# KFM 13: Materials for Storage and Conversion of Energy (joint session MM/KFM)

Time: Tuesday 10:15–11:30                                              Location: H46

KFM 13.1    Tue 10:15    H46

**How Important are Long-Range Electrostatics in Machine-Learning Potentials for Battery Materials?** — •Carsten Staacke[1], Hendrik Heenen[1], Christoph Scheurer[1], Gabor Csanyi[2], Karsten Reuter[1], and Johannes Margraf[1] — [1]Fritz Haber Institut, Berlin, Germany — [2]Engineering Department, Cambridge University, UK

All-solid-state Li-ion batteries promise gains in safety and durability by combining high Li-ion conductivity and mechanical ductility. In this respect, solid-state electrolytes (SSE) such as the $Li_7P_3S_{11}$ glass-ceramic have gained much attention. Modern machine learning (ML) potentials are increasingly being adopted as a tool for modeling SSEs at the atomistic level. However, the local nature of these ML potentials typically means that long-range contributions arising, e.g., from electrostatic interactions are neglected. To this end, we have combined short-ranged machine-learning potentials based on the Gaussian Approximation Potential (GAP) approach with a classical electrostatic model in the long-range (ES-GAP). We will present a first-principles validation of both, the pure GAP potential and the new ES-GAP for the LPS SSE. In particular, the role of Coulomb interactions in isotropic vs. non-isotropic system simulations will be evaluated. In standard isotropic simulation tasks, such as determining ionic conductivities, both GAP and ES-GAP yield similar results. In contrast, simulations on non-isotropic systems show the importance of ES contributions and provide new insights into interface stability of $Li_7P_3S_{11}$.

KFM 13.2    Tue 10:30    H46

**Oxygen Hole Formation Controls Stability in $LiNiO_2$ Cathodes: DFT Studies of Oxygen Loss and Singlet Oxygen Formation in Li-Ion Batteries** — •Annalena Genreith-Schriever[1,3], Hrishit Banerjee[1,2,3], Clare P. Grey[1,3], and Andrew J. Morris[2,3] — [1]Yusuf Hamied Department of Chemistry, University of Cambridge, Cambridge, United Kingdom — [2]School of Metallurgy and Materials, University of Birmingham, Birmingham, United Kingdom — [3]The Faraday Institution, Harwell Science and Innovation Campus, Didcot, United Kingdom

Ni-rich cathode materials achieve both high voltages and capacities in Li-ion batteries but are prone to structural instabilities and oxygen loss via the formation of singlet oxygen. Using ab initio molecular dynamics simulations, we observe spontaneous $O_2$ loss from the (012) surface of delithiated $LiNiO_2$, singlet oxygen forming in the process. We find that the origin of the instability lies in the pronounced oxidation of O during delithiation, i.e., O plays a central role in Ni-O redox in $LiNiO_2$, as analysed with density-functional theory and dynamical mean-field theory calculations based on maximally localised Wannier functions. The $O_2$ loss route observed here consists of 2 surface $O^{\cdot -}$ radicals combining to form a peroxide ion, which is oxidised to $O_2$, leaving behind 2 O vacancies and 2 $O^{2-}$ ions: effectively 4 $O^{\cdot -}$ radicals disproportionate to $O_2$ and 2 $O^{2-}$ ions. Singlet oxygen formation is caused by the singlet ground state of the peroxide ion, with spin conservation dictating the preferential release of $^1O_2$.

KFM 13.3    Tue 10:45    H46

**Defects and Phase Formation in Non-Stoichiometric $LaFeO_3$: A Combined Theoretical and Experimental Study** — •Daniel Mutter[1], Roland Schierholz[2], Daniel Urban[1], Sabrina Heuer[2,3], Thorsten Ohlerth[2,3], Hans Kungl[2], Christian Elsässer[1,4], and Rüdiger-A. Eichel[2,3] — [1]Fraunhofer IWM, Freiburg — [2]Forschungszentrum Jülich, IEK-9 — [3]RWTH Aachen, Institute of Physical Chemistry — [4]FMF, Universität Freiburg

Defect engineering of perovskite compounds has become increasingly popular as it offers the possibility to influence their catalytic properties for applications in energy storage and conversion devices such as solid-oxide fuel- and electrolyser cells. We present results of a combined theoretical and experimental study exploring the feasibility for an active manipulation of the La stoichiometry, and thereby the valence state of Fe, in $LaFeO_3$, which can be regarded as a base compound of the family of catalytically active $La_{1-x}A_xFe_{1-y}B_yO_{3-\delta}$ compounds. Concentrations of point defects are presened, derived from formation energies which were calculated by first-principles DFT+U calculations as a function of experimental processing conditions, resulting in predictions of achievable stoichiometry ranges. In the experimental part, LFO was synthesized with a targeted La-site deficiency, and we analyzed the phases in detail by X-ray diffraction and various electron microscopy methods (STEM, EDS, EELS). Instead of a variation of the La/Fe ratio, a mixture of two phases, $Fe_2O_3/LaFeO_3$, was observed, resulting in an invariant charge state of Fe, which is in line with the theoretical results.

KFM 13.4    Tue 11:00    H46

**Can we improve thermoelectric properties by microstructural manipulations?** — •Leonie Gomell[1], Tobias Haeger[2], Moritz Roscher[1], Hanna Bishara[1], Ralf Heiderhoff[2], Thomas Riedl[2], Christina Scheu[1], and Baptiste Gault[1] — [1]Max-Planck-Insitut für Eisenforschung GmbH, Düsseldorf, Deutschland — [2]Institute of Electronic Devices, University of Wuppertal, Deutschland

Thermoelectric (TE) materials convert (waste) heat into electrical energy. Several material properties determine TE performance, with the influence of microstructure being the least understood. However, the microstructure plays a crucial role in the performance of TE materials.

We present microstructural investigations of $Fe_2VAl$, synthesized via laser surface remelting. Scanning electron microscopy and atom probe tomography were used to bridge the scale from nanometer to micrometer. The local electrical resistivity was analyzed by an in-situ four-probe technique and the thermal conductivity by scanning thermal microscopy.

We observed a high dislocation density in the order of $10^{13}$ $m^{-2}$ and small grains separated by low-angle grain boundaries. Segregation of V and N was found at grain boundaries and dislocations, observed by atom probe tomography. These defects scatter electrons and phonons, influencing their transport within the material.

We conclude that by manipulating the microstructure, we were able to improve the properties of $Fe_2VAl$. The combination of detailed microstructural analysis and local measurement of properties offers the possibility of understanding the microstructure-property relationship.

KFM 13.5    Tue 11:15    H46

**Enhanced efficiency of graphene-silicon Schottky junction solar cell through inverted pyramid arrays texturation** — •Jiajia Qiu[1,2], Huaping Zhao[1], Wenhui Ma[2], and Yong Lei[1] — [1]Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany — [2]State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, China

Recently, a growing interest of incorporating graphene (Gr) with silicon (Si) to develop Gr-Si Schottky junction solar cells is considered as a potential low-cost alternative to the conventional p-n junction silicon solar cells. In this work, silicon nanowries (SiNWs) and silicon inverted pyramid arrays (SiIPs) were introduced on surface of Gr-Si solar cell through silver and copper-catalyzed chemical etching, respectively. The effects of SiNWs and SiIPs on carrier lifetime, optical properties and efficiency of Gr-SiNWs/SiIPs solar cell were systematically analyzed. The results show that the inverted pyramid arrays have ability of balance of antireflectance and surface area simultaneously. Compared to the Gr-SiNWs solar cells, power conversion efficiency (PEC) and carrier lifetime of Gr-SiIPs devices increase by 62% and 34%, respectively. Finally, the Gr-SiIPs cell with efficiency of 5.63% was successfully achieved through doping nitric acid. This work proposes a new strategy to introduce the inverted pyramid arrays for improving the performance of Gr-Si solar cells.