

# Slow Li<sup>+</sup> Self-Diffusion in Li Intercalated Nanometer-Sized Needlelike Rutile TiO<sub>2</sub> as Probed by Mixing Time Dependent <sup>7</sup>Li Stimulated Echo NMR Spectroscopy

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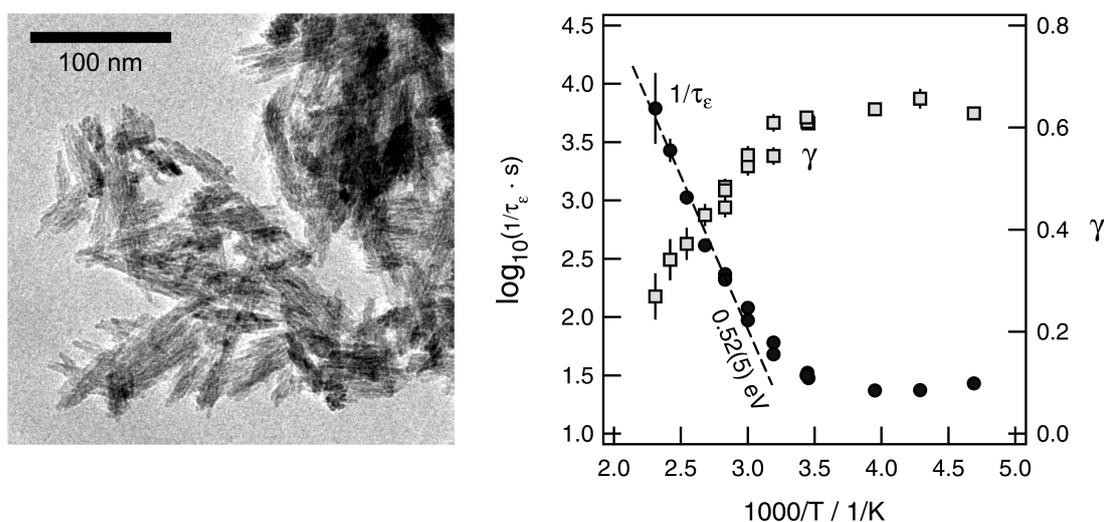
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The role of nanocrystalline materials in addressing the current challenges in energy storage has attracted large attention. Besides nanostructured B-type TiO<sub>2</sub> [1], being the fifth polymorph of titanium dioxide, Li intercalated nanocrystalline rutile is considered to act as a potential anode in inherently safe secondary Li ion batteries. In contrast to its coarse-grained counterpart, which is electrochemically inactive, nanocrystalline Li<sub>x</sub>TiO<sub>2</sub> (rutile) shows a high capacity, high rate performance, and good cycleability when used as an electrode material [2] demonstrating that nanostructuring is a promising strategy to meet the high power and high energy density requirements for Li-based energy storage devices. The advantages of nano-electrodes over those composed of micrometer-sized bulk materials are due to their shorter lengths for both electronic and Li<sup>+</sup> transport, a higher electrode-electrolyte contact area, and a much better compensation of the strain arising during Li<sup>+</sup> insertion and extraction.

Li diffusion in rutile is reported to be highly anisotropic [3], and Li insertion, which can be carried out chemically, electrochemically or by ball-milling of nanocrystalline TiO<sub>2</sub> with Li foil, is mainly a surface effect which seems to be due to slow Li diffusion in the *ab* planes preventing the Li ions to reach the thermodynamically preferred octahedral vacancies. Furthermore, repulsive Li-Li interactions in the *c*-channels seem to play an important role when Li is inserted into the rutile structure. Here, needlelike, nanocrystalline rutile TiO<sub>2</sub> (NanoAmor) of less than 20 nm in diameter and approximately 100 nm in length (see Fig. 1a) was treated with a solution of *n*-BuLi in hexane at room temperature. SEM images and X-ray diffraction patterns of the so obtained highly air-sensitive powder of Li<sub>x</sub>TiO<sub>2</sub> (cobalt blue) confirmed that the rutile structure is fully retained during Li insertion. This clearly indicates that a Li content *x* of less than 0.5 Li atoms per formula unit was obtained, because at higher values of *x* the material can undergo several phase transformations [4].

In order to study the Li self-diffusion parameters of the mixed conducting product, we carried out <sup>7</sup>Li stimulated echo NMR measurements being sensitive to changes of the electric environment of the Li ions when jumping between distinct crystallographic sites in Li<sub>x</sub>TiO<sub>2</sub>, see Ref. [5] for details of the method. By utilizing the Jeener-Broekaert pulse sequence, (90°)<sub>X</sub> – *t*<sub>p</sub> – (45°)<sub>Y</sub> – *t*<sub>m</sub> – (45°)<sub>φ</sub> – echo at *t*<sub>p</sub>, we measured mixing time (*t*<sub>m</sub>) dependent spin-alignment echo (SAE) NMR single-spin correlation functions *S*<sub>2</sub> of the quadrupole nucleus <sup>7</sup>Li (spin-quantum number *I* of 3/2). Two-time correlation functions were recorded at a fixed preparation time *t*<sub>p</sub> of 10 μs ensuring that interfering homonuclear dipole-dipole interactions of the Li spins are largely suppressed.

$S_2(t_p, t_m, t = t_p)$ , which is the amplitude of the stimulated echo read out at  $t = t_p$  here, measures the probability to find an Li ion at a time  $t_m$  in a position equal to that at the beginning, *i.e.*, at  $t_m = 0$ . Thereby, the choice of  $t_m$ , which can be varied from 10  $\mu\text{s}$  to some seconds, depending on the NMR spin-lattice relaxation time  $T_1$ , determines the length scale on which the Li diffusion process is monitored. Up to now several NMR studies have shown that SAE-NMR is sensitive to macroscopic diffusion parameters which are, in contrast to dc-conductivity or tracer measurements, probed via a microscopic, *i.e.*, atomic-scale, point of view, see Ref. [5] for an overview. The measured correlation functions  $S_2$ , which were recorded as a function of temperature and at a resonance frequency of 77.8 MHz, can be well parameterized with stretched exponentials,  $S_2(t_p = 10 \mu\text{s}, t_m, t = t_p) \propto \exp(-(t_m / \tau_\varepsilon)^\gamma)$ . The corresponding decay rates  $\tau_\varepsilon^{-1}$  and stretching exponents  $\gamma$  are shown in Fig. 1 as a function of the inverse temperature  $1/T$ .



**Fig. 1** Left: TEM micrograph of nanocrystalline  $\text{TiO}_2$ . The needlelike shape of the crystallites is clearly visible. X-ray diffraction confirmed the phase purity of the material. Right: Arrhenius plot of the  $^7\text{Li}$  SAE NMR decay rates which were recorded at 77.8 MHz. Above  $T = 330$  K the rates follow Arrhenius behavior (dashed line) with an activation energy of about 0.52 eV. Below  $T = 285$  K the  $S_2$ -decay curves are controlled by other effects such as spin diffusion or non-diffusion induced NMR spin-lattice relaxation, *e.g.*, presumably due to coupling of the Li spins with conduction electrons.

Whereas below 285 K echo damping is induced by non-diffusive effects, the decay rates  $\tau_\varepsilon^{-1}$  exhibit Arrhenius behavior above 330 K revealing slow Li exchange processes in  $\text{Li}_x\text{TiO}_2$  which are characterized by an activation energy of approximately 0.52 eV. Faster Li diffusion processes, if there are any, remain invisible for SAE NMR. Such processes ought to be characterized either by Li jumps between electrically equivalent sites or by extremely fast  $\text{Li}^+$  exchange between electrically *inequivalent* sites but leading to a mean, *i.e.*,  $t_m$ -independent, quadrupole frequency “sensed” by the Li ions so that  $S_2$  is not affected. However, neither NMR line shape nor spin-lattice relaxation measurements (in both the laboratory and rotating frame of reference) indicate such a fast exchange process.

Obviously, the good performance of the material in a Li battery mainly benefits from the short diffusion lengths rather than from extremely fast Li diffusion.

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