Fast Interfacial Li^+ Diffusion in Nanostructured LiF and LiF-Al_2O_3 composites as Seen by NMR Spectroscopy

Veronika Pregartner, Stefan Breuer, and Martin Wilkening

Institute for Chemistry and Technology of Materials, and Christian Doppler Laboratory for Lithium Batteries, Graz University of Technology (NAWI Graz), Stremayrgasse 9, 8010 Graz, Austria

e-mail: breuer@tugraz.at

Understanding ionic diffusion in solids is a very vital topic in material science. Currently we put much effort into finding suitable materials that meet the needs to develop leading-edge energy storage devices and sensors. Besides studies driven directly by applications, also fundamentally oriented investigations are required to shine further light on the structure-property relationships determining fast ion transport.[1,2] LiF attracted our attention as it has a versatile range of application. It can be used as a component for electrode materials with high capacity;[3] moreover, it is a fundamental component of the solid electrolyte interface (SEI).[4] Understanding ionic transport in and across the SEI is a topic of utmost importance.[5]

Here we studied ionic transport in nanocrystalline LiF and nanocrystalline LiF:Al_2O_3 composites to study interfacial ion transport properties. It is well known that the properties of materials with nm-sized structures, particularly if we consider ionic transport, can be significantly different from those of their coarse-grained counterparts.[6] To investigate the relationship between macroscopic and microscopic ion dynamics, we used conductivity spectroscopy and ^{7}Li, ^{19}F nuclear magnetic resonance (NMR) spectroscopy. The former method, which is sensitive to long-range ion transport, reveals significant higher conductivity values for the nanocrystalline LiF compared to the microcrystalline sample. Joint milling the ionic conductor with an insulator successfully enhances the conductivity even more. We observed an increase in ion transport by up to three orders of magnitude for LiF:Al_2O_3 (70:30 vol %). Variable-temperature NMR line shapes recorded under static conditions reveal a fast and a slow Li spin reservoir at elevated temperatures. Obviously, the interfacial regions at the LiF:Al_2O_3 contacts provide fast diffusion pathways for the Li ions. These atomistic insights available by NMR support earlier concepts that interfacial disorder and strain as well as space charge zones considerably influence overall ion transport in (nanocrystalline) conductor:insulator composites.[8-11]

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