

## CPP 42: Battery Materials (joint session KFM/CPP)

Chair: Prof. Dr. Anna Grünebohm (Ruhr-University Bochum)

Time: Thursday 9:00–12:35

Location: POT 51

CPP 42.1 Thu 9:00 POT 51

**Materialanalyse von NMC111 Kathodenmaterial aus recycelten Lithium-Ionen-Batterien mittels XRD, AFM und EDX/REM** — ●CLAUDIA SCHÖBERL, HANNO KÄSS und STEPHAN APPEL — Hochschule Esslingen, Kanalstraße 33, 73728 Esslingen, Deutschland

In einem industriellen Recyclingverfahren für Lithium-Ionen-Batterien wird Kathodenmaterial von der Trägerfolie mit Wasser abgestrahlt und getrocknet. In einem an der Hochschule Esslingen laufenden Forschungsprojekt wird die so gewonnene Schwarzmasse, die hauptsächlich aus NMC111 besteht, mittels Röntgendiffraktometrie (XRD), Rasterelektronenmikroskopie (REM) und elementanalytischen Methoden untersucht, um Hinweise auf die chemische Zusammensetzung und auf strukturelle Veränderungen zu erhalten. Ziel ist es unter anderem, passende Auswahlkriterien für die Qualität des Recyclingmaterials zu definieren, das nach Verarbeitung erneut in Lithium-Ionen-Batterien eingesetzt werden soll. Dazu zählen, neben dem Rest-Bindemittelgehalt, der Kohlenstoffanteil sowie der Anteil an Fremdelementen wie Kupfer und Aluminium. Das wiedergewonnene, recycelte Aktivmaterial wird bei einem Projektpartner zur Herstellung neuer Kathodenfolien verwendet, die in einer Messzelle elektrisch charakterisiert werden. Mittels Rasterkraftmikroskopie (AFM) werden diese neu präparierten Kathodenfolien an der Hochschule Esslingen untersucht. Mit Hilfe eines speziellen Messmodus, der quantitativen nanoskaligen mechanischen Charakterisierung, wird insbesondere die Korrelation von Strukturmerkmalen und mechanischen Eigenschaften überprüft.

CPP 42.2 Thu 9:20 POT 51

**Structural response in NCA-type battery cathodes** — ●TOBIAS HÖLDERLE<sup>1,2</sup>, PETER MÜLLER-BUSCHBAUM<sup>1,2</sup>, and ANATOLIY SENYSHYN<sup>2</sup> — <sup>1</sup>TUM School of Natural Sciences, Chair for Functional Materials, Garching, Germany — <sup>2</sup>MLZ, TUM, Garching, Germany

Battery-powered electric drivetrains in electric vehicles (EVs) are heavily limited and constrained to the performance of the energy storage device, i.e. battery. Batteries with higher power/energy densities, capacities, and cycling life are needed to increase EVs' performance and reduce greenhouse gas emissions. Mixed high nickel content  $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA) cathode material is one of a few today that simultaneously possess high energy and power densities at lower costs. However, NCA materials suffer from poor thermal stability and limited power density. They display capacity fading/efficiency loss due to antisite defects (cation mixing) in their structure, actively discussed in literature. In order to address the issue of cation mixing, a systematic ex-situ neutron powder diffraction study was done for a series of electrochemically delithiated NCA cathodes. The collected set of structural data was modeled using full-profile Rietveld method and results were discussed in line with observed electrochemical behavior. It is observed that lithium occupancies showed a decreasing character upon charging, independent from transition metal occupancies and indicating an absence of antisite defects (cation mixing) in the commercial NCA material during cell operation.

CPP 42.3 Thu 9:40 POT 51

**Dynamic structure evolution of extensively de-lithiated high voltage spinel LNMO** — NICOLA JOBST<sup>1</sup>, ●NEELIMA PAUL<sup>2</sup>, PREMYSL BERAN<sup>3,4</sup>, MARILENA MANCINI<sup>1</sup>, RALPH GILLES<sup>2</sup>, MARGRET WOHLFAHRT-MEHRENS<sup>1</sup>, and PETER AXMANN<sup>1</sup> — <sup>1</sup>Accumulators Materials Research (ECM), ZSW Centre for Solar Energy and Hydrogen Research Baden-Württemberg, DE-89081 Ulm, Germany — <sup>2</sup>Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, DE-85747 Garching, Germany — <sup>3</sup>Nuclear Physics Institute CAS, CZ-25068 Rez, Czech Republic — <sup>4</sup>European Spallation Source ERIC, Box 176, SE-221 00 Lund, Sweden

High voltage spinel is one of the most promising next-generation cobalt-free cathode materials for Li-ion batteries. Besides the typical compositional range of  $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$   $0 < x < 1$  in the voltage window 4.90 to 3.00 V, additional 1.5 mol of Li per formula unit can be introduced into the structure, in an extended voltage range to 1.50 V. Theoretically, this leads to significant increase of the specific energy

from 690 to 1190 Wh/kg. However, utilization of the extended potential window leads to rapid capacity fading, voltage polarization that lack a comprehensive explanation. In this work, we conducted potentiostatic entropymetry, operando XRD and neutron diffraction on the ordered stoichiometric spinel  $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  within  $0 < x < 2.5$  in order to understand the dynamic structure evolution and correlate it with the voltage profile. We were able to provide a conclusive explanation for the additional voltage step at 2.10 V, the sloping voltage profile below 1.80 V, and the additional voltage step at  $\sim 3.80$  V.

CPP 42.4 Thu 10:00 POT 51

**Computational Screening of Oxide Perovskites as Insertion-Type Cathode Material** — ●JOHANNES DÖHN<sup>1</sup> and AXEL GROSS<sup>1,2</sup> — <sup>1</sup>Institute of Theoretical Chemistry, Ulm University, Germany — <sup>2</sup>Helmholtz Institute Ulm, Germany

The intermittency of wind and solar power - the solely sustainable energy sources which are considered to be abundantly available - leaves only one consequence: For the transition towards renewable energy systems, efficient and reliable storage technologies are needed. Batteries are one of the most widely used storage devices but current technology based on the transfer of Li-ions faces several challenges including their dependence on critical materials with respect to both, scarcity and toxicity.

In our contribution we will discuss atomic-scale investigations of potential future battery materials carried out using density functional theory (DFT). We employed a high-throughput approach in order to screen the well known material class of oxide perovskites as insertion-type cathode materials and we derived several crucial battery properties including voltage and theoretical energy density for in total 280 compounds. For those candidate materials with promising properties, we evaluated additional features such as the voltage profile and diffusion barriers for ionic transport.

Such in silico investigations significantly narrow down the potential materials space for experimental coworkers and thereby contribute to finding green, cheap and reliable devices for energy storage.

CPP 42.5 Thu 10:20 POT 51

**Construction of cobalt oxyhydroxide nanosheets with rich oxygen vacancies as high-performance Lithium-ion Battery anodes** — ●YONGHUAN FU<sup>1,2</sup>, HUAPING ZHAO<sup>1</sup>, JIANHONG LIU<sup>2</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>Graphene Composite Research Center, College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, P. R. China

Cobalt oxyhydroxide (CoOOH) is a promising anode material for lithium-ion batteries (LIBs) due to its high electronic conductivity and theoretical specific capacity. Herein, CoOOH nanosheets are successfully obtained using a facile one-pot method, and a hierarchical nanoporous structure is formed by oxidizing cobalt hydroxide (Co(OH)<sub>2</sub>) in NaOH and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution. The CoOOH anode shows better electrochemical performance compared to Co(OH)<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> electrodes when applied to LIBs. The hierarchical nanoporous structure and high electronic conductivity of the CoOOH anode contribute to its outstanding initial discharge capacity, high initial coulombic efficiency, and excellent cyclability. Experiments and density functional theory (DFT) calculations confirmed that the high ICE and prominent rate capability of the nanosheets could be ascribed to the rapid and complete conversion reaction of CoOOH upon lithiation/delithiation facilitated by hydroxyl groups and oxygen vacancies. This study provides new insights into the structure-property relationship of transition-metal oxyhydroxide anode materials for LIBs.

CPP 42.6 Thu 10:40 POT 51

**The dielectric behaviour of lithium intercalated graphite anodes - as a function of the state of charge** — ●SIMON ANNIES, CHIARA PANOSSETTI, and CHRISTOPH SCHEURER — Fritz Haber Institut Berlin

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 graphite, i.e. the empty state of charge (SOC).

Utilizing our recently developed DFTB parametrization [1] which is 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% - finding a linear dependency from around  $\epsilon_r=7$  at 0% SOC to around 25 at 100% SOC. We achieve this by sampling the Coulomb interactions between pairs of Li-ions and vacancies in large cells with varying intercalant concentrations in the adjacent layers.

Our results agree with experiments in the limit of "empty" graphite, as well as for (bilayer-) graphene, which we consider a validation of our approach. With this, we lay an important piece of foundation for the understanding and multi-scale modelling of entire charging and discharging cycles of graphite anodes in Li-ion batteries.

[1] Anniés, Simon, et al., *Materials* 14.21 (2021): 6633.

CPP 42.7 Thu 11:00 POT 51

**Hypothetical t-LGPO as a good ionic conductor, and the influence of Li core electrons on diffusion** — GIULIANA MATERZANINI<sup>1</sup>, ●NICOLA MARZARI<sup>2,3</sup>, and GIAN-MARCO RIGNANESE<sup>1</sup> — <sup>1</sup>Modelling Division, Université catholique de Louvain, 1348 Louvain-la-Neuve, Belgium — <sup>2</sup>Theory and Simulations of Materials (THEOS), Ecole Polytechnique Federale de Lausanne, CH-1015 Lausanne, Switzerland — <sup>3</sup>National Centre for Computational Design and Discovery of Novel Materials (MARVEL), Ecole Polytechnique Federale de Lausanne, CH-1015 Lausanne, Switzerland

Following the computationally found high Li-ion conductivity in tetragonal Li<sub>10</sub>GeP<sub>2</sub>O<sub>12</sub> (t-LGPO), we study here the role of Li core electrons on Li diffusion in this hypothetical superionic material. We calculate Li diffusivity from two sets of Car-Parrinello canonical molecular dynamics simulations, one using Li pseudopotential with all electrons (1s2s1), and one with just one electron (2s1). The Arrhenius plots show a marked influence of the Li 1s electrons on the Li-ion diffusivity in t-LGPO, being the diffusion coefficient at 600 K one order of magnitude larger, and the activation barrier between 600 and 1200 K 1.5 times smaller, for the Li all-electrons with respect to the Li one-electron calculations. Similar sets of simulations performed for the analogue sulfide material, tetragonal Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> (LGPS), show, oppositely, that for LGPS the influence of Li 1s electrons on Li diffusivity is minimal. The different response of Li mobility to the explicit treatment of 1s electrons reveals fundamental differences in the ionic conductivity mechanism in these two classes of materials.

## 15 min. break

CPP 42.8 Thu 11:35 POT 51

**Sodiation-induced reactivation of micro-nano flower for ultra-long cycling life sodium-ion batteries** — ●YULIAN DONG, HUAPING ZHAO, and YONG LEI — Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany

A rational micro-nano hierarchical structure is demonstrated to prolong the cycle life of sodium-ion batteries (SIBs) by relieving the volume expansion and preventing active material agglomeration. In this work, micro-nano flower 3D-VSx was fabricated as an anode electrode for SIBs. The advanced features of micro-nano flower and the unique crystal structures of NiAs-type vanadium sulfides synergistically contribute to enhancing the electrochemical kinetics of 3D-VSx, and finally achieved remarking electrochemical performances with an ultra-

high capacity (961.4 mAh/g at 2 A/g) and an ultra-long cyclability (more than 1500 cycles). Furthermore, ex situ X-ray diffraction, Raman, and SEM bring to light a gradual reactivation process of 3D-VSx for sodium storage. Fortunately, upon reactivation, the electrochemical impedance of the 3D-VSx anode gradually weakens, and the diffusion-controlled charge storage mode further dominates compared to the capacitively-controlled mode, all of which facilitate the 3D-VSx to maintain a stable sodium storage capability. This work presents a general approach for preparing super-high specific capacity and rate capacity electrode materials for further improving the SIBs performance.

CPP 42.9 Thu 11:55 POT 51

**Sodium diffusion mechanism in NASICON solid electrolyte materials studied via quasi-elastic neutron scattering** — ●IVANA PIVARNÍKOVÁ<sup>1,2</sup>, STEFAN SEIDLMEYER<sup>1</sup>, MARTIN FINSTERBUSCH<sup>3</sup>, GERALD DÜCK<sup>3</sup>, NIINA JALARVO<sup>4</sup>, PETER MÜLLER-BUSCHBAUM<sup>1,2</sup>, and RALPH GILLES<sup>1</sup> — <sup>1</sup>TUM, MLZ, Garching, Germany — <sup>2</sup>TUM School of Natural Sciences, Chair for Functional Materials, Garching, Germany — <sup>3</sup>FZJ, IEK-1, Jülich, Germany — <sup>4</sup>ORNL, Oak Ridge, TN, USA

The sodium superionic conductor materials, also known as NASICON, have been a widely studied class of solid electrolytes for Na-ion based all-solid-state batteries. The aim of this work is to clarify the reason for extremely high conductivity exhibited by Na<sub>1+x</sub>Zr<sub>2</sub>SixP<sub>3-x</sub>O<sub>12</sub> (0-x-3) and to explain the role of the monoclinic to rhombohedral phase transition for the material with x=2.4, which supposedly occurs at around 170°C. We also investigate the overall temperature dependence of the ionic conductivity in the temperature range of 297-640K. The quasi-elastic neutron scattering (QENS) is used to measure the spatial and temporal dynamic properties of diffusion of Na-ions in the crystal structure. The Na-ion diffusion mechanism can be described by the right choice of the diffusion model. Important parameters, such as diffusion coefficients, activation energies, jump distances between the occupation sites and residence times are extracted from the measured and modelled QENS data. Temperature dependent X-ray diffraction data have been obtained and analysed in order to confirm the results obtained from the QENS data.

CPP 42.10 Thu 12:15 POT 51

**3D flower-like MnV<sub>12</sub>O<sub>31</sub> center dot 10H<sub>2</sub>O as a high-capacity and long-lifespan cathode material for aqueous zinc-ion batteries** — ●YAN RAN<sup>1</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>Yunnan Key Laboratory of Carbon Neutrality and Green Low-carbon Technologies, Yunnan University, 650091 Kunming, China

In this work, MnV<sub>12</sub>O<sub>31</sub> center dot 10H<sub>2</sub>O (MnVO) synthesized via one-step hydrothermal method is proposed as a promising cathode material for AZIBs. Because its stable layered structure and hierarchical morphology provide a large layer space for rapid ion transports, this material exhibits a high specific capacity (433 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup>), outstanding long-term cyclability (5000 cycles at current density of 3 A g<sup>-1</sup>), and sufficient energy density (454.65 Wh kg<sup>-1</sup>). To illustrate the intercalation mechanism, ex-situ X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) are adopted, uncovering a H<sup>+</sup>/Zn<sup>2+</sup> dual-cation co-intercalation processes. Besides, density functional theory (DFT) calculation analysis shows that MnVO has a delocalized electron cloud and the diffusion energy barrier of Zn<sup>2+</sup> in MnVO is low, which promotes the Zn<sup>2+</sup> transport and, consequently, improves the reversibility of the battery upon deep cycling. The results provide key and enlightening insights for the design of high-performance vanadium-oxide-based cathode materials for AZIBs.