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Li Conductivity of Nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Prepared by a Sol-Gel Method and High-Energy Ball Milling

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Abstract. Spinel-type structured $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ ($0 \leq x \leq 3$) is actually one of the most promising anode materials for Li ion batteries. In its nanostructured form it is already used in some commercially available Li ion batteries. As was recently shown by our group (Wilkening et al., Phys. Chem. Chem. Phys. 9 (2007) 1239), Li diffusivity in microcrystalline $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ with $x = 0$ is rather slow. In the present contribution the Li conductivity in nanocrystalline samples of the electronic insulator $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared by different routes is investigated using impedance spectroscopy. The mean crystallite size of the samples is about 20 nm. The ionic conductivity of nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ obtained by mechanical treatment is higher by about two orders of magnitude compared to that found for a material which was prepared following a sol-gel method. The latter resembles the behaviour of the microcrystalline sample with an average particle size in the μm range rather than that of a nanocrystalline ball milled one with a mean crystallite size of about 20 nm. The larger conductivity of the ball milled sample is ascribed to a much higher defect density generated when the particle size is reduced mechanically.

Introduction

High-energy ball milling serves as a versatile tool to reduce and control the particle size of ion conducting ceramics [1]. Depending on the milling conditions set and the type of mill used to prepare the nanocrystalline samples, after a few hours of milling the crystallite size usually reaches a value of about 20 nm [2]. The mechanically treated samples are characterized by a large number fraction of interfacial regions which often provide fast diffusion pathways for the ions. Quite recently, we have shown how mechanical treatment can be used to increase the room temperature Li conductivity of the poor ionic conductor LiTaO_3 by about six orders of magnitude [3]. An analogous study on LiNbO_3 [4,5] has revealed that this enhancement cannot be traced back solely to a size effect. Instead a careful analysis of the microstructure of the materials revealed that structurally perfect, i.e., less defective nanocrystals, which were prepared by a wet-chemical sol-gel method, do not show this colossal enhancement [5]. In the previous studies, the Li diffusivity and conductivity, respectively, was investigated complementarily by ^7Li nuclear magnetic resonance (NMR) spin-lattice relaxation and lineshape measurements as well as by impedance spectroscopy.

In the present contribution, we draw the readers' attention to the question whether the findings for LiNbO_3 are also valid for another nanocrystalline material, viz $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which can be easily prepared by both ball milling and a sol-gel method. $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ with ($0 \leq x \leq 3$) is known as a zero-strain

Li insertion material for anodes in Li ion batteries [6]. The host material ($x = 0$) can accommodate up to three Li atoms per unit cell. Quite recently, we have already quantified the rather low Li diffusivity in μm -sized polycrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by two-time ^7Li stimulated echo NMR spectroscopy. The activation energy probed by this NMR technique turned out to be about 0.86 eV [7], which is in agreement with that found by dc conductivity measurements at somewhat higher temperatures [7]. Whereas $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is an electronic insulator, the material with $x > 0$ is a mixed ion-electron conductor showing a drastically increased Li diffusivity as compared to the host material with $x = 0$. The latter was quantified recently by recording the diffusion induced ^7Li NMR spin-lattice relaxation rate maximum in the rotating frame of reference [8].

Experiment

The source material $\text{Li}_4\text{Ti}_5\text{O}_{12}$ used to prepare the ball milled samples was provided by the Süd-Chemie AG (Munich, Germany). The material was milled for 0.5, 2, 4, 8, 16 and 24 hours in an Al_2O_3 (99.5%) vial set. The ball-to-powder weight ratio used was about 2:1. Mechanical treatment with a SPEX 8000M shaker mill was carried out in Argon atmosphere using an air-tight beaker made of steel into which the alumina vial was placed. Nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was also synthesized via a sol-gel route. The corresponding samples, labeled as sg1 and sg2, which differ in crystallite size only, were synthesized from lithium metal and titanium isopropoxide as precursors. For details of sample preparation and characterization see Ref. [9]. The average crystallite size of all nanocrystalline samples was estimated from X-ray diffraction (XRD) peak broadening utilizing the method introduced by Scherrer. XRD patterns were measured at Bragg-Brentano geometry with CuK_α radiation on a Philips PW 1800 diffractometer.

Samples for dc conductivity measurements were prepared in the form of pellets of 8 mm diameter and thicknesses between 0.5 and 2 mm. The powders were pressed at room temperature under an uniaxial pressure of 1 GPa together with platinum powder (Merck 99.9%) in a sandwich configuration thus forming the electrodes. For the impedance measurements between 5 Hz and 13 MHz mainly an HP 4192A analyzer was employed which can measure dc conductivities down to about 10^{-8} S. Lower values were probed using a Novocontrol broadband dielectric spectrometer (BDS 40) working between 0.1 Hz and 10 MHz. In order to get rid of residual water on the surface of the nanoparticles, prior to the conductivity measurements the samples were kept for several hours at a temperature of 140 – 150 °C. The influence of water was registered by the observed decrease of the dc conductivity until a constant value was reached (usually after some hours).

Preliminary static ^7Li NMR line shape measurements were performed using an MSL 400 spectrometer and a modified MSL 100 console connected to a 9.4 T and a field-variable (0 – 7 T) Oxford cryomagnet, respectively. Standard pulse sequences were used to record ^7Li NMR spectra between 150 and 450 K. The pulse length was about 5 μs .

Results and Discussion

X-ray diffraction. Fig. 1 shows the XRD powder patterns of nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared by the two different routes, *viz* mechanically via high-energy ball milling and chemically utilizing a sol-gel method. The diffraction pattern of microcrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which served as source material to prepare the ball milled samples, is shown for comparison, too. The peak positions are in agreement with values reported in the literature [10]. No mechanochemical phase transformations take place during the milling process. As can be seen from Fig. 1 when the peak at $2\theta = 18.34^\circ$ is regarded, after two hours of milling the width of the peak is increased by about 15 %. This roughly holds also for the other peaks. Further milling leads to a drastic peak broadening which can be ascribed to a reduction of the crystallite size as well as to strain effects. Using the Scherrer equation [3, 11], the mean crystallite size $\langle d \rangle$ reduces from about 86 nm (2 h) to 44 nm (4 h) reaching $\langle d \rangle = 20$ nm after

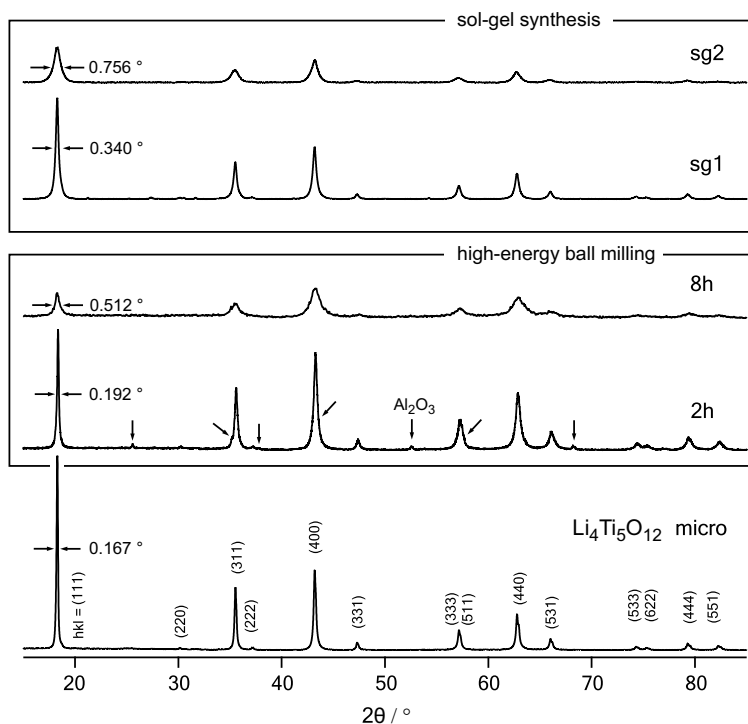


Fig. 1: XRD profiles of microcrystalline and mechanically treated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ high-energy ball milled for 2 and 8 h (bottom and intermediate). The XRD patterns of the chemically prepared materials (labeled as sg1 and sg2, respectively) are shown at the top. Small arrows indicate Al_2O_3 due to abrasion from the vial, see Ref. [14].

milling the microcrystalline material for 8 h in the shaker mill. Milling times longer than 8 h do not lead to significantly smaller values. Prior to this evaluation the K_{α_1} and K_{α_2} contributions of the XRD peaks were separated by means of the Rachinger procedure [12]. To what extent strain contributes to the observed increase particularly at large diffraction angles can be estimated following the method introduced by Williamson and Hall [13]. Such an analysis, for which the harmonic peaks (111) and (444) were taken, yields mean crystallite sizes being somewhat larger than those via the Scherrer equation, *viz* 77 and 33 nm compared to 44 and 20 nm for milling times of 4 h and 8 h, respectively.

The XRD patterns of the nanocrystalline samples prepared following the sol-gel route are also included in Fig. 1. For the sample labeled as sg1 an average crystallite size of 37 nm (Scherrer) and 42 nm (Williamson-Hall), respectively, is obtained. The analysis of the corresponding XRD pattern of the other sample (sg2) shows a much smaller crystallite size. Both methods yield 12-13 nm for the mean crystallite size.

Impedance Measurements and ^7Li NMR spectra. The impedance spectra of ball milled $\text{Li}_4\text{Ti}_5\text{O}_{12}$ consist of a typical dc plateau in the low-frequency regime and a dispersive part at higher frequencies. As an example, the corresponding spectra of ball milled $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are shown in Fig. 2a). Up to a frequency $\nu = \omega/2\pi$ of about 1 MHz the real part of the conductivity $\sigma'(\nu)$ can be fitted roughly with Jonscher's empirical power law $\sigma'(\nu) = \sigma_{\text{dc}} + A\omega^s$ with s ranging between 0.5 and 0.7. In Fig. 2b) $\sigma_{\text{dc}}T$ of all nanocrystalline samples is plotted *vs* reciprocal temperature according to the Arrhenius relation $\sigma_{\text{dc}}T \propto \exp(-E_a/(k_B T))$ where E_a denotes the activation energy and k_B Planck's constant. Interestingly, the ionic conductivities of the nanocrystalline samples obtained by the sol-gel method (sg1 and sg2) resemble that of microcrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ rather than those of the ball milled samples. Li transport in samples sg1 and sg2 is characterized by an activation energy of 0.84(1) eV which is identical to that obtained for microcrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ serving as a reference material, here.

It is reasonable that sample sg2, having the smallest mean crystallite size (12 nm, see above) of the materials studied here, shows a slightly higher ionic conductivity than sample sg1 (42 nm). This

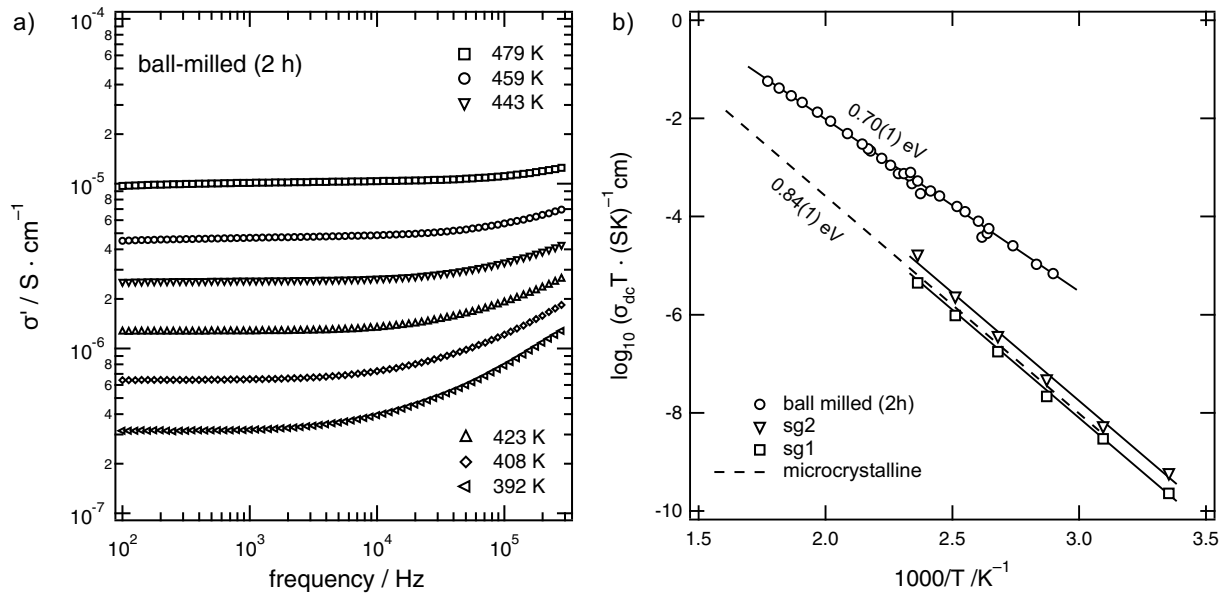


Fig. 2: a) Impedance spectra of nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared by high-energy ball milling of the microcrystalline source material in a shaker mill for 2 h. b) Temperature dependence of the dc conductivity of ball milled $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in comparison with that of nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared chemically using a sol-gel (sg) method. For comparison, the dashed line indicates the corresponding dc conductivity values of the μm -sized material which served as starting material to prepare the milled samples.

increase might be explained in terms of space charge regions similar to the situation in Ref. [15], where the anion conductivity of nanocrystalline CaF_2 prepared by inert-gas condensation was investigated. However, for the ball milled materials the influence of structural disorder introduced during mechanical treatment has to be considered when interpreting the results of the conductivity measurements. The samples prepared by ball milling for 2 h and longer yield identical conductivity values, which are by about two orders of magnitude larger than those of microcrystalline and sol-gel prepared nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Consistently, the corresponding activation energy is reduced to 0.70(1) eV, see Fig. 2b). Thus, although the crystallite size (and the interfacial area) of a sample prepared by ball milling for 2 h is comparable with that of a sol-gel prepared one, the transport parameters differ significantly. This is in agreement with the recently published ^7Li NMR and impedance spectroscopy studies on LiNbO_3 [5, 16] and LiTaO_3 [3]. In the latter case, a colossal enhancement of the ionic conductivity was found even when the material was mechanically treated for only 30 min.

Let us note for comparison that ball milled LiNbO_3 represents a structurally highly disordered material whereas a nanocrystalline LiNbO_3 sample prepared by a sol-gel method shows a high degree of crystallinity as probed by high-resolution transmission electron microscopy (TEM) and extended X-ray absorption fine structure (EXAFS) spectroscopy [5]. In particular, such structural differences can be enlightened by recording ^7Li NMR spectra taking advantage of quadrupole interactions between the quadrupole moment of the spin-3/2 nucleus with a non-vanishing electric field gradient (EFG) being present at the nuclear site [3, 5]. Significant local distortions of the site symmetry are directly reflected, e.g. in a pronounced broadening or even a disappearance of the NMR quadrupole powder pattern.

In Fig. 3 the ^7Li NMR spectra of micro- and nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ recorded at 173 K are shown. At this temperature motional narrowing of the central line width has not started yet. The mean Li jump rate at this temperature in both microcrystalline and nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (irrespective of the preparation method) is estimated to have a value much less than 10^3 s^{-1} . Therefore, at 173 K the shape of the NMR spectrum is definitely not influenced by Li motions. The spectra of the microcrystalline and the sol-gel prepared samples are partially identical (Fig. 3a)). They are both

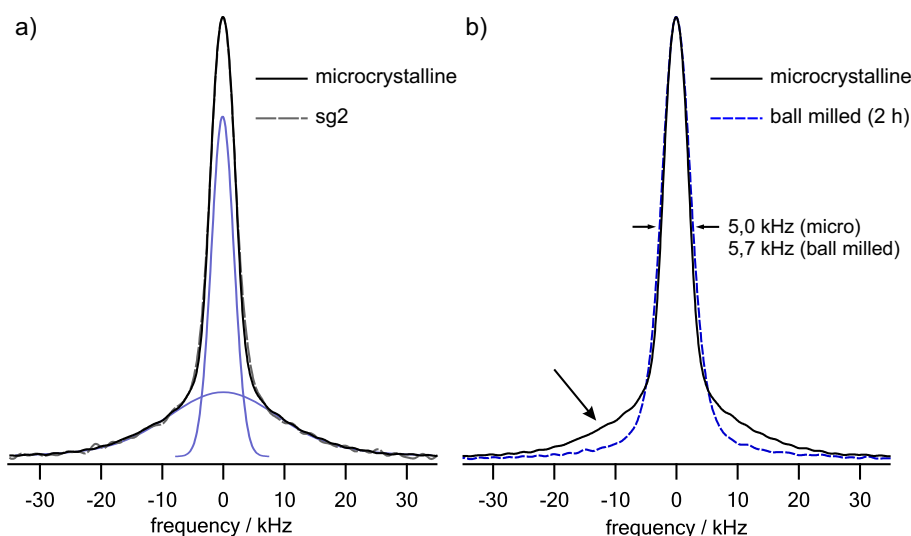


Fig. 3: a) Rigid lattice ${}^7\text{Li}$ NMR spectra of micro- and chemically prepared nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (sample sg2, see above) recorded at a resonance frequency of 155.4 MHz. At 173 K the spectrum of sg2 is a superposition of a Gaussian shaped central line and a quadrupole foot. b) Rigid lattice ${}^7\text{Li}$ NMR spectra of microcrystalline and ball milled $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (77.7 MHz). In the case of the latter one the quadrupole part (see arrow) is hardly detected indicating the presence of a very broad distribution of electrically different Li sites.

composed each of an intense central line and a less intense but broad and Gaussian shaped quadrupole part (Fig. 3a)). The shape of the latter reflects a broad distribution of EFGs present in $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In fact, in the spinel structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ the Ti^{4+} cations are randomly distributed over the 16d positions leading, according to quantum chemical calculations of the EFGs [17], to a large number of electrically different Li sites. In contrast to the ${}^7\text{Li}$ NMR spectrum of the microcrystalline source material, in the case of the mechanically treated samples this quadrupole contribution is smeared out, i.e., largely broadened, and therefore difficult to detect even when a solid echo experiment is carried out. Thus, in the case of the mechanically treated samples the quadrupole foot is additionally affected by extrinsically introduced structural disorder leading to a still broader distribution of EFGs. This is also corroborated by a slightly larger line width Δ (full width at half maximum) of the central line ($\Delta_{\text{ball milled}} = 5.7$ kHz) of the milled samples as compared to those observed for the microcrystalline as well as the sol-gel prepared samples ($\Delta_{\text{micro}} = 5.0$ kHz), respectively (see Fig. 3b)). Presumably, this observation can be attributed to a broader distribution of ${}^7\text{Li}$ chemical shifts in the mechanically treated samples.

Summary and Conclusion

Lithium transport properties in the nanocrystalline host material $\text{Li}_4\text{Ti}_5\text{O}_{12}$, prepared either chemically or mechanically, was investigated by impedance spectroscopy. Li conductivity of nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which was synthesized following a sol-gel route, strongly resembles that of the corresponding microcrystalline material. However, high-energy ball milling of microcrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for 2 h in a SPEX shaker mill leads to a highly defective material with a large number of interfacial regions and grain boundaries. The material features a Li conductivity which is by about two orders of magnitude higher than that of the source material. Milling times longer than 2 h do not cause further conductivity increase. Obviously, nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ obtained by a sol-gel process is structurally strongly related to the microcrystalline material providing no additional fast diffusion pathways for the Li cations which is, on the contrary, definitely the case for the ball milled material. It might be expected that an anode made of high-energy ball-milled $\text{Li}_4\text{Ti}_5\text{O}_{12}$ increases the rate (power) capability of an Li ion battery significantly.

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