

MM 2: Computational Materials Modelling: Energy Materials

Time: Monday 10:15–13:00

Location: H44

MM 2.1 Mon 10:15 H44

Importance of electronic correlations in exploring the exotic phase diagram of Li ion battery cathodes — ●HRISHIT BANERJEE^{1,2}, CLARE P. GREY¹, and ANDREW J. MORRIS² — ¹Department of Chemistry, University of Cambridge, UK — ²School of Metallurgy and Materials, University of Birmingham, UK.

We explore electronic and magnetic states of layered Li_xMnO_2 , a well known cathode material for Li ion batteries, as a function of states of charge x , using *ab-initio* dynamical mean-field theory. Projecting onto low-energy subspace of Mn $3d$ states, and solving a multi-impurity problem, we find that an antiferromagnetic insulating state appears in LiMnO_2 , with a moderate Néel temperature in agreement with experimental studies. As the system is delithiated we find various exotic states emerge such as ferrimagnetic correlated metals, charge ordered ferromagnetic correlated metals with large quasiparticle weight, ferromagnetic metals with small quasiparticle weight, as a function of various states of delithiation of LiMnO_2 and finally an antiferromagnetic insulator for the fully delithiated state, which is albeit unstable. At moderate states of charge, $x=0.67-0.33$, a mix of $+3/+4$ formal oxidation states of Mn is observed, while its overall nominal oxidation state changes from $+3$ in LiMnO_2 to $+4$ in MnO_2 . In all these cases the high-spin state emerges as the most likely state. The quasiparticle peaks in the correlated metallic states could be attributed to polaronic states. We explore the temperature vs. state of charge phase diagram and conclude that the state of charge is a key ingredient for the emergence of the exotic correlated phase transitions in this material.

MM 2.2 Mon 10:30 H44

Quantum-mechanical characterization of sulfur/carbon copolymer cathodes for Li-S batteries — ●POUYA PARTOVI-AZAR — MLU Halle-Wittenberg, Germany

Lithium-sulfur (Li-S) batteries are among the candidates for next-generation energy-storage systems thanks to their high energy density which arises from a high lithium capacity of elemental sulfur. However, cycling performance of Li-S batteries is drastically declined by a reversible capacity fade which is brought about by the diffusion of soluble Li-polysulfides through the electrolyte.^[1,2]

It has been recently shown that polymeric sulfur cathodes exhibit a promising performance in limiting the shuttle effect during the discharge.^[2] However, a clear atomistic picture on the favorable structures and their lithiation mechanism is still not fully established.

Here, we report our recent works on structural and electronic properties as well as finite-temperature vibrational spectra of polymeric sulfur cathodes, namely sulfur/1,3-diisopropenylbenzene^[3] and sulfur/polyacrylonitrile-based nanofiber^[4] co-polymers obtained through quantum-mechanical calculations.

[1] Qing Zhang *et al.*, *Adv. Sci.* 2103798 (2021); [2] G. Bieker *et al.*, *Commun. Mater.* 2, 37 (2021); [3] R. Kiani *et al.*, *ChemPhysChem*, doi: 10.1002/cphc.202100519; [4] P. Partovi-Azar *et al.*, *Phys. Rev. Applied* 1, 014012 (2018); P. Partovi-Azar, *under review* (2022)

MM 2.3 Mon 10:45 H44

Si nanostructure formation in quenched AlSi μ -droplets for application as anode material in lithium-ion-batteries — ●DAVID TUCHOLSKI and KARL-HEINZ HEINIG — Helmholtz-Center Dresden-Rossendorf, Dresden, Germany

We report on 3D lattice kinetic Monte Carlo (3DkMC) simulation of nanostructure formation during rapid quenching in gas-atomization (up to 10^8K/s) of droplets of AlSi alloy melt. The nanostructured Si particles (with the Al selectively etched away) promise to enable about 10x the capacity of the current state-of-the-art graphite in lithium-ion batteries by mitigating Si pulverization.

This work reproduces the experimentally found nanosponge and core-shell particles and reveals heteronucleation at Al_2O_3 sites resulting from trace oxygen at the surface as the formation mechanism for core-shell particles.

The computer simulation uses a memory-efficient bit-encoded lattice, enabling large scale atomistic calculations, while kinetics is implemented via CPU-efficient bit-manipulation for atom jumps between lattice sites. The jump probabilities are described by the metropolis algorithm with a look-up-table of energies calculated with an angular

dependent potential for the Si-Al-Au system in LAMMPS.

This work is supported by the federal ministry for economic affairs and climate protection under grant number 01221755/1.

MM 2.4 Mon 11:00 H44

Tackling structural complexity in $\text{Li}_2\text{S-P}_2\text{S}_5$ solid-state electrolytes using Machine Learning — ●TABEA HUSS, CARSTEN STAACKE, JOHANNES MARGRAF, KARSTEN REUTER, and CHRISTOPH SCHEURER — Fritz-Haber-Institut der MPG

The lithium thiophosphate (LPS) material class provides promising candidates for solid-state electrolytes (SSE) in lithium ion batteries due to high lithium ion conductivities, non-critical elements, and low material cost. LPS materials are characterized by complex thiophosphate microchemistry and structural disorder influencing the material performance. *Ab-initio* studies probing lithium ion conductivity are constrained in system size and simulated time scales. This limits the transferability of computational results to industrial applicable LPS materials. Therefore, we present the development of a data efficient training protocol for the LPS material class using the Gaussian Approximation Potential (GAP). The GAP model can likewise describe crystal and glassy materials and different P-S connectivities P_mS_n . We apply the GAP model to probe lithium ion conductivity and discuss the influence of poly-anions on the latter. The sampling approach allows for a variety of extension and transferability to other SSE.

MM 2.5 Mon 11:15 H44

Exploration of cathode-stable layered solid-state electrolytes — ●SINA ZIEGLER, CHRISTOPH SCHEURER, and KARSTEN REUTER — Fritz-Haber-Institut der MPG, Berlin, Germany

Promising higher safety and capacity, all-solid-state lithium batteries are envisioned to replace standard lithium-ion batteries in the future. Lithium thiophosphates achieve the highest Li ion conductivities of SSEs to date exceeding liquid electrolytes at 10 mS/cm [1].

Until now, the instability of most SSEs towards high-performance electrodes remains a critical challenge, with hardly any known SSE withstanding the reducing/oxidizing conditions at the lithium metal anode and/or high-voltage cathodes or forming electrochemically benign interfaces with the electrode active materials.

To address this issue, we investigate the concept of rare earth lithium halides as a material-efficient, nm thick cathode coating in contact with thiophosphate electrolytes as they provide wide electrochemical stability windows ($0.36-6.71\text{ V vs Li/Li}^+$) as well as good chemical and thermodynamic stability [2,3].

In order to validate this approach, the thermodynamic stabilities of the emerging SSE / halide interfaces are examined by *ab initio* thermodynamics to screen reaction free enthalpies of possible interface reactions. Furthermore, (stable) products of selected material combinations are surveyed for sufficient lithium ion mobility.

[1] C. Wang *et al.*, *Energy Environ. Sci.*, 2021, 14, 2577 [2] J. Liang *et al.*, *Acc. Chem. Res.* 2021, 54, 1023-1033 [3] K. Kim *et al.*, *Chem. Mater.* 2021, 33, 10, 3669-3677

15 min. break

MM 2.6 Mon 11:45 H44

Ab-initio core spectroscopy of LiCoO_2 and CoO_2 — DANIEL DUARTE RUIZ and ●CATERINA COCCHI — Carl von Ossietzky Universität Oldenburg, Institut für Physik, Oldenburg, Deutschland

X-ray absorption spectroscopy (XAS) is one of the most widely used technique to study the electronic structure of cathode active materials in operando conditions. From a theoretical point of view, many-body perturbation theory on top of density-functional theory [1] is the state of the art in the prediction of XAS and in the interpretation of corresponding experimental results. In this work, we investigate core spectroscopy in LiCoO_2 and CoO_2 , considering excitations from the Co K- and L23-edges as well as from the O K-edge. Our results, in agreement with experimental data, indicate that excitonic effects are negligible for the absorption spectra. The spectral fingerprints are well reproduced already by the independent particle approximation and, on a qualitative level, by the atomic, orbital features in the projected density states. These findings suggest that monitoring the electronic structure of LiCoO_2 during the delithiation process is sufficient to capture

the evolution of XAS signatures even in a possible high-throughput fashion.

[1] C. Vorwerk et al. *Electron. Struc.* 1, 037001 (2019)

MM 2.7 Mon 12:00 H44

High-throughput computational screening of fast Li-ion conductors — •TUSHAR THAKUR, LORIS ERCOLE, and NICOLA MARZARI — THEOS, EPFL, Switzerland

We present a high-throughput computational screening to find fast Li-ion conductors to identify promising candidate materials for application in solid-state electrolytes. Starting with $\sim 30,000$ experimental structures sourced from COD, ICSD and MPDS repositories, we performed highly automated calculations using AiiDA at the level of Density Functional Theory (DFT) to identify electronic insulators and to estimate lithium ion diffusivity using the pinball model [1] which describes the potential energy landscape of diffusing lithium at near DFT level accuracy while being orders of magnitude faster. We present the workflow where the accuracy of the pinball model is improved self-consistently and which is necessary in automatically running the thousands of required calculations and analysing their results. Promising conductors are further studied with first principles Molecular Dynamics simulations.

[1] Kahle, L. et al Modeling lithium-ion solid-state electrolytes with a pinball model. *Phys. Rev. Mater.* 2, 65405 (2018)

MM 2.8 Mon 12:15 H44

Adaptive kinetic Monte Carlo driven by local environment recognition — •KING CHUN LAI, SEBASTIAN MATERA, CHRISTOPH SCHEURER, and KARSTEN REUTER — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Efficient lattice kinetic Monte Carlo (kMC) simulation generally relies on a complete prior-understanding of the possible elementary processes and their corresponding energy barriers. Adaptive kMC (akMC) overcomes this limitation by searching for those kinetics during the simulation, but the transition state searches (TSSs) become a bottleneck. To address this, we augment akMC with machine learning on local atomistic environments. Assigning a Smooth Overlap of Atomic Positions vector to each found process, we build up a database during simulation. This database is used to propose initial guesses for TSSs on basis of the proximity of the current local environments and the database entries. This proximity measure is self-adjusted based on statistics from TSSs on-the-fly. As the database fills, the proposed guesses from the database become close to the true transition states. These high quality TSS guesses improve simulation efficiency in two ways. First, the number of TSSs per kMC step gets significantly reduced by avoiding unsuccessful or repeating random TSSs. Second, damped Newton-Raphson becomes practical, which completes a proposed TSS in only a handful iterations. Taking a Pd surface as an illustrative example, we demonstrate the performance of the approach and also discuss how clustering and proximity learning can improve

the TSS guesses further.

MM 2.9 Mon 12:30 H44

Atomistic Simulation Study of Li-Aluminosilicate Glass Scintillators — •EL MEHDI GHARDI, PRINCE RAUTIYAL, FIONA PEARCE, ANITA CROMPTON, LEE EVITS, SIMON MIDDLEBURGH, WILLIAM LEE, and MICHAEL RUSHTON — Nuclear Futures Institute, Bangor University, Gwynedd, LL57 2DG, United Kingdom

Radiation sensors are an important enabling technology in a number of fields, such as medicine, research, energy, military and homeland security. Glass base scintillators have been in use for more than 50 years and offer some benefits including their ability to respond to different types of radiation, and to be formed into various shapes. There is, however the possibility to discover and improve glass scintillators. With this in mind, this work provides insight from atomic scale simulations on the cerium doped Li-Aluminosilicate ($SiO_2 - Al_2O_3 - MgO - Li_2O - Ce_2O_3$) glass scintillators. Three glass compositions were studied using Molecular Dynamics (MD) and Density functional Theory (DFT) to investigate the effect of the ratio $R = ([Al_2O_3])/([MgO] + [Li_2O])$ (with $R = [0.3, 0.8 \text{ and } 2]$) on structural, electronic and optical properties. The effect of R on the complex structure of the system of interest was mainly associated to the increase of Q_4 population that replaced Q_3 's within the network, while electronic mid gap defects were found to be present when $R < 1$. The optical properties including absorption coefficients and energy loss spectra are calculated and analysed based on the electronic structures.

MM 2.10 Mon 12:45 H44

Bonding descriptor based approach for analysing and finding new Photovoltaic absorbers — •JAKOB JOHANNES LÖTFERING and MATTHIAS WUTTIG — RWTH Aachen University, Aachen, Germany

The discovery of Halide Perovskites as good Photovoltaic absorbers and their rapid optimization lead to the question whether there are other materials yet undiscovered for Photovoltaic applications. In order to find new Photovoltaic absorbers, many approaches focus on structural data. We propose a bonding descriptor based approach using two quantities called electrons shared (ES) and electrons transferred (ET), which can be calculated using Density Functional Theory (DFT) calculations. ES and ET are derived from the Quantum Theory of Atoms in Molecules (QTAIM). The first quantity we employ is twice the delocalization index ($\delta(\Omega', \Omega)$) between neighboring atoms. The second one is the number of electrons transferred to/from an atom compared to the unbonded atom. $\delta(\Omega', \Omega)$ is a measure for the number of electron pairs shared between two atoms. It can be obtained by integrating the exchange-correlation pair density over two domains Ω and Ω' , which correspond to the two atoms. ES and ET have already shown to be good bonding descriptors and property predictors, e.g. for Halide Perovskites and Phase Change Materials. We propose that these quantities can also be used to analyse chemical bonding in Photovoltaic absorbers and predict novel materials in this category.