MM 32: Transport in Materials: Diffusion, Charge or Heat Conduction

Battery Materials, Effects of Defects

Time: Thursday 15:00–17:45 Location: H22

MM 32.1 Thu 15:00 H22

Kinetic analysis of lithium transport in silicon anode using operando optical microscopy — •Shihao Wei, Monica Mead, Yug Joshi, and Guido Schmitz — Institute of Materials Science University of Stuttgart, 70569 Stuttgart, Germany

The performance of silicon(Si) anodes in lithium(Li)-ion batteries is significantly influenced by the kinetics of Li insertion and migration, particularly at the phase boundaries formed during cycling. Traditional techniques, such as EIS, SIMS, and NMR, are limited in providing detailed kinetic information at internal phase boundaries. This study proposes a novel approach to measure Li migration across phase boundaries in Si-based anodes. First, reflectance spectroscopy is employed to examine the optical response of Si thin films sputtered onto copper current collectors at various charge states, revealing reversible electrochromic behavior and the effect of Li content on spectral characteristics. Based on this, operando optical microscopy is developed to track the lithiation front, by using SU-8 photoresist as a patterning tool. The lithiation process is predominantly governed by diffusion-controlled parabolic growth, with minimal evidence of interface-controlled linear growth. Interestingly, applying the same method during delithiation, a significant slow-down of delithiation front appears. In addition, temperature-dependent diffusion behaviors are explored, quantified with an Arrhenius-like model. By altering the geometry of the photoresist patterns, the transport dynamics are analyzed under two distinct scenarios: a 1D semi-infinite planar configuration and a 2D finite circular configuration.

MM 32.2 Thu 15:15 H22

Crossing Boundaries? Probing Ion Conduction across Interfaces in Solid Electrolytes using Computational NMR Spectroscopy — •Tabea Huss[1], Federico Civaia[1], Simone Köcher[2,1], Karsten Reuter[1], and Christoph Scheurer[1,2] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Institute of Energy Technologies (IET-1), Forschungszentrum Jülich GmbH

Grain boundaries are critical, yet poorly understood factors affecting ion transport in solid-state electrolytes. The spin-alignment echo (SAE) nuclear magnetic resonance (NMR) experiment is a versatile tool to study the manifold transport processes of quadrupolar ions in these solid state materials. However, assigning the measured decay coefficients to physical transport phenomena often proves to be challenging. We have previously demonstrated that we can replicate the SAE experiment for bulk materials using a multi-scale machine learning framework.[1] This framework simulates both the atomic structure and dynamics of solid-state systems, along with generating solid state NMR observables. Our approach has already allowed us to predict electric field gradients over molecular dynamics trajectories and use them to compute decay constants that align with ion hopping times in bulk lithium thiophosphates. In this work, we extend our methodology to explore ion transport in grain boundary structures of the solid-state electrolyte $Li_{10}GeP_2S_{12}$. We extract SAE time constants and differentiate among various decay processes, advancing another step towards direct comparability with experimental results.

[1] A. F. Harper *et al.*, Faraday Discuss., (2024).

MM 32.3 Thu 15:30 H22

Theoretical Investigation of Electron Transport in the $LiMnPO_4$ Battery Material — •Franz Winkler[1,2] and Harald Oberhofer[1,2] — [1]University of Bayreuth — [2]Bavarian Center for Battery Technologies

Developing better batteries and thus battery materials is a crucial step in humanity's urgent energy transition. Thereby, theory can play an important role in characterizing and understanding the properties of the involved materials. In this contribution we present our work on $LiMnPO_4$ which exhibits some desirable properties such as a high energy density and a high potential and thus operating voltage. However, its adoption is hampered by a bad electronic conductivity.

Using electronic density functional theory (DFT), we compute the parameters of conductivity for both band- and polaronic hopping transport, to identify possible bottlenecks and thus possible future improvements of the material. For this we consider both the paramagnetic and antiferromagnetic configuration of $LiMnPO_4$. Due to the well known failures of plain semi-local DFT to represent both localized polaronic configurations and complex spin structures, we thereby use Hubbard-corrected DFT for the bulk of our calculations and range-separated hybrid DFT as a reference. Improvements suggested by our theoretical results can then help experimental collaborators to establish synthetic routes towards more efficient battery materials.

MM 32.4 Thu 15:45 H22

Lithium transport in Lithium Manganese Oxide as a function of temperature, concentration and grain size measured by operando optical microscopy — •Monica Mead[1], Yug Joshi[2], and Guido Schmitz[1] — [1]Institut für Materialwissenschaft, Universität Stuttgart, Heisenbergstr.3, 70569 Stuttgart — [2]Max-Planck-Institut für Nachhaltige Materialien, Max-Planck-Straße 1, 40237 Düsseldorf

Common methods for the determination of diffusion coefficients in electrode materials require critical interpretation, as their formal derivations rely on restrictive assumptions (e.g. galvanostatic/potentiostatic intermittent titration technique (G/PITT), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV)). Alternatively, an optical method for studying ion transport in battery electrodes through operando microscopy can be applied. Here, the measurement of diffusion coefficients is done on thin films in lateral diffusion geometry and is based on an optical response upon ion intercalation. This allows measuring the diffusion coefficient as a function of temperature, concentration and grain size. In this work, diffusion of Li ions in Lithium Manganese Oxide (LMO) is studied by operando microscopy. The temperature dependence of the diffusion coefficient, providing the activation energy via the Arrhenius relation, and the diffusion coefficients for the bulk/grain boundaries of LMO can be determined. Additionally, it is possible to find the concentration dependence by an inverse Boltzmann-Matano method on concentration profiles derived from the intensity profiles along the diffusion direction.

MM 32.5 Thu 16:00 H22

Charge Transport Simulation in the High State-Of-Charge using Kinetic Monte Carlo — •Roya Ebrahimi Viand, Chiara Panosetti, Christoph Scheurer, Karsten Reuter, and Sebastian Matera — Fritz-Haber-Institut der MPG, Berlin

Understanding charge transport in solids is crucial for improving energy storage systems such as lithium-ion batteries. The diffusion of particles in solid materials typically involves rare transitions between low-energy sites, making kinetic Monte Carlo (kMC) an effective tool for studying the long-time dynamics. To address the computational challenges posed by long-range Coulomb interactions, we utilize fast rules for updating the process rates at each kMC step. We investigate ion transport on an isotropic rectangular lattice as well as in lithium graphite structures at high states of charge. We find that small changes in the ion concentration can significantly influence ion mobility, depending on temperature and dielectric response. This happens near stoichiometric concentrations, where the ions freeze in a Coulomb superlattice where effective motion is energetically uphill. Introducing defects or excess ions then opens effective pathways for diffusion. Finally, we discuss the possibility of multiple quasi-stationary states manifesting in different mobilities under the same applied conditions and concentrations.

15 min. break

MM 32.6 Thu 16:30 H22

Electrical characterization of the gate length dependence in graphene field-effect transistors — •Daniel Nickel[1], Daniele Capista[1], Rasuole Lukose[1], Christian Wenger[1,2], and Mindaugas Lukosius[1] — [1]IHP - Leibnitz Institute for High Performance Microelectronics, Im Technologiepark 25, 15236 Frankfurt (Oder), Germany — [2]BTU Cottbus Senftenberg, Platz der Deutschen Einheit 1, 03046 Cottbus, Germany

Integrating graphene into silicon complementary metal-oxide semiconductor technology for electronic and optoelectronic applications holds

great promise but faces challenges such as limited graphene mobility. This work addresses this limitation by using graphene field-effect transistors (GFETs) to analyze the influence of fabrication parameters on the electrical properties of graphene and to investigate the gate length dependence of sheet mobilities at $T = 300$ K. The GFET devices are fabricated with a wolfram back-gate on a 200 mm SiO_2/Si wafer, transferring chemical vapor deposition-grown graphene, patterning it, and forming graphene channel contacts with Pd/Au and Ni. The Dirac point is well detected in electrical measurements, indicating the transition between p- and n-type conduction. Graphene mobility is evaluated using the transconductance method and total resistance fit, revealing peak mobilities of $\mu_p = 715$ cm^2/Vs for the p-branch and $\mu_n = 986$ cm^2/Vs for the n-branch, with dependencies on channel length and contact metals used. Funding was provided by the EU's Horizon 2020 research and innovation program under the Graphene Flagship grant agreement no. 101189797.

MM 32.7 Thu 16:45 H22

Structural and electronic impact of defective sites and their effects on the thermoelectric properties of scandium nitride thin films — •Luigi Cigarini, Urszula Danuta Wdowik, and Dominik Legut — IT4Innovations, VŠB Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic

The Landauer model provides a theoretical tool to understand the electronic transport mechanisms that deeply govern at the atomic scale the thermoelectric conversion of interesting materials. Transition metals nitrides are currently studied for potential applications in energy conversion. Modeling the effects on electronic transport that result from the electronic and structural modifications produced by oxygen impurities and spatial vacancies in scandium nitride (ScN), we propose a theoretical interpretation for new experimental results revealing a strong dependence of the thermoelectric properties of ScN thin films on procedural changes during their fabrication. We find that the thermoelectric properties of ScN are actually decisively determined by the structural and electronic factors caused by the presence of these defects or impurities. Evaluating to what extent these material's overall properties are influenced by these features necessarily requires a theoretical approach. This is particularly true as the presence of oxygen, which proves to be a decisive factor, is extremely difficult to control in standard fabrication processes and experimental conditions. The results presented in this contribution demonstrate the potential of this theoretical approach in studying the thermoelectric properties of these materials uncovering future strategies for improvement.

MM 32.8 Thu 17:00 H22

Helium Interaction with Atomic Level Defects in TungstenStudied by Positron Annihilation Spectroscopy — •Vassily Vadimovitch Burwitz[1,2], Annemarie Kärcher[1,3], Maik Butterling[4], Eric Hirschmann[4], Emma Huntley[2], Adrian Langrehr[1,2], Maciej Oskar Liedke[4], Lucian Mathes[1,2], Thomas Schwarz-Selinger[3], Christoph Springl[1,2], Monia Vadrucci[5,6], Andreas Wagner[4], and Christoph Hugenschmidt[2] — [1]TU München, School of Natural Sciences, Physikdepartment — [2]TU München, MLZ — [3]MPI für Plasmaphysik, Garching — [4]HZDR, Institute of Radiation Physics — [5]ENEA, Development of Particle Accelerators and Medical Applications, Frascati (RM), Italy — [6]Italian Space Agency, Science and Innovation Directorate, Rome

Understanding the type and evolution of lattice defects in tungsten (W) is of interest in nuclear fusion materials research. We therefore investigated W(111) mono-crystals by positron annihilation Doppler-broadening spectroscopy (DBS) and positron annihilation lifetime spectroscopy (PALS). Both complementary methods are sensitive tools for the examination of the defect type and concentration. The literature currently lacks conclusive experimental work regarding the influence of He decoration of vacancies on PAS. We therefore irradiated samples by 4.5 MeV electrons to different damage levels in order to specifically produce mono-vacancies in W. We will present DBS and PALS measurements, both performed with a slow positron beam, before and after plasma loading with 50 eV He ions. The implantation energy is chosen low enough to prevent displacement damage.

MM 32.9 Thu 17:15 H22

Formation energies and charge transition levels of charged point defects in Hematite — •Hao Chen, Christoph Freysoldt, Mira Todorova, and Jörg Neugebauer — Max-Planck-Institut für Nachhaltige Materialien GmbH, Düsseldorf, Germany

Hematite (Fe_2O_3), an iron oxide fundamental to the process of iron ore reduction, exhibits rich defect physics and off-stoichiometric features, as iron can occur as either Fe^{3+} and Fe^{2+}. Charged point defects and the associated Fe^{2+}/Fe^{3+} transitions play an important role in phenomena such as thermodynamic stability, phase transitions between iron oxides, and electronic structure modulation. In order to correctly account for these effects in the prediction of defect equilibria, phase diagrams, diffusion, and related properties, a robust framework for understanding defect thermodynamics and constructing a comprehensive defect model at the ab initio level is essential. Here, we employ DFT+U as an efficient tool for studying strongly correlated systems. In view of the delocalization error of standard functionals, DFT+U is crucial to investigate Fe^{2+} ions as distinct species. Moreover, it systematically opens the band gap of the bulk iron oxides. Since Hubbard U parameter has a direct influence on the band structure and Fe-related defect states in the band gap, we investigate the impact of U values on the computed formation energies of vacancies and interstitials. Our results show that the defect formation energies have a surprisingly weak dependence on U, thus allowing reliable predictions. We analyze the electronic structures of the defects in detail to uncover the underlying physical mechanisms.

MM 32.10 Thu 17:30 H22

Contribution of damped collective modes to thermopower in the strange metal phase of cuprates — •Giovanni Mirarchi[1], Sergio Caprara[2,3], Carlo Di Castro[2], Götz Seibold[4], and Marco Grilli[2,3] — [1]Institute of Theoretical Physics and Astrophysics, University of Würzburg, Am Hubland, 97074 Würzburg, Germany — [2]Dipartimento di Fisica, Sapienza Università di Roma, P. le Aldo Moro 5, 00185 Roma, Italy — [3]ISC-CNR, Unità di Roma Sapienza, P. le Aldo Moro 5, 00185 Roma, Italy — [4]Institut für Physik, BTU Cottbus-Senftenberg - PBox 101344, D-03013 Cottbus, Germany

The strange-metal behavior, which is still an unsolved problem in condensed matter physics, is typically signaled by anomalies in thermodynamic and transport properties, including the famous linear-in-temperature resistivity [1]. The best-known case of strange-metal behavior in literature is that of high-temperature superconducting cuprates, whose strange-metal phase seems to always be accompanied by some kind of dynamical charge order [2]. Based on the experimental evidence of damped short-ranged charge density collective modes in the strange-metal phase of cuprates [3], we propose a scenario in which these collective modes can affect the phenomenology of this phase by interacting with electrons and by directly contributing to thermodynamics and transport [4]. In this talk, the concept of heat current in the presence of damping is discussed and used to describe the Seebeck effect in cuprates through a mechanism analogous to phonon drag. [1] Nat. Phys. 15, 142-147 (2019). [2] Science 337, 821 (2012). [3] Science 365, 906-910 (2019). [4] Commun. Phys. 5, 10 (2022).