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Nuclear Magnetic Resonance Methods for Studying Li^+ Diffusion in Micro- and Nanocrystalline as well as Amorphous Materials

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Sustainable energy storage in the form of secondary Li ion batteries requires both the preparation of advanced materials as well as the development of techniques being capable to characterize the transport properties of ionic conductors preferably on large time and length scales. By combining the various techniques of nuclear magnetic resonance (NMR) [1], which, in particular, include the generation and analysis of stimulated echoes, Li jump rates with values ranging from a few jumps per second up to rates of the order of some millions of jumps per millisecond can be studied [2-4]. In Fig. 1 an overview of the time windows accessible by various NMR techniques is given [2-4].

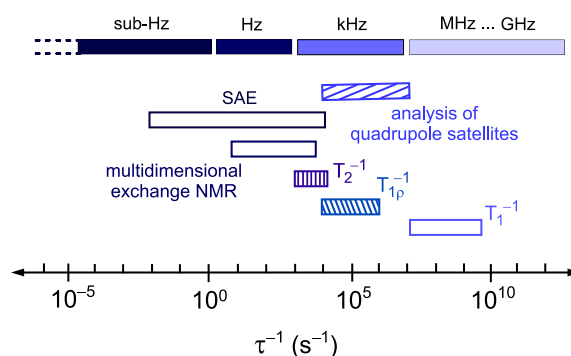


Fig. 1 By the combination of different NMR techniques, comprising besides conventional spin-spin and spin-lattice relaxation NMR measurements also spin-alignment echo (SAE) and multidimensional exchange NMR, Li diffusion parameters such as the jump rate τ^{-1} can be probed over a dynamic range of about 10 orders of magnitude (T_1^{-1} : NMR spin-lattice relaxation rate in the laboratory frame, $T_{1\rho}^{-1}$: NMR spin-lattice relaxation probed in the rotating frame of reference, T_2^{-1} : NMR spin-spin relaxation rate or analysis of the NMR line width as a function of temperature.)

Besides the very broad time and length scales covered by NMR spectroscopy, the different techniques are universally applicable to measure Li dynamics also in a large variety of materials, *i.e.*, from structurally well ordered via highly defective, including nanocrystalline, to amorphous solids [3,4]. The materials, whether in the form of powders or single crystals, were usually fire-sealed in quartz tubes

ensuring a full protection from water moisture or oxygen which is of particular importance for air-sensitive samples and long-time NMR measurements.

We give a brief overview of recent diffusion studies performed in Hannover, see, *e.g.*, Refs. [2-9], using ^7Li as well as ^6Li NMR spectroscopy, including techniques such as measuring temperature-dependent spin-lattice (T_1^{-1}) and spin-spin relaxation rates (T_2^{-1}) as well as recording mixing-time dependent amplitudes of stimulated, *i.e.*, spin-alignment, echoes (SAE). The latter technique, which we have applied to characterize Li ion hopping in several microcrystalline [2,8-15] and nanostructured [16,17] as well as glassy (amorphous) ionic conductors [9,18], served as a formidable tool to enable a direct and atomic-scale access to (long-range) Li diffusion parameters at moderate temperatures [10]. Whereas spin-lattice relaxation NMR experiments, when performed in the laboratory frame of reference, are sensitive to very fast Li diffusion processes with jump rates of the order of the Larmor frequency (MHz range), with SAE-NMR measurements extremely slow Li motions can be probed (see Fig. 1). The latter technique takes advantage of the relatively small quadrupole interactions of ^7Li or, in particular, ^6Li with non-vanishing electric field gradients at the nuclear sites [1,11,15]. This enables a non-selective excitation of the entire NMR spectrum. In addition, by preparation-time dependent SAE-NMR measurements also information about the diffusion pathways can be obtained [2].

Between the dynamic limits marked by T_1 - and SAE-NMR, Li diffusion parameters are usually obtained via $T_{1\rho}^{-1}$ and T_2^{-1} measurements giving access to Li jump rates in the range from 10^3 to 10^5 s^{-1} [3,4]. In the case of $T_{1\rho}^{-1}$ measurements, *i.e.*, spin-lattice relaxation (SLR) NMR experiments performed in the rotating frame of reference [3], the external magnetic field, whose strength is of the order of ten Tesla, is formally replaced by a much weaker spin-lock field of the order of one milli Tesla only. Thus, after the initial perturbation with a short radio frequency pulse, the spins effectively relax in a magnetic field which corresponds to a locking frequency of some kHz. Provided the relaxation of the spin system back into its equilibrium state is driven by Li diffusion only, the SLR rate, when plotted as a function of inverse temperature, passes through a characteristic maximum [3,19]. The flanks of this rate peak yield information not only about diffusion parameters but also about the extent of correlation effects and the dimensionality of the diffusion pathway [2,3]. In particular, the latter can be probed by frequency-dependent SLR-NMR measurements. Up to now, only few low-dimensional Li conductors were studied in such a way, see, *e.g.*, Ref. [20].

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