

## KFM 17: Focus Session: Battery Materials – Experimental Characterisation and Safety Testing (joint session KFM/MM)

The focus session is dedicated to the characterization of microstructure, electrochemical, thermal and safety properties of Lithium-ion and Post-Lithium cells and their individual active and passive materials. This is required to obtain quantitative and reliable data, which are necessary to improve the current understanding in order to design and develop better and safer materials and cells. Potential topics include, but are not limited to electrochemical characterization techniques, thermal characterisation techniques, safety testing, development of safer materials and cell designs, thermodynamic modelling of materials, modelling of thermal runaway and propagation.

Chair: Carlos Ziebert (KIT Karlsruhe)

Time: Wednesday 15:00–19:05

Location: EMH 225

### Invited Talk KFM 17.1 Wed 15:00 EMH 225

**Reversible and irreversible heat effects in batteries and battery materials** — ●ANDREAS JOSSEN — Technical University of Munich, School of Engineering and Design, Department of Energy and Process Engineering, Chair for Electrical Energy Storage Technology, Arcisstrasse 21, 80333 Munich, Germany

Heat generation within batteries is caused by different effects, as entropy, over-potentials and voltage hysteresis. These effects depend on the state of charge and the state of health of the battery and the resulting temperature strongly influences the performance of the system. Therefore measuring of these heat effects is of high interest to support the material and cell design development. Especially of large format cells, as used in electric vehicles, the heat balance strongly influences the fast charge capability on system level. The presentation introduces the different effects and describes measurement methods (calorimetric and electrical based) and discusses the challenges for the different methods. Improved measurement methods are presented and measurement examples for some high-energy materials are discussed. An example where upscaling from a material level to large format cell is shown

### KFM 17.2 Wed 15:30 EMH 225

**Temperature dependency of the heat capacity of Lithium-ion batteries during Heat-Wait-Seek Tests in Accelerating Rate Calorimetry** — ●PHILIPP FINSTER, HANS J. SEIFERT, and CARLOS ZIEBERT — Karlsruhe Institute of Technology (KIT), Institute of Applied Materials - Applied Materials Physics (IAM-AWP), Eggenstein-Leopoldshafen, Germany)

The Heat-Wait-Seek test in Accelerating Rate Calorimeter (ARC) can be used to estimate the safety performance of Lithium-ion cells by extracting parameters such as critical temperatures or generated heat. To calculate the generated heat, it is essential to know the heat capacity of the cell as a function of temperature.

In this study we show an accurate way to calculate the heat capacity of the cell, based on its individual components with respect to temperature. Additionally, we will discuss time dependency of the heat capacity, for instance while melting of the separator or venting. Using this dependence of temperature results in a significant difference in the calculated heat capacity of about 15 % in the temperature range from 298 K to 498 K. In this work the approach is applied to commercial type 21700 cells. The cells were measured in an ES-ARC from Thermal Hazard Technology, UK. The generated heat was compared for either fresh cells or cells after cyclic aging.

With this approach the generated heat in abuse tests can be predicted more accurately to simulate the propagation of heat during a single cell failure in a pack or to calculate the appropriate thickness of a heat barrier for safer battery packs.

### KFM 17.3 Wed 15:50 EMH 225

**Thermal Runaway analysis of lithium-ion batteries with different electrolyte compositions** — ●KARSTEN GEUDER, HANS JÜRGEN SEIFERT, and CARLOS ZIEBERT — Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany

Investigation of the safety of lithium-ion batteries, particularly with respect to thermal runaway, is critical because of the wide application of these batteries. This study specifically examines the influence of electrolyte and additives on battery safety and aims to improve our understanding of thermal runaway in full cells through comparative analysis.

Unlike commercial lithium-ion batteries, the electrolyte composi-

tion is well known. The control electrolyte of the 1Ah pouch cells is a 3:7 mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC). In addition, we used the control electrolyte with either 5% vinylene carbonate (VC) or 5% fluoroethylene carbonate (FEC). To assign the different thermal processes and reactions in the full cells, the dry cells were disassembled and the components were analyzed by differential scanning calorimetry. The full cells were characterized for their thermal runaway behavior using both Heat-Wait-Seek and over-charge tests in accelerating rate calorimeters. We were able to correlate the endothermic behavior of the full cell at about 115 °C with the onset of separator melting. A comprehensive understanding of thermal runaway is critical to ensuring the safety of lithium-ion batteries. An accurate understanding of the electrolyte composition provides deeper insight into its safety implications.

### KFM 17.4 Wed 16:10 EMH 225

**Comparison of thermal safety of new and aged commercial 21700 lithium-ion batteries with different cathode materials by Accelerating Rate Calorimetry (ARC)** — ●SEBASTIAN OHNESEIT, NILS UHLMANN, HANS JÜRGEN SEIFERT, and CARLOS ZIEBERT — Karlsruhe Institute of Technology (KIT), Institute for Applied Materials - Applied Materials Physics (IAM-AWP), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Cylindrical lithium-ion batteries (LIB) of type 21700 have multifaceted usage applications, such as consumer goods, battery electric and hybrid electric vehicles. In consequence, their safety in new and aged state is of particular interest. In this experimental study, the different cathode materials NMC, NCA and LFP were compared, as well as high power and high energy cells. Calendar and cyclic aging with different test conditions (temperature, discharge rate) was performed on the listed cell types and subsequently safety tests were performed on the aged cells, in comparison to results of new cells of the same type. Thermal abuse was done by the heat-wait-see test in an Accelerating Rate Calorimeter (ARC). Several critical temperatures and temperature rates, as well as exothermal data, were determined. Furthermore, the grade of destruction and mass loss was determined, and all data was compared for aged and unaged cells. It was found that, for aged NMC and NCA cells, the aging parameter modified the exothermal reaction onset and overall, a lower maximum temperature was found for the aged cell state. LFP cells reacted, as expected, at significantly higher temperatures, making the cell chemistry considerably safer.

### KFM 17.5 Wed 16:30 EMH 225

**Are Li-ion cells safe for 2nd-Life Applications - The Case of Lithium Plating** — ●THOMAS WALDMANN<sup>1,2</sup>, GABRIELA G. GEROSA<sup>1</sup>, MAX FEINAUER<sup>1</sup>, MARKUS HÖLZLE<sup>1</sup>, and MARGRET WOHLFAHRT-MEHRENS<sup>1,2</sup> — <sup>1</sup>Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW), Helmholtzstrasse 8, D-89081 Ulm — <sup>2</sup>Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Helmholtzstrasse 11, D-89081 Ulm

Increased sustainability and reduced dependence on foreign critical resources (e.g. Co, Ni, Li) go hand in hand with increased cycle life and re-use of aged Li-ion batteries in 2nd-life applications before recycling. However, there is a lack of knowledge on the safety of aged cells with the mechanism of lithium plating. Lithium plating leads to fast aging of Li-ion cells due to reaction of the deposited lithium with electrolyte and formation of "dead lithium". We show results on the influence of lithium plating in commercial Li-ion cells in the 1st-life on safety in 2nd-life. Possibilities to detect and avoid lithium plating which we investigated recently are discussed. Arrhenius plots of the

aging rate in the 1st-life show the typical V-shape and the transition to lithium plating as main aging mechanism below 25°C. Our safety tests show higher hazard levels for cells with lithium plating after the 1st-life. Therefore, lithium plating is an aging mechanism which is to be avoided. Possibilities are shown to avoid Li plating and for early detection of unsafe behavior.

### 15 min. break

KFM 17.6 Wed 17:05 EMH 225

**Microstructural Impact on Filament Growth in All Solid-state Sodium Batteries** — ●ZIMING DING<sup>1</sup>, YUSH TANG<sup>1</sup>, TILL ORTMANN<sup>2</sup>, JANIS KEVIN ECKHARDT<sup>2</sup>, MARCUS ROHNKE<sup>2</sup>, GEORGIAN MELINTE<sup>1</sup>, CHRISTIAN HEILIGER<sup>2</sup>, JÜRGEN JANEK<sup>1,2</sup>, and CHRISTIAN KÜBEL<sup>1,3</sup> — <sup>1</sup>Institute of Nanotechnology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany — <sup>2</sup>Institute for Physical Chemistry and Center for Materials Research, Justus Liebig University Giessen, Giessen, Germany — <sup>3</sup>Karlsruhe Nano Micro Facility, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany

Although the intergranular growth mechanism in inorganic solid electrolytes (SEs) based lithium-based all solid-state batteries (ASSBs) is well studied, there is still much to be learned for sodium-based ASSBs. The polycrystalline Na-β<sup>2</sup>-alumina is selected as a model material to investigate its microstructural impact on Na-filament growth. Using in situ biasing transmission electron microscopy, the Na-filament growth at the interface between the SE and electrode and grain boundaries (GBs) within the SE, were observed during Na deposition. The relationship between the microstructure of SE and filaments is further studied through the orientation analysis and correlative imaging. It is found that anisotropic ion transport due to layered crystal structure can contribute to distinctive Na-ion transport behaviors at different GBs during operation and influence the Na-filament growth. This work helps to understand Na-filament formation and how a critical filament network might form leading to failure of the battery.

KFM 17.7 Wed 17:25 EMH 225

**Computational and experimental investigation of Na and Y co-doping on electrochemical performance of LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> cathode material for Li-ion batteries** — SAHAR ZIRAKI<sup>1</sup>, ●MANSOUR KANANI<sup>1</sup>, BABAK HASHEMI<sup>1</sup>, and MOHAMMAD MOHSEN LOGHAVI<sup>2</sup> — <sup>1</sup>Department of Materials Science and Engineering, School of Engineering, Shiraz University, Shiraz, Iran — <sup>2</sup>Department of Energy Storage, Institute of Mechanics, Shiraz, Iran

LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA) has attracted a lot of attention owing to its high voltage, specific energy density, and specific capacity. However, the cycle durability of the NCA material is still a challenge. In this study, the addition of sodium (Na) on Li-site and yttrium (Y) on metal-site, and their co-doping into NCA material, were investigated experimentally and theoretically. For the first time, we proposed a framework for parameterization of the structural and thermal stability of NCA during the lithiation/delithiation process in terms of first-principle density functional theory (DFT) calculations. The computational results confirmed the positive effect of Na<sup>+</sup> and Y<sup>3+</sup> on the structural and thermal stability of the NCA cathode systematically. Following those outcomes, different percentages of the dopants were added to the cathode material experimentally, and electrochemical tests were performed. The underlying mechanisms of observed experimental improvements were interpreted and discussed according to the computational outcomes.

KFM 17.8 Wed 17:45 EMH 225

**Pits and Traps in the Impedance Analysis of Ionic Conductors** — ●JANIS K. ECKHARDT<sup>1,2,3</sup>, SASCHA KREMER<sup>2,3</sup>, MATTHIAS T. ELM<sup>2,3,4</sup>, PETER J. KLAR<sup>3,4</sup>, JÜRGEN JANEK<sup>2,3</sup>, and CHRISTIAN HEILIGER<sup>1,3</sup> — <sup>1</sup>Institute for Theoretical Physics, Justus Liebig University, Giessen D-35392, Germany — <sup>2</sup>Institute of Physical Chemistry, Justus Liebig University, Giessen D-35392, Germany — <sup>3</sup>Center for Materials Research (ZfM), Justus Liebig University, Giessen D-35392, Germany — <sup>4</sup>Institute of Experimental Physics I, Justus Liebig University, Giessen D-35392, Germany

The development of innovative electrochemical storage systems, such as solid-state batteries, is critical for achieving climate neutrality and sustainability goals. Several hurdles must be overcome before such technologies are ready for the market. Impedance spectroscopy is a powerful method for characterizing the electrical transport properties

of new materials and for monitoring systems in operation. Although it is an older measurement technique, the interpretation of data for inhomogeneous solid-state systems lacks established concepts for reliable results. Thus, we use 3D electrical network models for spatially-resolved transport simulations and systematic investigation of the influence of sample microstructure and solid-solid interface morphology. The material-specific transport quantities derived from 1D models (e.g., brick layer model) sometimes exhibit inaccuracies of several orders of magnitude. In addition, the impedance response of the system exhibits geometric signatures that cannot be adequately represented in 1D physically motivated circuit models, e.g., current constriction.

KFM 17.9 Wed 18:05 EMH 225

**Vacancies on the Lithium-Sublattice in the Solid-State Electrolyte LLZO employing Positron Annihilation Spectroscopy** — DOMINIK BORAS<sup>1</sup>, ANDREAS KOHRMANN<sup>1</sup>, DANIEL WAGNER<sup>1</sup>, DANIEL GÖBEL<sup>1</sup>, JANEZ KOSIR<sup>2</sup>, TANJA KALLIO<sup>2</sup>, and ●TORSTEN E.M. STAAB<sup>1</sup> — <sup>1</sup>Institute for Functional Materials and Biofabrication, Julius-Maximilians Universität Würzburg, D-97070 Würzburg, Röntgenring 11 — <sup>2</sup>Department of Chemistry, Aalto University, Kemistintie 1, FIN-02015 Espoo

We characterise the electrolyte LLZO for all solid-state batteries. LLZO (Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>) samples have been synthesised via the mixed-oxide route, i.e. grinding and calcination, grinding again, then pressing and finally sintering the pellets. We varied the doping (Fe, Al) and the excess Li content. The formed phases (cubic and tetragonal) have been characterised by XRD, while the lattice defects have been investigated by the method of positron annihilation lifetime spectroscopy (PALS). By PALS we were able to see clear differences after calcination when varying the lithium excess. Measuring powder with increasing Li-excess a lifetime component, which could be related to the bulk crystal significantly decreases from 220ps to 190ps. This may be an indication of more and more filled Li-lattice site after the calcination step. Sintered pellets showed two different positron lifetimes (190 / 200ps and 326 / 374ps) for both un-doped / Al-doped samples. This first attempt shows the potential of PALS to characterise all solid-state electrolytes with respect to defects and the occupation of crystal lattice site influencing the mobility of Li ions.

KFM 17.10 Wed 18:25 EMH 225

**Exploring Polaron Stability and Defect Structures in Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO): A Combined Theoretical and Experimental Approach** — ●YU-TE CHAN<sup>1</sup>, MATTHIAS KICK<sup>2</sup>, CRISTINA GROSU<sup>2</sup>, CHRISTOPH SCHEURER<sup>1</sup>, and HARALD OBERHOFER<sup>3</sup> — <sup>1</sup>Fritz-Haber-Institut der MPG, Berlin — <sup>2</sup>Massachusetts Institute of Technology, Cambridge, USA — <sup>3</sup>University of Bayreuth

Spinel Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO) is a promising anode material for next-generation all-solid-state Li-ion batteries (ASSB) due to its "zero strain" charge/discharge behavior. Pristine, white LTO possesses poor ionic and electronic conductivity. Through tailoring the sintering protocol, one can produce oxygen vacancies accompanied by polaron formation, resulting in a performant, blue LTO material.

By performing Hubbard corrected density-functional theory (DFT+U) calculations we are able to show that polaron formation and a possible polaron hopping mechanism play a significant role in enhancing electronic conductivity and in boosting Li<sup>+</sup> diffusion, in line with the experimentally observed improved conductivities.[1] We pair these findings with positron lifetime spectroscopy (PALS) to study the charge carriers' (polaron and Li<sup>+</sup>) behavior and the defect structures produced in the sintering. We developed a machine-learned potential to study the dynamics of the polaron and the structural defects measured from PALS, reaching a rather complete picture of the bulk vs. surface defect chemistry in LTO particles.

[1] M. Kick *et al.*, J. Phys. Chem. Lett. **11**, 2535 (2020); ACS Appl. Energy Mater. **4**, 8583 (2021).

KFM 17.11 Wed 18:45 EMH 225

**Partially substituted metal sulfide anodes for high-performance sodium-ion batteries** — ●ZIDONG WANG — Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany

Due to sodium resources' abundance and easy availability, sodium-ion battery technology has attracted extensive research interest and made significant progress in recent years. Among the various anode materials used for sodium-ion battery anodes, transition metal sulfides, especially bimetallic sulfides, have great potential due to their high capacity and electrochemical activity. In this work, the original bimetallic sul-

vide cations were partially replaced to improve the performance further. In this strategy, the synergistic effect of multi-metal cations will result in superior energy absorption and enhancement. Metal elements with different oxidation states can produce higher capacity through syn-

ergistic effects with each other. Mn-Ni-Co-S with 10% substitution showed satisfactory capacity (721.09 mAh/g at 300 mA/g and 662.58 mAh/g after 20 cycles) and excellent cycle life (85.41% capacity retention after 1000 cycles at 2000 mA/g).