

## SYLI 4: NMR studies

Time: Tuesday 10:15–11:30

Location: IFW A

SYLI 4.1 Tue 10:15 IFW A

**Investigation of the Li ion conduction behavior in the solid electrolyte Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> by multidimensional NMR** — ●MARC PAULUS<sup>1</sup>, MAGNUS GRAF<sup>1</sup>, PETER NOTTEN<sup>1,4</sup>, RÜDIGER-ALBERT EICHEL<sup>1,3</sup>, and JOSEF GRANWEHR<sup>1,2</sup> — <sup>1</sup>FZ Jülich, Institut für Energie- und Klimaforschung, D-52425 Jülich, Germany — <sup>2</sup>RWTH Aachen, ITMC, D-52074 Aachen, Germany — <sup>3</sup>RWTH Aachen, IPC, D-52074 Aachen, Germany — <sup>4</sup>Department of Chemical Engineering and Chemistry, TU/e, 5600 MB Eindhoven, The Netherlands

The biggest challenge to overcome in solid electrolytes is the relatively slow and still poorly understood lithium ion migration at solid electrolyte/electrode interfaces as well as at grain boundaries in solid-state electrolytes. Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> is one of the best Li-ion conductors and therefore an interesting candidate as electrolyte material in Li-ion batteries. To link lithium migration mechanisms with different structural features of LGPS by correlation of spin lattice relaxation and spin alignment echo NMR a pulse sequence with two independently varied evolution times was developed. The obtained data was processed with an algorithm for discrete Laplace inversion. The resulting spin lattice-spin alignment correlation map of LGPS provided several signal components that were assigned to different morphologies and dynamic regions in LGPS. In addition, the experiment facilitated a direct distinction between relaxation-controlled and mobility-induced components in the  $\tau_c$  distribution. Further analysis of the spectral NMR dimension in comparison with SEM and XRD measurements yielded a diverse model of lithium motion for the LGPS powder sample.

SYLI 4.2 Tue 10:30 IFW A

**Solid-state MAS and in-situ NMR spectroscopy for studying battery systems** — WOLFRAM MÜNCHGESANG<sup>1</sup>, VIKTOR KOROTEEV<sup>2</sup>, TATIANA ZAKHARCHENKO<sup>3</sup>, DANIIL M. ITKIS<sup>4</sup>, DIRK C. MEYER<sup>1</sup>, and ●ANASTASIA VYALIKH<sup>1</sup> — <sup>1</sup>Institut für Experimentelle Physik, TU Bergakademie Freiberg, Freiberg, Germany — <sup>2</sup>Nikolaev Institute of Inorganic Chemistry SB RAN, Novosibirsk, Russia — <sup>3</sup>Department of Material Science, Moscow State University, Moscow, Russia — <sup>4</sup>Department of Chemistry, Moscow State University, Moscow, Russia

Current research efforts in the field of energy storage are directed towards improving cost and performance of lithium ion batteries as well as evaluating post lithium ion concepts. Deep understanding of electrochemical processes requires quantitative information on a molecular level, on the one hand, and with temporal resolution, on the other hand. In our studies we apply ex-situ analysis using high-resolution magic angle spinning (MAS) NMR in combination with in-situ NMR, in order to characterize the electrochemical intermediates and reaction products as well as to monitor the formation of solid electrolyte interface (SEI) and surface microstructures in operating cells. The NMR results demonstrate the structural transformations in lithium ion batteries based on vanadia composite and <sup>13</sup>C-isotop enriched carbon electrodes.

SYLI 4.3 Tue 10:45 IFW A

**<sup>7</sup>Li NMR studies of lithium ion dynamics in 70Li<sub>2</sub>S-30P<sub>2</sub>S<sub>5</sub> materials** — ●MICHAEL HAAKS<sup>1</sup>, STEVE MARTIN<sup>2</sup>, and MICHAEL VOGEL<sup>1</sup> — <sup>1</sup>Institut für Festkörperphysik, TU Darmstadt, Germany — <sup>2</sup>Department of Materials Science and Engineering, Iowa State University, Ames, USA

Rising energy demand makes it important to improve the performance of lithium ion batteries. For this purpose it is important to understand the dynamics of lithium ions, in particular, in heterogeneous materials, which are used in modern strategies for material optimization. With combination of <sup>7</sup>Li NMR spin-lattice relaxation, diffusion measurements, line-shape, and stimulated-echo analyses it is possible to investigate lithium ionic motion in wide range of time and length scales in

0.5Li<sub>2</sub>S-0.5(xGeS<sub>2</sub>-(1-x)GeO<sub>2</sub>)[1] and 70Li<sub>2</sub>S-30P<sub>2</sub>S<sub>5</sub> glasses[2]. We exploit there capabilities to ascertain the effect of ceramization in 70Li<sub>2</sub>S-30P<sub>2</sub>S<sub>5</sub>. We find that the large variety of lithium environments results in broad distributions of correlation times for the jump motion of the lithium ions. Our results for 70Li<sub>2</sub>S-30P<sub>2</sub>S<sub>5</sub> allow us to relate the enhancement of electronic conductivity under ceramization[3] to faster lithium ion dynamics on various length scales.

[1] Gabriel et al., Solid State Nuclear Magnetic Resonance 70, 53 (2015)

[2] Haaks et al., work in progress

[3] Mizuno et al., Advanced Materials 17, 918 (2005)

SYLI 4.4 Tue 11:00 IFW A

**Combined DFT and solid-state NMR study of ionic mobility in Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>** — ●SIMONE KÖCHER<sup>1,2</sup>, ANDREAS GARHAMMER<sup>2</sup>, HENDRIK HEENEN<sup>2</sup>, MAGNUS GRAF<sup>1</sup>, JOSEF GRANWEHR<sup>1</sup>, RÜDIGER-A. EICHEL<sup>1</sup>, KARSTEN REUTER<sup>2</sup>, and CHRISTOPH SCHEURER<sup>2</sup> — <sup>1</sup>IEK-9 - Fundamental Electrochemistry, Forschungszentrum Jülich, Jülich, Germany — <sup>2</sup>Chair 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, experimental spectra of novel high-capacitance electrodes such as the configurationally disordered defect spinel oxide Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO) are highly complex. Support by independent first-principles based calculations is indispensable to achieve an unambiguous interpretation. We establish a corresponding framework for <sup>7</sup>Li spin-alignment echo NMR studies of LTO by providing first-principles reference values for chemical shielding and quadrupolar coupling from density-functional theory calculations. A detailed comparison of experimental and theoretical data suggests that a local Li ion mobility faster than the experimental time resolution must have a considerable impact on the observed NMR quantities. We present first steps towards accounting for this local dynamics in the simulation of the autocorrelation function of the NMR experiment within a kinetic Monte Carlo model.

SYLI 4.5 Tue 11:15 IFW A

**Li-ion batteries cathode materials from extended Hubbard-corrected functionals** — ●MATTEO COCOCCIONI and NICOLA MARZARI — Theory and Simulations of Materials (THEOS) and NCCR-MARVEL, EPFL, Lausanne, Switzerland

Predictive modeling of the atomistic structure and electronic properties of transition-metal (TM) compounds is essential for the development of several emerging technologies. This is particularly true for materials explored as electrodes in Li-ion batteries. Unfortunately, most approximate energy functionals fail to capture the localization of electrons on TM ions during the charge/discharge transients, thus compromising the energetics of these systems and the assessment of their performance.

Hubbard-corrected DFT functionals (DFT+U) improve significantly the description of localized valence electrons and have become the standard choice to the modeling of these TM compounds when computational efficiency is required (e.g., for screening large numbers of compounds). This work shows that an extended formulation of DFT+U, including on-site (U) and inter-site (V) interactions, improves the description of mixed valence materials. Focusing on Li<sub>x</sub>MPO<sub>4</sub> (M = Fe, Mn, Ni, Co) we discuss their equilibrium structure and electronic properties in dependence of Li content. Contradicting a common practice, we provide theoretical justification to using computed interaction parameters. We also show this is crucial to reliably compare the energy of different phases, to assess the thermodynamic stability of intermediate compositions and to evaluate the voltage of the resulting battery.