MM 7: Materials for Storage and Conversion of Energy II (joint session MM/KFM)

Time: Monday 11:45–13:00   Location: C 264

MM 7.1   Mon 11:45   C 264

Symmetry Matters: Machine Learning EFG Tensors for NMR Parameter Simulations — •Angela F. Harper[1], Simone Köcher[1,2], Karsten Reuter[1], and Christoph Scheurer[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]IEK-9 Forschungszentrum Jülich

Electric field gradient (EFG) tensors are directly probed by experimental solid-state Nuclear Magnetic Resonance (NMR), and are crucial for deciphering the atomic-scale structure and dynamics of Li-ion battery materials. By employing a machine learning approach we devise a model capable of learning complete EFG tensors, using equivariant descriptors. We further show that it is not sufficient to simply learn scalar quantities derived from a tensor such as quadrupolar shift or asymmetry. To assess the model's performance, we curate an extensive dataset comprising over 60,000 EFG tensors calculated for a diverse set of equilibrium and non-equilibrium crystal structures of $Li_4Ti_5O_{12}$ (LTO), a well-studied zero-strain insertion anode material in Li-ion batteries. We finally show that we predict the quadrupolar frequency to within a few kHz for the ^7Li nucleus, which is well within the level of error required to make meaningful predictions for ^7Li NMR. This work represents a significant step towards realizing *in silico* spectroscopy: the ability to calculate spectroscopic signals such as EFG tensors with the same accuracy as experimental spectroscopy, using machine learning.

MM 7.2   Mon 12:00   C 264

Design criteria for zero-strain cathode materials of the tungsten bronze type compounds A_xFeF_3 (A=Li, Na, K) by first-principles — •Aljoscha F. Baumann[1], Daniel Mutter[2], Daniel F. Urban[1,2], and Christian Elsässer[1,2] — [1]Freiburg Materials Research Center, 79104 Freiburg, Germany — [2]Fraunhofer IWM, 79108 Freiburg

Mechanical stresses in the microstructure of cathode materials during charge/discharge cycles can reduce the long-term stability of intercalation-type alkali-metal-ion batteries. In this context, crystalline compounds exhibiting *zero-strain* (ZS) behavior are of particular interest. For instance, near zero-strain sodiation was experimentally measured in the tetragonal tungsten-bronze (TTB) type compound Na_xFeF_3. [Han, J. Mater. Chem. A, 4, 7382] By atomistic simulations, using a first-principles method based on density functional theory, we investigated the potential of iron-based fluoride compounds with tungsten-bronze structures as ZS cathode materials. The simulations were conducted systematically to study the intercalation of the alkali metal ions Li^+, Na^+, and K^+ into the TTB and two related tungsten-bronze structures of the perovskite and hexagonal types. As the alkali-metal ions intercalate, the oxidation state of the Fe ions decreases, which leads to an enlargement of their surrounding Fluorine octahedra. We found that this effect can be partially compensated by the volume reduction of the F- polyhedra surrounding the alkali ions. We discuss the structural and chemical prerequisites of the host lattice for enabling a ZS insertion mechanism for ions in crystals.

MM 7.3   Mon 12:15   C 264

Construction of cobalt oxyhydroxide nanosheets with rich oxygen vacancies as high-performance Lithium-ion Battery anodes — •Yonghuan Fu[1,2], Huaping Zhao[1], Jianhong Liu[2], and Yong Lei[1] — [1]Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany — [2]Graphene Composite Research Center, College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, P. R. China

Cobalt oxyhydroxide (CoOOH) is a promising anode material for lithium-ion batteries (LIBs) due to its high electronic conductivity and theoretical specific capacity. Herein, CoOOH nanosheets are successfully obtained using a facile one-pot method, and a hierar-chical nanoporous structure is formed by oxidizing cobalt hydroxide (Co(OH)2) in NaOH and (NH4)2S2O8 solution. The CoOOH anode shows better electrochemical performance compared to Co(OH)2 and Co3O4 electrodes when applied to LIBs. The hierarchical nanoporous structure and high electronic conductivity of the CoOOH anode contribute to its outstanding initial discharge capacity, high initial coulombic efficiency, and excellent cyclability. Experiments and density functional theory (DFT) calculations confirmed that the high ICE and prominent rate capability of the nanosheets could be ascribed to the rapid and complete conversion reaction of CoOOH upon lithiation/ delithiation facilitated by hydroxyl groups and oxygen vacancies. This study provides new insights into the structure-property relationship of transition-metal oxyhydroxide anode materials for LIBs.

MM 7.4   Mon 12:30   C 264

Preparation of Prussian blue analogue materials and their application to sodium ion storage — •Ping Hong, Huaping Zhao, and Yong Lei — Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany

The development of a new generation of energy storage systems is necessary due to the limited availability of non-renewable energy resources and the substantial environmental impact associated with the utilization of renewable energy. Sodium ion batteries are likely to become the next generation of large-scale commercial energy storage systems because of their low cost and high energy density. Among various materials, Prussian blue analogs (PBAs) have received great attention for their open three-dimensional framework structure and rapid sodium ion insertion/de-insertion capability. And derivatives synthesized using PBAs as templates have been widely studied. Therefore, in this work, PBAs with a well-defined structure were prepared as cost-effective electrode materials by a simple co-precipitation method. The PBAs materials were applied to sodium ion batteries, showing excellent performance. To achieve outstanding performance, a series of adjustments were made to the binder, electrolyte, and voltage range used in the batteries. at a current density of 100 mA g-1 within the voltage range of 2.0-4.2 V, the capacity remains around 120 mAh g-1. Even at ultra-high loadings, the material demonstrates excellent capacity and cycling stability.

MM 7.5   Mon 12:45   C 264

Multiscale defective FeCu interfaces for sodiophilic and catalytic-enhanced Na-CO2 batteries — •Changfan Xu, Tzuchin Huang, Huaping Zhao, and Yong Lei — Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany

Sodium-carbon dioxide (Na-CO2) batteries are hindered by challenges such as unmanageable sodium deposition/ volume changes at anode and sluggish CO2 reduction/ evolution reaction (CO2RR/ CO2ER) kinetics at CO2 cathode upon cycling. Here, we propose a dual-functional electrode with multiscale defective FeCu interfaces (CP@FeCu) that acts as Na metal hosts and CO2 cathode simultaneously. Microstructural, electrochemical reaction, and theoretical calculations investigations collectively reveal that multiscale defective FeCu interfaces are responsible for the enhancement of sodiophilicity for Na plating/stripping at anode and catalytic activity for CO2RR/ CO2ER at CO2 cathode. Consequently, the CP@FeCu anode enables the uniform deposition of dendrite-free sodium, and the CP@FeCu cathode exhibited low overpotentials and exceptional long-term cycling stability. Significantly, implementation of a symmetrical Na-CO2 battery with CP@FeCu@Na anode and CP@FeCu cathode demonstrates significantly improved electrochemical properties. The introduction of multiscale defective FeCu interfaces with sodiophilic and catalytic dual centers offers an effective method for the tailoring and optimization of sodium metal batteries with high energy density.