive delivered the capacity increasing over 20 cycles, eventually enhancing the capacity by 10%. According to the change in the differential capacity (i.e., dQ/dV profiles), the increased capacity is most likely resulting from the enhanced redox reaction of sulfide-based anion-building blocks, e.g., PS_4^{3-}, not due to the redox of VCl_3 itself. To further investigate the effect of metal halides, we quantitatively analyzed the ion transport within the composites by analyzing impedance spectra with transmission line models, revealing the enhancement in the effective ionic conductivity of the composites with the VCl_3 additives. In the presentation, we will discuss the mechanistic understanding and the methodology to assess transport within the composites. This work provides the designing strategies and means for quantitative assessment of the composite cathodes with functional additives.

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Mitigating oxygen release in lithium-rich manganese oxide cathodes to enable high-energy-density solid-state lithium batteries

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Solid-state lithium batteries using high-voltage, high-capacity cathodes, such as lithium-rich manganese oxides (LRMO; >250 mAh/g, 4.6 V vs. Li^+/Li), hold the potential to achieve energy densities up to 500 Wh/kg. However, LRMO faces challenges, including low electronic conductivity (~10^{-8} S cm^{-1}), the need for electrolytes stable at high voltages, and complex anion redox chemistry that leads to the release of lattice oxygen, which in turn causes harmful oxidation of the electrolytes. To address the latter issue, we chemically engineered the LRMO surface using a hetero-atomic-containing agent, which we hypothesize to suppress oxygen release at higher voltages. Indeed, when employed in a solid-state battery using $Li_3InCl_{5.4}F_{0.6}$ as solid electrolyte significant improvements have been achieved. For instance, the surface engineered LRMO exhibits a significant improvement in its initial discharge capacity and coulombic efficiency, increasing from 131 mAh/g to 220 mAh/g and from 75.46% to 84.83%, respectively, at 0.1C, compared to the pristine LRMO. When tested at 1C, the initial discharge capacity increased from 83 mAh/g to 153 mAh/g and the capacity retention remarkably increased from 83% to 95% after 500 cycles.

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Fluoropolymer Binders for Cathode Composites in All-Solid-State Batteries

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All-solid-state batteries (ASSBs) utilizing argyrodite sulfide electrolytes, such as Li_6PS_5Cl, have garnered significant attention for electric vehicle applications owing to reduced flammability and higher energy density compared to conventional lithium-ion batteries. However, the development of roll-to-roll manufacturing for cathode electrodes remains limited by the absence of compatible binders for slurry-based processes. A key issue is the chemical instability of Li_6PS_5Cl in polar solvents, which complicates the preparation of solid electrolyte and cathode material (e.g., NCM) mixtures with polar binders. Several approaches have employed non-polar or weakly polar binders, such as rubber-based materials, necessitating solvents with matching polarity. However, these binders often fail to establish adequate interfacial contact within the composite, thereby limiting their effectiveness.

In this study, we explored the use of polyvinylidene fluoride (PVdF) copolymers as binders, which are well-established in battery applications. By incorporating weakly polar groups into the PVdF copolymer, we successfully achieved slurry processing with weakly polar solvents. Compared to acrylonitrile butadiene rubber, PVdF-based binders allow higher Li_6PS_5Cl coverage on the cathode materials, attributed to uniform distribution of PVdF binder, which leads to improved cycling stability and rate performance. Post-cycling analysis revealed distinct surface characteristics on the cathode composites relying on binders. I will present further details on the impact of PVdF-based binders in enhancing cathode composite performance in the poster presentation.

Paper-like anodes of 100% Si integrated with Argyrodite Li_6PS_5Cl Solid Electrolyte

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We present the integration of 100 vol. % Si with Li_6PS_5Cl solid electrolyte (SE) and study of their electrochemical properties and post-cycling microstructure. The anodes are paper-like networks of aggregated Si nanowires (SiNW) attached to a Cu current collector, with dimensions above 100cm^2 and possibility to adjust mass loading (0.1 – 3 mg/cm^2). They are produced using a slurry-free continuous dry aerosol process and are currently under industrial scale-up.

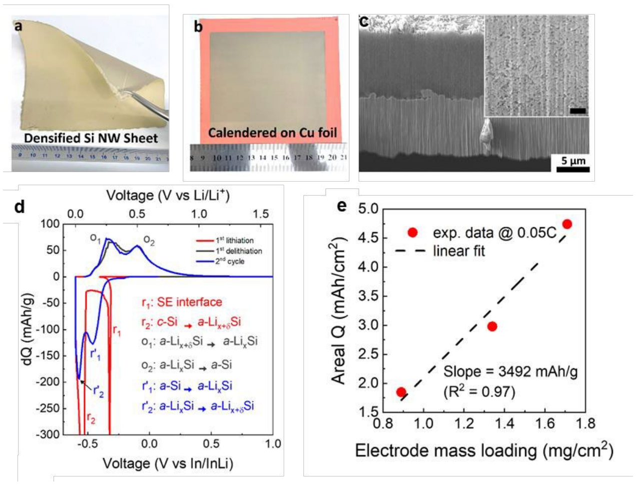

Figure 1. Photograph of SiNW paper (a) and calendered anode on Cu (b) and the cross-sectional microstructure (c). Differential capacity plot with reactions during lithiation/delithiation (d) and low-rate capacity for different mass loadings.

The anodes are integrated in half cells Si|Li_6PS_5Cl|InLi by consecutive pressing of each layer. Si anodes provide >2.5 Ah/g capacity, including at a high mass loading of 1.7 mg/cm^2 (~5 mAh/cm^2). Cross-sectional microscopy shows that the method produces a planar 2D electrolyte/SiNW interface. The corresponding EIS data is modelled by three series elements representing ion transport resistance in the SE separator, the combined interfacial resistances, and the electrode charge transfer contribution, all of which remain stable. We also determine the Li+ diffusion coefficient (2.4×10^{-13} cm^2/s). Finally, we present cyclability data and discuss the roles of anode porosity, electrolyte compaction and stress generated at the anode/electrolyte interface.

(COI: JJV has a financial interest in Floatech, which commercializes Si anodes)

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Improved Lithium Metal Cycling Performance via Mild Sintering Treatment of Li_6PS_5Cl for All-Solid-State Batteries

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The argyrodite Li_6PS_5Cl (LPSCl) solid electrolyte (SE) with its high ionic conductivity and low temperature processing holds the promise to enable lithium metal in all-solid-state batteries. However, lithium dendrites initiated at the Li/SE interface propagate through the SE, hindering the stable cycling at high current density. [1] Herein, a mild sintering treatment of the LPSCl pellet at low temperature shows higher bulk densification and better Li/SE interfacial contact leading to a significant cycling performance improvement of the thin lithium metal. The pellet is fabricated at 380 MPa at room temperature, followed by a sintering treatment at 50 MPa under vacuum in the temperature from 60 °C to 100 °C. After sintering, the LPSCl structure stability and the chemical composition are investigated by XRD, XPS and EIS, showing phase stability in the bulk yet the occurrence of excessive side reactions with the current collector producing oxidized sulfur and phosphorus at the surface under 100 °C. The sintering steps decrease the resistance of SE from 450 Ω to 146 Ω at 20 MPa, emphasizing the increase of the electrolyte ionic conductivity. As a best optimized condition sintering at 80 °C has been chosen, where no SE oxidation is detected, and reasonable pellet densification is achieved. The sintered pellet exhibits a more uniform surface with reduced voids and smaller pores, contributing to lower porosity and better Li/SE contact. The sintering treatment enhances the critical current density from 1.1 mA cm^{-2} to 1.6 mA cm^{-2} for symmetric cells. This approach also enables Li | NCM811 full cells to achieve rate capability at 3 mA cm^{-2} with a capacity of 1 mAh cm^{-2} and to operate more than hundreds of cycles at 1 mA cm^{-2} with a capacity of 1.6 mAh cm^{-2}.

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Solution-Processed Non-crystalline Sodium Thin Film Solid Electrolytes for Sodium-Metal Batteries

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Advanced batteries containing Na metal anodes (NMA) are needed to enable the clean economy and meet ambitious climate targets. Currently, NMA batteries are limited by dendrite propagation due to the non-uniform plating and stripping of Na. The non-crystalline solid electrolyte (SE) thin film, lithium phosphorus oxynitride (LiPON) has demonstrated stable Li plating/stripping at appreciable rates, aiding in the inhibition of dendrite propagation. However, LiPON is typically produced via expensive and low throughput vacuum deposition methods. [1]

Here, we report a study on non-crystalline sodium thin films, which are synthesised via spin coating from aqueous solutions and subsequent annealing in air. Homogenous, dense, flat layers were synthesised with sub-micron thickness at temperatures as low as 275 ℃. Our study investigates the effect of compositional variation and annealing on the ionic conductivity and structural properties. We hope that our findings relating to NAPO should be of value when engineering non-crystalline SEs for a variety of Na-metal battery technologies, whilst providing an insight into optimising the conductivity properties of non-crystalline thin films.

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Title: Scalable Free-Standing Amorphous Solid Electrolyte Films for Advanced Lithium Batteries

Motivation:

- Lithium phosphorous oxynitride enhances lithium batteries *via* preventing dendrite growth and enabling stable battery operation but is costly due to vacuum deposition methods.
- Amorphous lithium-aluminum-phosphorus-oxide (LAPO) thin films, produced by spin-coating, present a cheaper, scalable solution with better ionic conductivity *via* specific element doping and annealing techniques[2-3].
- Research focuses on overcoming production challenges of LAPO films to advance lithium battery technology.

Abstract:

- This study focuses on developing scalable, free-standing amorphous LAPO electrolyte films with enhanced ionic conductivity, rivaling LiPON, using a low-temperature, cost-effective process. The LAPO films were optimized through multi-element doping and a one-dimensional heating method with a PDMS sacrificial substrate via spin-coating. These advancements position LAPO as a promising thin film electrolyte for TFLB, offering potential for high-energy-density all-solid-state lithium metal batteries.

Drop-In Ability of Solid-State Batteries (Oxide, Polymer, and Sulfide)

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After several years of research for conventional Li-ion battery since the 1990s, [1] this technology appears to reach its physicochemical limits. [2] Innovative concepts are crucial to surpass the possibilities of this technology, and solid-state batteries (SSB) promises improvements in terms of energy density, power density and stability while maintaining safety and a wider operating window. [3] While the expectations for Li-SSB are strongly driving industrial and scientific efforts, several challenges remain on the pursuit for commercialization including the uncertainties for cell processing and production, costs, and safety. [4] As battery cell factories are associated with high costs, competitive SSB concepts may need effective integration into mass production, necessitating in-depth examination and comparison of cell manufacturing infrastructures as the prerequisites for cost-benefit calculations. In addition, SSB cell materials must be tailored to exploit the full potential of SSB technology. With a suitable design, the costs of a production change can be minimized - a decisive factor for the integration of new technologies. Herein we present the results of an extensive study about drop-in abilities to produce SSB cells. Therefore, a factory for conventional Li-ion battery cells is being redesigned using factory planning tools and comparing process sequences for the manufacturing of SSB cells. Our major focus is this evaluation for three different concepts with i) sulfide (LPSCl), ii) oxide (LLZO), and iii) polymer (PEO) electrolytes, each with a Li metal anode and Ni-rich cathode active materials. In addition, we take a closer look at the process flow and cell materials involved.

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Dry coating of sulfide-based components for All-Solid-State Batteries

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All-solid-state batteries (ASSBs) based on sulfidic electrolytes are one of the most promising technologies for the next-generation energy storage systems. Safer and with higher energy density than the common lithium-ion batteries, ASSBs have attracted great interest from both academic and industrial communities. However, full-scale commercialization is hindered by a lack of process technology that can transfer ASSBs to a higher Technology Readiness Level. Indeed, the incompatibility of sulfidic electrolytes with commonly used solvents (NMP, water) requires new concepts for component manufacturing. Dry electrode processes could potentially eliminate the solvents and further provide savings in energy consumption and equipment footprint.

In this study, a scalable and continuous process for sulfide-based materials, in solid-state cathode and separator manufacturing is demonstrated. The patented solvent-free coating technology DRYtraec® is applied here. This calender technology is using a speed differential concept to apply shearing forces to PTFE-based dry mixtures. Further parameters such as roll speed, temperature, force, gap width and coating width can be tuned, allowing versatile dry film production. While manual manufacturing of dry electrodes was already shown in previous work [1], here a step forward on the prototype-scale production is made.

With a content of 1% PTFE, laminated NMC on Al-foil was obtained, over 325 cm length on 10 cm width. A quasi-linear relationship between shearing ratio (speed differential of the rolls) and loading is also shown. Moreover, two types of solid electrolyte layer (SEL) as separator can easily be manufactured with DRYtraec® process: free-standing and laminated. To pave the way for the future development of ASSBs, the SEL was laminated on cathode material. Electrochemical characterization of each component are being evaluated to highlight the relevance of DRYtraec® process for solid-state batteries manufacturing.

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Towards a higher energy density by production of free-standing thin SE–films in a role-to-role process

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All-solid-state batteries (ASSB) show great promise for the advancement of high-energy batteries. To maximize the energy density, a key research interest lies in the development of ultrathin and highly conductive solid electrolyte (SE) layers. In this work, thin and flexible sulfide solid electrolyte membranes are fabricated and laminated onto a non-woven fabric using a scalable and solvent-free role-to-role process (Figure 1). The membranes show significantly improved tensile strength compared to unsupported sheets, which facilitates cell assembly and allows a continuous component production using a single-step calendering process (DRYtreac®).

Thickness and mass loading can be varied, thus following a compression step densified membranes with thicknesses from 40 - 160 µm can be obtained. The resulting SE membranes retain a high ionic conductivity (1.6 mS cm^{-1}) at room temperature. An excellent rate capability was demonstrated in an ASSB pouch cell with a Li_2O–ZrO_2-coated $LiNi_{0.9}C_{0.05}Mn_{0.05}O_2$ cathode, a 55 µm thin SE membrane, and a columnar silicon anode fabricated by a scalable physical vapor deposition process. On cell-level, promising volumetric energy densities were achieved, showcasing the potential for high energy densities by reducing the SE membrane thickness while enabling good mechanical properties.

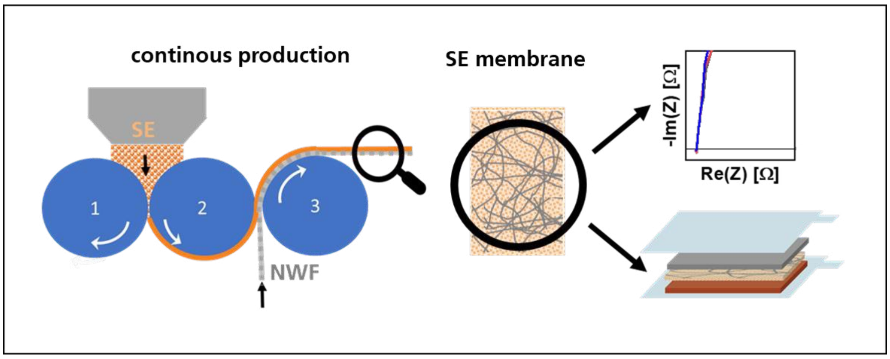

Figure 1: Schematic of the production and characterization of the SE membranes

Characterization of the Calendering Process for Sulfide-Based Solid-Electrolyte Separators

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Industrializing solid-state batteries is crucial for advancing energy storage technologies as solid-state batteries offer a promising alternative to conventional lithium-ion batteries [1]. Reducing the porosity and enhancing the solid-to-solid contact between particles has shown to improve the performance of solid-state batteries [2]. Achieving a scalable process for the densification of sulfide-based solid-electrolyte separators is a key step [3]. This study investigates the calendering process as a method to achieve this goal, aiming to replace the predominantly used uniaxial pressing technique.

This work examines the influence of key process parameters such as line load, calendering speed, and roll temperature on the solid-electrolyte separator using a pilot-scale calender for both sheet-based and coil-based materials. The interactions between these parameters and the resulting microstructural, mechanical, and electrochemical properties of the solid-electrolyte separators are analyzed. This work finds that calendering significantly reduces the porosity of solid-electrolyte separators and presents a promising alternative to uniaxial pressing, offering a scalable and efficient approach for the production of solid-electrolyte separators.

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Development of 20 Ah semi solid state pouch cell with an in-situ solidified gel polymer electrolyte

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Semi-solid state batteries (sSSBs) technology based on an in-situ electrolyte solidification approach has several advantages over all-SSBs as (a) versatile electrolyte chemistry (electrolyte precursor can be handled as a liquid electrolyte), (b) direct use of high loading porous electrodes, (c) no need of solid electrolyte film manufacturing and handling processes, (d) excellent "electrolyte/electrode" contact, (e) low operational pressure, and (f) easy scalability and compatibility with high throughput processes on existing LIB manufacturing facilities, resulting in high performing and safe battery with a similar cost to LIB commercial benchmark.

In this connection, CIDETEC has developed a 20 Ah semi-SSB prototype (stack size 140 x 230 mm^2) based on "*Graphite-SiO$_x$ / NMC622*" chemistry with in-situ solidified gel polymer electrolyte. The developed 20 Ah pouch cell prototype demonstrated relevant energy density (220 Wh/kg, 550 Wh/L) and promising electrochemical performance at 25 ºC (**Figure 1**). Our contribution will reveal more details about design and electrochemical performance of the developed semi-SSB technology.

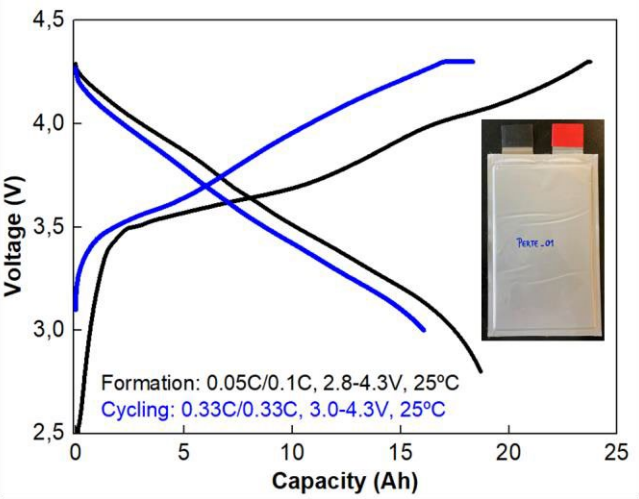

Figure 1. Charge-discharge profiles of the developed 20 Ah pouch cell prototype. *Cycling conditions: 25ºC, 62 kPa (initial pressure). Inset: digital photo of the 20 Ah cell.*

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Industrial solutions towards the manufacturing of semi- solid and sulfide- based all solid state batteries

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A123 Systems is pursuing a progression of semi- to all- solid state battery technologies to deliver safe and cost- effective energy storage solutions. Targeted chemistries of interest leverage much of the existing lithium- ion battery manufacturing infrastructure. Nevertheless, advanced materials, process and cell level modifications are required to accommodate the unique chemo- electro- mechanical properties while satisfying scalability and end- user requirements. Herein will be presented methods developed and lessons learned while pursing materials and manufacturing solutions for solid- state batteries.

A wholistic approach is shared highlighting the need for solutions that balance architectural mechanics with practical electrochemical performance. In particular, strategies for evaluating how process routes impact electrode and cell level performance, as supported by experimental data, will be discussed. Furthermore, differentiation between solutions required for the unique demands of semi- vs. full solid state is provided, acknowledging trade- offs accompanying various design strategies. Modifications where necessary are discussed on the backdrop of efforts to control costs and complexity by a thorough understanding of materials- level interactions and their impact on performance metrics such as stability and high- rate performance. The goal is to identify and explore scientific and technical challenges on the path to realizing commercial solutions to this promising future battery technology.

Material interaction between Ni-rich NCM cathode active material and substituted garnet LLZO:X (X = Ta, Al, Ga) solid electrolyte

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All-solid-state batteries with a lithium-metal anode, a garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) separator, and a high-capacity composite cathode show significant potential as intrinsically safe next-generation batteries. However, they suffer from severe capacity fading due to degradation of the cathode/solid electrolyte interface. Thus, stabilizing the garnet electrolyte against the cathode active material, under high-temperature processing conditions, is essential. Previous research has provided valuable insights into the interaction between lithium cobalt oxide (LCO) and LLZO [1]. This study extends this understanding to $LiNi_xCo_yMn_{1-x-y}O_2$ (NCM) cathode active material.

Our work explores cation diffusion between Ni-rich NCM cathode and a LLZO separator during co-sintering. Our investigation focuses on how LLZO composition (Ta, Al or Ga doping) influences material interaction at the cathode/separator interface during conventional co-sintering and advanced processing by field-assisted sintering / spark plasma sintering (FAST/SPS). We examined as prepared separator pellets and co-sintered half cells with XRD, SEM, EDS and Raman spectroscopy. Results show that initial density, microstructure, and phase purity of the separators are important indicators for secondary phase evolution and distribution in the in the LLZO separator. The influence of cation interdiffusion on the ionic conductivity of the separators was investigated by electrochemical impedance spectroscopy (EIS). In an attempt to minimize LLZO degradation, innovative, low temperature FAST/SPS with very short dwell times was successfully applied for the fabrication of half-cells.

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Characterization of composite cathodes in all-solid-state lithium batteries by different electrochemical scanning probe microscopy techniques

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In the recent decade all-solid-state batteries (ASSB) got high attention in the field of energy storage due to the high safety factor by replacing flammable organic liquid electrolytes with non-flammable solid electrolytes. Many years the focus was only on the synthesis of electrolytes with high ionic conductivity in order to enhance the battery performance. Today promising electrolytes were introduced and intensively studied. However, further improvements in material and cell design rely on a detailed knowledge of interfacial reactions and charge transport through the battery components [1, 2]. Therefore, the battery performance strongly depends on the conduction networks and maintaining stable interfaces in ASSBs. Using different scanning probe microscopy (SPM) techniques allows the investigation of local electrochemical properties with high spatial resolution on nanoscale level [3].

In this work SPM techniques based on atomic force microscopy are used for visualizing electrochemical properties in composite cathodes in bulk type batteries, containing an amorphous sulfide-based solid electrolyte and lithium cobalt oxide (LCO) as an active material. For our studies we operate with different advanced techniques, such as kelvin probe force microscopy (KPFM), conductive atomic force microscopy (cAFM) and electrochemical strain microscopy (ESM). By cycling the batteries and *in-situ* characterization of ASSB cathodes in different state of charges we are interested in showing local changes of electrochemical properties. However, interpreting information from ESM to locally probe ion movement is still challenging due to different signal contributions, such as electrostatic forces [4].

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Understanding Impedance Spectra of Bulk-Type All-Solid-State Batteries

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Bulk-type all-solid-state Li batteries (ASSBs) are currently of great interest due to the improved battery safety compared to conventional lithium-ion batteries containing liquid electrolytes. [1] Furthermore ASSBs can potentially achieve higher energy densities than state-of-the-art lithium-ion batteries. [1,2] The performance of ASSBs depends critically on the contacts between cathode active material (CAM) particles and solid electrolyte (SE) particles inside the composite cathodes. The Li^+ exchange current density at the CAM | SE interfaces is determined by these contacts. Nonetheless experimental studies on Li^+ exchange current densities are almost non-existent for ASSBs, which is most likely due to the poor understanding of the impedance spectra of such batteries.

In order to obtain more information on exchange current densities, a comparative case study was carried out using different cathode active materials (CAM), namely single crystalline $LiCoO_2$ particles and single crystalline $LiNi_{0.83}Mn_{0.06}Co_{0.11}O_2$, an In-Li alloy as anode, and a sulphide-based solid electrolyte. The determination of the cathode exchange current density is based on: (i) Impedance measurements on In−Li | SE | In−Li symmetric cells in order to determine the anode impedance together with the anode | separator interfacial impedance; (ii) Variation of the composite cathode thickness in order to differentiate between the ion transport resistance and the charge transfer resistance of the composite cathodes; (iii) Impedance simulations based on the transmission-line model [3-5].

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ToF-SIMS investigation of solid-state electrolyte degradation behavior against different conducting agents

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Solid-state batteries promise higher energy densities and greater safety but also come with challenges related to cycle life.[1] Especially the reactions at the carbon solid-state electrolyte interphase are of special importance.[2] Understanding these reactions may be one of the key factors to unlock long lasting solid state-batteries.

One key instrumentation used for interphase analysis is ToF-SIMS as it enables high lateral resolution imaging of molecular and atomic distributions. Especially in combination with cross sections ToF-SIMS enables the visualization of different chemical environment in solid state batteries.

This study aims to understand the role of mixing and the conducting agent can play by combining an argyrodite type electrolyte with different conducting agents at different ball milling speeds. The resulting composite was built against LiIn in full cells and electrochemically evaluated. Electrochemical analysis revealed that higher mixing energy consistently resulted in greater capacity and thus decomposition.[3] Finally, the interphases of the cycled composites were investigated *via* FIB ToF-SIMS to map the different chemical compositions in detail.

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Cracking the Surface: Analyzing Argyrodite Stability with Lithium Alloying Anode Materials

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Sulfide-based electrolytes are one of the most promising candidates for solid state electrolytes (SSEs), showing ionic conductivities similar to those of liquid electrolytes, while their soft nature allows room-temperature processing [1]. However, these sulfidic electrolytes are challenged when combined with lithium metal, as microstructural issues such as pore formation and current constrictions due to surface roughness set boundaries for critical current densities [2]. Moreover, the sulfidic SSEs are not chemically stable towards lithium metal and a layer of low ionic conductivity forms at the anode electrolyte interface [3].

To overcome these issues, alloying anode materials (AAMs) are attracting increasing attention. Possible candidates for AAMs include silicon (3579 mAh g^{-1}), tin (993 mAh g^{-1}), aluminum (990 mAh g^{-1}) and zinc (410 mAh g^{-1}) [4]. Some have already been implemented with sulfide-based SSEs, while others are still to be investigated in sulfidic ASSB context [5,6].

This study aims to examine the chemical stability of the argyrodite SSE $Li_{5.5}PS_{4.5}Cl_{1.5}$ towards possible AAM candidates. Different anode compositions were synthesized *via* ball-milling. Solid state analytics were applied to investigate the reactivity of AAMs and the SSE. Combined with electrochemical characterization, conclusions are drawn about the compatibility of AAMs in sulfide-based ASSBs.

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In Situ Derived Protection of the Anode|Electrolyte Interface for Semi-Solid Structural Batteries

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Structural batteries combine high energy storage capabilities with mechanical load-bearing functions, while simultaneously serving as both a power source and a structural element. As such, they are considered an optimal choice for automotive, nautical, and aeronautic vehicles, as they reduce the overall weight of the whole system, thus, enhancing the energy density [1]. Among the various choices of electrolyte systems for structural batteries, ceramic/polymer hybrid electrolytes stand out due to their high mechanical strength and excellent thermal stability, both of which are crucial for the safety and structural integrity of these bifunctional batteries. However, the unstable electrode|electrolyte interface between NASICON-type $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) solid-state electrolytes and the two electrodes poses a significant challenge to the cycling stability [2]. Specifically, the reduction of Ti^{4+} at the anode|LATP interface leads to performance degradation. To address this issue, an *in situ* polymerized protection layer was developed to isolate the LATP from the anode, aiming to mitigate the detrimental side reactions with the LATP/PVdF-TrFE/ionic liquid composite electrolyte. This approach enabled a substantially stabilized interface and, thus, a superior cycling stability of graphite||NMC_{811} full-cells. These performance improvements underscore the potential of advanced structural batteries for next-generation applications.

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Electrochemical Investigation of the Li-ion Transport at the Sulfide Solid Electrolytes Interfaces

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The solid-state Li-ion battery (SSB) is an up-and-coming energy storage technology [1]. However, fully utilising the stored energy is not easy due to the limited interface area between solid materials. Hence, SSBs must decrease the resistance of Li-ion transfer at the solid-solid interface to facilitate further enhancements. To mitigate the interfacial resistance, it is essential to identify the predominant factor hindering the transfer of ions at the interface. In this study, we report a solid-state electrochemical four-electrode cell to analyse the resistance between two sulfide SEs [4]. Argyrodite Li_6PS_5Cl (LPSCl), glass-ceramic Li_2S-P_2S_5-LiI (LPSI) and crystalline $Li_{10.35}Ge_{1.35}P_{1.65}S_{12}$ (LGPS) were used as solid electrolytes. The ionic conductivities and activation energies of the LPSCl, LPSI, and LGPS were measured to be 0.83, 2.7, and 7.1 mS cm^{-1} and 40.5, 29.8, and 37.0 kJ mol^{-1}, respectively. The four-electrode cells were built by stacking two pellets incorporating reference electrodes (REs, **Figure 1**). **Figure 2** shows the impedance spectrum of the four-electrode cell with a LPSCl-LPSI interface. Two semicircles, P_1 and P_2, were found at higher and lower frequencies, respectively. The distance between REs was changed to attribute each resistance component to the bulk or interface. As a result, P_1 only showed dependency on the distance between REs, referring to P_1 as a lithium-ion transfer process in the bulk and P_2 as a lithium-ion transfer process between the solids. The activation energy of each interfacial resistance is also discussed in the presentation.

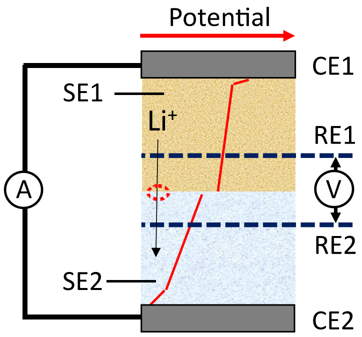

Fig. 1 The schematic of a solid-state four-electrode cell.

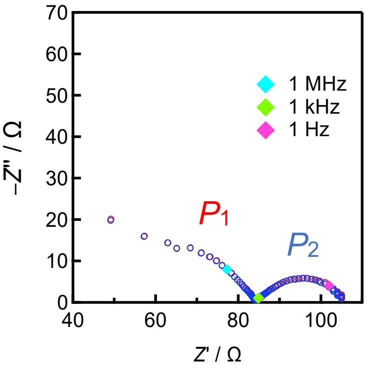

Fig. 2 Impedance spectrum of the LPSCl-LPSI cell.

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Enhancing Electrochemical Stability in All-Solid-State Batteries through Halide Incorporation in Lithium Argyrodites $Li_{6-x}PS_{5-x}X_{1+x}$ (X= Cl and Br)

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Abstract:

All-solid-state batteries with lithium argyrodite as a solid electrolyte are a promising technology for next-generation batteries, offering improved safety and high energy density, particularly when Li/Si is considered as the anode material. Despite their advantages, lithium argyrodite-based solid electrolytes often suffer from a limited electrochemical stability window, which can lead to decomposition. This study focuses on the synthesis and characterization of halide-enriched lithium argyrodite, $Li_{6-x}PS_{5-x}X_{1+x}$ (where X = Cl and Br), to investigate the effects of halide incorporation on structural and ionic transport properties under varying synthesis conditions. We optimized the halide-enriched lithium argyrodite to achieve higher ionic conductivity, reaching up to 14 mS/cm in cold pressing. Additionally, electrochemical stability tests demonstrated that increasing halide content significantly enhances the stability window. Notably, substituting sulfur with halide, increases halide content at the 4d site and more lithium vacancies, which contribute to improved oxidation stability and reduction potentials. A comparative analysis of $Li_{5.5}PS_{4.5}Br_{1.5}$, $Li_{5.5}PS_{4.5}Cl_{1.5}$, and commercially available Li_6PS_5Cl (NEI) highlighted substantial improvements in the electrochemical stability window for these materials. This research demonstrates the potential of halide incorporation as a viable strategy to address fundamental challenges in all-solid-state battery development, paving the way for more robust and efficient energy storage solutions.

Polymerized ionic liquids as multifunctional cathode coatings for sulfide-based solid-state batteries

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Sulfide-based solid-state batteries (SSBs) with Nickel-rich cathode materials (i.e., $LiNi_xCo_yMn_{1-x-y}O_2$, $x \geq 0.8$) are emerging as a top contender for next-generation batteries with improved safety and energy density. However, they face several chemomechanical challenges at the cathode-electrolyte interface, such as decomposition of the solid electrolyte, cathode particle cracking, and contact loss. To overcome these challenges, polymerized ionic liquids (PIL) have been previously used as coatings at the cathode particle surface. [1]

In this study, we investigate the effect of incorporating lithium salts into PIL cathode coatings on Li^+ transport and cathode surface protection in sulfide-based SSBs. Nickel-rich $LiNi_{0.82}Co_{0.11}Mn_{0.07}O_2$ (NMC82) was coated with the PIL poly(diallyldimethy-lammonium) bis(trifluoro-methanesulfonyl)imide (PDDATFSI) with and without a lithium salt, and the performance of coated and uncoated powders was evaluated in SSBs with argyrodite Li_6PS_5Cl electrolyte. While both the coated NMC82 powders showed improved capacity retention compared to uncoated NMC82, the coating with the Li salt (Li-PIL) also resulted in improved rate performance and a capacity retention of 82.7% after 500 cycles at 0.2C (2.8−4.3 V vs Li+/Li). Two-dimensional exchange solid-state nuclear magnetic resonance (2D EXSY ssNMR) spectroscopy suggested that the Li-PIL coating facilitates Li^+ transport across the cathode/electrolyte interface, in addition to both coatings effectively mitigating chemical and mechanical degradation. These findings highlight the effectiveness of Li-PIL as a multifunctional cathode coating in sulfide-based SSBs.

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Influence of the current collector on Na all solid-state anode-free batteries

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Sodium solid-state batteries present a viable alternative to lithium batteries due to the abundance and low cost of sodium, as well as its electrochemical properties that closely resemble those of lithium. Metallic anodes in these batteries can achieve higher energy densities than conventional carbon-based which can be improved with the reduced weight, volume of "anode-free" batteries. These batteries form the anode in situ during the first charge cycle, enhancing also safety during assembly and reducing costs. A key challenge for these systems is the creation of a CC/Na metal/SE interface that facilitates a uniform current distribution during cycling with high reversibility, preventing the formation of resistance constrictions and current hotspots.

In this work, a sodium NaSICON-type electrolyte with the composition $Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$ is used. This electrolyte is characterized by its high ionic conductivity (up to $5*10^{-3}$ Scm^{-1}) [1,2], excellent air resistance, and high energy density. Various metals have been selected as current collectors to study how sodium interacts with each metal and whether it forms alloys, examining how this interaction can impact the performance. Metals such as Sn, In, Au, and Cu have been used. A favourable CC-Na-SE interaction can promote lower nucleation overpotentials and a more homogenous Na platting/stripping, which benefits the battery's cycling performance. It's important, however, that the reaction occurring are reversible, otherwise, sodium loss from the system could lead to a rapid decline of coulombic efficiency [3].

Characterization measurements of the solid electrolyte and its surface have been conducted, including XRD, Raman, XPS and SIMS measurement. Electrochemical measurements have also been performed using blocking electrodes to determine conductivity values, and cycling of symmetric and anode-free cells to study the influence of different electrolyte surfaces and current collectors.

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Interfacial Stabilization by Prelithiated Trithiocyanuric Acid as an Organic Additive in Sulfide-based All-Solid-State Lithium Metal Batteries

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Interfacial degradation at the lithium metal anode (LMA) remains one of the biggest challenges in sulfide-based all-solid-state batteries, causing poor electrochemical performance. To stabilize the interface, protection of the LMA with an artificial SEI and/or modification of the SSE composition using metal substitution have been actively pursued. [1]

In contrast, we have introduced an organic additive approach, the mixing of prelithiated trithiocyanuric acid, Li_3TCA, with Li_6PS_5Cl, to establish a stable interface. [2] Including 2.5 wt% Li_3TCA enables a rise in the critical current density from 1.0 to 1.9 mA cm^{-2} in Li/Li symmetrical cells and stable cycling for over 750 hours at a high current density of 1.0 mA cm^{-2} (figure 1b). SEI formation is studied using coulometric time titration analysis (CTTA), [3] where Li is plated and consumed into SEI on a current collector. Post-mortem analysis of this current collector using XPS showed reduced Li_2S and increase P in the SEI, indicating a more stable interface (figure 1c).

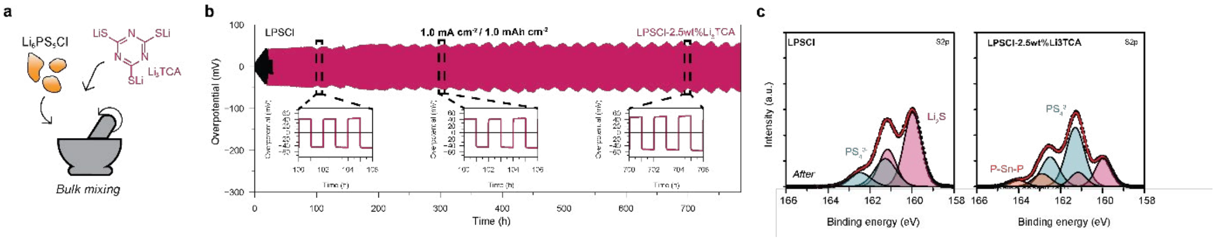

Figure 1: a) Simple organic functionalization strategy of mortar mixing of LPSCl with Li_3TCA b) Li plating and stripping at 1.0 mA cm^{-2} and 1.0 mAh cm^{-2} symmetrical cells c. XPS after CTTA experiment showing reduced Li_2S in presence of additive.

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Unveiling Surface Chemistry of Ultrafast-Sintered LLZO Solid-State Electrolytes for High-Performance Li-Garnet Solid-State Batteries

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Ultrafast (UF) sintering emerges as a game-changing sintering methodology for fabricating $Li_7La_3Zr_2O_{12}$ (LLZO) solid-state electrolytes, representing a pivotal stride toward the advancement and prospective commercialization of Li-garnet solid-state batteries.[1, 2] Despite its widespread use in the fabrication of LLZO ceramics, the chemical composition of the UF-sintered LLZO surface remains largely unexplored. This study presents an in-depth analysis of the surface chemistry of UF-sintered LLZO using comprehensive techniques, including depth-profiling X-ray photoelectron spectroscopy (XPS) and focused-ion-beam time-of-flight secondary ion mass spectroscopy (FIB-TOF-SIMS). Our investigation uncovers a striking difference between the surface of UF-sintered and conventionally-sintered LLZO, revealing a predominant surface contamination by Li_2O up to ca. 40 nm depth in the case of UF processing. Comparative synchrotron X-ray diffraction data during UF and conventional sintering elucidate the origin of surface contamination. We propose a viable solution to this issue through an additional heat-treatment (HT) step at 900 °C after UF sintering, as corroborated by XPS, and FIB-TOF-SIMS measurements. Furthermore, we present a comparative assessment of the electrochemical performance of Li/LLZO/Li symmetric cells based on UF-sintered LLZO pellets, both with and without the post-HT step, underscoring the pivotal role of an uncontaminated LLZO surface.

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The Stability of the Solid Electrolyte Interphase of Argyrodite Solid Electrolytes

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The solid electrolyte interphase that forms on argyrodite solid electrolytes has been reported to continually grow through a diffusion controlled process, yet this process in not fully understood.[1] Through a combination of cyclic voltammetry, x-ray photoemission spectra and coulometric titration time analysis (CTTA) the stability of the SEI itself is probed. These findings reveal that the SEI is not stable and suggest an explanation for the diffusion driven solid electrolyte interphase (SEI) growth mechanism. In addition, a solid-state ring reference electrode is developed which when used in combination with CTTA allows for the resistance of a growing SEI to be studied through electrochemical impedance spectroscopy.

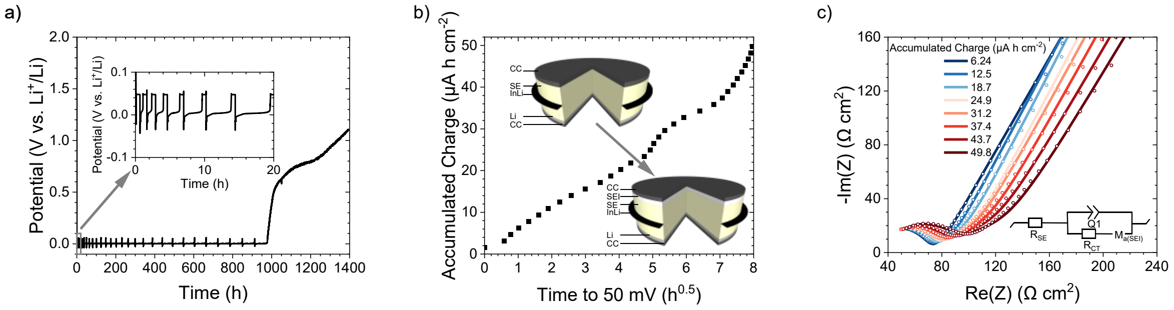

Figure 1 - Three electrode CTTA measurement. a) CTTA with PEIS conducted once a 50 mV OCV was reached, b) relationship between accumulated charge and the square root of OCV time to consume Li metal, c) PEIS of a growing SEI.

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Standardized Processing, Measuring and Evaluation of Solid Electrolyte Impedance Data for Reliable Characterization of Solid Electrolytes

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All-solid-state batteries are the target technology of new and established players on the battery market. The further development of solid electrolytes has a fundamental issue at the electrochemical characterisation level. The absence of standardized protocols in sample preparation and measuring procedures leads to large uncertainties in the determination of the ionic conductivity. This has been shown in a round-robin study using argyrodite solid electrolytes.[1] On the other hand, it has also been shown in a case-study using oxide electrolytes, that harmonized procedures can lead to more reproducible results.[2] Sample fabrication procedures and the applied pressure during the measurement were also identified as major influences in the resulting ionic conductivities.[3] In order to improve the reliability of ionic conductivity determination, there is a need for standardized methods. We aim to identify optimized measuring and preparation conditions for sulfide, oxide, and polymer electrolytes as major material classes. Screening conditions include pre-processing pressure, contact materials, pressure during the measurement, temperature, and AC amplitude as well as different cell designs.

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Tailoring $CsSnCl_3$ based Solid Electrolyte for High-Performance Solid-State Chloride-Ion Batteries

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Solid-state chloride-ion batteries (SS-CIBs) offer potential advantages over conventional lithium-ion batteries, including higher energy density and improved safety. However, liquid chloride ion batteries are susceptible to electrode material dissolution within the electrolyte, which can significantly impact their performance. $CsSnCl_3$, a perovskite-type halide, has emerged as a promising solid electrolyte for SS-CIBs due to its high ionic conductivity and stability. [1] However, its performance can be further enhanced through doping strategies. This study investigates the effects of various dopants [2] on the structural, electrochemical, and ionic conductivity properties of $CsSnCl_3$. We explore the incorporation of different cations (e.g.,alkaline earth metals, and transition metals) into the $CsSnCl_3$ lattice. Characterization techniques such as X-ray diffraction (XRD), impedance spectroscopy is employed to elucidate the impact of doping on the crystal structure, phase stability, and ionic transport. By optimizing the doping composition and synthesis conditions, we aim to develop high-performance solid electrolytes that can drive the advancement of SS-CIB technology.

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The riddle of succinonitrile based polymer electrolytes: an NMR perspective

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The main bottleneck in the practical implementation of all solid state rechargeable lithium metal batteries is the solid state electrolyte which should ideally possess high safety, a wide electrochemical stability window, favourable ion conductivity and the ability to form conformal interfacial contact with the electrodes. Polymer based hybrid solid electrolytes are an interesting category which embody many of the positive attributes of the constituents. Succinonitrile (SN, a solid state plastic crystal) embedded elastomeric electrolytes (SEEs) have emerged as promising hybrid electrolyte systems which showed conductivity of 10^{-3} S cm^{-1} at ambient temperature along with electrochemical stability against high voltage cathodes. [1]

Although SEEs are widely reported in the literature, their Li-ion transport mechanism is unclear. For instance, most literature claim that Li ion conductivity occurs only through the SN phase. To verify this, we synthesized the PCEE (plastic crystal embedded elastomer electrolyte) system which is well known and explored it through various 1D and 2D solid state nuclear magnetic resonance (ssNMR) spectroscopy experiments and we find that the polymer does take part in the ion transport which is evidenced in EXchange SpectroscopY experiments. Further we also analysed the decomposition products of SN at the Li surface which is a prime concern in long term cycling of SEEs. Herein we report these results and in light of this we expect to utilise the full potential of SEE towards high energy battery applications [2]

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Fully reduced electrolytes for Li metal and Silicon anodes in solid state batteries

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To beat conventional lithium ion batteries in terms of energy density requires low-potential, high-energy-density anodes such as Si or Li-metal anodes. Most highly-conducting solid electrolytes decompose at the low potentials of Si and Li metal anodes, leading to irreversible Li-loss – particularly an issue for industrially-attractive “zero-Li-excess” battery-cells. One way to mediate this is to design solid-electrolytes that are fully-reduced, and thus thermodynamically stable at the operating potentials of low-potential anodes. “Fully-reduced” means that all elements (except for Li) in the solid carry their lowest possible formal oxidation state and thus cannot be further reduced.

The challenge of most known fully reduced phases is their relatively low conductivity and low oxidation stability. In this study, we report new families of fully-reduced solid electrolytes having the antifluorite structure that reach conductivities above 0.2 mS cm^{-1}. We demonstrate how structural disorder is the key towards reaching high conductivities, by calculating activation barriers and using these for percolation analysis. The electrochemical stability towards Li metal and silicon anodes is evaluated, demonstrating the possibilities of fully-reduced materials to work as protective solid electrolyte layer in all-solid state batteries.

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Halogen Substitution Effects on Structure, Ionic Conductivity, and Electrochemical Stability of Solid Electrolytes $Li_3YBr_xCl_{6-x}$

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Solid-state batteries are attracting significant attention due to their superior safety and potential for high energy density. Achieving these benefits requires solid electrolytes that can simultaneously enhance ionic conductivity and electrochemical stability, ensuring compatibility with high-energy electrodes. In this context, ternary halides such as Li_3YX_6 (X = Cl, Br) have been developed, offering high ionic conductivity (~1 mS/cm) and a wide electrochemical window, enabling stable operation with $LiCoO_2$ cathode materials [1]. Introducing Br to Li_3YCl_6 has been shown to further increase ionic conductivity; however, thermodynamic calculations suggest a potential reduction in oxidative stability. [2] This observation underscores the need for a deeper understanding of the relationship between structure, ionic conductivity, and the electrochemical window.

In this study, we experimentally investigate the substitution series $Li_3YBr_xCl_{6-x}$ (x = [0, 6], in steps of 1.5) to examine how halogen composition influences crystal structure, ionic conductivity, and the electrochemical stability window [3]. We found that the composition $Li_3YBr_xCl_{6-x}$ (x = 1.5) offers a favorable balance, significantly increasing ionic conductivity (5.36×10^{-3} S/cm at 303 K) compared to Li_3YCl_6, while maintaining the higher oxidative stability of Li_3YCl_6 (3.5 V) relative to the bromide end member. This work, for the first time, provides a more precise electrochemical window assessment of the halide system by testing the (de)lithiation potentials, broadening the perspective on how to optimize solid electrolytes for both ionic conductivity and electrochemical stability.

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Degradation Mechanisms in $LiFePO_4$-based All-Solid-State Batteries containing a Hybrid Electrolyte with Garnet $Li_7La_3Zr_2O_{12}$ designed for Maritime Applications

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The development of commercial solid-state batteries has been delayed due to the distinct limitations of both inorganic and organic solid electrolytes, prompting the exploration of hybrid approaches. However, the ion conductivity of hybrid solid electrolytes at room temperature remains inadequate, particularly because the role and influence of the inorganic and organic interphases are not yet well understood. [1]

Based on recent publications, the promising composition of a hybrid electrolyte layer involves polyethylene oxide (PEO) paired with a lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) salt and $Li_7La_3Zr_2O_{12}$ (LLZO) inorganic filler to achieve high ionic conductivity together with satisfactory mechanical properties. [2] Pairing the electrolyte layer with an $LiFePO_4$ (LFP) cathode can potentially meet the requirements set by maritime industry with regard to safety, cost, and long-term performance.

In this work, we conduct a comparative study on the aforementioned system, investigating the performance of the battery upon modification of incorporation methods (self-standing films, direct coatings, tape-cast, pellets), electrode/electrolyte composition (%wt ratios, involved materials such as plasticizers, ionic liquids), and electrode coatings to reduce the interfacial resistance. The main purpose of the study is conducting post-mortem analysis for the identification of main degradation mechanisms impeding the desired performance of the battery.

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Tape casting Li_6PS_5Cl: Effect of particle size distribution and densification pressure

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In energy storage, solid-state batteries are an attractive, safer alternative to traditional lithium-ion batteries with higher power and energy densities but transitioning from lab-scale to commercially viable pouch cells remain a major commercialization challenge [1]. One of the major challenges related to the manufacturing of solid-state batteries is synthesizing electrolytes with controlled microstructure [2]. Efforts to develop large-scale synthesis techniques for Li_6PS_5Cl solid electrolyte have led to its commercial availability, however unlike lab-scale synthesis, commercial production often results in varied particle sizes and distributions. This causes challenges like poor densification and low-quality percolation networks, with some particles even exceeding the separator or cathode thickness, leading to suboptimal kinetics.

In this study, we present a procedure to tune the particle size distribution (PSD) of commercially available Li_6PS_5Cl while maintaining high Li-ion conductivity. We will examine the impact of different PSDs on the densification of tapes, composed of 97.5% Li_6PS_5Cl and 2.5% binder, using cold uniaxial pressing at pressures ranging from 0 to 1000 MPa. Finally, we will discuss the correlation between the microstructure of the tapes (e.g., porosity and connectivity) and Li-ion transport, analysed using XRD, FIB-SEM tomography, TEM, and temperature- and pressure-dependent impedance spectroscopy.

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Lithiation-driven cascade dissolution coprecipitation of sulfide superionic conductors

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The high-cost lithium sulfide (Li_2S) precursor and limited dry methods using the ball-milling technique have prevented mass production of Li_6PS_5Cl (LPSCl).[1] Herein, we developed the one-pot wet synthesis of LPSCl using granule Li metal, naphthalene (NAP), elemental S, P_2S_5, and LiCl in tetrahydrofuran (THF). It particularly produces Li_6PS_5Cl of high quality (5.7 mS cm^{-1} of ionic conductivity at 25 °C) at a material cost of one-tenth of previously reported methods.[2] The synthesis process, featuring a cascade-dissolution-coprecipitation mechanism, is investigated using electrospray ionization mass spectrometry (ESI-MS) and ^{31}P nuclear magnetic resonance (NMR) with the aid of the density functional theory (DFT) calculation. The one-pot Li_6PS_5Cl-based ASSBs with a $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ cathode and a Li-In anode provide a high initial capacity (190 mAh g^{-1} at a 0.1 C rate, 55 °C) and hold a capacity retention of > 80 % after 1,000 cycles at a 2.0 C rate.

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Potassium-Ion Conducting Chloride Solid Electrolyte with High Voltage Stability

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Due to its abundance and low potential (0.104 V vs. Li/Li$^+$), potassium chemistry in rechargeable batteries may be promising for achieving cost-effectiveness with high energy density, making it desirable for large-scale energy storage systems. Furthermore, following the development paths of Li and Na technologies, the introduction of all-solid-state K or K-ion batteries with inorganic K$^+$ solid electrolytes (SEs) has the potential to improve safety and energy density when compared to liquid electrolyte-based batteries.

In this study, we report the synthesis of a novel potassium SE using a mechanochemical method: cubic $KTaCl_6$, which has a remarkable K$^+$ conductivity of 1.0×10^{-5} S cm^{-1}. This value represents a 1000-fold enhancement over that of samples obtained using heat treatment. Using X-ray diffraction, Rietveld analysis, and bond valence energy landscape calculations, we reveal three-dimensional K$^+$ migration paths that are enabled by face-sharing KCl_{12}^{11-} cuboctahedra through structural characterization. This configuration is in contrast to that of the monoclinic $KTaCl_6$ produced through annealing, which features discontinuous K$^+$ migration pathways. These pathways are formed by the edge- or corner-sharing of KCl_{12}^{11-} anti-cuboctahedra, resulting in a significantly reduced K$^+$ conductivity. Theoretical calculations and cyclic voltammetry measurements employing three-electrode cells confirm high electrochemical stability up to ≈3.9 V (vs. K/K$^+$).

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Improving the ionic conductivity of low cost and scalable solid electrolytes through cation disorder in Li-rich halides

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Different families of SEs, such as ternary ordered spinels (i.e., Li_2MgCl_4 and Li_2ZnCl_4) has been previously studied. These materials were synthetised thorough long thermal solid-state synthesis, which typically were carried out at 150ºC for 3-4 months leading to a ordered spinel structure (*Fd*-3*m*) with the Li and the Zn on the octahedral and tetrahedral sites, respectively. Interestingly, the Li_2ZnCl_4 undergoes a phase transition from 215 ºC to an olivine (*Pnma*) polymorph. However, the olivine structure showed a degree of disorder, with Li sitting on tetrahedral 8*a* sites. These studies suggested that the tetrahedral Li environment plays a pivotal role on the ionic conductivity of these materials, leading to a huge increase up to $2\cdot10^{-4}$ $S\cdot cm^{-1}$ (280 ºC) in the case of the olivine polymorph compared to $1\cdot10^{-7}$ $S\cdot cm^{-1}$ (125 ºC) for the fully ordered spinel.[1,2]

It has been pointed out that the Li-site disorder introduced through this M deficiency contributes to a 3D Li+ diffusion within all the crystalline structure.[3]

Here we report on the development of a fast Li conductors disordered spinel ($Li_2Zn_{1/3}Zr_{1/3}Cl_4$ and $Li_2Zr_{1/3}Mg_{1/3}Cl_4$) based on non-critical elements and scalable processing with bulk conductivities around $1\cdot10^{-4}$ and $4\cdot10^{-4}$ $S\cdot cm^{-1}$ respectively, which represents a 5 orders of magnitude increase compared to the Li_2ZnCl_4 fully ordered counterpart. These materials were prepared by means of a High Energy Ball Milling within 1h without further steps. High-frequency electrochemical impedance spectroscopy has been used in order to deconvolute the bulk and grain boundary contribution to the ionic conductivity. The electrochemical stability window of these materials has been studied and joint synchrotron x-ray and neutron powder diffraction studies has been used in order to fully describe the crystalline structure and Li^+ diffusion pathways on these new SEs.

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Linking the manufacturing method and the Li$^+$ ion diffusion in Hybrid Solid Polymer Electrolytes

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Hybrid Solid Polymer Electrolytes (HSPEs) enhance the safety and stability of SSBs,[1] particularly by combining well known polymers, like polyethylene oxide (PEO), with inert fillers such alumina (Al_2O_3). However, scaling up HSPEs from lab scale is challenging, since the processing method strongly affects the properties of the final membrane. For instance, extrusion of PEO with LiTFSI and Al_2O_3 has demonstrated exceptional cycling performance, superior coulombic efficiency, and strong resistance to dendritic growth when the final thickness is set ca. of 70 μm. The efficacy is mainly linked to the efficient transport of lithium ions across the thin HSPE combined with the improvement of the mechanical properties induced by the added filler.[2] Therefore, understanding the movement of lithium ions through the membrane is of utmost importance in the field of energy storage and electrochemical systems.

In this study, a comprehensive analysis and evaluation of various factors affecting lithium ion movement of different membranes processed either by extrusion or solvent casting will be done. Particularly, this study will correlate the lithium movement aspects with the, up to now, rather unexplored effect of the manufacturing method, including the determination of the Li$^+$ diffusion constant, the concentration polarization, the ionic mobility and the lithium depletion of the HSPEs manufactured either by extrusion or solvent casting. These insights, obtained only on electrochemical tests, allows for understanding how the lithium movement in the HSPE is impacted by the chemistry of the components, but also by the selected manufacturing method and shed light on one of the most unknown aspects of HSPE manufacturing.

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Exploring the Electrochemical Oxidation of $LiBH_4$ and $Li_2B_{12}H_{12}$ for High-Voltage All-Solid-State Batteries

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Hydridoborates represent a promising class of solid electrolytes, offering high ionic conductivity at room temperature (> 10^{-3} S cm^{-1}), low density (~1 g cm^{-3}), ease of dry and solution processing, and stability under both reducing conditions with lithium and sodium metals and oxidizing conditions above 3 V vs Li^+/Li [1]. Notably, certain Li^+ and Na^+ solid electrolytes composed of two cage-like closo-hydridoborate anion species can form a highly ion-conductive, passivating interphase, making them suitable for use with 4 V-class cathodes. Despite these advantages, the precise chemical nature of the electrochemical decomposition products of hydridoborates and their variation with electrochemical potential remain unclear.

In this study, using a combination of experimental and theoretical approaches, we demonstrate that $LiBH_4$ undergoes electrochemical oxidation to form $Li_2B_{12}H_{12}$ above 2.0 V vs Li^0/Li^+. Additionally, we provide evidence that the $[B_{12}H_{12}]^{2-}$ anion is further oxidized to larger boron-hydrogen clusters above 3.8 V vs Li^+/Li. These findings on the solid-state electrochemical oxidation products are applicable to other systems, regardless of cation species and hydridoborate anion structures, thereby contributing to cathode design strategies for high-voltage all-solid-state batteries.

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Reducing Overpotential in Quasi-Solid-State Lithium Sulfur Batteries by Integrating Solid-State Electrolyte into the Cathode Slurry

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The lithium-sulfur (Li-S) battery is a promising energy storage system due to its high theoretical energy density; however significant challenges, particularly poor cycling performance has hindered its practical deployment. Quasi-solid-state (QSS) Li-S batteries offer a potential route to mitigating this by avoiding the production of Li-polysulfides upon operation. This comparatively new concept offers substantial opportunities for electrode design to improve the performance of the battery. This study demonstrates and improved electrode which can be deployed in QSS Li-S cells to address these issues by integrating solid-state electrolyte $Li_{10}GeP_2S_{12}$ (LGPS) into the positive electrode slurry.

The traditional use of N-Methyl-2-pyrrolidone (NMP) in Li-S battery cathode slurry reacts with solid-state electrolytes like LGPS. To avoid this, ethyl acetate (EA) is used as an alternative solvent. Due to EA’s incompatibility with polyvinylidene fluoride (PVDF) binder, polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) is used instead. Although EA's low boiling point complicates coating, adding hexyl butyrate (HB) as a co-solvent improves the coating quality[1]. This optimized system enhances LGPS integration, reduces overpotential, and boosts the electrochemical performance and lifespan of quasi-solid-state Li-S batteries.

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Isovalent substitution for optimising scalable thin-film amorphous solid electrolytes

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Rechargeable lithium batteries are increasingly essential for applications ranging from portable electronic devices to electric vehicles. However, the prevailing Li-ion batteries face significant safety concerns and have reached a plateau in energy density. All-solid-state Li batteries offer the promise of improved energy density and longer lifespans, yet large-format cells are still challenged by Li dendrite formation. The amorphous solid electrolyte (SE) lithium phosphorous oxynitride (LiPON), is known for its excellent stability against Li metal electrodes and its ability to inhibit dendrite growth by directing Li plating/stripping. [1] Despite these advantages, the production of LiPON requires vacuum deposition techniques, which are costly and feature low throughput, limiting its broader applicability. In previous work, our group introduced a scalable thin-film amorphous SE based on Li-Al-P-O chemistry (LAPO) that can be processed using an aqueous precursor solution and low-temperature annealing in air. [2] However, its ionic conductivity was much lower than that of LiPON, falling below the commercially viable range (~10^{-6} S/cm).

This work focuses on optimising LAPO SE through Al substitution. This substitution has significantly enhanced the ionic conductivity to 10^{-6} S/cm while maintaining low electronic conductivity (10^{-12} to 10^{-14} S/cm), indicating its ability to prevent Li dendrite growth. [3] Furthermore, we have systematically investigated the scalability of the SE thickness. The enhanced ionic conductivity and excellent scalability of the optimised LAPO SE offer promising potential for the success of all-solid-state Li batteries.

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Exploring Pressure and Strain Effects in Argyrodite Solid Electrolytes for Enhanced Solid-State Batteries

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The global shift towards sustainable energy solutions necessitates advancements in battery technology, prompting a transition from conventional lithium-ion batteries towards more efficient alternatives. Solid-state batteries have emerged as a promising candidate due to their potential for enhance safety, energy density, and lifespan. This research focuses on exploring the viability of argyrodite materials for solid-state battery applications through computational modelling techniques. Utilising tools such as *ab initio* molecular dynamics (AIMD) and density functional theory (DFT), the research investigates the effects of varying pressure and strain on the structural and electrochemical properties of argyrodite materials. Argyrodites demonstrate remarkable characteristics such as high ionic conductivity, wide electrochemical stability window and compatibility with various electrode materials. By elucidating the intricate relationships between material structure and battery performance, this research aims to highlight the potential of argyrodite materials as a key component in the development of next-generation solid state batteries. The utilisation of argyrodite materials could lead to significant improvements in battery efficiency, cycle life, and safety, thereby accelerating the transition towards sustainable energy solutions.

A High-Throughput Technique for Unidirectional Critical Current Density Testing of Solid Electrolyte Materials

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Work on solid electrolytes for rechargeable lithium-based batteries is motivated by the potential benefits of lithium-metal anodes for a variety of applications, including electric vehicles. Dendrite formation has been the key challenge preventing commercialization of rechargeable lithium-metal batteries, so establishing, validating, and improving the dendrite resistance of electrolytes is a key enabler of progress in the field. Typical symmetric cycling tests of Li-Li cells introduce operational and theoretical limitations which compromise the data produced and the conclusions which can be drawn from such testing. A high-throughput technique for unidirectional critical current density testing is presented which has allowed the development of a solid electrolyte capable of withstanding current densities of at least 300 mA cm^{-2}. The theoretical and empirical basis for this testing methodology is outlined, results are presented and analyzed, and best practices for critical current density testing of solid electrolyte materials are proposed.

Parameter Sensitivity Analysis and Calibration of Discrete Element Models for Optimizing All-Solid-State-Battery Cathode Microstructures

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Optimizing the microstructure of all-solid-state battery (ASSB) cathode composites, particularly those with sulfide-based solid electrolytes (SEs), is essential for enhancing performance and energy density. Understanding the impact of material properties, compositions, and processing parameters on microstructural behavior is crucial to inform effective design strategies. The Discrete Element Method (DEM) offers valuable insights for optimizing cathode microstructures; however, its effective application is limited by parameter variability and the lengthy fitting process, which may lead to inaccurate predictions.

This study conducts a parameter sensitivity analysis on DEM inputs to identify which material parameters most affect microstructure outcomes, including cathode active materials (CAM) utilization, SE network percolation, and composite porosity. Through a systematic exploration of the parameter space, we identify the parameters with the greatest influence on simulation results, allowing for more targeted model calibration. Our findings emphasize the importance of sensitivity analysis in DEM, providing insights for efficient calibration strategies and addressing limitations in traditional parameter fitting. By examining both global and local optimization, this research identifies optimal conditions for various scenarios and provides guidelines for the effective use of DEM models in ASSB microstructure optimization.

Influence of Layered Electrode Designs on the Performance of All-Solid-State Batteries

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Sulphide-based all-solid-state batteries (ASSBs) offer a promising route to safer batteries with superior energy density compared to conventional Li-ion batteries. However, design and optimization of the composite cathode is one of the key aspects requiring intensive research. [1,2] Achieving both high energy and power density remains challenging due to limitations in ionic conductivity and active material loading. Using structure-resolved simulations, we investigate the potential of electrode structuring to enhance ASSB performance. [3] While simulations of electrode designs with electrolyte channels predict only moderate increase in cell performance, two-layer cathode designs promise significant improvement in practical energy density. The layered structure effectively balances improved ionic transport due to increased solid electrolyte fraction at the separator and substantial active material loading through increased active material fraction at the current collector. Taking these design considerations to the next level, electrodes with a three-layer design have been fabricated. Electrochemical tests and complementary simulations confirm the beneficial effect of this approach. This opens up a large design space for electrode fabrication. On our poster we present an efficient approach to screen the various design options and identify an optimized composite cathode for ASSBs.

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Unravelling the Role of Sulfur/Halide Local Disorder in Argyrodites: Pathways to Enhanced Ionic Diffusion

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Understanding the mechanisms behind high ionic conductivity is crucial for optimizing solid electrolytes. This study analyses sulfur/halide disorder and local environments coordinating lithium transport in $Li_{7-x}PS_{6-x}Br_x$ argyrodites using ab initio molecular dynamics. Contrary to common assumptions [1,2], such as the roles of bromine content, site occupancy, and configurational entropy, we find that maximum conductivity is primarily achieved through an even distribution of sulfur and bromine across the 4a and 4d sublattices. A detailed analysis of local sulfur/bromine environments and their impact on jump activation energies reveals that an even distribution of sulfur and bromine enhances ionic transport by balancing high- and low-energy jump pathways. Additionally, we introduce the "ionic potential" as a universal descriptor to quantify the strength of attraction between diffusing cations and anions, which reliably predicts conductivity trends across various experimental compositions. Our analysis suggests that maximum conductivity is achieved by minimizing and equalizing ionic potentials across the 4a and 4d sites, offering a new framework for designing advanced argyrodite electrolytes.

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Influence of Surfaces on Ion Transport and Stability in Anti-Perovskite Solid Electrolytes at the Atomic Scale

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Solid-state batteries are widely considered as a next-generation technology capable of revolutionising energy storage as they combine several potential advantages, such as energy density gains and safety enhancements. Nonetheless, interfacial issues still stand as one of the greatest barriers to their large-scale success. The understanding of such regions and the surfaces that form them is thus vital for practical applications. [1] Recently, anti-perovskite solid electrolytes have captivated great interest due to their promising ionic conductivity and structural versatility. [1, 2]

Here, density functional theory calculations are used to explore the stability, defect chemistry, electronic properties, and ionic migration barriers across the bulk and at the surfaces of a range of M_3OX (M = Li or Na; X = Cl or Br) anti-perovskites. We find that the metal-halide terminated (100) surfaces are the most thermodynamically stable surface type for all analysed systems. Our simulations predict that the formation of any vacancy type at any site is more energetically favourable in systems containing Na instead of Li, regardless of their halide content. The analysis of the electronic properties reveals that Na-based systems could potentially present lower electrochemical stabilities. Our migration energy barriers results suggest the existence of a complex trade-off between maximizing atomic polarizability and bottleneck size in the lattice for enhancing ion migration. Such findings provide critical insights for the design of anti-perovskite surfaces that promote ion transport in solid-state batteries.

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Electrochemical Behavior of Silicon Nitride in Solid-State Batteries

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Solid-state batteries (SSBs) are known for their safety and high energy density. Among various anode materials, silicon (Si) is considered promising due to its high theoretical capacity and low lithium insertion potential [1]. However, Si suffers from low conductivity and significant volume expansion, leading to an unstable solid-electrolyte interphase (SEI) and mechanical instability [2]. To address these issues, silicon nitride (SiNx) has emerged as a promising alternative, forming Li-Si-N phases with strong ionic conductivity during cycling [3]. While SiNx has shown stability in liquid electrolytes [4], its role in SSBs remains underexplored.

This study investigates the electrochemical behavior of SiNx in SSBs using impedance spectroscopy to understand lithiation and decomposition mechanisms within sulfide-based solid electrolytes. Our findings show that intermediate Li-Si-N phases provide high conductivity, supporting stable cycling without carbon additives. However, carbon significantly influences the initial conductivity of the anode composite and the lithiation kinetics, impacting overall cycle stability. In-situ impedance spectroscopy and cycling reveal different lithiation behaviors in carbon-containing versus carbon-free systems.

Overall, this study offers valuable insights into the lithiation processes and interface stability, improving our understanding of SiNx performance in SSBs and advancing its application potential.

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Impact of Cathode Design on All-Solid-State Sodium-Sulfur Battery Performance

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The sodium-sulfur battery chemistry has recently garnered attention for its high theoretical capacity (1672 mAh g^{-1}) and diffuse availability of raw materials [1]. The performance of Na-S batteries is, however, critically hindered by the shuttling of polysulfides upon cycling, leading to the passivation of the anode and self-discharge. Replacing the liquid electrolyte with an inorganic solid ion conductor can suppress the formation and migration of polysulfides, enhancing battery safety.

The optimization of ionic and electronic transport inside the sulfur cathode plays a central role in achieving high energy density and rate performance. Sulfur has an extremely low ionic and electronic conductivity; thus, the sulfur redox reactions can only occur at the triple phase boundary between the catholyte, the electronically conductive carbon additive and the sulfur particles [2]. Optimized transport in the cathode composite is crucial to address the need for high cathode loading (> 3 mAh cm^{-2}) required for practical applications.

In this work, we investigated the effect of the cathode design and processing on the performance of all-solid-state Na-S batteries with a chlorine-substituted Na_3PS_4 electrolyte. In particular, the discharge kinetic, cycling stability and efficiency of the Na-S battery were evaluated and analyzed in relation to the ionic and electronic transport within the cathode architecture.

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The role of nanoporous carbon materials for thiophosphate-based all solid state lithium sulfur battery performance

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Due to their high theoretical energy density, all solid state lithium sulfur batteries (ASSLSBs) represent one of the most promising candidates for next-generation energy storage systems. Whilst high addressability of sulfur has been published for several cathode compositions and preparation methods in recent years, there is still a lack of clarity regarding the influence of the used carbon. Furthermore, ASSBLSBs face challenges in up-scaling, since the common preparation methods including high energy ball milling are time consuming, batch-wise and require high energy impact. In this study, high sulfur utilization > 1600 mAh g_S^{-1} and reversibility with 80 % of initial discharge capacity after 60 cycles is achieved, using a more time-efficient preparation method with significantly lowered energy impact by selecting a suitable carbon[1]. Furthermore, the influence of the carbon porosity and particle morphology on the electrochemical performance is discussed. This study provides guidance in selecting nanostructured carbon materials to enable cost-efficient, up-scalable preparation methods for ASSBLSBs without compromising on the excellent electrochemical performance.

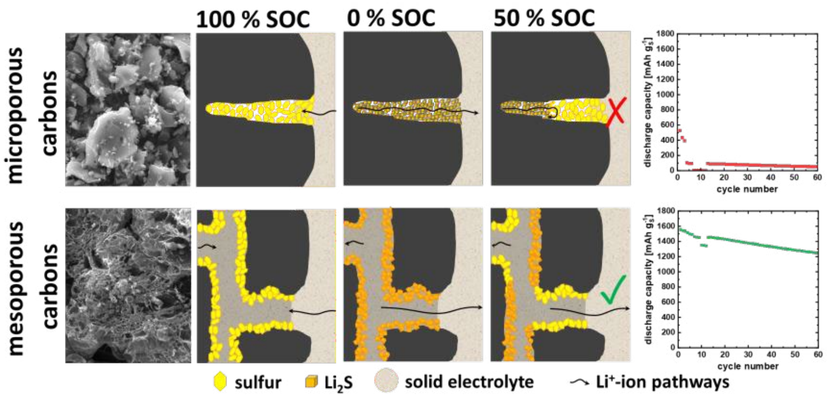

Figure 1: Assumed transport of Li^+-ions within the pores of carbons with different porous structure.

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Identification and quantification of kinetic limitations of thiophosphate-based solid-state cathodes by chronoamperometry

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All-solid-state batteries (ASSBs) are emerging as a promising next-generation energy storage device, but their performance is currently constrained by several limitations. Appropriate characterization methods are essential to accelerate the development process. This study demonstrates the use of chronoamperometry (CA) to rapidly evaluate the performance of ASSB cathodes. It provides rate capability information comparable to conventional galvanostatic testing, but with a shorter measurement time and increased data output. The increased data output enables more accurate modelbased analysis to identify rate-limiting mechanisms, leading to better utilization of the active material. This was demonstrated using a Li6PS5Cl (LPSCl) solid electrolyte with different active cathode materials. Chronoamperometry was used to determine ratelimiting mechanisms, such as electrical or diffusional limitations, as well as the maximum utilization of active materials at low rates.

Further the CA-method is used for validating the capacity and rate performance of LPSCl composite cathodes in ASSB. Quantitative analysis of chronoamperometric data distinguishes between resistive and diffusive rate limitations in NCM811-LPSCl cathodes of varying morphology and composition. It is found that increasing the ratio of active material to solid electrolyte increases the diffusive limitations, especially in single crystal NCM811 cathodes with high active material content (above 84%). The diffusive limitations originate due to a reduction of the NCM811-LPSCl active contact area. The use of small particle catholyte significantly improves the contact area, mitigating diffusion limitations and improving rate performance.

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