

## 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 SiO<sub>2</sub>, 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

Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (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<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> battery materials** — •MANUEL MUNDZINGER<sup>1</sup>, TOBIAS WÄLDE<sup>1</sup>, JÖRG BERNHARD<sup>1</sup>, MICHAEL KINYANJUI<sup>1</sup>, MARILENA MANCINI<sup>2</sup>, PETER AXMANN<sup>2</sup>, MARGRET WOHLFAHRT-MEHRENS<sup>2</sup>, UTE GOLLA-SCHINDLER<sup>1</sup>, and UTE KAISER<sup>1</sup>

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Ion channelling contrast [1] was utilized to characterize the crystallinity and crystalline architecture of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> particles [2] for battery

cells. The LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> 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 Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> 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 (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, 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** —

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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<sub>x</sub>TM<sub>1-x</sub>O<sub>y</sub>F<sub>1-y</sub> 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).