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Li Diffusion in $Li_2Ti_3O_7$ Probed by ^{7}Li Stimulated Echo NMR

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1. Introduction

During the last years the interest in fast lithium ion conductors has considerably increased due to their promising potential applications in, e. g., smart windows, sensors and secondary ion batteries [1]. Among others, metal-doped $Li_2Ti_3O_7$ (ramsdellite structure) is currently examined as high voltage anode material for new generation Li ion batteries [2]. The present study on Li diffusion in $Li_2Ti_3O_7$ is somewhat more fundamentally oriented towards an investigation of Li jump rates and diffusion pathways in $Li_2Ti_3O_7$ having a channel structure.

The channel structure of $Li_2Ti_3O_7$ (space group *Pbnm*) is shown in Fig. 1. The Li^+ ions occupy sites within the channels (c) as well as share common sites with Ti cations in the framework (f) according to the notation $[Li_{1,77}\square_{2,23}]_c[(Ti_{3,43}Li_{0,52}\square_{0,05})O_8]_f$ [3] wherein vacancies are represented by □. Li transport in $Li_2Ti_3O_7$ is anticipated to take place mainly within the channels which would imply one-dimensional (1D) diffusion. However, there is also a noticeable interchannel hopping of Li^+. Thus, the conductivity anisotropy is significant but is not sufficient to classify this material as a true 1D conductor [4]. In the present work Li diffusion in $Li_2Ti_3O_7$ has been investigated with various nuclear magnetic resonance (NMR) techniques [5]. In particular, ^{7}Li spin-alignment echo (SAE) NMR spectroscopy was used to trace extremely slow Li motions with jump rates smaller than $\sim10^4$ 1/s [6]. The latter jump rates are compared with results extracted from dc conductivity measurements.

2. Experimental

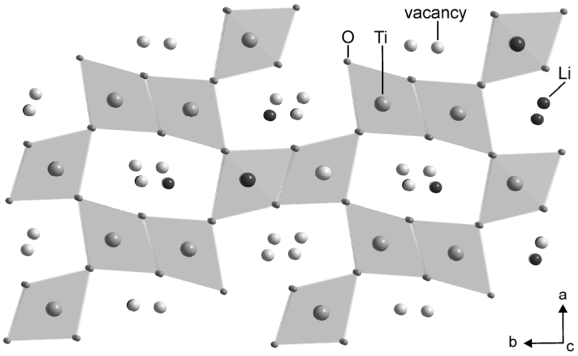

Fig. 1: Crystal structure of $Li_2Ti_3O_7$.

Polycrystalline $Li_2Ti_3O_7$ was prepared from Li_2CO_3 and TiO_2 (anatase) via a solid state reaction [7]. The sample was enriched with ^{6}Li to enlarge the average ^{7}Li-^{7}Li distance in order to reduce dipolar interactions (the ratio ^{7}Li : ^{6}Li is 57 : 43). ^{7}Li SAE-NMR two-time correlation functions were recorded with a Bruker MSL 400 spectrometer working at a radio frequency of 155 MHz. ^{7}Li NMR stimulated echoes were measured with the Jeener-Broekaert pulse sequence, $90_x^\circ – t_p – 45_y^\circ – t_m – 45^\circ$ [8], at fixed pre-

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paration time t_p (10 μs) but for variable mixing times t_m ranging from 10^{-5} s to 10 s. For the conductivity measurements an HP 4192A impedance analyzer working at frequencies from 5 Hz to 13 MHz was employed.

3. Results and Discussion

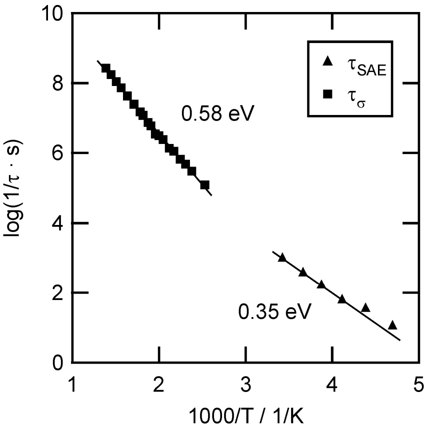

Fig. 2: $1/\tau_{SAE}$ and $1/\tau_\sigma$ as a function of the inverse temperature. Whereas $1/\tau_\sigma$ probes Li transport on a long-range length scale, $1/\tau_{SAE}$ is additionally sensitive to spatially confined Li^+ motions.

In Fig. 2 the ^{7}Li NMR spin-alignment echo decay rates $1/\tau_{SAE}$ are displayed as a function of inverse temperature. The rates show Arrhenius behaviour with an activation energy of 0.35 eV. For comparison, hopping rates $1/\tau_\sigma$ which were extracted from dc conductivity data via the Nernst-Einstein and Einstein-Smoluchowski equations are shown in Fig. 2, too (see, e.g., Ref. [9] for an analogous study on a glassy material). The rates here were obtained by assuming 1D uncorrelated motion. Because 1D is not strictly true ([4], see above), this introduces an error which is at most 20 %. The jump distance was assumed to be 0.16 nm, which is the distance between two Li sites within the channels in a staggered way. Interestingly, the activation energy (0.58 eV) is much larger than that obtained from SAE NMR. Moreover, extrapolation of $1/\tau_\sigma$ to lower temperatures clearly shows that the rates do not agree with those obtained from SAE NMR. Presumably, some of the Li jumps within the channels lead efficiently to an echo damping but do not necessarily contribute to long-range transport as probed by dc conductivity measurements. This reflects the rather complex Li diffusion properties of $Li_2Ti_3O_7$, which are being further elaborated by, e. g., spin-lattice relaxation NMR measurements in the rotating frame of reference. These are also able to detect slow diffusion processes and will be compared with the present SAE NMR measurements.

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