# Influence of Anion Substitution on the Lithium Diffusivity in Hexagonal $Li_xTiS_{2-y}Se_y$

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*Presented at the Bunsen Colloquium: Spectroscopic Methods in Solid State Diffusion and Reactions
September $24^{th} - 25^{th}$, 2009, Leibniz University Hannover, Germany*

Diffusion processes play a crucial role in the design of new components for, *e.g.*, rechargeable batteries, electrochemical sensors and electrochromic devices [1]. In order to systematically develop suitable materials for these applications, the diffusion properties of ion conductors have to be well understood. Among manifold aspects, the influence of dimensionality as well as substitution effects on ionic motion have to be taken into account when promising materials are tailored further in order to improve their transport properties.

Layered $Li_xTiS_2$ turned out to be an excellent model system in order to study the elementary steps of Li self-diffusion within the van-der-Waals gap between the $TiS_2$ layers [2,3] where Li diffusion is strictly confined to two dimensions [2,3].

The present work tries to go one step further and is concerned with the question what kind of influence the substitution of $S^{2-}$ with $Se^{2-}$ in $Li_xTiS_2$ has on the Li diffusivity. Layered $Li_xTiS_ySe_{2-y}$ ($0 \leq y \leq 2$) is single phase and shows the same crystal structure as the end members $Li_xTiS_2$ and $Li_xTiSe_2$ which is $P\bar{3}m1$. Here, we have restricted our measurements to samples with a Li content $x$ of $x = 0.7$. Li diffusivity was studied from a microscopic point of view by rotating-frame spin-lattice relaxation (SLR) NMR measurements at moderate temperatures ranging from 150 to 500 K. Details of the technique are described in, *e.g.*, Refs. [5,6]. When plotted as a function of the inverse temperature, the diffusion-induced NMR relaxation rate $T_{1\rho}^{-1}$, which can be recorded by the well-known spin-lock technique, see, *e.g.*, Ref. [6] , passes through a characteristic maximum when $\omega_1\tau \approx 0.5$ is fulfilled. While $\tau$ denotes the correlation time, $\omega_1$ is the angular locking frequency, which is of the order of a few kHz. In the present study we have recorded $T_{1\rho}^{-1}$ rates at about 14 kHz by using an MSL 100 spectrometer (Bruker) in combination with a field-variable Oxford cryomagnet of a nominal external magnetic field of 4.7 T. This corresponds to a resonance frequency of 77.7 MHz.

In Fig. 1 Arrhenius representations of the SLR NMR rates $T_{1\rho}^{-1}$ of $Li_xTiSe_2$ as well as $Li_{0.7}TiS_{0.4}Se_{1.6}$ are shown. In both cases the diffusion-induced rate peak is clearly detected. As an

example, for $Li_xTiSe_2$ the maximum shows up at $T_{max,\rho} = 322$ K. Using the above mentioned maximum condition this leads to an Li jump rate of approximately $1.8 \times 10^5$ s$^{-1}$. For comparison, the corresponding jump rate of the sulfide analogue is $2 \times 10^6$ s$^{-1}$ at this temperature [3]. Obviously, Li diffusion in $Li_xTiS_2$ is by more than one order of magnitude faster than in Li intercalated titanium diselenide. Substitution of $Se^{2-}$ for $S^{2-}$ shifts the maxima of the rate peaks to lower temperatures. For example, the SLR NMR rate maximum of $Li_xTiS_{0.4}Se_{1.6}$ appears, when recorded at the same locking frequency of 14 kHz, at $T = 280$ K.



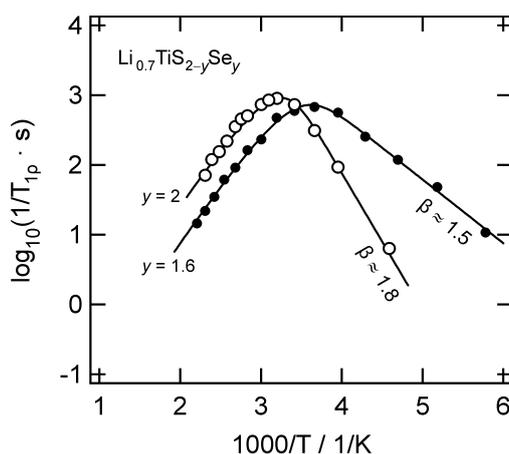**Fig. 1** $^7$Li NMR spin-lattice relaxation rates $1/T_{1\rho}$ of polycrystalline, $Li_{0.7}TiSe_2$ and $Li_{0.7}TiS_{0.4}Se_{1.6}$ plotted as $\log_{10}(1/T_{1\rho})$ vs. $1000/T$. Data were recorded at $\omega_0/2\pi = 77.7$ MHz and $\omega_1/2\pi \approx 14$ kHz. $\beta$ denotes the frequency dependence of the relaxation rates on the low-$T$ flanks of the diffusion-induced rate peaks (see text).

Whereas the slope of the high-$T$ flank, reflecting long-range Li diffusion, is nearly independent of the composition $y$, that of the low-$T$ side of the diffusion induced rate peak is reduced by more than a factor of two. The corresponding (low-$T$) activation energy decreases from about 0.37 eV ($y = 2$) to values of approximately 0.15 eV ($y \approx 1$).

Solid lines in Fig. 1 show fits based on Richards' modified expression for the spectral density function $J(\omega,\tau)$ of a 2D ionic conductor, $J(\omega,\tau) \propto \tau \cdot \ln(1+(\omega\tau)^{-\beta})$, incorporating a logarithmic frequency dependence of the rate $T_{1\rho}^{-1}$ in the limit $\omega_1\tau \ll 1$ [5] as well as a non-BPP-type frequency dependence on the low-$T$ flank being expressed by $1 < \beta < 2$ [4,6]. The later takes into account correlation effects such as structural disorder and Coulomb interactions, see, *e.g.*, Refs. [6,8,9]. The so obtained activation energy, which characterizes long-range Li transport, is about 0.4 eV and does not change much with composition. However, the $\beta$-values pass through a maximum located at $y = 1.0$, *i.e.*, at the composition which produces the highest degree of mixing in the anion sublattice.

The activation energies probed when just the low-$T$ flank is analyzed (see above) are in good agreement with those obtained from calculations using the density-functional-Hartree-Fock one-parameter hybrid method PW1PW (see [10] and Refs. therein), which were performed on samples with the composition $y = 1$. Such small values are found when an Li ion can jump from an octahedron with mixed anions to another one composed of $S^{2-}$ anions, only.

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