

MM 16: Energy Conversion

Time: Tuesday 10:15–13:00

Location: SCH A 215

MM 16.1 Tue 10:15 SCH A 215

Spins at Work: Probing Charging and Discharging of Organic Radical Batteries by Electron Paramagnetic Resonance Spectroscopy — ●ILIA KULIKOV¹, NAITIK PANJWANI¹, ANATOLIY VERESHCHAGIN², DOMENIK SPALLEK¹, DANIL LUKIANOV², ELENA ALEXEEVA², OLEG LEVIN¹, and JAN BEHREND¹ — ¹Berlin Joint EPR Lab, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin — ²St. Petersburg, 199034, Russian Federation

We report on the development of an operando setup for spectroelectrochemical Electron Paramagnetic Resonance (EPR) measurements on redox conductive polymers for organic radical batteries. [1]

Quantitative EPR experiments performed on electrochemical cells with a TEMPO containing polymer cathode demonstrate a strong decrease in the number of paramagnetic centres upon oxidation. [2] The distinct EPR signatures of the polymer are used to study its degradation upon repeated cycling. A comparison between the EPR and electrochemical data is used to monitor the degradation process.

Low-temperature ex-situ pulse EPR measurements on an oxidized cathode film reveal a spectrum of dilute nitroxide species, which indicates formation of electrochemically inactive islands. These experiments pave the way for studying organic radical battery materials by advanced EPR techniques.

[1] I. Kulikov et al., *Energy and Environmental Science*, 2022, 15, 3275.

[2] A. A. Vereshchagin et al., *Batteries & Supercaps* 2021, 4, 336.

MM 16.2 Tue 10:30 SCH A 215

Revisiting the storage capacity limit of graphite battery anodes: spontaneous lithium overintercalation at ambient pressure — CRISTINA GROSU^{1,2}, ●CHIARA PANOSSETTI¹, STEFFEN MERZ², PETER JAKES², SEBASTIAN MATERA¹, RÜDIGER-A. EICHEL², JOSEF GRANWEHR², and CHRISTOPH SCHEURER^{1,2} — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²IEK-9, FZ Jülich, Germany

The market quest for fast-charging, long-lasting, safe batteries drives the exploration of new energy storage materials, but also promotes fundamental studies of those already widely used—primarily graphite anodes for Li-ion batteries. We focus on the upper intercalation limit in the morphologically quasi-ideal highly oriented pyrolytic graphite, with a LiC₆ stoichiometry corresponding to 100% state of charge. A sample prepared by immersion in liquid Li at ambient pressure, investigated by ⁷Li nuclear magnetic resonance (NMR), shows unexpected signatures of superdense intercalation compounds, LiC_{6-x}. These were ruled out for decades, as the highest geometrically accessible composition, LiC₂, can only be prepared under high pressure. We monitored the sample upon calendar aging and employed DFT calculations to rationalize NMR findings. Computed free energies reveal that non-negligible overintercalation proceeds spontaneously beyond the currently accepted capacity limit. Challenging the widespread notion that any additional intercalation beyond LiC₆ is not possible under ambient conditions, we highlight the implications for performance-crucial phenomena and critically discuss possible quantitative characterization routes[1].

[1] C. Grosu et al., arXiv:2107.11137 (2021)

MM 16.3 Tue 10:45 SCH A 215

Computational investigation of carbon based anode materials for Li- and post-Li ion batteries — ●JAFAR AZIZI¹, HOLGER EUCHNER², and AXEL GROSS¹ — ¹Institute of Theoretical Chemistry, Ulm University, 89069 Ulm, Germany — ²Institute of Physical and Theoretical Chemistry, University of Tübingen, 1572076 Tübingen, Germany

With respect to sodium ion batteries, traditional graphite anodes exhibit a severe limitation due to their inability to intercalate sodium atoms. Hard carbon materials, on the other hand, provide a promising alternative for Na-ion and K-ion batteries with high theoretical capacities and low reaction potentials. The presence of the particular nanostructure of these functionalized carbon-based materials have been shown to be responsible for these features. The major obstacle for a continued development and improvement is a lack of a functional understanding of the role of these structural features with regard to the intercalation and storage mechanism. To overcome these problems, the intercalation of Li, Na, and K in the presence of distinct defects have been investigated by density functional theory (DFT) calculations.

It will be shown how the combination of phonon simulations with electronic band structure calculations allows for a validation of the so-called modified card house model for the alkali metal storage in hard carbon.

MM 16.4 Tue 11:00 SCH A 215

Detailed structural and electrochemical comparison between high potential layered P2-NaMnNi- and doped P2-NaMnNiMg-oxides — ●MANUEL DILLENZ¹, CORNELIUS GAUCKLER², MOHSEN SOTOUDEH¹, HOLGER EUCHNER³, MARIO MARINARO², and AXEL GROSS^{1,4} — ¹Institute of Theoretical Chemistry, Ulm University, Mez-Starck-Haus, Oberberghof 7, 89081 Ulm — ²ZSW-Zentrum für Sonnenenergie und Wasserstoff-Forschung, Helmholtzstrasse 8, 89081, Ulm, Germany — ³Institute of Physical and Theoretical Chemistry, Universität Tübingen, Auf der Morgenstelle 15, 72076 Tübingen, Germany — ⁴Helmholtz Institute Ulm (HIU) for Electrochemical Energy Storage, Helmholtzstraße 11, 89069 Ulm, Germany

Manganese-based transition metal oxides with a P2 structure are promising cathode materials for sodium ion batteries. Although these materials exhibit high working potential vs Na⁺/Na and high capacity, they are affected by Na⁺ ion/vacancy ordering transitions and phase transformations at high voltages, resulting in poor reversibility. Here we present a combined experimental/theoretical approach to investigate the effect of magnesium doping on the layered P2-Na_{0.67}Mn_{0.75}Ni_{0.25}O₂ cathode material. The Mg-doped material showed stabilization of the high potential plateau and improved cycle life. Based on our experimental data and periodic density functional theory (DFT) calculations, phase stabilities of the O2, P2, and OP4 phases for the pristine and Mg-doped systems were investigated to elucidate the origin of the "Z"-phase formation in the Mg-doped systems.

MM 16.5 Tue 11:15 SCH A 215

Coarse-Grained Simulation of Dendrite Growth in Lithium Metal Batteries — ●LEN KIMMS, DIDDO DIDDENS, and ANDREAS HEUER — Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster

In this talk, we will present a simulation study that investigates the formation and growth of dendrites. Due to the increasing demand for portable high-capacity energy storage, there is a renewed interest in Lithium metal batteries (LMBs). In LMBs one electrode is replaced by lithium metal anchored on a current collector. Lithium metal is electrochemically plated on the anode side when charging the battery. Depositing the metal uniformly is a hugely challenging undertaking. The intrinsically high reactivity of lithium metal, electric field effects, and spatial variations of the local composition in the electrolyte all drive dendritic deposition. We employ a versatile coarse-grained model to understand the influence of various electrochemical conditions on the dendrite morphology. The model allows not only the investigation of fundamental driving forces like the electric field and the cation concentration but also the evaluation of more intricate procedures e.g. pulse charging. Different particle types with varying reactivity are implemented, which allows the representation of local passivation. Also, a solid electrolyte interface (SEI) layer can be incorporated either explicitly with a particle layer on the surface or implicitly by modifying the cationic diffusion locally. Here we report results on how to suppress non-uniform deposition by employing charging, microstructured electrode surfaces, and SEI effects.

15 min. break

MM 16.6 Tue 11:45 SCH A 215

Modelling Hard Carbon with High-Dimensional Neural Network Potentials — ●ALEXANDER L. M. KNOLL^{1,2}, JAFAR AZIZI³, HOLGER EUCHNER⁴, AXEL GROSS³, and JÖRG BEHLER^{1,2} — ¹Lehrstuhl für Theoretische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany — ²Research Center Chemical Sciences and Sustainability, Research Alliance Ruhr, 44780 Bochum, Germany — ³Institut für Theoretische Chemie, Universität Ulm, 89081 Ulm, Germany — ⁴Institut für Physikalische und Theoretische Chemie, Eberhard Karls Universität Tübingen, 72076 Tübingen, Germany

Hard carbon (HC) is widely regarded as a promising anode material

for lithium and sodium ion batteries. However, this material is notoriously difficult to characterise experimentally, as its properties strongly depend on the carbon precursor and the conditions of preparation. *Ab initio* investigations could help to illuminate its structure, but are severely hampered by its complexity involving large graphitic domains as well as amorphous motifs. To bypass these challenges, we present a high-dimensional neural network potential (HDNNP) for HC that accurately reproduces short-range and dispersion interactions in the system. We show that elaborate structural models can be constructed with this potential using various simulation protocols and demonstrate their validity through comparison to experimental data.

MM 16.7 Tue 12:00 SCH A 215

Computational Studies on the Electrochemical Performance of Doped and Substituted Ti_3C_2Tx ($T = O, OH$) MXene — ●MANDIRA DAS¹ and SUBHRADIP GHOSH² — ¹Indian Institute of Technology Guwahati, Guwahati, Assam, India — ²Indian Institute of Technology Guwahati, Guwahati, Assam, India

Using Density functional theory (DFT) in conjunction with a solvation model, we have investigated the phenomenon of electrode-electrolyte interaction at the electrode surface and its consequences on the electrochemical properties like the charge storage and total capacitance of doped and substituted functionalized Ti_3C_2Tx ($T = O, OH$) supercapacitor electrode. We have studied nitrogen-doped, nitrogen substituted, and molybdenum substituted MXenes in acidic electrolyte H₂SO₄ solution. By considering nitrogen doping at different sites, we found that the greatest capacitance is obtained for doping at functional sites. Our results agree well with the available experiment. We also found that the enhancement in capacitances due to nitrogen doping is due to amplifications in the pseudocapacitance. We propose that the primary mechanism leading to the enhanced value of the capacitances due to nitrogen doping is surface redox activity. The performances of substituted systems, on the other hand, are degraded compared to the pristine ones. This suggests that better storage capacities in Ti_3C_2Tx electrode can be obtained by doping only. We provide insights into the reasons behind contrasting behavior in doped and substituted systems and suggest ways to further improve the capacitances in the doped system.

MM 16.8 Tue 12:15 SCH A 215

Structure-property relationships in functionalized metal organic framework from first-principles high-throughput screening — ●JOSHUA EDZARDS¹, HOLGER-DIETRICH SASSNICK¹ und CATERINA COCCHI^{1,2} — ¹Institut für Physik, Carl von Ossietzky Universität Oldenburg, 26129 Oldenburg — ²Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, 12489 Berlin

Metal organic frameworks (MOFs) are novel materials with high potential in many fields of application, ranging from gas storage and catalysis to optoelectronics. MOFs are constituted by metal atoms bound together by linker molecules which can be modified by functional groups. This leads to an enormous variety of MOFs with different structural properties, which can in turn affect their band structures, projected density of states, charge density distribution, etc. In this project, we perform high-throughput first-principles calculations on MOF-5 a well-

known member of the MOF family. We scan all possible structures that arise by exchanging the metal ion Zn with alkaline-earth metals, and by functionalizing the linker molecule (1,4-benzodicarboxylate) with Br, CH₃, Cl, COOH, NO₂, and OH. We investigate the electronic properties of the stable structures and assess how they are influenced by the choice of the metal ion and by the functionalization of the linkers.

MM 16.9 Tue 12:30 SCH A 215

Lithium diffusion visualized in $Li_{4+x}Ti_5O_{12}$ using optical microscopy (revealing slow-moving phase boundary) — ●YUG JOSHI, ROBERT LAWITZKI, and GUIDO SCHMITZ — Chair of Materials Physics, Institute of Materials Science, University of Stuttgart, Stuttgart, Germany

Lithium titanate ($Li_4Ti_5O_{12}$) undergoes a phase transformation from spinel structured ($Li_4Ti_5O_{12}$) to rock-salt ($Li_7Ti_5O_{12}$). The material has been reported to show sluggish mobility of lithium in fully lithiated and delithiated phases. This challenges the high-rate performance observed in this material. To elucidate this behavior, optical microscopy and the electrochromic character of the material have been used to visualize the phase transformation. The kinetics of lithium transport is observed in a constrained region of sputter-deposited thin-film samples. This enables a study of the lateral transport on the length scales of tens of micrometers. Furthermore, with a thermostatically controlled cell, the Arrhenius-like temperature dependence of lithium diffusivity is revealed. Our quantitative findings demonstrate that indeed the end phases have poor diffusivity. Surprisingly, the phase boundary moves slowly upon lithiation, which has been refuted in prior reports, however, it is confirmed here by the linear growth kinetics of the Li-rich phase in the initial stages of the lithium transport. Interestingly, the partial solubility of lithium in the spinel structured $Li_{4/3+\delta}Ti_5/3O_4$ phase increases the diffusivity of lithium drastically. This increase in diffusivity along with the reduction in size of the electrode seems to be compensating the kinetic hindrance induced by the phase boundary.

MM 16.10 Tue 12:45 SCH A 215

Photocatalytic water splitting from Koopmans spectral functionals: The case of TiO_2 polymorphs — ●MARIJA STOJKOVIC¹, EDWARD LINSKOTT¹, and NICOLA MARZARI^{1,2} — ¹Theory and Simulations of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland — ²Laboratory for Materials Simulations, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

Photocatalytic water splitting has drawn considerable attention for renewable energy production. Since the first reported photocatalytic water splitting by titanium dioxide, this material remains one of the most promising photocatalysts, due to its suitable band gap and band-edge positions. However, estimating both of these properties is a challenging task for standard DFT functionals. Here we show how Koopmans spectral functionals can accurately predict the band structure and level alignment of rutile, anatase and brookite, demonstrating the advantage of orbital-density dependent functionals for predicting the spectral properties of materials.