MM 12: Materials for the Storage and Conversion of Energy

Non-Lithiumbased Materials, Characterisation and Simulation Methods

Time: Tuesday 10:15–13:00 Location: H22

MM 12.1 Tue 10:15 H22

Where Electrons Rest After Dark: Polaron Stability in Opto-Ionic 2D Niobium Titanate — •Christoph Dähn[1], Yang Wang[2], Risov Das[2], Bettina V. Lotsch[2], Karsten Reuter[1], and Christian Carbogno[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]MPI für Festkörperforschung, Stuttgart

Two-dimensional Niobium Titanate in alkaline solution is promising for opto-ionic energy applications, since it can store photo-generated charge carriers over macroscopic time scales. Although experiments suggest polarons to play a key role for charge storage, identifying the atomistic and electronic mechanisms active in this material has so far proved challenging, also due to the intrinsic disorder of this compound. In this work, we shed light on these aspects by performing hybrid density-functional theory calculations. In a first step, we explore the vast amount of possible lattice decorations resulting from the partial occupation of Ti-sites with Nb, from which we identify a representative set of stable configurations for this disordered material. In a second step, we investigate the stability of polarons at different lattice sites in these configurations. To qualitatively rationalize these results, a fuzzy classification scheme [1] is applied to group comparable polarons according to their local environment. This allows us to analyze how the local environment influences polaron stability and, in turn, long-term charge retention and its underlying mechanisms [2].

[1] K. C. Lai *et al.*, *J. Chem. Phys.* **159**, 024129 (2023).
[2] Y. Wang *et al.*, *J. Am. Chem. Soc.* **146**, 25467(2024).

MM 12.2 Tue 10:30 H22

Beyond Ion Dynamics: Efficient Charge Transport Simulations including Polarons at Battery Scales — •Matteo Rinaldi, Karsten Reuter, and Christian Carbogno — Fritz-Haber-Institut der MPG, Berlin

Polarons have long been recognized as fundamental for charge transport in battery materials - be it as charge carrier or as ion-transport enhancer [1]. Nonetheless, a quantitative modeling of polaron dynamics in such materials has, so far, remained elusive. On the one hand, the activated dynamics of polarons requires time and length scales that are inaccessible with first-principles methods. On the other hand, (machine learned) interatomic potentials do not capture electronic charge transport by construction. In this work, we overcome this hurdle by exploiting force-field models that explicitly account for the electronic viz. polaronic degrees of freedom in a semi-classical, adiabatic fashion. We demonstrate the viability of the approach for lithium titanium oxide (LTO), a prototypical anode material for which polaron hopping is known to play a decisive role [1]. To this end, we train an equivariant message-passing model to density-functional theory data obtained with hybrid functionals. By then performing large-scale molecular-dynamics simulations with this force-field, we investigate both ionic and polaronic transport in LTO as well as their dynamic coupling. We show that polarons diffuse orders of magnitude faster than ions and discuss the implications for the design of battery materials.

[1]M. Kick, C. Scheurer, and H. Oberhofer, ACS Appl. Energy Mater. 4, 8583 (2021).

MM 12.3 Tue 10:45 H22

Tuning electronic structure of CoNi LDHs via surface Fe doping for achieving effective oxygen evolution reaction — •Yunli Shi[1,2], Huaping Zhao[1], Junqi Li[2], and Yong Lei[1] — [1]Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany — [2]School of Materials Science and Engineering, Shaanxi University of Science and Technology, Xian 710021, China

Cobalt and nickel-based layered double hydroxides (LDHs) are promising oxygen evolution reaction (OER) catalysts, but their performance is limited by poor conductivity and low intrinsic catalytic activity. In this study, CoNi LDHs were used as a matrix, with iron sites introduced onto the surface via cation replacement (Fe-CoNi LDHs). Unlike ternary Fe-CoNi LDHs synthesized through conventional one-step methods, the iron sites in Fe-CoNi LDHs are primarily located on the surface and edges of nanosheets, ensuring abundant exposure of reactive sites. Surface doping was found to optimize the coordination environment and electronic structure, reducing the binding energy between reactants and active sites. As a result, Fe-CoNi LDHs exhibit an overpotential of only 260 mV at 10 mA cm-2, demonstrating superior OER performance. This study elucidates the electronic structure and mechanism of enhanced activity, highlighting the potential of surface doping to advance electrocatalytic applications.

MM 12.4 Tue 11:00 H22

Ferromagnetic chiral hybrid organic-inorganic perovskites — •Muskan Nabi and Alessandro Stroppa — CNR - Institute for SuPerconductors, INnovative materials, and devices Italy

In recent years, chiral hybrid organic-inorganic perovskites where the organic cations are the *source* of chirality, have received great attention from the physics and chemistry community. Their functional properties enable the control of light, charge, and electron spins in the same materials. Here, we discuss the intriguing *chirality transfer mechanism* in newly synthesized ferromagnetic chiral hybrid inorganic perovskite and their interplay with magnetism. Although the organic cations are chiral and polar molecules, their arrangement in the crystal structure results in a chiral non-polar space-group P212121. Moreover, we discuss a new chirality order parameter such as the electronic chirality measure (ECM) aiming at quantify the molecular cation chirality taking into account ionic and electronic degrees of freedoms simultaneously. Also, the relation of ECM to physical properties of chiral hybrid perovskites will be discussed.

MM 12.5 Tue 11:15 H22

Enhanced Supercapacitor Performance of Sr-Doped Barium Stannate (BaSnO3) Nanostructures: Synthesis, Characterization, and Electrochemical Insights — Alaa Farid[1,2], •Diaa EL-Rahman Rayan[1,3], Moataz Fayed[4], Saad Mohamed[4], Abdel Hakim Kandil[2], Mohamed Abd El-Nasser[2], and Mohamed Rashad[1] — [1]Central Metallurgical Research and Development Institute (CMRDI), P.O. Box: 87 Helwan, 11421, Egypt — [2]Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt — [3]Department of Physics, Deraya University, New Minia, Minya, Egypt — [4]Mining and Metallurgy Engineering Department, Tabbin Institute for Metallurgical Studies, (TIMS), Tabbin, Helwan, Cairo Egypt

This study investigates the structural, morphological, thermal, and electrochemical properties of Sr-doped barium stannate. The annealing of undoped BaSnO3 at various temperatures leads to the formation of cubic BaSnO3 phase predominating at 1100 °C. The increasing Sr ion doping induces lattice strain, with slight shifts in the (110) peak. HR-TEM analysis confirms high crystallinity with a significant reduction in particle size from 125.3 to 22.6 nm due to Sr doping. Electrochemical performance tests in a three-electrode configuration show that Sr doping significantly enhances charge storage capacity, with Ba0.8Sr0.2SnO3 achieving a maximum specific capacitance of 1902 F.g-1 at 1 A.g-1. Additionally, the device demonstrated an impressive energy density of 65.6 Wh.kg-1 at a power density of 1633.54 W.kg-1.

15 min. break

MM 12.6 Tue 11:45 H22

Advanced Electron Energy Loss Spectroscopy techniques in catalyst analysis — •Daniela Ramermann, Michael Poschmann, Christoph Göbel, Wenchao Wan, Elisabeth H. Wolf, Saskia Heumann, Holger Ruland, and Walid Hetaba — Max-Planck-Institut für Chemische Energiekonversion, Mülheim an der Ruhr

Electron energy loss spectroscopy (EELS) is a powerful technique that gives access to the electronic structure of the sample, enabling analysis of elemental composition, chemical bonding and oxidation states. Combined with the high spatial resolution of a scanning transmission electron microscope, detailed analysis of a catalyst can be carried out, to gain knowledge about the structure-function relationship. In addition to spatially resolved oxidation state analysis, accessing spectra at higher energy losses than commonly used was recently reported.

We apply these techniques to investigate the oxidation states of a CuZn-based MeOH catalyst system spatially resolved, using selfmeasured standards. Furthermore, we give examples of the utilization of EELS at high energy losses on a Co-based ammonia decomposition catalyst.

MM 12.7 Tue 12:00 H22

Rapid Identification of Ion Migration in Solid-State Ion Conductors from Machine-Learning Raman Spectroscopy — Manuel Grumet[1], Takeru Miyagawa[1], Karin S. Thalmann[2], Tomáš Bučko[3,4], •Waldemar Kaiser[1], and David A. Egger[1] — [1]TUM School of Natural Sciences, Technical University of Munich — [2]Institute of Physics, University of Freiburg — [3]Faculty of Natural Sciences, Comenius University of Bratislava — [4]Institute of Inorganic Chemistry, Slovak Academy of Sciences

Raman spectroscopy is a rapid, non-invasive, and widely available technique that provides a fingerprint of atomic vibrations within solid-state materials. In this work, we demonstrate evidence of Raman signatures that arise from the migration of ions within solid-state ion conductors. We use a rapid computational framework, which consists of machine-learning molecular dynamics simulations [1] and machine-learned polarizability tensors [2], to predict finite-temperature Raman spectra of two classes of superionic conductors, i.e. AgI [3] and Na_3PnS_4 (Pn=P,Sb) [4]. Our simulation results indicate pronounced and broad low-energy Raman intensities due to the host lattice that are correlated with the diffusion of cations. These insights can open novel synergies with experiments to rapidly screen novel compounds for future battery materials. [1] Miyagawa, et al. J. Mater. Chem. A. 12, 11344-11361 (2024) [2] Grumet, et al. J. Phys. Chem. C, 128, 15, 6464-6470 (2024) [3] Brenner, et al. Phys. Rev. Mater. 4, 115402 (2020) [4] Brenner, et al. J. Phys. Chem. Lett. 13, 25, 5938-5945 (2022)

MM 12.8 Tue 12:15 H22

Ion Dynamics in Li-Garnet Electrolytes from Machine-Learning Molecular Dynamics and Raman Spectroscopy — •Takeru Miyagawa[1], Hyunwon Chu[2], Willis O'Leary[2], Manuel Grumet[1], Jennifer L.M. Rupp[1,2], Waldemar Kaiser[1], and David A. Egger[1] — [1]TUM School of Natural Sciences, Technical University of Munich — [2]Department of Materials Science and Engineering, Massachusetts Institute of Technology

Lithium lanthanum zirconate (LLZO) is a promising electrolyte compound for solid-state batteries. Despite subtle differences in the structural properties, its cubic phase, often stabilized by doping, strongly exceeds the tetragonal counterpart in its ionic conductivity. Here, we study the interplay of Li ion migration and host lattice dynamics in tetragonal and cubic LLZO, and compare the ion dynamics to Ta-doped LLZO, using machine-learning molecular dynamics benchmarked in our previous study [1]. We observe a strongly correlated Li-ion migration in the undoped cubic LLZO at increased temperatures, whereas the tetragonal phase showed no Li ion conduction. In contrast, Li ion hopping is the dominant mechanism in Ta-doped cubic LLZO. Additionally, we compute finite-temperature Raman spectra [2] of the LLZO materials and correlate them to experiments. Our predicted Raman results accurately align with measured Raman spectra, allowing us to reveal concrete vibrational motifs that may be utilized to screen LLZO films for the presence of the conductive cubic phase. [1] Miyagawa, et al. J. Mater. Chem. A 12, 11344 (2024) [2] Thomas, et al. Phys. Chem. Chem. Phys. 15, 6608-6622 (2013)

MM 12.9 Tue 12:30 H22

Extracting Gibbs free energies from local composition fluctuations in atom probe data — •Parisha Diwan, Jianshu Zheng, Rüya Duran, Guido Schmitz, and Sebastian M. Eich — University of Sttugart

In this work, thermodynamic fluctuation theory which is traditionally used for liquids has been extended to solids by incorporating an additional elastic work component to account for local composition variations, which is not present in liquids. In solids, composition fluctuations are quantified through the relative variance of the composition histogram, which is influenced by the evaluation volume size and interface effects. These fluctuations are key to determining the Gibbs free energy of mixing in solid alloys. The technique most suitable for identifying local composition fluctuations is Atom Probe Tomography (APT), which provides high-resolution, 3D spatial chemical information at the atomic level. This allows for the detection of local composition variations in solid materials, making it an ideal tool for the evaluation of the extended fluctuation theory. The study applies this theory to a Cu-Ni alloy, using experimental APT data and spatial frequency distribution analysis. By comparing the results with existing phase diagram data, the method demonstrates its effectiveness in extracting the Gibbs free energy of mixing from local composition fluctuations in solids. The comparison with the latest CALPHAD depiction of the miscibility gap further supports the reliability of the method, showing that the proposed approach can accurately predict thermodynamic properties in solid alloys based on atomic-scale data.

MM 12.10 Tue 12:45 H22

Nanoscopic Bubble Formation during Hydrogen Desorption: Insight from Simulations and Neutron Scattering at the Nanometer Scale and its Impact on Hydrogen Storage Performance — •Arnab Majumdar[1], Neslihan Aslan[1], Martin Müller[1,2], and Sebastian Busch[1] — [1]GEMS at MLZ, Helmholtz-Zentrum Hereon — [2]Kiel University

Chemical hydrogen storage using complex hydrides is promising; characterizing the process at various length scales is crucial for optimizing this approach. At the nanometer length scale and below, neutron scattering is a powerful non-destructive technique, in particular because of hydrogen's significant scattering interaction with neutrons. Additionally, neutrons scatter differently depending on the isotope, allowing deuterium to be used in place of hydrogen.

Small Angle Neutron Scattering (SANS) is suited for characterizing structures at the nanometer length scale. In situ measurements confirmed the occurrence of the hydrogen storage process but the measurements alone could not provide complete details about the processes.

Computer simulations were performed; the most suitable model described the nanoscopic structure using the probability distribution of different compounds. The evolution of initial to final probability distribution was modelled according to different chemical kinetic models. This approach qualitatively reproduces the experimental data, suggesting the presence of trapped gas at the nanometer scale during desorption. This key insight enables an estimate of volumetric performance at the engineering scale, which shows a good match with experiments.