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Diffusion in lithium ion conductors – From fundamentals to applications

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Lithium ion conductors and concomitantly the topic of Li solid state diffusion have become enormously popular in recent years. The annual number of publications increased from 1991, the year when the Li ion battery was introduced into the market, up to this day by factors of some tens. This is mainly due to the quest for better materials and performances of Li ion batteries, the leading electrochemical energy storage system. However, fundamental research on diffusion of the lightest ion besides H^+, comprising questions about, e.g., the dimensionality of diffusion or the influence of structural disorder, has been intensified as well.

Here, exemplary results of our group are reviewed. Starting from early studies on ionic motion by ^{8}Li-beta-NMR [1], the first example of a battery cathode material, which at the same time turned out be a model system for an unambiguous proof of two-dimensional Li diffusion via frequency-dependent ^{7}Li-NMR spin-lattice relaxation time measurements, was layer-structured Li_xTiS_2 as a polycrystal [2]. This system, partly also in its nanocrystalline and amorphous forms [3], has developed into a true playground for diffusion-related NMR studies, where also the potential of ^{7}Li spin-alignment echo NMR was demonstrated [4]. Another potential cathode material is Li_3VF_6 where detailed insights into the Li diffusion process were obtained by ^{6}Li 2D exchange MAS NMR [5]. Actual or potential anode materials studied by us primarily from a fundamental point of view have been Li_xC_6 ($0 < x \leq 1$) [6], $Li_{4+x}Ti_5O_{12}$ ($0 < x < 3$) [4] and, among the silicides, $Li_{12}Si_7$ [7]. In $Li_{12}Si_7$ very fast quasi one-dimensional Li diffusion was detected. While the fast ion conductor Li_3N still plays a role as an excellent model system where the whole arsenal of NMR techniques has been applied [1, 4], $Li_7La_3Zr_2O_{12}$ is presently regarded as one of the most promising electrolytes for all-solid-state Li ion batteries and simultaneously serves for studying the influence of doping and defects on Li diffusivity [8].

Thus, diffusion in Li ion conductors is a topic *par excellence* in the tension field of fundamentals and applications with considerable cross-fertilization between the two. Methodologically, it extensively involves NMR techniques, but also impedance spectroscopy, mass spectrometry and neutron scattering are being applied.

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