CPP 55: Materials for Energy Storage and Conversion - Battery and Fuel Cell Materials (joint session MM/CPP)

Time: Tuesday 14:15–15:45   Location: IFW D

CPP 55.1   Tue 14:15   IFW D

Atomistic simulation of working interfaces: Towards understanding the role of complex multiphase grain boundaries in all-solid-state Li-ion batteries — •Sina Stegmaier[1], Roland Schierholz[2], Christoph Scheurer[1], and Karsten Reuter[1] — [1]Theoretische Chemie, TU München — [2]IEK-9, Forschungszentrum Jülich

All-solid-state batteries (ASSBs) present a next-generation technology, promising increased operation safety and lifetime as compared to state-of-the-art Li-ion cells. The performance of solid-state electrolytes (SSEs) in ASSBs, though, is severely limited by poorly understood interfacial processes. Atomistic insight into the structure and transport processes at working SSE grain boundaries (GBs) [1] is required to enable rational progress.

To this end, we employ molecular dynamics (MD) simulations with a first-principles parametrized force field and study complex multiphase GBs in the SSE material LATP. An experimentally guided sinter protocol is established to model the formation of semi-amorphous domains at the interface of crystalline LATP grains. The resulting structural atomistic models enable the investigation of anisotropic lateral and transverse ion transport and the comparison to macroscopically accessible observables such as ion conductivity. Following this approach, we leverage experimental input for computational modeling and studying of more realistic solid-solid working interfaces.

[1] A. Mertens et al., Solid State Ionics 309, 180 (2017).

CPP 55.2   Tue 14:30   IFW D

Polaron Hopping Mechanism as a source for electronic conductivity in $Li_4Ti_5O_{12}$ (LTO) Batteries — •Matthias Kick[1], Cristina Grosu[1,2], Markus Schuderer[1], Christoph Scheurer[1], and Harald Oberhofer[1] — [1]Technische Universität München — [2]Forschungszentrum Jülich

State of the art lithium ion batteries rely on graphite as anode material due its remarkable lithium-intercalation properties. However due to the low intercalation potential of graphite, Li dendrite growth can occur during rapid charge processes, rendering a potential risk of having short-circuits in a battery cell. In addition, the large volume change during (dis)charging the battery results in unfavorable strain damaging the anode. Lithium titanium oxide $Li_4Ti_5O_{12}$ (LTO) shows the potential of being an excellent alternative to graphite anodes, as its volume stays stable during charge cycles and its high intercalation potential prevents Li dendrites to form. Unfortunately, the low conductivity of LTO still limits its use. To improve on this drawback, an elegant way is to introduce oxygen vacancies resulting in formation of Ti^{3+} centers. As a result, this blue colored LTO shows a lowering in its electronic resistance with improved electronic conductivity. By performing *Hubbard corrected density functional theory* (DFT+U) calculations we are able to show that in fact polaron formation and a possible polaron hopping mechanism can play a significant role in the experimental observed improved conductivities. Morevover we are able to gauge polaronic charge mobility by explicitly calculating polaron hopping barriers.

CPP 55.3   Tue 14:45   IFW D

Exploring defect structures in $Li_4Ti_5O_{12}$ (LTO): A combined theoretical and experimental approach — •Yute Chan[1], Cristina Grosu[1,2], Karsten Reuter[1], and Christoph Scheurer[1] — [1]TU München — [2]IEK-9, FZ Jülich

Spinel $Li_4Ti_5O_{12}$ (LTO) is a fascinating anode material for next-generation all-solid-state Li-ion batteries (ASSB). Its "zero strain" charge/discharge behavior promises high safety and long cycling lifetimes. Nonetheless, pristine, white LTO possesses poor ionic and electronic conductivity. The latter can be increased by tailoring the sintering protocol to produce oxygen vacancies, resulting in a performant, blue LTO material. Heretofore, the detailed structure and distribution of the vacancies are unknown. Thus, powerful analytic techniques are needed to identify the defect structure inside the material. Positron lifetime spectroscopy (PALS) stands out from other experimental methods by the ability to sensitively collect positron lifetimes that correlate to different material defects. Data measured at the Garching positron source indicates that the positron lifetimes for LTO

bulk and surface are distinguishable. To invert these lifetimes and gain information for the respective regions, we construct a series of LTO bulk and slab models and calculate theoretical lifetimes using two different self-consistent schemes within the framework of two-component density functional theory. We will discuss the relationship between experimental and theoretical lifetimes of LTO bulk and surface.

CPP 55.4   Tue 15:00   IFW D

A Neural Network Potential for Lithium Manganese Oxides — •Marco Eckhoff[1], Peter E. Blöchl[2], and Jörg Behler[1] — [1]Universität Göttingen, Institut für Physikalische Chemie, Theoretische Chemie, Tammannstraße 6, 37077 Göttingen, Germany — [2]Technische Universität Clausthal, Institut für Theoretische Physik, Leibnizstraße 10, 38678 Clausthal-Zellerfeld, Germany

The lithium manganese oxide spinel $Li_xMn_2O_4$, with $0 < x < 2$, is an important cathode material in lithium ion batteries. The recently introduced local hybrid density functional PBE0r yields an accurate description of this material in good agreement with experiment. However, the accessible system size of molecular dynamics and Monte Carlo simulations is very limited when using density functional theory directly. Building on PBE0r data, we thus constructed a high-dimensional neural network potential, which provides a first-principles quality description of the potential energy surface at a fraction of the computational costs. This potential enables large-scale simulations of $Li_xMn_2O_4$ to study phase transitions and lithium diffusion.

CPP 55.5   Tue 15:15   IFW D

One parabola to fit them all: A response surface approach to computational catalyst screening — •Frederic Felsen, Christoph Scheurer, and Karsten Reuter — TUM, Munich, Germany

In the pursuit of sustainable power-to-fuel (P2X) technologies methanol fuel from renewable resources is one promising route towards reducing global carbon dioxide emissions. One of the many obstacles to overcome on the way to this ambitious goal is the efficient conversion of CO_2 rich syngas to methanol. Intricate interface structures are characteristic for all commonly employed catalyst materials for this process, like the state of the art $CuZnOAl_2O_3$ [1]. Understanding these surface effects is key for a rational improvement and design of future catalysts.

We present an approach to efficiently characterize solid-solid interface structures by a well defined set of single point DFT calculations. Exploiting ideas from response surface methodology [2], we actively distort interface structures to evaluate the response of the system on geometric changes. Resulting observables such as adsorption energies of reaction intermediates may directly provide insight into the catalytic activity of the respective interfaces. Furthermore, this novel interface characterization may enable computational screening for multi component catalyst materials. As a first test case metal thin films supported on transition metal oxides will be studied.

[1] M. Behrens et al., *Science*, 336, (2012).
[2] R. H. Myers et al., Response Surface Methodology, *Wiley*, (2009).

CPP 55.6   Tue 15:30   IFW D

Analysis of $Li_xMn_2O_4$ for catalysis of the oxygen-evolution-reaction (OER) using STEM-EELS — •Florian Schönewald[1], Max Baumung[1], Marcel Risch[1,2], and Cynthia Volkert[1] — [1]Institut für Materialphysik, Universität Göttingen — [2]Helmholtz-Zentrum Berlin für Materialien und Energie

Controlling the OER is an important step for achieving a sustainable renewable energy future. The process of generating molecular oxygen from water by chemical means is severely kinetically limited. Here $Li_xMn_2O_4$ is studied as a model electrocatalyst. To understand the role of manganese valence and covalency for the OER these are manipulated by electrochemical de-/lithiation. Characterisation of the particles is performed before and after OER, for different lithiation states. Specific attention is given to Mn at the surface since it is directly involved in electron transfer.

With EELS of the O K- and Mn L-edge a surface layer with strongly reduced Mn has been discovered and attributed to changes in Mn/O ratio. This state is also preserved under delithiation. In previous stud-

ies, this effect has been explained by tetragonal Mn_3O_4 forming at the surfaces [1]. However, no second phase matching Mn_3O_4 or related structures was identified by X-ray powder diffraction. According to the estimated surface volume share of about $10\,\%$, Mn_3O_4 formation can be excluded. Instead, a combination of oxygen vacancies and additional manganese on tetrahedral sites as antisite defects is taken into account to explain the apparent Mn valence change at surfaces.

[1] Daichun Tang et al, Chem. Mater. 2014, 26, 11, 3535-3543