

## MM 8: Materials for Storage and Conversion of Energy

Time: Monday 15:45–18:30

Location: H46

MM 8.1 Mon 15:45 H46

**Atomistic analysis of Li migration in  $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  (LATP) solid electrolytes** — ●DANIEL PFALZGRAF<sup>1,2</sup>, DANIEL MUTTER<sup>2</sup>, DANIEL URBAN<sup>1,2</sup>, and CHRISTIAN ELSÄSSER<sup>1,2</sup> — <sup>1</sup>Freiburg Materials Research Center (FMF), University of Freiburg, Stefan-Meier-Straße 21, 79104 Freiburg, Germany — <sup>2</sup>Fraunhofer IWM, Wöhlerstraße 11, 79108 Freiburg, Germany

We present an examination of the ionic migration of Li in LATP [ $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ] solid electrolytes from an atomistic viewpoint based on density functional theory calculations [1]. In our study, we vary the Al content and investigate its effects on the crystal structure of LATP and on the migration energy landscape of interstitial Li ions. The energy profiles governing the Li diffusion are found to be systematically influenced by the position of Al ions in direct vicinity of the migration path, and we derive a simplified classification scheme of three universal energy profile shapes. The overall influence of the Al/Ti-ratio on the Li migration is analyzed by a separation into chemical and geometrical aspects. This work provides a solid basis for a resource-efficient computational examination of the ionic conductivity of Li in LATP with varying Al/Ti concentrations.

[1] D. Pfalzgraf, D. Mutter, and D.F. Urban, *Solid State Ionics* 359, 115521 (2021)

MM 8.2 Mon 16:00 H46

**Diffraction tomography studies of lithium distribution in 18650-type Li-ion cells** — ●ANATOLIY SENYSHYN<sup>1</sup>, VLADISLAV KOCHETOV<sup>2</sup>, DOMINIK PETZ<sup>3</sup>, and MARTIN MÜHLBAUER<sup>4</sup> — <sup>1</sup>Forschungszentrum Heinz Maier-Leibnitz, Technische Universität München, Garching, Germany — <sup>2</sup>Institut für Physik, Universität Rostock, Rostock, Germany — <sup>3</sup>Physik Department, Technische Universität München, Garching, Germany — <sup>4</sup>Institute for Applied Materials, Karlsruhe Institute of Technology, Karlsruhe, Germany

At the moment Li-ion batteries are dominating in the segment of energy storage for portable electronics and electric drivetrains. Despite its overall popularity and widespread, the Li-ion technology has a high improvement potential, especially in the aspects concerning power and energy density, power fading, safety etc. Besides the variety of different factors, the chemical, mechanical and morphological uniformity of the cell components is one of the aspects crucial for optimization, estimation and prediction of cell parameters and cell behavior during standard operation and misuse. In the current contribution a series of diffraction-based methods (spatially resolved diffraction using radial oscillating collimators and/or conical slits as well as X-ray and neutron diffraction tomography) applied to probe inner structure of samples (either on example of dedicated phantom sample or cylindrical-type Li-ion battery) will be briefly introduced and reviewed.

MM 8.3 Mon 16:15 H46

**Li diffusion in perovskite materials for battery applications** — ●WEI WEI<sup>1</sup>, JULIAN GEBHARDT<sup>1,2</sup>, DANIEL URBAN<sup>2,3</sup>, and CHRISTIAN ELSÄSSER<sup>1,2,3</sup> — <sup>1</sup>Cluster of Excellence livMatS, University of Freiburg, Germany — <sup>2</sup>Fraunhofer Institute for Mechanics of Materials IWM, Freiburg, Germany — <sup>3</sup>Freiburg Materials Research Center (FMF), University of Freiburg, Germany

Metal halide perovskites are promising photovoltaic (PV) absorber materials, with the highest power conversion efficiency values currently exceeding 22%. Furthermore, unlike most of the traditional PV materials, hybrid perovskites have a strong ionic character. Therefore, these materials have recently been reported to have good ionic conductivity and lithium storage potential,<sup>[1]</sup> allowing in principle the combination of a solar cell and a Li-ion battery in a single device. Here, we investigate this possibility by a Li-CsPbI<sub>3</sub> model system. By means of density-functional-theory calculations, we consider two scenarios: 1) Li in the rigid cubic perovskite structure, and 2) Li in the perovskite structure with flexible tilted bonds, which is the more realistic scenario at room temperature. The results of our simulations show that in the less symmetric structure the interstitial Li sites become nondegenerate and Li ions migrate along more complicated paths and have to overcome higher barriers than in the cubic structure. Nevertheless, diffusing Li ions have to overcome only moderate energy barriers of 0.16-0.33 eV, corroborating the potential use of metal-halide perovskites as Li-ion conducting PV materials.

[1] Zhen Li et al. *Energy Environ. Sci.*10 (2017) 1234

MM 8.4 Mon 16:30 H46

**Analytical TEM studies of LiCoO<sub>2</sub> thin film electrode for Li-ion batteries** — ●ARDAVAN MAKVANDI<sup>1</sup>, SANDRA LOBE<sup>2</sup>, MICHAEL WOLFF<sup>2</sup>, MARTIN PETERLECHNER<sup>1</sup>, CHRISTOPH GAMMER<sup>3</sup>, SVEN UHLENBRUCK<sup>2</sup>, and GERHARD WILDE<sup>1</sup> — <sup>1</sup>Institute of Materials Physics, University of Münster, Münster, Germany — <sup>2</sup>Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), Forschungszentrum Jülich GmbH, Jülich, Germany — <sup>3</sup>Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

LiCoO<sub>2</sub> is the mostly used cathode material in commercial Li-ion batteries. However, only half of its theoretical capacity can be used due to the structural and chemical instability of its surface at charge voltages higher than 4.2 V. In general, interfaces (e.g. active material/coating, electrode surface/electrolyte) determine the local Li-ion transport kinetics and finally the electrochemical performance. Therefore, it is necessary to study the structure and chemistry of electrodes and electrode/electrolyte interfaces. In this work, the structure and chemistry of the bulk and surface regions of LiCoO<sub>2</sub> thin film before and after cycling are studied using transmission electron microscopy (TEM). In this case, the effect of an Al-doped ZnO-coating layer on the stability of the electrode surface upon cycling at high charge voltage has been studied.

MM 8.5 Mon 16:45 H46

**Investigation of volume changes in the colquiriite structure due to Li insertion from first principles** — ●ALJOSCHA BAUMANN<sup>1,2</sup>, DANIEL MUTTER<sup>2</sup>, DANIEL URBAN<sup>1,2</sup>, and CHRISTIAN ELSÄSSER<sup>1,2</sup> — <sup>1</sup>Freiburger Materialforschungszentrum, Stefan-Meier-Straße 21, 79104 Freiburg — <sup>2</sup>Fraunhofer IWM, Wöhlerstraße 11, 79108 Freiburg

The long-term stability of lithium-ion batteries (LIB) is often negatively affected by mechanical stresses in the cathode material during charge/discharge cycles. Materials that show a zero-strain (ZS) behavior, i.e. their volume changes hardly during insertion or extraction of Li ions, are therefore of great interest. For individual compounds of the material class of colquiriites,  $\text{LiA}^{\text{II}}\text{M}^{\text{III}}\text{F}_6$ , ZS behavior has already been predicted theoretically and observed experimentally, e.g. for  $\text{Li}_{1+x}\text{CaFeF}_6$ , which exhibited a volume change of less than 0.5 % upon insertion of lithium ions up to  $x=0.8$ .

In order to identify the mechanism responsible for the ZS behavior we calculated the variation of the equilibrium volume due to varying Li concentration using density-functional theory (DFT). The analysis of the electronic and magnetic structure and local structure parameters at equilibrium volumes indicates that the total volume is influenced by a combination of expanding fluorine octahedra around the transition-metal ions due to the changing oxidation state, the distortion of octahedra around the Ca ions, and a decrease of repulsion between fluorine anions due to the inserted Li ions.

15 min. break

MM 8.6 Mon 17:15 H46

**Cu<sup>2+</sup> Intercalated Vanadium Pentoxide Grown on Carbon Cloth as Binder-Free Cathodes for Reversible Aqueous Zinc Ion Batteries** — ●PING HONG<sup>1,2</sup>, YUDE WANG<sup>2</sup>, HUAPING ZHAO<sup>1</sup>, and YONG LEI<sup>1</sup> — <sup>1</sup>Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany — <sup>2</sup>School of Materials Science and Engineering, Yunnan University, Kunming, People's Republic of China

Aqueous zinc batteries (ZIBs) with low cost, safety, environmentally friendly, and high theoretical capacity are a promising electrochemical energy storage technology. Vanadium based materials have been widely studied as cathode materials for ZIBs because of their safety, diverse crystal structure, abundant resources, low cost and high theoretical capacity. In the reported cathode materials, the mass loading of the cathode is usually less than 4 mg/cm<sup>2</sup> is not sufficient enough for practical applications. Herein, Cu<sup>2+</sup> intercalated vanadium pentoxide (CVOH@CC) with high loading (~7 mg/cm<sup>2</sup>) were directly grown on carbon cloth via hydrothermal method. The as-prepared CVOH@CC

has a distinct 3D interconnected nested structure. When applying as binder-free cathode for ZIBs, CVOH@CC electrodes exhibited a high capacity of 223.4 mAh/g at 1.0 A/g and a long cycling performance of over 2000 cycles. The intercalation resulted in a better capacitive response and faster diffusion rate for the cathode compared to pure vanadium pentoxide (VOH@CC), which means better rate performance and cycling stability, providing a viable design proposal for the production of industrial grade ZIBs.

MM 8.7 Mon 17:30 H46

**Reversible hybrid Na-CO<sub>2</sub> batteries with low charging voltage and long-life** — ●CHANGFAN XU — Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany — School of Metallurgy and Environment, Central South University, Changsha 410083, China — Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China

A reversible and long-life hybrid Na-CO<sub>2</sub> battery was proposed by using Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub> solid electrolyte as a separator, the saturated NaCl solution as an aqueous electrolyte, and nitrogen-rich graphitic carbon framework with well-defined morphology and dense bimetallic Fe-Cu sites (Fe-Cu-N-C) as cathodic catalyst. Besides having high Na<sup>+</sup> ion conductivity, Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub> solid electrolyte also can prevent potential contamination from H<sub>2</sub>O and CO<sub>2</sub> to sodium anode and avoid the internal short-circuit touch of Na dendrite with the cathode, thus improving the battery safety. The aqueous electrolyte can facilitate the dissolution of insulated discharge products, which overwhelmingly improves the reaction kinetics. The Fe-Cu-N-C cathodic catalyst can facilitate the fast evolution and degradation of flocculent discharge products. Finally, the hybrid Na-CO<sub>2</sub> battery exhibited an excellent long-term cyclability with up to 1550 cycles (over 600 h). The reaction mechanism of Na-CO<sub>2</sub> battery was revealed by in-situ Raman, SEM and XRD analyses.

MM 8.8 Mon 17:45 H46

**Revisiting the storage capacity limit of graphite battery anodes: spontaneous lithium overintercalation at ambient pressure** — CRISTINA GROSU<sup>1,2</sup>, ●CHIARA PANOSETTI<sup>1</sup>, STEFFEN MERZ<sup>2</sup>, PETER JAKES<sup>2</sup>, SEBASTIAN MATERA<sup>1</sup>, RÜDIGER-A. EICHEL<sup>2</sup>, JOSEF GRANWEHR<sup>2</sup>, and CHRISTOPH SCHEURER<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut, Berlin, Germany — <sup>2</sup>IEK-9, Forschungszentrum Jülich, Germany

The market quest for fast-charging, safe, long-lasting, and performant batteries drives the exploration of new energy storage materials, but also promotes fundamental investigations of those already widely used. Presently, revamped interest in anode materials is observed – primarily graphite electrodes for Li-ion batteries. We focus on the upper intercalation limit in the morphologically quasi-ideal highly oriented pyrolytic graphite (HOPG), with a LiC<sub>6</sub> stoichiometry corresponding to 100% state of charge (SOC). We prepared a sample by immersion in liquid lithium at ambient pressure. Investigation by static <sup>7</sup>Li nuclear magnetic resonance (NMR) resolves unexpected signatures of superdense intercalation compounds, LiC<sub>6-x</sub>. These were ruled out for decades, since the highest geometrically accessible composition, LiC<sub>2</sub>, can only be prepared under high pressure. We thus challenge the widespread notion that any additional intercalation beyond LiC<sub>6</sub> is not possible under ambient conditions. We monitored the sample upon calendaric

aging and employed *ab initio* calculations to rationalise the NMR results. The computed relative stabilities of different superdense configurations reveal that non-negligible overintercalation does proceed spontaneously beyond the currently accepted capacity limit.

MM 8.9 Mon 18:00 H46

**The dielectric behaviour of Lithium intercalated graphite anodes as a function of the state of charge** — ●SIMON ANNIÉS<sup>1,2</sup>, CHIARA PANOSETTI<sup>2</sup>, MARIA VORONENKO<sup>1</sup>, and CHRISTOPH SCHEURER<sup>2</sup> — <sup>1</sup>Theoretical Chemistry, Technical University Munich, Germany — <sup>2</sup>Fritz Haber Institut, Berlin, Germany

The dielectric behaviour of battery materials is a crucial piece of information for understanding atomistic mechanics and modelling diffusion- and charging processes. However, for the most common anode material in today's Lithium ion batteries (Lithium intercalated graphite), literature results regarding this property are sparse, conflicting and only available for the empty state of charge (SOC).

Utilizing our recently developed DFTB parametrization (based on a machine-learned repulsive potential), we are - for the first time - able to compute the dielectric behaviour of Lithium intercalated graphite for the entire range of charge from 0% to 100%. Our results agree with experiments for 'empty' graphite, as well as for (bilayer-) graphene, which we use for an additional benchmark of our approach.

With increasing state of charge, we find a linear dependency of the dielectric constant, growing from around 7 at 0% SOC to around 29 at 100% SOC. With this, we lay an important piece of foundation for the understanding and multi-scale modelling of entire charging and discharging processes of Li-ion batteries.

MM 8.10 Mon 18:15 H46

**In-situ analysis of SEI formation and cycle behavior on Sn by combined QCM-CV** — ●KE WANG and GUIDO SCHMITZ — Chair of Materials Physics, Institute for Materials Science, University of Stuttgart, Heisenbergstr. 3, 70569 Stuttgart, Germany

Sn (Tin) could in principle be a promising candidate for a lithium-ion battery anode since it offers larger capacity than commercially graphite. But, researchers are still confused about the capacity fade especially caused by the formation of solid electrolyte interface (SEI). Here, we perform an in-situ characterization to clarify the mechanisms of SEI formation. Cyclic voltammetry has been conducted in combination with a quartz crystal microbalance to measure the growth of the SEI. Beside the overall mass increase, evaluating the mass change per charge (MPE) even enables identification of the ab/desorbed species. In advanced analysis, we combine three different characteristics including mass spectra, real-time MPE and average MPE, for the different stages of the long-term SEI formation. Except the SEI layer formed in first cycle, the SEI is continuously affected by the formation of Li<sub>2</sub>O during lithiation and the oxidation of Sn during de-lithiation. In addition, the influence of the voltage window and the thickness of the electrodes on SEI formation are investigated. Remarkably, the SEI thickness reveals a linear relation to the electrode thickness which is linked to continuous cracking and major oxidization of Sn bulk. Particularly, the inorganic part of the SEI formed during lithiation in the specific voltage range of 0.36 - 0.27 V plays an important role on the microstructure of electrode and stabilizing the electrode.