

## CPP 56: Focus: Computational Methods for the Energy Transition: Paving the Road to Future Materials and Storage Systems - organized by Stephan Kramer and Jochen Zausch

Time: Thursday 15:00–18:00

Location: H14

### Invited Talk

CPP 56.1 Thu 15:00 H14

**Microstructure resolved simulations and theory based modeling: Tools for exploring the inner life of a battery** — ●ARNULF LATZ — DLR at Helmholtz Institute Ulm for Electrochemical Energy Storage, Germany

Theory, Modeling and Simulation are important tools for creating insights in electrochemical processes from the atomistic scale to the scale of electrochemical devices. They also form the base for a future knowledge based and theory driven development of better electrochemical storage systems. Spatially resolved simulations on electrode scale can help to create a more intuitive picture of transport processes and degradation phenomena in batteries. Despite the impressive increase of in situ and operando techniques, there are still local phenomena in batteries which cannot be explored experimentally. Simulations can supplement this lack of information, if it is ensured that they can capture the spatio-temporal phenomena caused by the highly nonlinearly coupled electrochemical, multi-physics processes in batteries. This can be achieved by using as much as possible rigorous theoretical methods to derive coupled transport- electrochemistry models from fundamental principles, which try to minimize purely phenomenological assumptions. In the presentation, the development of advanced theories for electrolytes is demonstrated for the examples of solid electrolytes and ionic liquids. The impact of morphological defects and grain boundaries in all solid state batteries as well as binder distributions on the capacity, impedance and degradation of batteries is discussed with the help of pore resolved simulations.

CPP 56.2 Thu 15:30 H14

**Optimizing the performance of batteries using digital material engineering** — ●LONA GLATT, FABIAN BIEBL, CHRISTIAN WAGNER, and ANDREAS WIEGMANN — Math2Market GmbH, Kaiserslautern, Germany

Key challenges to transform renewable energies into a reliable energy supply lie in optimizing its storage through increased performance of batteries. The battery performance is strongly influenced by the microstructure of the battery materials. Thus, engineering better batteries depends on understanding the impact of the micro-structure on material properties. Here, we use the simulation software GeoDict to show such an optimization on a cathode, containing a blend of the active materials Lithium Nickel Cobalt Aluminum Oxide (NCA) and Lithium Cobalt Oxide (LCO). The starting point for the optimization is a 3d-scan of the NCA-LCO cathode. Using the import module of GeoDict, the structure is segmented into three materials: electrolyte, binder and active material. The two active materials cannot be discerned based on gray values alone. In a next step, the GrainFind module is used to assign each grain to be NCA or LCO based on its shape. The result is a fully segmented cathode material containing electrolyte, binder, NCA, and LCO. Next, we use GeoDict to run a battery charging simulation and to compute other important material properties such as pore-sizes, diffusivity, conductivity, tortuosity, and mechanical properties for this cathode. Finally, we focus on finding the optimal amount of binder in the cathode by varying its amount and running geometrical analyses and a charging simulation on the resulting structure.

### Invited Talk

CPP 56.3 Thu 15:45 H14

**Increasing the rate capability of thick graphite electrodes: Insights from MRI, NMR and porous electrode theory modelling** — ●JAMIE FOSTER — University of Portsmouth, Portsmouth, UK

Utilization of thicker electrodes is one route towards improving the energy density of Li-ion batteries because it decreases the number of electrodes per cell, thereby increasing the ratio of active material to current collectors. However, the increased thickness means that it is difficult to achieve sufficiently fast transport of the lithium to supply the deep regions of the electrode with reactant. At even moderate (dis)charge rates, thick electrodes exhibit significant polarization and undesirable under-utilization of capacity.

We report experimentally determined lithium concentration profiles in a 300 micron thick graphite electrode under operation. The observed behavior clearly shows the phase transforms that are known to occur within graphite during (de)lithiation; there are sharp bound-

aries between graphite areas lithiated to different stages. Comparison with porous electrode theory modelling reveals that a portion of the Li is temporarily stored in the electrode surface film prior to intercalation. Although it is often difficult to fully lithiate the thick electrode, we demonstrate that the inclusion of a short current reversal, facilitates more complete lithiation. We also demonstrate the value of this high-fidelity experimental data to the modelling community, by showing how it can be used for high-confidence parameter estimation when combined with inverse modelling techniques.

CPP 56.4 Thu 16:15 H14

**Combining physical and network modeling for the simulation of lithium ion batteries** — ●DION WILDE and JOCHEN ZAUSCH — Fraunhofer-Institute for Applied Mathematics, Kaiserslautern, Germany

For battery development numerical simulation methods can help to optimize and understand cell properties or to investigate degradation behavior. In this context physical continuum models play an important role. The drawback of these models is that the numerical solutions of the partial differential equations require significant computational effort. In applications an electrical equivalent circuit model (ECM) is often sufficient to describe the effects of interest and can be solved more efficiently. However, the parameterization of such models typically require parameter fitting since the input parameters don't have direct physical meaning. In our approach we combine a physically correct electrochemical model and the computationally fast equivalent-circuit model to formulate a physics-based equivalent circuit model which is directly linked to electrochemical parameters. The ECM is derived from the Newman model containing an element modeling the Butler-Volmer equation as well as a state-of-charge dependent voltage source representing the OCV of the designed material and resistors for electron/ion diffusion in the solid/electrolyte. Also the extension to electrochemical impedance spectroscopy is straight-forward. The system is solved by the mesh current method in python. In this contribution we will present our physical and ECM models and present a comparison between the two approaches.

### 15 min. break

### Invited Talk

CPP 56.5 Thu 16:45 H14

**Numerical Simulation and Machine Learning in Virtual Materials Design** — ●JAN HAMAËKERS — Fraunhofer Institute for Algorithms and Scientific Computing SCAL, Sankt Augustin, Germany

An essential basis for designing novel materials is the understanding of their properties on the nanoscale and their effects on the macroscale. Besides theory, experiment and measurement, computational science established themselves as a new field in research and development over the last decades. In particular multiscale modeling and efficient numerical simulation techniques are powerful tools in the framework of materials design. The large amount of newly generated data from experiments and simulations together with new techniques of data analysis and machine learning have recently opened the new promising field of data-driven research. In this talk we will give an overview on selected topics in computational and data-driven science and on our recent research results and software tools.

CPP 56.6 Thu 17:15 H14

**Simulating Curved Graphene Supercapacitors** — ●JANNES SEEBECK<sup>1</sup> and ROBERT MEISSNER<sup>1,2</sup> — <sup>1</sup>Hamburg University of Technology, Institute of Polymer and Composites, Hamburg, Germany — <sup>2</sup>MagIC Magnesium Innovation Centre, Institute of Materials Research, Helmholtz Zentrum Geesthacht, Geesthacht, Germany

Supercapacitors are promising storage devices for electrical energy that offers a high power density but typically low energy density. Their storage performance is due to a reversible ion adsorption by forming an electric double layer on the electrode surface. Molecular dynamics (MD) simulations offer the possibility to gain insights into the molecular mechanisms of forming electric double layers and pore filling. However, simulations show that in supercapacitors with an ionic liquid as electrolyte, the mean-field approach for calculating the differential capacitance leads to false results due to the strong correlation of ions.

By using a free energy approach for the calculation of the differential capacity from the fluctuating charge density on the electrode surfaces it is possible to show a non-linear behaviour of the ionic liquid on the capacitance. Furthermore, MD-Simulations show a different orientation of the ionic liquid to the electrode interface depending on the applied potential, which can be a reason for the fluctuation of the capacity. By simulating curved graphitic electrodes, with a convex and concave pore-like structure, in combination with a diluted ionic liquid as electrolyte it is possible to examine the impact of curvature on the orientation of the ionic liquid, and finally the resulting capacity.

CPP 56.7 Thu 17:30 H14

**Computational Analysis of Composition-Structure-Property-Relationships in NZP-type Materials for Li-Ion Batteries** — •DANIEL MUTTER<sup>1,2</sup>, DANIEL F. URBAN<sup>1</sup>, and CHRISTIAN ELSÄSSER<sup>1,2</sup> — <sup>1</sup>Fraunhofer IWM, Wöhlerstraße 11, 79108 Freiburg — <sup>2</sup>Freiburger Materialforschungszentrum FMF, Stefan-Meier-Str. 21, 79104 Freiburg

Compounds crystallizing in the structure of  $\text{NaZr}_2(\text{PO}_4)_3$  (NZP) are considered as promising materials for solid state electrolytes in Li-ion batteries. Using density functional theory (DFT), a systematic computational screening of 18 NZP compounds, namely  $\text{LiX}_2(\text{LO}_4)_3$  with  $X = \text{Ti, V, Fe, Zr, Nb, Ru, Hf, Ta, Os}$ , and  $L = \text{P, Mn}$  is performed with respect to their activation energies for vacancy-mediated Li migration. It is shown how the different ionic radii of the cationic substitutions influence structural characteristics such as the octahedron volumes around Li ions on the initial and transition state sites, which affect the activation energies ("composition-structure-property"-relationships). The prevalent assumption that structural bottlenecks formed by triangularly arranged oxygen atoms at a certain location along the migration path determine the energy barriers for Li migra-

tion is not supported by the DFT results. Instead, the ionic neighborhood of the migrating ion in the initial and in the transition state need to be taken into consideration to relate the structure to the activation energies. This conclusion applies to Na containing NZP compounds as well.

CPP 56.8 Thu 17:45 H14

**The origin of unstable sodium graphite intercalation compounds** — OLENA LENCHUK and •DOREEN MOLLENHAUER — Institute of Physical Chemistry, Justus-Liebig University Giessen, Heinrich-Buff-Ring 17, D-35392 Giessen, Germany

First principles investigations can contribute to the understanding of intercalation mechanisms and compounds chemistry important for supporting the development of battery materials such as sodium-ion batteries (SIBs). [1] The commonly used negative electrode graphite for lithium-ion batteries does not intercalate sodium ions in high concentrations [2,3] whereas intercalation of potassium is possible. In order to understand the origin of Na-GICs (binary graphite intercalation compounds) instability compared to stable Li- and K-GIC we performed dispersion corrected density-functional theory (DFT) calculations. We analyzed and compared in detail the interplay between the structural deformation and binding contributions of the different alkali metal-GIC. This allows us to identify main factors for the instability of Na-GICs [4].

[1] M. Goktas, C. Bolli, E. J. Berg, P. Novak, K. Pollok, F. Langenhorst, M. v. Roeder, O. Lenchuk, D. Mollenhauer, P. Adelhelm, *Adv. Energy Mater.* 2018, 1702724. [2] K. Nobuhara, H. Nakayama, M. Nose, Sh. Nakanishi and H. Iba, *J. Power Sources* 243 (2013) 585-587. [3] Zh. Wang, S.M. Selbach and T. Grande, *RSC Adv.* 4 (2014) 4069-4079. [4] O. Lenchuk, P. Adelhelm, D. Mollenhauer, Manuscript to be submitted.