

Symposium Interfacial Challenges in Solid-State Li Ion Batteries (SYLI)

jointly organized by
the Metal and Material Physics Division (MM),
the Surface Science Division (O), and
the Semiconductor Physics Division (HL)

Rüdiger-A. Eichel
Institut für Energie- und Klimaforschung
Forschungszentrum Jülich
Ostring O10
52425 Jülich
r.eichel@fz-juelich.de

Karsten Reuter
Lehrstuhl für Theoretische Chemie
Technische Universität München
Lichtenbergstr. 4
85747 Garching
karsten.reuter@ch.tum.de

The electrification of road transportation is generally considered the next important frontier for electrochemical energy storage, and it is currently debated whether prevailing Li ion batteries will ever be suitable for full mass-market electrification. Presently, a wave of optimism is building in the battery community that most of the limitations of conventional Li ion batteries for electric vehicles (safety, limited energy densities) can be addressed by using a solid-state electrolyte (SSE) in place of the traditional liquid one. Unfortunately, present-day all-solid-state batteries are still largely characterized by extremely low current (power) densities. This is ascribed to interfacial resistances, possibly arising from imperfect morphology or chemistry (in particular Li depletion layers) at the interfaces. The use of super-ionic SSEs, nanostructured interfaces, or blending with ion-conducting polymer gels appear as promising routes to overcome these resistances. However, as the exact reason for interfacial resistances is not even known for simple model systems, research along these lines is thus far largely empirical. A more directed exploration and therewith shortened innovation cycles require a detailed, atomic-scale characterization and concomitant understanding of the structures and the ionic transport at the buried electrode-SSE interfaces. This symposium will highlight corresponding studies and discuss current frontiers.

Overview of Invited Talks and Sessions

(Lecture room HSZ 02)

Invited Talks

| | | | | |
|----------|-----|-------------|--------|---|
| SYLI 1.1 | Mon | 9:30–10:00 | HSZ 02 | Interfacial challenges in solid-state Li ion: some perspectives from theory — •ALAN LUNTZ, SASKIA STEGMAIER, JOHANNES VOSS, KARSTEN REUTER |
| SYLI 1.2 | Mon | 10:00–10:30 | HSZ 02 | Will solid electrolytes enable lithium metal anodes in solid state batteries? — •JÜRGEN JANEK, DOMINIK WEBER, WOLFGANG ZEIER |
| SYLI 1.3 | Mon | 10:30–11:00 | HSZ 02 | Hybrid Electrolytes for Solid-State Batteries — •HANS-DIETER WIEMHÖFER |
| SYLI 1.4 | Mon | 11:15–11:45 | HSZ 02 | Neutron diffraction on solid-state battery materials — •HELMUT EHRENBERG, ANATOLIY SENYSHYN, MYKHAILO MONCHAK, SYLVIO INDRIS, JOACHIM BINDER |
| SYLI 1.5 | Mon | 11:45–12:15 | HSZ 02 | Sulfate-based Solid-State Batteries — •YUKI KATOH |

Sessions

| | | | | |
|--------------|-----|-------------|--------|---|
| SYLI 1.1–1.5 | Mon | 9:30–12:15 | HSZ 02 | Symposium Interfacial Challenges in Solid-State Li Ion Batteries |
| SYLI 2.1–2.4 | Mon | 15:45–16:45 | IFW A | Interface-dominated behaviour |
| SYLI 3.1–3.3 | Mon | 17:15–18:00 | IFW A | Sulphate- and phosphate-based electrolytes |
| SYLI 4.1–4.5 | Tue | 10:15–11:30 | IFW A | NMR studies |
| SYLI 5.1–5.4 | Tue | 11:45–12:45 | IFW A | Structure - property relationships I |
| SYLI 6.1–6.5 | Wed | 10:15–11:30 | IFW A | Defects, structure and thermodynamics |
| SYLI 7.1–7.4 | Wed | 11:45–12:45 | IFW A | Hybrid and structured electrolytes |
| SYLI 8.1–8.4 | Wed | 15:45–16:45 | IFW D | Structure - property relationships II |

SYLI 1: Symposium Interfacial Challenges in Solid-State Li Ion Batteries

Time: Monday 9:30–12:15

Location: HSZ 02

Invited Talk

SYLI 1.1 Mon 9:30 HSZ 02

Interfacial challenges in solid-state Li ion: some perspectives from theory — •ALAN LUNTZ¹, SASKIA STEGMAIER¹, JOHANNES VOSS¹, and KARSTEN REUTER² — ¹Stanford University, Stanford, CA, USA — ²Technical University of Munich, Munich, Germany

Unfortunately, interfacial challenges severely limit power and cycle life in all solid-state Li ion batteries. We use theory to investigate some of the origins of these limitations with both continuum theory and DFT. The obvious ones are electrochemical stability of the electrolyte at the anode/cathode interfaces and mechanical issues relating to maintaining interfacial contact during cycling while inhibiting Li dendrite growth. We are especially trying to understand if any fundamental limitations exist from the structures of the double layers that form at the solid electrolyte-electrode or other interfaces in the solid-state stack. These can be quite different than in conventional liquid Li ion batteries. We use Li3OCl as a prototypical Li ion superionic conductor and discuss its properties and discuss its interface with model electrode interfaces.

Invited Talk

SYLI 1.2 Mon 10:00 HSZ 02

Will solid electrolytes enable lithium metal anodes in solid state batteries? — •JÜRGEN JANEK, DOMINIK WEBER, and WOLFGANG ZEIER — Institut für Physikalische Chemie, Justus Liebig-Universität, Gießen, Germany

In order to achieve solid state lithium batteries with higher energy densities [1], lithium metal anodes are one of the primary options. However, reversible and morphologically stable plating of thick lithium metal films is difficult, as void formation and dendrite growth may occur - leading to impedance growth and/or short-circuits. Ceramic electrolytes are considered as a potential solution to this problem. In this lecture the interface between solid electrolytes and lithium metal anodes will be discussed in depth, and the occurrence of both thermodynamic and kinetic instabilities will be highlighted. In particular, the existence of SEI ("solid electrolyte interphases"), forming between lithium metal and the solid electrolyte, will be demonstrated for a number of solid electrolytes. It will also be shown that the growth of these SEI layers follows a typical square-root law-type behavior in SEI formation in liquid electrolytes.

[1] J. Janek and W. Zeier, Nat. Energy 1 (2016) 16141

Invited Talk

SYLI 1.3 Mon 10:30 HSZ 02

Hybrid Electrolytes for Solid-State Batteries — •HANS-DIETER WIEMHÖFER — Inst. Inorganic & Analyt. Chem., WWU Münster — Helmholtz-Institute Münster

Rechargeable lithium batteries with largely increased energy and power densities are a primary goal at present world wide. At the same time, enhanced safety concerns cause the need to replace current liquid electrolytes by new high performance electrolytes combining higher mechanical, thermal and electrochemical stability. Finally, this leads to the development of hybrid electrolytes. The primary idea is to construct electrolytes fulfilling a multitude of requirements based on a combination of components and phases, often coupled with approaches to achieve stable meso or micro porous networks down to chemically designed nanostructures. Starting from ion conducting inorganic solids and glasses, the combination with polymers and salt-in-polymer systems opens a wide range for possibilities for chemical design, tailoring

and fine tuning of electrolyte properties of such hybrid systems. The concept will be illustrated with a number of examples, for instance, self organized block-copolymer networks acting as porous containers for fast ion conducting channels. Future all solid state batteries are expected to profit from hybrid concepts as well. For instance, volume changes during charging/discharging of active electrodes need an elastic polymer network acting as a glue and stabilizing a good contact and charge transfer kinetics of solid electrolyte/solid electrode interfaces.

15 min. break**Invited Talk**

SYLI 1.4 Mon 11:15 HSZ 02

Neutron diffraction on solid-state battery materials — •HELMUT EHRENBERG¹, ANATOLIY SENYSHYN², MYKHAILO MONCHAK¹, SYLVIO INDRIS¹, and JOACHIM BINDER¹ — ¹Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM) — ²Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Garching, Germany

Solid-state batteries are a promising approach to safer electrochemical energy storage and higher energy densities. Bottle necks are interface reactions and transport limitations in the solids. Advanced and optimized materials must provide dedicated properties, for example a good Li-ion conductivity for sufficiently high current densities and only small volume changes to preserve mechanical integrity. Neutron diffraction offers unique features to elucidate the underlying structure-property relationships, which determine the resulting performance parameters on cell level. Selected examples are shown, which demonstrate the capabilities of neutron diffraction to reveal Li-ion diffusion pathways as in the $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) superionic conductor, Li occupation numbers at intermediate states of charge as for LiCoPO_4 or a comparison of volume changes between commercial and alternative zero-strain electrode materials. The capabilities of solid-state batteries are discussed.

Invited Talk

SYLI 1.5 Mon 11:45 HSZ 02

Sulfate-based Solid-State Batteries — •YUKI KATOH — Toyota Motor Europe NV/SA, Hoge Wei 33, Zaventem, Belgium

Large-scale batteries are in high demand for applications such as plug-in electric hybrid or electric vehicles, and smart electric power grids. The all-solid-state battery is the most promising candidate for future battery systems, due to the high energy density obtaining by direct-series-stacking of the battery cells. However, the poor electrochemical characteristics of the all-solid-state battery, due to higher cell-resistivity than conventional liquid electrolyte batteries, still remain as an unsolved issue. We will demonstrate an all-solid-state battery with extremely high power performance that employs the superionic conductors having the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -type crystal structure. The battery can operate over a wide temperature range with extremely high current drains of 3 mAcm⁻² (-30 °C), 100 mAcm⁻² (25 °C), and 1000 mAcm⁻² (100 °C). Careful electrochemical examination of the all-solid-state battery with the same battery configuration as a liquid electrolyte system revealed that the rate characteristics are simply dependent on the difference in state of electrolyte. The very high power characteristics of solid state battery comes from intrinsic ion transportation mechanism of solid electrolyte.

SYLI 2: Interface-dominated behaviour

Time: Monday 15:45–16:45

Location: IFW A

SYLI 2.1 Mon 15:45 IFW A

Interfacial double layers in all-solid-state Li-ion batteries: theoretical insights — ●JOHANNES VOSS¹, SASKIA STEGMAIER², KARSTEN REUTER³, and ALAN LUNTZ^{1,2} — ¹SLAC National Accelerator Laboratory, Menlo Park, CA, USA — ²Stanford University, Stanford, CA, USA — ³Technische Universität München, Germany

Neglecting potential electrochemical and mechanical stability issues of the interface between battery electrode and solid Li-ion conducting electrolyte, we present a theoretical study of charge double layers at ideal solid-solid interfaces. Based on DFT calculations for Li_3OCl , we discuss ionic charge carrier stabilities and interactions in the bulk and at interfaces to electrodes. We furthermore employ continuum models parametrized with DFT energies to understand charging at both the anode and cathode interfaces, respectively, and discuss how spacer materials could mitigate related potential interfacial issues.

SYLI 2.2 Mon 16:00 IFW A

Separation of Intra Grain and Grain Boundary Processes in Solid Electrolytes by High-Resolution Impedance Spectroscopy — ●ANDREAS MERTENS, SHICHENG YU, DENIZ GUENDUEZ, HERMANN TEMPEL, ROLAND SCHIERHOLZ, HANS KUNGL, RÜDIGER-A. EICHEL, and JOSEF GRANWEHR — Forschungszentrum Jülich, Institute of Energy and Climate Research, IEK-9, D-52425 Jülich, Germany

Solid electrolytes are intensively researched for the next generation lithium-ion batteries. Yet their ion transport mechanisms must be better understood to improve their still too low ionic conductivity. Especially distinguishing between contributions from intra grain and grain boundary processes proved to be particularly challenging. This is mainly due to similar time constants of both processes at room temperature, leading to a strong overlap of their impedance contributions.

In this work we use a distribution of relaxation times analysis (DRT) in two dimensions (2D-DRT) to increase the resolution of impedance data measured at $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) solid electrolyte samples sintered between 950°C and 1100°C. The second dimension of the 2D-DRT is given by data measured at varying temperatures between 10°C and 50°C. With the 2D-DRT it is possible to quantify the resistances and thus the activation energies of the intra grain and the grain boundary ionic charge transport processes under realistic battery operation conditions. Moreover, the ionic conductivity within the grain and the grain boundary could be determined.

SYLI 2.3 Mon 16:15 IFW A

Microstructural Properties of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ Solid-State Electrolyte — ●DENIZ CIHAN GUNDUZ^{1,2}, ROLAND

SCHIERHOLZ¹, SHICHENG YU^{1,2}, ANDREAS MERTENS^{1,2}, HERMANN TEMPEL¹, HANS KUNGL¹, and RÜDIGER-A EICHEL^{1,2,3} — ¹Forschungszentrum Jülich, Institute of Energy and Climate Research, IEK-9, 52425 Jülich, Germany — ²RWTH Aachen University, Institute of Physical Chemistry, 52074 Aachen, Germany — ³Jülich-Aachen Research Alliance, Section JARA-Energy, Germany

Lithium-ion batteries are important in daily life. One task is to replace liquid electrolytes by solid ones and $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) is a promising candidate exhibiting high ionic conductivities. For further development it is important to understand the influence of the microstructure on the ionic conductivity. Solid state electrolytes have been mainly investigated via means of electron microscopy (Scanning Electron Microscopy as well as Transmission Electron Microscopy). Here we combine these techniques with Laser Scanning Microscopy (LSM) to study the microstructure, such as grain size, grain boundary width, porosity and secondary phase content and distribution of LATP pellets sintered at different temperatures; and draw a relation to impedance measured on these pellets.

SYLI 2.4 Mon 16:30 IFW A

Development of Bulk-type All-Solid-State Lithium-ion Battery Based on Phosphate Backbone Materials — ●SHICHENG YU, HERMANN TEMPEL, ANDREAS MERTENS, DENIZ CIHAN GUNDUZ, SVENJA BENNING, ROLAND SCHIERHOLZ, FLORIAN HAUSEN, HANS KUNGL, and RÜDIGER-A EICHEL — Forschungszentrum Jülich, Institute of Energy and Climate Research, IEK-9, D-52425 Jülich, Germany

Considerable efforts have been devoted to the development of thick-film solid-state batteries while less achievement has been published owing to the poor interfacial compatibility between electrodes and electrolytes as well as low lithium ion transfer kinetics in solid materials. Here, we demonstrate the fabrication and performance of thick-film monolithic all-phosphate ceramic solid-state Li-ion batteries with high power density and cycling stability at ambient temperature based on $\text{LiTi}_2(\text{PO}_4)_3/\text{C}/\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3/\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$. Theoretically, due to the crystal structure matchup of $\text{LiTi}_2(\text{PO}_4)_3$, $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, the solid-solid interface between $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ electrolyte and $\text{LiTi}_2(\text{PO}_4)_3$ anode is expected to facilitate smooth contact while partially matched on the other side for the solid-solid contact of solid electrolyte and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode. Besides, the operation voltage of the electrode pair is highly matched with the electrochemical window of solid electrolyte. Excitingly, by optimizing the morphology of electrode materials and composition of each layer, the all-solid-state lithium-ion battery, which has a controllable thickness from 0.7 up to 2 mm, showed high capacity and more than 300 stable cycles.

SYLI 3: Sulphate- and phosphate-based electrolytes

Time: Monday 17:15–18:00

Location: IFW A

SYLI 3.1 Mon 17:15 IFW A

Aliovalent substitution in garnet type solid-state electrolytes for solid-state lithium-ion batteries — ●ANJA PAULUS¹, MAIKE WIRTZ¹, SABRINA HEUER¹, PETER JAKES¹, HANS KUNGL¹, and RÜDIGER ALBERT EICHEL^{1,2} — ¹Fundamental Electrochemistry (IEK-9), Institute of Energy and Climate Research, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany — ²Institut für Physikalische Chemie (IPC), RWTH Aachen University, D-52074 Aachen, Germany

Conventional lithium-ion batteries consist of an electrolyte containing toxic, flammable organic liquids which lead to several safety issues such as leakage and burning of the battery. In order to overcome these safety issues solid-state electrolytes could be an alternative to obtain powerful lithium-ion batteries. The garnet type electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ shows promising properties in terms of high lithium-ion conductivity and a good stability against lithium. There are two modifications known for this material, on the one hand a tetragonal one which is thermodynamically stable at room temperature and on the other hand a cubic high temperature modification. The cubic structure shows a lithium conductivity of two orders of magnitude higher than the conductivity of the tetragonal one. One possibility to stabilize the cubic structure at

room temperature or lower temperatures is by aliovalent substitution. Aluminum substitution on the lithium site shows a lithium conductivity of $3.41 \cdot 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ for $\text{Li}_{6.4}\text{Al}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$ at room temperature [1]. Our focus is to study the influence of aliovalent substitution on the properties of garnet type solid-state electrolytes by various techniques. 1.C.Tsai et al., J. Electroceram., 2015, 35, 25-32.

SYLI 3.2 Mon 17:30 IFW A

Defect chemistry of solid electrolyte $\text{Li}_4\text{P}_2\text{S}_6$ by first-principles calculations — ●MARCEL SADOWSKI, SABRINA SICOLO, and KARSTEN ALBE — Institute of Materials Science, Technische Universität Darmstadt, Jovanka-Bontschits-Str. 2, 64287 Darmstadt, Germany

Glassy, glass-ceramic and crystalline lithium thiophosphates have attracted interest as solid electrolytes for all-solid-state batteries. Despite similar structural motifs, these materials exhibit a wide range of compositions, structures and ionic conductivities. For the glass-ceramic consisting of crystalline $\text{Li}_4\text{P}_2\text{S}_6$ and glassy $\text{Li}_4\text{P}_2\text{S}_7$, for example, contradictory ionic conductivities were reported. In this contribution we present density functional theory (DFT) calculations on the

defect thermodynamics and kinetics of crystalline $\text{Li}_4\text{P}_2\text{S}_6$. [1] Despite the existence of low energy diffusion paths, the overall conductivity is inhibited by high defect formation energies. This supports the hypothesis that the conductivity of the $\text{Li}_4\text{P}_2\text{S}_7/\text{Li}_4\text{P}_2\text{S}_6$ composite material is determined by the relative amount of glassy and crystalline phases.

Furthermore, thermodynamics predict the instability of $\text{Li}_4\text{P}_2\text{S}_6$ against metallic lithium. Corresponding interface models for different surface terminations of $\text{Li}_4\text{P}_2\text{S}_6$ show the barrierless formation of an interphase reminiscent of Li_2S , which might act as a passivating layer and protect the electrolyte from further decomposition.

[1] C. Dietrich, M. Sadowski, S. Siculo, D. A. Weber, S. J. Sedlmaier, K. S. Weldert, S. Indris, K. Albe, J. Janek, W. G. Zeier, *Chem. Mater.* DOI:10.1021/acs.chemmater.6b04175 (2016).

SYLI 3.3 Mon 17:45 IFW A

Systematic Search for Lithium Ion Conducting Compounds by Screening of Compositions Combined with Atomistic Simulation — •DANIEL MUTTER^{1,2}, DANIEL URBAN², and CHRISTIAN ELSÄSSER^{1,2} — ¹Freiburger Materialforschungszentrum (FMF), Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Straße 21, 79104

Freiburg — ²Fraunhofer Institut für Werkstoffmechanik (IWM), Wöhlerstraße 11, 79108 Freiburg

Solid state electrolytes (SSEs) with high Li conductivity can significantly improve Li ion accumulators in terms of electrochemical efficiency, thermal and mechanical stability, and environmental compatibility, leading to an enhanced range of applications for these high energy density batteries. Compounds crystallizing in the structure of $\text{NaZr}_2(\text{PO}_4)_3$ (NZP) are regarded as promising SSEs, mainly because of their three-dimensional diffusion network enabling fast transport of Li ions through well defined channels. Starting from $\text{LiTi}_2(\text{PO}_4)_3$, we analyzed a large variety of NZP compounds by systematically screening the relevant parts of the periodic table, replacing atoms on the Ti and P sublattices by isovalent elements. The influence of these elemental substitutions on structural stability, preferred Li sites, ionic mobility, migration paths and diffusion mechanisms were analyzed by means of a combined approach of multiple computational methods with different levels of accuracy, ranging from static energy landscape and molecular dynamics simulations with ionic bond valence potentials to density functional theory calculations combined with the nudged elastic band method.

SYLI 4: NMR studies

Time: Tuesday 10:15–11:30

Location: IFW A

SYLI 4.1 Tue 10:15 IFW A

Investigation of the Li ion conduction behavior in the solid electrolyte $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ by multidimensional NMR — •MARC PAULUS¹, MAGNUS GRAF¹, PETER NOTTEN^{1,4}, RÜDIGER-ALBERT EICHEL^{1,3}, and JOSEF GRANWEHR^{1,2} — ¹FZ Jülich, Institut für Energie- und Klimaforschung, D-52425 Jülich, Germany — ²RWTH Aachen, ITMC, D-52074 Aachen, Germany — ³RWTH Aachen, IPC, D-52074 Aachen, Germany — ⁴Department of Chemical Engineering and Chemistry, TU/e, 5600 MB Eindhoven, The Netherlands

The biggest challenge to overcome in solid electrolytes is the relatively slow and still poorly understood lithium ion migration at solid electrolyte/electrode interfaces as well as at grain boundaries in solid-state electrolytes. $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ is one of the best Li-ion conductors and therefore an interesting candidate as electrolyte material in Li-ion batteries. To link lithium migration mechanisms with different structural features of LGPS by correlation of spin lattice relaxation and spin alignment echo NMR a pulse sequence with two independently varied evolution times was developed. The obtained data was processed with an algorithm for discrete Laplace inversion. The resulting spin lattice-spin alignment correlation map of LGPS provided several signal components that were assigned to different morphologies and dynamic regions in LGPS. In addition, the experiment facilitated a direct distinction between relaxation-controlled and mobility-induced components in the τ_c distribution. Further analysis of the spectral NMR dimension in comparison with SEM and XRD measurements yielded a diverse model of lithium motion for the LGPS powder sample.

SYLI 4.2 Tue 10:30 IFW A

Solid-state MAS and in-situ NMR spectroscopy for studying battery systems — WOLFRAM MÜNCHGESANG¹, VIKTOR KOROTEEV², TATIANA ZAKHARCHENKO³, DANIL M. ITKIS⁴, DIRK C. MEYER¹, and •ANASTASIA VYALIKH¹ — ¹Institut für Experimentelle Physik, TU Bergakademie Freiberg, Freiberg, Germany — ²Nikolaev Institute of Inorganic Chemistry SB RAN, Novosibirsk, Russia — ³Department of Material Science, Moscow State University, Moscow, Russia — ⁴Department of Chemistry, Moscow State University, Moscow, Russia

Current research efforts in the field of energy storage are directed towards improving cost and performance of lithium ion batteries as well as evaluating post lithium ion concepts. Deep understanding of electrochemical processes requires quantitative information on a molecular level, on the one hand, and with temporal resolution, on the other hand. In our studies we apply ex-situ analysis using high-resolution magic angle spinning (MAS) NMR in combination with in-situ NMR, in order to characterize the electrochemical intermediates and reaction products as well as to monitor the formation of solid electrolyte interface (SEI) and surface microstructures in operating cells. The NMR results demonstrate the structural transformations in lithium ion batteries based on vanadia composite and ^{13}C -isotope enriched carbon

electrodes.

SYLI 4.3 Tue 10:45 IFW A

^7Li NMR studies of lithium ion dynamics in $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$ materials — •MICHAEL HAAKS¹, STEVE MARTIN², and MICHAEL VOGEL¹ — ¹Institut für Festkörperphysik, TU Darmstadt, Germany — ²Department of Materials Science and Engineering, Iowa State University, Ames, USA

Rising energy demand makes it important to improve the performance of lithium ion batteries. For this purpose it is important to understand the dynamics of lithium ions, in particular, in heterogeneous materials, which are used in modern strategies for material optimization. With combination of ^7Li NMR spin-lattice relaxation, diffusion measurements, line-shape, and stimulated-echo analyses it is possible to investigate lithium ionic motion in wide range of time and length scales in $0.5\text{Li}_2\text{S}-0.5(\text{xGeS}_2-(1-\text{x})\text{GeO}_2)[1]$ and $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$ glasses[2]. We exploit there capabilities to ascertain the effect of ceramization in $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$. We find that the large variety of lithium environments results in broad distributions of correlation times for the jump motion of the lithium ions. Our results for $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$ allow us to relate the enhancement of electronic conductivity under ceramization[3] to faster lithium ion dynamics on various length scales.

[1] Gabriel et al., *Solid State Nuclear Magnetic Resonance* 70, 53 (2015)

[2] Haaks et al., work in progress

[3] Mizuno et al., *Advanced Materials* 17, 918 (2005)

SYLI 4.4 Tue 11:00 IFW A

Combined DFT and solid-state NMR study of ionic mobility in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ — •SIMONE KÖCHER^{1,2}, ANDREAS GARNHAMMER², HENDRIK HEENEN², MAGNUS GRAF¹, JOSEF GRANWEHR¹, RÜDIGER-ALBERT EICHEL¹, KARSTEN REUTER², and CHRISTOPH SCHEURER² — ¹IEK-9 - Fundamental Electrochemistry, Forschungszentrum Jülich, Jülich, Germany — ²Chair for Theoretical Chemistry and Catalysis Research Center, Technische Universität München, Garching, Germany

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful tool to gain detailed understanding of the ionic mobility in battery materials. Notwithstanding, experimental spectra of novel high-capacitance electrodes such as the configurationally disordered defect spinel oxide $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) are highly complex. Support by independent first-principles based calculations is indispensable to achieve an unambiguous interpretation. We establish a corresponding framework for ^7Li spin-alignment echo NMR studies of LTO by providing first-principles reference values for chemical shielding and quadrupolar coupling from density-functional theory calculations. A detailed comparison of experimental and theoretical data suggests that a local Li ion mobility faster than the experimental time resolution must have a considerable impact on the observed NMR quantities. We present first steps

towards accounting for this local dynamics in the simulation of the autocorrelation function of the NMR experiment within a kinetic Monte Carlo model.

SYLI 4.5 Tue 11:15 IFW A

Li-ion batteries cathode materials from extended Hubbard-corrected functionals — ●MATTEO COCCIONI and NICOLA MARZARI — Theory and Simulations of Materials (THEOS) and NCCR-MARVEL, EPFL, Lausanne, Switzerland

Predictive modeling of the atomistic structure and electronic properties of transition-metal (TM) compounds is essential for the development of several emerging technologies. This is particularly true for materials explored as electrodes in Li-ion batteries. Unfortunately, most approximate energy functionals fail to capture the localization of electrons on TM ions during the charge/discharge transients, thus

compromising the energetics of these systems and the assessment of their performance.

Hubbard-corrected DFT functionals (DFT+U) improve significantly the description of localized valence electrons and have become the standard choice to the modeling of these TM compounds when computational efficiency is required (e.g., for screening large numbers of compounds). This work shows that an extended formulation of DFT+U, including on-site (U) and inter-site (V) interactions, improves the description of mixed valence materials. Focusing on LiMPO_4 ($M = \text{Fe, Mn, Ni, Co}$) we discuss their equilibrium structure and electronic properties in dependence of Li content. Contradicting a common practice, we provide theoretical justification to using computed interaction parameters. We also show this is crucial to reliably compare the energy of different phases, to assess the thermodynamic stability of intermediate compositions and to evaluate the voltage of the resulting battery.

SYLI 5: Structure - property relationships I

Time: Tuesday 11:45–12:45

Location: IFW A

SYLI 5.1 Tue 11:45 IFW A

Hierarchically Structured Electrode Materials for Lithium-Ion Batteries — ●MICHAEL FISCHER, XIAO HUA, PRESTON SUTTON, and ULLRICH STEINER — Adolphe Merkle Institute, Chemin des Verdiers 4, 1700 Fribourg, Switzerland

We present a facile synthetic approach for the fabrication of hierarchically structured electrode materials for lithium-ion batteries. Amphiphilic block copolymers are known to form well-defined morphologies on a mesoscale. By confining sol-gel chemistry to one of the blocks of the polymer these structures can be transferred to various inorganic materials, including functional materials that find use in batteries. Blending the sol-gel precursor/block copolymer mixture with a homopolymer induces phase separation and leads to structure formation on a secondary (micrometre) scale. Following this method, we synthesized mesoporous microspheres of TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ as anode materials and hollow LiFePO_4/C nanospheres as a cathode. These compounds suffer from intrinsically low ionic and electronic conductivities but are of great interest due to their inherent stability and safety. The aforementioned morphologies circumvent this drawback by providing shortened solid-state diffusion distances, facilitating ionic transport. In addition, we can tune the mesopore size by employing block copolymers of different chemical composition and molecular weight. Studying the relationship between pore size and electrochemical performance enables us to identify design principles for the optimization of electrode architectures.

SYLI 5.2 Tue 12:00 IFW A

Comparison of different thin-film solid-state battery systems — ●SUSANN NOWAK, JULIANE MÜRTER, and GUIDO SCHMITZ — Heisenbergstr. 3, 70563 Stuttgart

Different systems of thin-film batteries will be compared in respect to their suitability of being used as a reasonable combination of materials in an all-solid-state battery. As the cathode lithium iron phosphate, lithium cobalt oxide and lithium manganese oxide are compared. The used electrolyte is LiPON and as the anodes tin, silicon and lithium are tested. All cells are prepared by ion-beam sputtering resulting in an overall thickness of one micrometer or less for the whole cell. Electrochemical and TEM investigations are used to evaluate the changes at the interfaces and in the electrodes during cycling and to show mechanisms of capacity loss in the system. The behavior of lithium iron phosphate is very different from the one of lithium cobalt oxide when covered with LiPON. The capacity of the LFP covered with LiPON is exponentially increasing with the temperature and reaching its theoretical value at around 70°C . In the case of all-solid-state batteries with other anodes than lithium, the capacity becomes dependent on the chosen balancing ratio of the cells.

SYLI 5.3 Tue 12:15 IFW A

Ion transport and phase transformation in thin film LiFePO_4 intercalation electrodes — ●GUIDO SCHMITZ¹, FABIAN WUNDE², and FRANK BERKEMEIER² — ¹Institut für Materialwissenschaft, Univ. Stuttgart, Heisenbergstr. 3, 70569 Stuttgart — ²formerly: Institut für Materialphysik, Univ. Münster

Thin film battery materials have an important potential to be applied in all-solid-state batteries. From the view point of physics, they offer a clearer model geometry than the usual particle-binder-compound electrodes. The phase diagram of LiFePO_4 predicts a phase separation in the Li intercalation. However, it is controversial whether phase separation might be suppressed in nanosystems due to elastic or kinetic constraints.

We study the intercalation kinetics of thin films under variation of the intercalation rate over more than 4 orders of magnitude. Also the layer thickness has been systematically varied. We show i) that the miscibility gap of the bulk system is essentially understood by elastic interaction, ii) that nanometric thin films clearly reveal phase separation and therefore undergo significant plastic relaxation, iii) that the grain boundaries represent fast transport paths with the electrochemical characteristics of an ion-conductor and iv) how the classic Randles-Sevcik analysis has to be modified in the case of a phase-separating material to derive proper diffusion coefficients.

SYLI 5.4 Tue 12:30 IFW A

First-Principles Calculations on Structure and Reactivity of Amorphous LiPON — ●SABRINA SICOLA and KARSTEN ALBE — Institute of Material Science, Technische Universität Darmstadt, Jovanka-Bontschits-Str. 2, 64287 Darmstadt, Germany

Despite their increasing popularity as solid electrolytes, the structure/property relationship of Lithium Phosphorus Oxynitrides has not yet been clarified. Theoretical work offers an invaluable insight into the atomistic properties of solids, provided the availability of valid structural models. The simulation of glassy structures represents a main challenge from a computational point of view, and is further complicated by their non-trivial composition. In this contribution, a new approach to the ab-initio simulation of amorphous structures of virtually any desired composition is described. A realistic composition has been suggested by experiments recently conducted by academic partners. The defect thermodynamics of LiPON suggests its instability against metallic lithium. [1] The formation of a solid-electrolyte interphase (SEI) at this interface has been recently observed and quantified experimentally. Following up on this result, the interfacial structural and electronic properties have been investigated with a special focus on reactivity. This work does not only describe a novel approach to the simulation of a more realistic electrolyte, but also provides unprecedented insights, supported by experimental results, into its stability and reactivity under operational conditions.

[1] S. Sicola, K. Albe, J. Power Sources 331, 382-390 (2016).

SYLI 6: Defects, structure and thermodynamics

Time: Wednesday 10:15–11:30

Location: IFW A

SYLI 6.1 Wed 10:15 IFW A

Structure, thermodynamics and Li storage of and in amorphous siliconoxycarbides: insights from first-principle calculations — •JOCHEN ROHRER and KARSTEN ALBE — FG Materialmodellierung, FB Material- und Geowissenschaften, Technische Universität Darmstadt

Precursor-derived amorphous siliconoxycarbides (SiOC) are attracting increased attention as potential anode material for Li-ion batteries. Capacities of 600 mAh/g and above have been achieved. Furthermore, SiOCs have been reported to be thermodynamically stable relative to the crystalline boundary phases cristobalite, SiC and graphite. On the microscale, SiOCs are well characterized and can be described by regions consisting of amorphous SiO₂, graphitic free carbon and mixed ternary regions. The details of the atomic structure within the ternary regions are, however, still under debate.

In this contribution we present strategies to model and determine local atomic characteristics of SiOC using density functional theory calculations. Using cluster models, we systematically investigate the bonding environment of carbon in ternary Si-O-C regions. Thereby we consider various coordinations and the possibility of hydrogen incorporation into the amorphous network [1]. Based on the predicted local C environment, we then design periodic supercell models with variable carbon content, compute thermodynamic stability and investigate Li storage in a way similar to our previous work on Si anodes [2].

[1] J. Rohrer et al., *submitted to Int. J. Mater. Res.* (Nov 2016).

[2] J. Rohrer and K. Albe, *J. Phys. Chem. C* **117**, 18796 (2013).

SYLI 6.2 Wed 10:30 IFW A

Oxygen Defects in LTO – Structural Models and Adapted DFT Treatments — •MARKUS SCHUDERER, KARSTEN REUTER, and CHRISTOPH SCHEURER — Technische Universität München, Germany

Li₄Ti₅O₁₂ (LTO) receives increasing interest as a zero-strain anode material for lithium ion batteries. One route pursued to improve its limited electronic conductivity is via the deliberate introduction of oxygen defects during synthesis. Little is presently known though, whether these defects enrich at the electrode-electrolyte interface and concomitantly contribute to structural or charge transfer limitations. Aiming to contribute to this context from the perspective of first-principles electronic structure calculations, we assess differing setups in terms of reliability and computational efficiency. This comprises a comparison of periodic supercell and solid-state embedded cluster approaches, as well as treatments on the semi-local or screened hybrid level of density-functional theory. While semi-local functionals delocalize the excess charge density associated with the defect and lead to metallic systems, the hybrid functional recovers the experimentally observed band gap and localizes the charge density on titanium ions directly coordinating the defect. We show that this localization can already be appropriately captured with small embedded clusters, rendering this approach numerically far more efficient in particular for studies of surface or interface defects.

SYLI 6.3 Wed 10:45 IFW A

Ion channelling contrast to reveal structure and growth behaviour of LiNi_{0.5}Mn_{1.5}O₄ battery materials — •MANUEL MUNDZINGER¹, TOBIAS WÄLDE¹, JÖRG BERNHARD¹, MICHAEL KINYANJUI¹, MARILENA MANCINI², PETER AXMANN², MARGRET WOHLFAHRT-MEHRENS², UTE GOLLA-SCHINDLER¹, and UTE KAISER¹

— ¹Ulm University, Central Facility for Electron Microscopy, Group of Electron Microscopy of Materials Science, Albert-Einstein-Allee 11, 89081 Ulm, Germany — ²Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), Helmholtzstrasse 8, 89081 Ulm

Ion channelling contrast [1] was utilized to characterize the crystallinity and crystalline architecture of LiNi_{0.5}Mn_{1.5}O₄ particles [2] for battery

cells. The LiNi_{0.5}Mn_{1.5}O₄ particles were cut by the focused ion beam (FIB) machine; then the FIB was used to produce channelling contrast revealing the polycrystallinity of the material, allowing to determine grain size distribution and architecture. For systematic investigations, differently sized particles (10-30 micrometre in diameter) were examined. We found that with increasing particle size the number and the average size of the grains increases. This allows to conclude that during growth new grains are formed as well as existing grains grow. SAED and HRTEM reveal that the structure is cubic. Ion channelling contrast and EBSD contrast were compared showing very similar results. This work was done in the LiEcoSafe project funded by the BMBF (03X4636C).

[1] C. A. Volkert et al, *MRS Bulletin*, 32:389-399, 5, 2007.

[2] P. Axmann et al, *Journal of Power Sources* 301 (2016) 151-159.

SYLI 6.4 Wed 11:00 IFW A

Modeling occupational disorder in Li₄Ti₅O₁₂ battery materials: Intrinsic complexity and its effect on ion mobility — •HENDRIK H. HEENEN, CHRISTOPH SCHEURER, and KARSTEN REUTER — Technische Universität München, Germany

Lithium-titanium-oxide (Li₄Ti₅O₁₂, LTO) is unique among battery materials due to its exceptional cyclability and high rate capability. This performance is assumed to derive at least partly from the occupational disorder introduced via mixed Li/Ti occupancy in the LTO spinel-like structure. Notwithstanding, the exact atomic-scale influence of this disorder on Li ion mobility remains an open question.

We explore the vast configuration space accessible during high-temperature LTO synthesis by Wang-Landau sampling. Use of a numerically efficient, density-functional theory validated interatomic potential [1] allows for extensive sampling in simulation cells large enough to appropriately capture the long-range disorder. The determined configurational ensemble is indeed characterized by a large degree of microscopic inhomogeneity. Subsequent room-temperature molecular dynamics simulations reveal the dominant fraction of Li ions in this ensemble to be immobile on nanosecond timescales. However, certain disorder motifs give rise to a novel correlated ion diffusion mechanism. We discuss this mechanism in the context of the evolution and morphology of the so-called two-phase reaction appearing during Li intercalation [2].

[1] M. Vijayakumar et al., *J. Power Sources* **196**, 2211 (2011)

[2] M. G. Verde et al., *ACS Nano* **10**, 4312 (2016)

SYLI 6.5 Wed 11:15 IFW A

Ab initio modeling of Li-rich transition metal oxyfluorides —

•HOLGER EUCHNER¹ and AXEL GROSS^{1,2} — ¹Helmholtz Institute for Electrochemical Energy Storage, Helmholtzstraße 11, 89081 Ulm — ²Institute of Theoretical Chemistry, Ulm University, Albert-Einstein-Allee 11, 89069 Ulm

Recently, Li-rich transition metal (TM) oxyfluorides, were identified as promising electrode materials in Li-ion batteries [1,2]. Due to the evidenced robustness of the underlying framework – a disordered rock salt structure (DRS), consisting of two disordered fcc sublattices, exhibiting TM/Li and O/F disorder, respectively – this class of materials is a potential candidate for future application in Li-ion technology.

To provide insight into underlying mechanisms and potential for improvement, we have conducted a computational study of a number of Li_xTM_{1-x}O_yF_{1-y} compounds. Using periodic density functional theory calculations, the impact of different TMs as well as different O/F concentrations on structural stability, (de-)lithiation behavior and Li diffusion is investigated. Apart from predicting open circuit voltage and energy density, we present an analysis of Li-diffusion pathways and corresponding barriers, which we relate to local environment and bonding characteristics of Li atoms.

[1] R. Chen et al., *Adv. Energy Mater.* **5**, 9 (2015).

[2] S. Ren et al., *Adv. Sci.* **2**, 10 (2015).

SYLI 7: Hybrid and structured electrolytes

Time: Wednesday 11:45–12:45

Location: IFW A

SYLI 7.1 Wed 11:45 IFW A

Morphology and conductivity of nanohybrid block copolymer electrolyte for lithium-ion batteries — ●EZZELDIN METWALLI, MAXIMILIAN KAEPPPEL, SIMON SCHAPER, and PETER MÜLLER-BUSCHBAUM — TU München, Physik-Department, LS Funktionelle Materialien, James-Frank-Str. 1, 85748 Garching

Polymer electrolyte membranes are promising alternatives to conventional liquid electrolytes in lithium-ion batteries [1]. A key challenge is to achieve a highly ionic conductive solid-state polymer membrane that maintains high-modulus, toughness, and chemical stability. The ionic conductivity in relation to the morphology of a ternary system composed of polystyrene-block-polyethylene oxide (PS-*b*-PEO) diblock copolymer (DBC) electrolyte, lithium salt and ionic liquid (IL) was investigated. An optimized functional morphology of the hybrid membrane was achieved by enabling highly interpenetrated hard PS and soft PEO/IL domains. The high-modulus glassy PS domain of the nanostructured hybrid membranes offers mechanical stability, while the Li-containing PEO/IL hybrid domain enables the requisite high ionic conductivity. The IL doping enhances the solubilization of the undissociated lithium salt at the PS/PEO domain interface. The pronounced conductivity enhancement of the current Li-ion/IL/DBC hybrid electrolyte compared to other previously reported DBC electrolyte systems is discussed. [1] E. Metwalli et al., ChemPhysChem 2015, 16, 2882.

SYLI 7.2 Wed 12:00 IFW A

Preparation of Electrodes for Li-Ion Batteries from Inexpensive Dirty Silicon — ●RICHARD SCHALINSKI¹, STEFAN L. SCHWEIZER¹, and RALF B. WEHRSPORN^{1,2} — ¹Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Halle 06099, Germany — ²Fraunhofer Institute for Mechanics of Materials IWM, Halle 06120, Germany

With the increased development of renewable energies and electric vehicles in our society, there is a greater demand for high capacity, safe and inexpensive storage technologies. Li-ion batteries are the technology of choice for the use in portable devices. To increase the capacity density of these batteries, nanostructured silicon was introduced as a material for the negative electrode. Commonly, either expensive silane or electrical grade silicon is used as the starting material. We introduce an alternative route by using inexpensive metallurgical grade silicon (purity 98%) as a starting material and purify it using metal assisted chemical etching followed by ball milling to obtain

silicon nanoparticles. The Si-nanoparticles were mixed with different binders (CMC, PVdF, Na-Alginate) to form slurries, which were coated onto Cu-substrates. The dried electrodes were investigated by SEM and introduced to further electrochemical testing in a half cell setup. A variation of the chemical contents and pretreatments of the substrates were carried out to optimize the capacity and cyclability of the electrodes.

SYLI 7.3 Wed 12:15 IFW A

Polymer patterning: Solid polymer electrolytes for lithium batteries — PRESTON SUTTON, ILJA GUNKEL, and ●ULLI STEINER — Adolphe Merkle Institute, Fribourg, Switzerland

Patterning materials at the nanoscale can dramatically influence the performance of batteries. At the Adolphe Merkle Institute (AMI) we are applying expertise in structural control to improve electrodes and electrolytes alike. Two goals of our research are: 1- Take advantage of polymer self-assembly as a facile method to attain predictable morphologies in block copolymers (BCPs) quantifying ionic conductivity as a function of grain size and crystallinity. 2- Use BCPs to decouple mechanical properties from ionic conductivity in electrolytes.

SYLI 7.4 Wed 12:30 IFW A

Modulation of the optical properties of LiMn₂O₄ via Li-ion transport — ●YUG JOSHI, SUSANN NOWAK, and GUIDO SCHMITZ — Institut für Materialwissenschaft, Universität Stuttgart

Extensive research has been carried out in the fields of Li-ion batteries and electrochromic materials. The present study combines both in investigating the changes in the optical properties of the lithium manganese oxide (LMO), a spinel structured cathode material during an electrochemical reaction. To study this behavior ion-beam sputtering is used to deposit LMO as the active layer onto a layer of platinum serving as a current collector, over an oxidized silicon wafer. The multilayered sample is then characterized using optical spectroscopy at different lithiation states. The measured data is fitted using Cauchy's model to extract the complex refractive index (refractive index and absorption coefficient) of LMO and its dependence on the lithium content. The reversibility of the optical changes is verified by in-situ optical measurements during multiple charging and discharging cycles of LMO. The study reveals a reversible change of the complex refractive index during an electrochemical reaction in the wavelength range of 850-1600nm, making it a suitable candidate for the application of optical switching.

SYLI 8: Structure - property relationships II

Time: Wednesday 15:45–16:45

Location: IFW D

SYLI 8.1 Wed 15:45 IFW D

Process monitoring of charging/discharging of lithium ion battery cathodes by operando SQUID magnetometry — ●ROLAND WÜRSCHUM¹, GREGOR KLINER¹, STEFAN TOPOLOVEC¹, HARALD KREN², STEFAN KOLLER², WALTER GOESSLER³, and HEINZ KRENN⁴ — ¹Inst. of Mater. Phys., Graz Univ. of Technology, Graz, Austria — ²VARTA Micro Innovation GmbH, Graz — ³Inst. of Chem., Univ. Graz — ⁴Inst. of Phys., Univ. Graz

The magnetic susceptibility χ of cathode materials, which contain transition metals, substantially changes during charging/discharging and, therefore, serves as a highly sensitive fingerprint for the charge state. A novel pathway in this direction has recently opened up by developing in-situ electrochemical techniques for magnetometry. Operando magnetic χ -measurements on Li_xCoO_2 [1] and $\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC) cathode materials [2] in a SQUID magnetometer during repetitive electrochemical cycling were performed enabling a continuous and bulk sensitive monitoring of the charge compensation process. Upon charging of NMC up to Li contents of $x = 1/3$ exclusively Ni undergoes oxidation, namely in two consecutive steps $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$ for $x > 2/3$ and $\text{Ni}^{3+} \rightarrow \text{Ni}^{4+}$ for $2/3 > x > 1/3$ [2]. Co oxidation for $x < 1/3$ is found to be irreversible [2]. In the case of Li_xCoO_2 , evidence is found for a nonmetal-metal transition of Anderson-type [1]. In addition to Co also O undergoes partial oxidation, as also observed for NMC.

[1] St. Topolevec et al., J. Sol. State Electrochem. 20 (2016) 1491.

[2] G. Klinser et al., Appl. Phys. Letters 109 (2016) 213901.

SYLI 8.2 Wed 16:00 IFW D

Enhancement of Sodium Ion Battery Performance Enabled by Oxygen Vacancies — ●YANG XU, MIN ZHOU, CHENGLIANG WANG, LIYING LIANG, FABIAN GROTE, YAN MI, and YONG LEI — Institute für Physics & IMN MacroNano (ZIK), Technische Universität Ilmenau, Ilmenau 98693, Germany

The utilization of oxygen vacancies (OVs) in sodium ion batteries (SIBs) is expected to enhance performance, yet it has rarely been reported. Taking the MoO_3 -x nanosheet anode as an example, for the first time we demonstrate the benefits of OVs on SIB performance. Moreover, the benefits at deep-discharge conditions can be further promoted by an ultrathin Al_2O_3 coating. Ex-situ electrochemical impedance and X-ray photoelectron spectroscopy measurements show that the OVs increase the electric conductivity and Na-ion diffusion coefficient, and the promotion from ultrathin coating lies in the effective reduction of cycling-induced solid-electrolyte interphase. The coated nanosheets exhibited high reversible capacity and great rate capability with the capacities of 283.9 mAh g⁻¹ at 50 mA g⁻¹ and 179.3 mAh g⁻¹ at 1 A g⁻¹ after 100 cycles. This work could not only arouse future attention on OVs for sodium energy storage, but also open up new

possibilities for designing strategies to utilize defects in other energy storage systems.

Reference

Y. Xu, M. Zhou, X. Wang, C. Wang, L. Liang, F. Grote, M. Wu, Y. Mi, Y. Lei, Angew. Chem. Int. Ed. 2015, 54, 8768.

SYLI 8.3 Wed 16:15 IFW D

Polycrystalline Na_xCoO_2 thin films on β -Alumina ceramics for solid state batteries — •PHILIPP KEHNE¹, CONRAD GUHL², RENÉ HAUSBRAND², and PHILIPP KOMISSINSKIY¹ — ¹Department of Materials Science, TU-Darmstadt, Advanced thin film technology — ²Department of Materials Science, TU-Darmstadt, Surface science

Good cycling performance was previously shown for rechargeable sodium ion batteries with layered-oxide cathode materials such as Na_xCoO_2 in combination with liquid electrolytes. However, studies of sodium-based solid state batteries are necessary to correlate the electronic structure of sodium-ion insertion materials with the battery performance. Here we report polycrystalline Na_xCoO_2 films grown on β -Alumina polycrystalline ceramic substrates with pulsed laser deposition. The sodium content in the films can be adjusted in the range of $x = 0.6$ * 1.1 by varying the post-deposition annealing conditions. The β -alumina substrates reveal ionic conductivities of 0.002 S/cm (25 °C) and can be used as electrolyte in solid-state sodium batteries. The fabricated Swagelok-type rechargeable batteries with Na_xCoO_2 thin-film cathodes, β -alumina electrolyte, and sodium anodes reveal an open circuit voltage of 2.75 V and a specific capacitance of $C = 80$ mAh/g. Investigations of the electronic structure of the materials and

interfaces in the fabricated batteries by in-situ XPS are in progress.

SYLI 8.4 Wed 16:30 IFW D

Large-scale highly ordered Sb nanorod arrays anode with high capacity and rate capability for sodium-ion batteries — •LIYING LIANG, YANG XU, CHENGLIANG WANG, LIAOYONG WEN, YAOGUO FANG, YAN MI, MIN ZHOU, HUAPING ZHAO, and YONG LEI — Institute for Physics and IMN MacroNano, Ilmenau University of Technology, Ilmenau 98693, Germany.

The poor electrochemical performance of Na-ion batteries is the major bottleneck for future development. Hence a performance-oriented electrode structure is proposed, which is 1D nanostructure arrays with large-scale high ordering, well vertical alignment, and large interval spacing. Benefiting from these structure merits, a great enhancement on electrochemical performance could be achieved. To Sb as an example, we firstly report large-scale highly ordered Sb nanorod arrays with uniform large interval spacing (190 nm). In return for this electrode design, high ion accessibility, fast electron transport, and strong electrode integrity are presented here. Used as additive-free anode for SIBs, Sb nanorod arrays showed a high capacity of 620 mAh g⁻¹ at the 100th cycle with a retention of 84% up to 250 cycles at 0.2 A g⁻¹, and superior rate capability for delivering reversible capacities of 579.7 and 557.7 mAh g⁻¹ at 10 and 20 A g⁻¹, respectively. A full cell coupled by P2-Na₂/3Ni/3Mn₂/3O₂ cathode and Sb nanorod arrays anode was also conducted, which showed a good cycle performance up to 250 cycles, high rate capability up to 20 A g⁻¹, and large energy density up to 130 Wh kg⁻¹.