

MM 7: Battery Materials

Advanced Magnetic Resonance

Time: Monday 11:45–13:00

Location: H 0106

MM 7.1 Mon 11:45 H 0106

NMR studies on ion dynamics in solid electrolytes for Li-ion batteries — •EDDA KLOTZ¹, STEFAN SPANNENBERGER², MICHAEL HAAKS¹, BERNHARD ROLING², and MICHAEL VOGEL¹ — ¹Condensed Matter Physics, TU Darmstadt, Germany — ²Department of Chemistry, University of Marburg, Germany

In order to improve safety, lifetime, and energy density in batteries, all-solid state ion batteries are of great significance in modern-day research. One of their key components are solid electrolytes with high ionic conductivities. In this area, various materials based on Li⁺-ions as well as Na⁺-ions have been investigated and found to have the potential to outperform the liquid electrolytes currently used in ion batteries.

The improvement of those materials depends directly on understanding the ion dynamics that determine the ion conductivity. By combining various NMR techniques such as spin-lattice relaxation, stimulated-echo and line-shape analysis, we are able to investigate local ion dynamics in a broad time range. Additionally, self-diffusion coefficients are determined using static field gradient NMR (SFG). We apply those methods to investigate the effects of ceramization in glassy Li-ion conductors [1]. We show that local dynamics and macroscopic diffusion can be consistently described by the same broad distributions of activation energies.

[1] Haaks et al., Phys. Rev. B 96, 104301 (2017)

MM 7.2 Mon 12:00 H 0106

Theoretical simulation of Li solid-state NMR in battery research — •SIMONE KÖCHER^{1,2}, JOSEF GRANWEHR¹, RÜDIGER-A. EICHEL¹, KARSTEN REUTER², and CHRISTOPH SCHEURER² — ¹IEK-9 - Fundamental Electrochemistry, Forschungszentrum Jülich, Jülich, Germany — ²Chair for Theoretical Chemistry and Catalysis Research Center, Technische Universität München, Garching, Germany

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful tool to gain detailed understanding of the ionic mobility in battery materials. Notwithstanding, configurational disorder and ionic dynamics increase the complexity and ambiguity of experimental spectra of Li ion electrode materials. Support by independent first-principles based calculations is indispensable to achieve an unambiguous interpretation. For correlating theoretically calculated magnetic resonance parameters with experiments, an accurate reference scale of different lithium compounds is required. We establish this reference scale through density-functional theory (DFT) calculations of chemical shifts for ideal periodic lithium salts with a focus on the influence of geometry, relativistic effects and computational method on the calculated chemical shieldings. For the novel high-capacitance electrode material Li₄Ti₅O₁₂ (LTO), we discuss ⁶Li magic angle spinning (MAS) NMR and ⁷Li spin-alignment echo NMR studies. The impact of ionic motion and configurational space is studied.

MM 7.3 Mon 12:15 H 0106

Nuclear Magnetic Resonance measurements on layered chalcogenides LiCuCh (Ch = Se, Te) — •LENA SPILLECKE¹, MARTIN VALLDOR¹, DARIA MIKHAILOVA¹, LARS GIEBELER¹, KWING-TO LAI², HANS-JOACHIM GRAFE¹, and BERND BÜCHNER¹ — ¹Leibniz Institute for Solid State and Materials Research, Helmholtzstraße 20, 01069 Dresden, Germany — ²Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong, Republic of China

Nuclear Magnetic Resonance (NMR) measurements were performed on the two novel chalcogenide compounds LiCuCh (Ch = Se, Te). These layered transition metal compounds are isostructural to anti-PbClF and, thus, also isostructural to the superconducting LiFeAs compound. Several Li containing transition metal compounds have recently become a focus of research interest because of their expected performance in electrochemical battery cells. Hence, temperature dependent mea-

surements of the spin-lattice (T_1) and spin-spin (T_2) relaxation times on the ⁷Li and the ⁶³Cu-site of the LiCuCh compounds were performed to investigate ⁷Li mobility and structural changes. In LiCuTe the diffusion of ⁷Li-atoms set in at a temperature of 302K, corresponding to an activation energy of 0.49 eV. The activation energy can be extracted separately from T_1 , T_2 and linewidth measurements. Furthermore, LiCuTe and LiCuSe show two inequivalent ⁷Li-sites which can be recognized from two differing spin-lattice relaxation times as well as from two observable peak-positions in the NMR-spectra, which is unexpected based on x-ray diffraction data.

MM 7.4 Mon 12:30 H 0106

In-operando EPR spectroscopy of lithium ion batteries — •ARVID NIEMÖLLER, PETER JAKES, SVITLANA EURICH, ANJA PAULUS, HANS KUNGL, RÜDIGER-A. EICHEL, and JOSEF GRANWEHR — Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung (IEK-9), 52425 Jülich, Germany

Redox mechanisms in battery cathode materials are challenging to be identified. Despite investigations using a wide range of different experimental techniques, exact mechanisms on atomic scales are still not well understood for many classes of materials. In-operando electron paramagnetic resonance (EPR) is a recently introduced technique with the potential to shed new light on oxidation states of transition metal ions in battery cathode materials. An electrochemical flat cell was developed that matches the requirements of the EPR spectrometer. It was used to cycle a LiNi_{0.5}Mn_{1.5}O₄ (LNMO) spinel cathode vs. lithium metal over 500 hours, proving the functionality and stability of the cell setup. EPR spectra show a broad LNMO EPR signal with weak amplitude that was recorded with sufficiently high sensitivity to unravel oxidation mechanisms in the cathode material during battery cycling. These results are compared with ex-situ SQUID measurements. In addition, the EPR linewidth varied continuously with the state of charge, suggesting the formation of a solid solution for slow cycling and a mixed model of solid solution and two-phase formation for fast cycling rates. Long-term EPR experiments complement the electrochemical measurements, allowing us to deduce a model for long-term material degradation of LNMO during battery cycling.

MM 7.5 Mon 12:45 H 0106

Conduction EPR spectroscopy with applied current — •LÉONARD KRÖLL¹, ARVID NIEMÖLLER¹, PETER JAKES¹, JOSEF GRANWEHR^{1,2}, and RÜDIGER-A. EICHEL^{1,3} — ¹Institute of Energy and Climate Research - Fundamental Electrochemistry (IEK-9), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany — ²Institut für Technische und Makromolekulare Chemie (ITMC), RWTH Aachen University, 52056 Aachen, Germany — ³Institut für physikalische Chemie (IPC), RWTH Aachen University, 52074 Aachen, Germany

The EPR signal evolution of a metallic lithium sample under a direct current (DC) has been investigated. The data show a significant change of the EPR signal. The Dysonian signal splits up at a threshold value resulting in two peaks with lower intensities.

Theoretical considerations show that the observation arises from the magnetic field induced by the DC. This field B_j interacts with the magnetization generating spins in two ways depending on the position of the spins in the sample. Firstly, B_j in- or decreases the main field B_0 leading to two peaks. Secondly, the interaction field B_1 , which induces the spin flips, is modified. The direction of the DC determines if the on- or the off-resonance part of B_1 is increased by B_j . In the first case the spin flipping process is strengthened, whereas in the second case it is not affected. Both factors together leads to an asymmetry in the signal originated by the direction of the DC.

In order to allow a comparison of the measured with the calculated data, the effect of the diffusion of the spin carrying electrons in the metal has to be incorporated. The results are shown within this work.