Understanding fast ion dynamics in sodiated Li$_4$Na$_x$Ti$_5$O$_{12}$: from interfacial to extended Li$^+$ and Na$^+$ dynamics in its mixed-conducting solid solutions

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Abstract

Climate change and energy crises require the development of new sustainable materials to realise reliable electrochemical energy storage devices. Spinel-type Li$_4$Ti$_5$O$_{12}$ (LTO) is one of the most promising anode materials not only for Li-based batteries, but also for those relying on sodium. While Li$^+$ ion dynamics at the early stages of lithiation has been studied already previously, almost no data on the diffusion properties of Na$^+$ ions can be found in the literature. Here, we used nucleus-specific $^7$Li and $^{23}$Na nuclear magnetic resonance (NMR) spectroscopy to quantify the motional processes in mixed-conducting Li$_4$Na$_x$Ti$_5$O$_{12}$ with $x = 0.1$, 0.5 and 1.5 on the angstrom length scale. Most importantly, our results reveal a strong increase in Li$^+$ diffusivity in the early stages of chemical sodiation that is accompanied by a sharp decrease in activation energy when $x$ reaches 0.5. The two-component $^7$Li NMR spectra point to the evolution of an interfacial solid solution at very low sodiation levels ($x = 0.1$). At $x = 0.5$, these regions emerge over almost the entire crystallite area, enabling rapid 8a-16c-8a Li$^+$ exchange (0.4 eV), which leads to facile long-range ion transport. We direct the attention of the reader towards the initial formation of solid solutions in LTO-based anode materials and their capital impact on overall ion dynamics. In contrast to macroscopic electrochemical testing, NMR is uniquely positioned to detect and to resolve these exceptionally fast ion dynamics during the initial stages of sodiation. As these processes crucially determine the fast-charging performance of LTO-type batteries, our study lays the atomistic foundations to establish a general understanding of why two-phase materials such as LTO can act as an impressive insertion host for both Li and Na ions.

1. Introduction

Electrochemical energy storage devices, which power mobile phones or notebooks, are an integral part of daily life in industrialised countries [1–3]. Lithium batteries of various types and sizes are employed in many fields of electric storage ranging from mobile to stationary necessities. In particular, these fields do also include the transport sector, for which powerful large-scale systems are needed [4–7]. A gradual exhaustion of the world’s lithium resources in the future, however, gives rise to thought about replacing Li as the ionic charge carrier in some of these systems. In particular, such considerations will affect the development of stationary, high-volume electrical storage systems. A highly abundant and, therefore, low-cost alternative would be sodium, Na.

Since the early stages of battery research, devices relying on ions such as Li$^+$ or Na$^+$ have been investigated in parallel. The commercialization of the first lithium-ion battery by Sony in 1991 [8, 9] led, however, to a slowing down of research on Na-ion batteries. In the future, the market of the aforementioned
large-scale systems that store electricity for the power grid is expected to be dominated by more eco-friendly sodium-based rechargeable batteries [10, 11].

Many earlier studies focused on the development and characterization of Na-bearing cathode materials, such as Na2CoO3 or Na3V2(P2O7)3/C, while others explore new anode materials [12–14]. Some of the established anode materials, such as hard carbon and Na3Ti2O7, may, however, suffer from low insertion potentials and, therefore, raise the risk of undesired sodium plating at the electrode surface [15–17]. Well known from lithium-ion batteries and most famous for its zero-strain properties is the pentatitanate Li4Ti5O12 (LTO) [18]. LTO entered the spotlight of battery research as a very powerful anode material many years ago [18–21].

Spinel-type LTO crystallizes with cubic symmetry (Fd3m). According to the Wyckoff notation, the general formula is given as follows [Li]a/8[Li2/3Ti5/3]a/16[O4]a/32, with the lithium ions fully occupying the 8a (tetrahedral) and partly occupying the 16d (octahedral) sites [22–24]. The 16d sites are mainly populated by the Ti4+ ions in a random fashion. During lithium insertion, the ions entering the structure are placed on the empty 16c (octahedral) sites immediately causing 8a-16c Li+–Li+ repulsive interactions. Hence, Li ions originally residing on the 8a positions are pushed to the vacant 16c sites [24]. Finally, rocksalt-type LTO, [Li2]a/16[Li2/3Ti5/3]a/16[O4]a/32 [25, 26] is formed if x in Li4+xTi5O12 reaches x = 3. Li+ ions on 16d positions are to be regarded as much less mobile than those on 8a and 16c [23]. These sites are expected to trap Li vacancies [27].

Upon electrochemical sodiation, a multi-step insertion process is suggested [28] that includes the formation of the sodium-rich Na4Li3Ti2O12 ([Na2]a/16[Li2/3Ti5/3]a/16[O4]a/32) phase and, simultaneously, the generation of Li-rich Li3Ti2O5. Hence, at least three phases altogether are assumed to be involved in the overall insertion process: LTO, Li7Ti5O12 and Na4Li3Ti2O12. Again, the occupation of the formerly vacant 16c sites by Na+ is accompanied by a shift of Li+ from 8a to 16c, leaving behind the vacant 8a sites [28, 29]. At this stage we should not underestimate the role of a cation-mixed solid solution, (Li3Na2)8/16LiTi16/16O4. Indeed, in situ x-ray diffraction points to the possible involvement and interfacial formation of such regions [30]. Moreover, transmission electron microscopy investigations of sodiated polycrystalline and single-crystalline LTO do not only show the coexistence of the aforementioned phases but also reveal the growth of a Na-rich phase starting from the surface to the inner region of a particle [31]. Lattice disorder has been observed along the surface of the two-phase system leading to local strain, dislocations and further defects extending over a region of ca. 15 Å in width [31].

Another study points towards the formation of a sodium-poor phase, that is, [Na]a/8[Li2/3Ti5/3]a/16[O4]a/32, which is suggested to be formed at intermediate to high Na-extraction rates ranging from 1 to 10 C. Due to the small volume changes between the sodium-poor and the sodium-rich phase, the synthesis and the use of this phase is expected to enable strain-free cycling of LTO-based sodium-ion batteries [32].

The present study aims at shedding light on the ion-specific Li+ and Na+ dynamic parameters governing overall ionic transport in mixed-conducting samples of LTO, which we prepared by chemical sodiation. We used 7Li and 23Na nuclear magnetic resonance (NMR) spectroscopy [33, 34] to quantify the elementary steps of ion hopping in Li4+xTi5O12 samples differing in Na composition (x = 0.1, 0.3 and 1.5). NMR is a uniquely positioned method to selectively study ion dynamics of the distinctly mobile ion charge carriers in LTO [35–40]. It helped us to identify any interrelations of cation dynamics in these mixed-conducting samples that also reveal clear electronic conduction properties. Such interrelations, or ion–ion correlations, have scarcely been touched in literature from a spectroscopic point of view providing information on the angstrom length scale. We will show that Na insertion greatly changes the Li+ diffusivity already at very low insertion levels of x = 0.1 and x = 0.5. Our NMR study provides both dynamic and mechanistic details which usually remain undetectable by employing macroscopic electrochemical testing of LTO-based insertion hosts.

2. Experiment

2.1. Starting material
Polycrystalline LTO, EXM 1037 purchased from SüdChemie AG, was mechanically treated to reduce the grain size of the initially microcrystalline powder. To obtain the nanocrystalline samples studied, we used high-energy ball milling (Fritsch Pulverisette 7 planetary mill, 5 mm ZrO2 balls, ZrO2 beaker (40 ml))). Milling was carried out in ethanol at rotational speeds of 600 rounds per minute for a duration of 200 min. Prior to the milling procedure, the powder obtained was dried at ambient conditions before stripping Li2CO3 residues from the particles at 573 K under vacuum. Any further handling of the samples was carried out in an Ar-filled glovebox (MBrann MB-G 200), that is, under strict inert gas atmosphere.

The corresponding x-ray powder diffraction (XRD) profile has already been presented elsewhere, as the same unsodiated LTO powder was used in an earlier study [41], see also for experimental details. XRD pointed to a highly pure starting material; 7Li NMR spectra, described below, revealed a slight contamination.
with Li$_2$TiO$_3$ that is almost invisible for XRD. We could not detect any other side phases or impurities of untreated LTO (see figure S1). Milling does not change the crystal structure; there are no mechanical transformations observed except those related to the broadening of the reflections due to size effects and were possibly strain introduced. Additionally, the low sodiation contents have only marginal influence on the positions of the Bragg reflections.

2.2. Sodiation procedure
Dimethoxyethane (DME), supplied by Fluka Chemicals, was mixed with Biphenyl in stoichiometric amounts to yield 1 M biphenyl-1,2-dimethoxythane. To form a dark blue sodiating agent, approximately 2.3 g of sodium metal were added to 100 ml of the aforementioned 1 M biphenyl-DME solution. LTO was immersed into the solution at a specific molar ratio to obtain different sodiation levels. The calculated ratios were 0.1:1, 0.5:1 and 1.5:1 mol Na per mol LTO, hereafter referred to as $x = 0.1$, 0.5 and 1.5. The sodiation was carried out by stirring LTO in the reducing medium for several hours. The higher the sodium content, the more titanium ions get reduced, resulting in a darkening of the blue colour. Unless the sodiating agent is used in excess, the completion of the sodiation process is indicated by the reagent fading in colour. To remove all reagent residues, the sodiated powder was washed three times with DME and afterwards dried in a vacuum for 24 h. The Na content was verified by inductively coupled plasma emission spectroscopy; the standard deviation turned out to be 10%. The final sodiated LTO samples were then fire-sealed in quartz tubes with a length of approximately 2 cm. Quartz wool was used to centre the powder sample in the tube and to prevent it from heating during the sealing process.

2.3. NMR investigations
NMR measurements were carried out using an Avance III spectrometer (Bruker) that is connected to an Ultrashield 500 MHz widebore magnet with a magnetic field of 11.7 T. This field corresponds to Larmor frequencies of $\omega_0/2\pi = 194$ MHz and $\omega_0/2\pi = 132$ MHz for $^7$Li and $^{23}$Na, respectively. At a constant power output of 200 W, the $\pi/2$ pulse lengths varied with temperature in a range from 2 to 4.8 $\mu$s for $^7$Li and from 2.2 to 2.9 $\mu$s for $^{23}$Na. $^{23}$Na and $^7$Li NMR spin-lattice relaxation (SLR) rates, $1/T_1 = R_1$, were acquired with the well-known saturation recovery pulse sequence, $10 \times \pi/2 - t_d - \pi/2$ - acquisition (acq.) [42]. The variable delay time ($t_d$) was chosen such that the complete magnetization transients $M_z(t_d)$ were probed. The transients were either analysed with a single exponential $M_z(t_d) \propto 1 - \exp(-t_d/T_1)\gamma$ or with a sum of two non-stretched exponentials. The stretching factor $\gamma' = \gamma_1$ ranged from 1 to 0, whereby $\gamma_1 = 1$ yields non-stretched functions.

Additionally, spin-lock SLR NMR measurements [33], were performed to investigate the temperature dependence of the corresponding $^7$Li NMR rate $1/T_1\rho \equiv R_1\rho$. This technique, $\pi/2 \rho(t_{\text{lock}}) - \text{acq.}$, features a variable spin-lock pulse $\rho(t_{\text{lock}})$ and was introduced by Ailion and Slichter [42–45]. To ensure comparability, the spin-locking frequency, $\nu_{\text{lock}}$, was set to 33.3 kHz for all experiments. Transversal magnetization transients $M_\rho(t_{\text{lock}})$ recorded as a function of the locking pulse length $t_{\text{lock}}$ were analysed with stretched exponentials according to $M_\rho(t_{\text{lock}}) \propto \exp\left(-t_{\text{lock}}/T_{1\rho}\gamma\right)$, $\gamma = \gamma_{1\rho}$ (see below).

$^6$Li magic angle spinning (MAS) NMR spectra were recorded using a 2.5 mm probe (Bruker) at a spinning frequency of 30 kHz. We accumulated 128 scans to obtain a single 1D NMR spectrum. To ensure full longitudinal relaxation of all magnetization components, the recycle delays were set to 600 s. Solid LiCl served as a reference to determine the NMR chemical shifts $\delta_{CS}$.

3. Results and discussion
3.1. $^7$Li NMR spectra and motional narrowing of the central transition
Recording $^7$Li (spin–quantum number $I = 3/2$) NMR lines as a function of temperature gives first insights into the structural, electric and dynamic features of the samples with their varying Li content. In figure 2 the $^7$Li NMR spectra of LTO samples with $x = 0.1$, $x = 0.5$ and $x = 1.5$ are shown. At low temperatures, that is, at 298 K, the line of Li$_x$Na$_{1-x}$Ti$_2$O$_{12}$ is composed of a broad component (III) that mirrors the so-called quadrupole transitions ($\pm 3/2 \leftrightarrow \pm 1/2$) of a powder sample [46–48]. This signal is superimposed by the central line ($\pm 1/2 \leftrightarrow \pm 1/2$) that is mainly broadened because of homonuclear Li–Li magnetic dipolar interactions (signals I and II). Sufficiently rapid $^7$Li exchange processes, characterised by jump rates $1/T_{\text{NMR}}$ in the kHz range, increasingly average these interactions with temperature [49]. This averaging process causes the central line to narrow, as is clearly seen figure 2(a). At temperatures at which $1/T_{\text{NMR}}$ reaches or exceeds the order of the width (full width at half maximum, FWHM) of the quadrupole component, the broad line (III) of the overall signal starts to narrow also. This narrowing process sets in at approximately 373 K (see figure 2(a)).
3.2. Very low sodiation levels \((x = 0.1)\): formation of an interfacial solid solution

Most importantly, the central line of \(\text{Li}_2\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}\) (figure 2(a)) reveals a so-called two-component narrowing process (see also the inset of figure 2(a)). We recognise that at 373 K the central transition is composed of two contributions (I and II). The narrow line (I) on top of the broader one (II) reflects \(\text{Li}^+\) ions being much more mobile than the majority of \(\text{Li}^+\) ions in LTO. Importantly, a non-sodiated sample (see the respective inset in figure 2(a)) does not show this component (see also below). Hence, we safely conclude that the introduction of \(\text{Na}^+/e^-\) significantly changes the \(\text{Li}^+\) diffusion properties of LTO.

Assuming that the \(\text{Na}^+\) ions occupy the empty 16c sites in the LTO framework, the neighbouring \(\text{Li}^+\) ions on 8a, which are connected to 16c by face sharing, are immediately subjected to strong Coulomb repulsions. To escape from the 8a site, \(\text{Li}^+\) jumps to the next empty 16c site. Again, on the new position it senses strong \(\text{Li}_{12}\text{Li}_{16c}\) interactions. Altogether, these local repulsions result in an overall frustrated situation [35] that gives rise to both strongly enhanced local and long-range \(\text{Li}^+\) ion dynamics, see below [22, 50]. The same 8a-16c diffusion pathway would be opened if \(\text{Na}^+\) kicks off the \(\text{Li}^+\) ions on 16d. The former 16d ions would occupy empty 16c sites leading to the same frustrated \(\text{Li}^+\) cation arrangement.

As has been shown for \(\text{Li}_3\text{[LiTi]}\text{O}_{12}\) through 2D \(^{6}\text{Li}\) MAS NMR exchange spectroscopy [23], the \(\text{Li}\) ions on 16d are much less mobile than those on 8a. Hence, we conclude that, also in the present case, the motional narrowing in \(\text{Li}_2\text{Na}_x\text{[LiTi]}\text{O}_{12}\) with \(x = 0.1\) is indeed predominantly governed by rapid 8a-16c \(\text{Li}^+\) exchange processes driven by the strong Coulomb interactions [35].

The situation seen for \(\text{Li}_4\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}\) is, however, not entirely comparable to that seen for \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) by some of us earlier [22]. In \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) the whole \(^7\text{Li}\) NMR line is affected by the doping effect, giving rise to the formation of a solid solution at low \(x\) values [22]. Here, we see that the central \(^7\text{Li}\) NMR line of \(\text{Li}_4\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}\) is composed of two contributions (I and II). The broader line labelled II reflects the untouched LTO phase. Hence, not all of the ions in \(\text{Li}_4\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}\) have access to fast exchange processes. The diffusion properties of most of them remain unaffected. This two-component line shape points to a segregation [24] of \(\text{Na}\) ions, most likely in the outer spheres, that is, in the interfacial regions of the particles (see the illustration in figure 2(b)). We still tend to ascribe the narrow line (I) to those ions located in a solid-solution-like region rather than to those residing in phases such as \(\text{Na}_6\text{[LiTi]}\text{O}_{12}\) and \(\text{Li}_7\text{[LiTi]}\text{O}_{12}\) [28]. These \(\text{Li}\)-rich [51] and \(\text{Na}\)-rich phases do not provide fast \(\text{Li}^+\) ions, which will be discussed below.

For comparison and to put the present results into a broader context, two-component NMR line shapes have frequently been observed for a number of nanocrystalline ceramics that can be described by core–shell features with fast \(\text{Li}\) ions in the interfacial regions and slower ones in the crystalline bulk areas [52–54]. In contrast to these systems studied so far, the unsodiated, nanocrystalline LTO sample does not show such a two-component feature. Thus, as mentioned above, the narrow line shows up only when \(\text{Na}\) is inserted, which switches on cation–cation repulsions mainly involving the face-sharing 8a and 16c \(\text{LiO}_6\) polyhedra (see figure 1(b)).

3.3. \(\text{Na}^+\) insertion levels \((x = 0.5)\): spatially extended solid-solution region through internal lithiation

For \(x = 0.5\), the aforementioned situation of cation–cation repulsions escalates even more. In agreement with enhanced \(\text{Li}_{8a}-\text{Li}_{16c}\) dynamics due to increasing cation–cation \(\text{Li}^+-\text{Li}^+\) and \(\text{Li}^+-\text{Na}^+\) repulsions, we observe that the \(^7\text{Li}\) NMR lines are subjected to strong motional narrowing effects (see figure 2(b) and its inset). To visualise these changes a better way, we plotted the FWHM of the three samples together with those of the unsodiated, microcrystalline LTO sample as a function of temperature (see figure 3). While motional
narrowing of microcrystalline (and nanocrystalline) unsodiated LTO starts at relatively high temperatures, i.e. slightly below 400 K, the curve of the sample with \( x = 0.1 \) and especially that belonging to the sample with a Na content of \( x = 0.5 \) are clearly shifted towards lower temperatures. For \( x = 0.5 \) motion-induced narrowing of the central line does already start at a temperature below 300 K, indicating extremely fast Li\(^+\) ion dynamics at these early stages of LTO sodiation. A separation into the lines I and II, as has been possible for lithiated LTO, but less pronounced [12], is shown at the top illustrate the formation of interfacially located solid-solutions (see figure 1(a)), extended solid solutions (see figure 1(b)) and the formation of a mixed material with solid-solution regions and the phases Li\(_5\)Ti\(_3\)O\(_12\) and Na\(_6\)Li\(_5\)Ti\(_3\)O\(_12\) (figure 1(c)). Fast Li\(^+\) ion dynamics is either found in the interfacial regions or in areas with solid-solution like (Na\(^{+}\), Li\(^{+}\)) mixed regions offering rapid 8a-16c-8a jump processes. See text for further explanation and details.

Here, we assume that the Na ions entering the structure, dislodge the Li\(^{+}\) ions and force them to occupy sites farther away from the surface regions. This internal lithiation process results in extended areas with fast Li\(^+\) diffusion. In this sense, Li\(^+\) hopping essentially follows the principles of an interstitialcy diffusion mechanism involving the regular site 8a and the interstitial site 16c [35], as illustrated in figure 3(b).

Li\(^+\) diffusivity in Li\(_{1-x}\)Na\(_x\)Ti\(_3\)O\(_12\) is high enough to average the site-specific electric quadrupole interactions. Consequently, the corresponding quadrupolar NMR signal (III) disappears at higher \( T \). Most likely, the rapid Li\(^+\) ions sense an averaged, almost vanishing electric field gradient and are no longer exposed to quadrupole interactions giving rise to a large (mean) coupling constant. This behaviour has also been observed for lithiated LTO, but less pronounced [22].

As a side remark, the drastic increase in Li\(^+\) diffusivity upon sodiation of LTO is exactly the opposite of what is seen for so-called mixed alkali glasses [55–60]. In glasses with a single charge carrier, such as Li\(^{+}\), a strong decrease in ionic conductivity is observed when a second one, e.g. Na, is added.

### 3.4. The multiphase regime at higher sodiation levels

For \( x = 1.5 \) the overall situation changes again. We observe a less pronounced NMR line-narrowing process at low \( T \), see figure 2(c). The corresponding motional narrowing curve shifts back to higher temperatures (figure 3). This observation shows that Li\(^{+}\) ion diffusivity slows down again. We explain this decrease in Li\(^+\) diffusivity by considering the following aspects. While Na ions on 16c destabilise Li\(^{+}\) on 8a leading to rapid frustration-driven Li exchange processes, at the same time the Na\(^{+}\) ions might block the 8a-16c-8a jump pathway if we assume a lower diffusivity of Na\(^+\) as compared with Li\(^{+}\). Indeed, a lower diffusivity is seen by \(^{23}\)Na NMR line shape measurements, as will be discussed below. The more Na ions enter the structure, the more 8a-16c-8a pathways, needed for through-going ion transport and effective averaging of the dipolar interactions, get blocked in the Na-rich regions of the solid solutions.

Figure 2. Evolution of the \(^7\)Li NMR spectra (194 MHz) of Li\(_{1-x}\)Na\(_x\)Ti\(_3\)O\(_12\) (\( x = 0.1, 0.5, 1.5 \)) with temperature. The spectra were recorded under static conditions at the temperatures indicated. Insets show selected spectra to identify region III, indicating the quadrupole intensities, as well as regions II and I belonging to the central transitions. The spectrum of LTO (see inset in figure 1(a)) was recorded at 116 MHz, which represents the NMR signal of unsodiated LTO, for comparison. The schematics shown at the top illustrate the formation of interfacially located solid-solutions (see figure 1(a)), extended solid solutions (see figure 1(b)) and the formation of a mixed material with solid-solution regions and the phases Li\(_5\)Ti\(_3\)O\(_12\) and Na\(_6\)Li\(_5\)Ti\(_3\)O\(_12\) (figure 1(c)). Fast Li\(^+\) ion dynamics is either found in the interfacial regions or in areas with solid-solution like (Na\(^{+}\), Li\(^{+}\)) mixed regions offering rapid 8a-16c-8a jump processes. See text for further explanation and details.
Lithiated LTO segregation effects, possibly also including the formation of nm-sized domain structures, are known for earlier continuously subdivides into a Na-rich and a Li-rich region upon sodiation, as has also been suggested that the diffusion barriers probed by NMR (see below) are independent of the insertion route. Effect on ion dynamics: it might block rapid diffusion pathways but could also open slower ones. Ions fully occupy the 16c sublattice leaving behind an empty 8a lattice. The Li-rich phase is Li$_8$[LiTi$_2$O$_{12}$]. As we showed earlier, the Li$^+$ diffusivity in this Li-7 phase, which is also formed when Li$_{4+x}$Ti$_2$O$_{12}$ is lithiated up to $x = 3$, is much lower than in the original Li-4 phase [22, 23, 50, 51]. Its NMR motional narrowing

At this insertion stage, we cannot exclude the involvement of other, alternative Li$^+$ diffusion pathways chosen by the ions. For example, it is possible that the empty tetrahedral sites 48f and 8b get involved in overall diffusion. The connection of these polyhedra with the Li bearing sites is illustrated in figure 1. While 8b is only connected to 8d (octahedral site) via face sharing, the 48f site is connected, again via face sharing, to both the Li 16c and the Li 16d sites, see below. Thus, the 48f site could indeed act as a suitable transition site to enable slow 16c-16d exchange processes coming into play at high x values. Such processes are expected to be characterised by higher activation energies than the 8a-16c-8a Li$^+$ jump process. Earlier results from NMR and broadband conductivity point in this direction [61]. Moreover, the stepwise decay of the $^7$Li NMR line width with increasing temperature (see figure 3) could indeed serve as an argument for several diffusion pathways the Li$^+$ ions have access to in sodiated LTO. This behaviour, which includes a large distribution of activation energies, is in contrast to that of lithiated LTO. For lithiated LTO such steps in the NMR narrowing curves are absent [22]. This absence shows that, in comparison to lithiation, Na insertion has a two-fold effect on ion dynamics: it might block rapid diffusion pathways but could also open slower ones.

Besides a possible Na ion blocking effect that might occur at sufficiently high values of $x$ we showed earlier, the Li$^+$ sites generated through sodiation; lattice expansion due to Na insertion leads to a compensating effect for $x = 1.3$ as the Na–Na distance increases. The curves of Li$_4$Ti$_2$O$_{12}$ and LTO (coarse grained samples) are shown for comparison; the same holds for the curve referring to the $^{23}$Na NMR line widths ($x = 1.5$). See text for further explanation.

**Figure 3.** (a) $^7$Li NMR motional line narrowing of sodiated Li$_x$Na$_y$Ti$_2$O$_{12}$, with $x = 0$, 0.1, 0.5 and 1.5. For the sample with $x = 0.5$, pronounced averaging of the dipolar interactions between the spins sets in at approximately $T = 300$ K. The final line widths are connected to the field inhomogeneity of the external magnetic field. The FWHM of the sample with $x = 0.1$ is governed by the sharp line on top of the broader resonance. In both cases we recognise a slightly stepwise narrowing behaviour that points to several diffusion pathways consecutively activated in sodiated LTO. For $x = 1.5$ the curve shifts back to higher temperatures. Most likely, the formation of Na-rich and Li-rich phases start to influence the overall FWHM values. These phases do not provide rapid Li$^+$ diffusion pathways. Any blocking effect of 16c Na$^+$ ions on the 8a-16c-8a diffusion pathway might play a role, too. At the inflexion point ($T = 325$ K) the mean Li$^+$ jump rate in Li$_8$Na$_{0.5}$Ti$_2$O$_{12}$ is in the order of 5.8 kHz $\times$ $2\pi \approx 3.6 \times 10^{-3}$ s$^{-1}$. A value of 5.8 kHz refers to the line width in the rigid lattice regime ($T \rightarrow 0$ K, $x = 0.5$). The inset shows the change in FWHM of the $^{23}$Na NMR line. (b) The same data as in (a) but normalised with respect to the rigid lattice value of FWHM. This value of FWHM increases with increasing amount of Ti$^{4+}$ centres generated through sodiation; lattice expansion due to Na insertion leads to a compensating effect for $x = 1.3$ as the Na–Na distance increases. The curves of Li$_4$Ti$_2$O$_{12}$ and LTO (coarse grained samples) are connected to the field inhomogeneity of the external magnetic field. The FWHM of the sample with $x = 0.1$ is governed by the sharp line on top of the broader resonance. In both cases we recognise a slightly stepwise narrowing behaviour that points to several diffusion pathways consecutively activated in sodiated LTO. For $x = 1.5$ the curve shifts back to higher temperatures. Most likely, the formation of Na-rich and Li-rich phases start to influence the overall FWHM values. These phases do not provide rapid Li$^+$ diffusion pathways. Any blocking effect of 16c Na$^+$ ions on the 8a-16c-8a diffusion pathway might play a role, too. At the inflexion point ($T = 325$ K) the mean Li$^+$ jump rate in Li$_8$Na$_{0.5}$Ti$_2$O$_{12}$ is in the order of 5.8 kHz $\times$ $2\pi \approx 3.6 \times 10^{-3}$ s$^{-1}$. A value of 5.8 kHz refers to the line width in the rigid lattice regime ($T \rightarrow 0$ K, $x = 0.5$). The inset shows the change in FWHM of the $^{23}$Na NMR line. (b) The same data as in (a) but normalised with respect to the rigid lattice value of FWHM. This value of FWHM increases with increasing amount of Ti$^{4+}$ centres generated through sodiation; lattice expansion due to Na insertion leads to a compensating effect for $x = 1.3$ as the Na–Na distance increases. The curves of Li$_4$Ti$_2$O$_{12}$ and LTO (coarse grained samples) are shown for comparison; the same holds for the curve referring to the $^{23}$Na NMR line widths ($x = 1.5$). See text for further explanation.
Figure 4. (a) $^6$Li 1D exchange NMR spectra of lithiated Li$_{4+x}$Ti$_5$O$_{12}$. The spectra were taken from literature and refer to a microcrystalline sample [23]. Here, they serve for a comparison with the $^6$Li spectra of sodiated LTO. (b) $^6$Li 1D exchange NMR spectra of sodiated Li$_{4+x}$Ti$_5$O$_{12}$, this work. The first spectrum is identical to that on the left side. Values in ppm indicate the chemical shifts $\delta_{CS}$ of the individual NMR lines. Solid lines show the deconvolution of the total signal with appropriate Voigt functions. See text for further details.

curve [22] is added in figure 2(b) for comparison. In pure Na$_6$[LiTi]O$_{12}$, Li$^+$ occupies only the 16$d$ sites that we identified as those sites that do not take part in rapid exchange processes (see above). Thus, in both phases, Na$_6$[LiTi]O$_{12}$ and Li$_6$[LiTi]O$_{12}$ [50, 51], we suspect the Li ions on 16$c$ and on 16$d$ to be much less mobile than those on 8$a$, that is, in the solid solutions of Li$_3$Na$_x$[LiTi]O$_{12}$ ($x < 1$).

Taken together, the sample characterised by $x = 1.5$ is, most likely, a mixture of at least three regions: the solid solution Li$_3$Na$_x$[LiTi]O$_{12}$ as well as the phases Li$_6$[LiTi]O$_{12}$ and Na$_6$[LiTi]O$_{12}$. The $^7$Li NMR line observed is thus a superposition of various NMR lines reflecting the Li ions in the individual phases. Na ion blocking effects and phases with poor Li$^+$ diffusivity lead effectively to a decrease in overall Li$^+$ diffusivity for $x = 1.5$. The small schematics included in figure 2 help illustrate the evolution of these phases upon sodiation.

3.5. 1D $^6$Li MAS NMR revealing fast 8$a$ Li ions

To support our conclusions on ion dynamics drawn, so far, from variable-temperature NMR line shape measurements, we recorded high-resolution 1D $^6$Li MAS NMR spectra to resolve the Li ions in the various phases and their distinct, site-specific dynamic properties (figure 4). The corresponding spectrum of LTO is composed of two lines [23, 63]. The ratio of the areas under the lines reflect the 8$a$ and 16$d$ occupation levels. No other sites are occupied in unsodiated LTO by Li$^+$. The signal around $-0.85$ ppm reveals a tiny amount of Li$_2$TiO$_3$, as has been discussed elsewhere [64]. This signal is also seen in the spectra shown in figure 4(b), slightly shifted towards $-0.95$ ppm (see arrows).

Upon sodiation ($x = 0.1$), we recognise that the line mirroring the 8$a$ ions reduces in line width. Hence, besides elimination of the dipolar couplings through external MAS, internal exchange processes lead to further averaging of the residual dipolar broadening. Despite these effects, the line clearly resembles that of
unsodiated LTO, supporting our interpretation that a surface-related Na-bearing solid-solution is formed at such low sodiation levels. At \( x = 0.1 \), many of the Li\(^+\) ions in the bulk regions do not sense the effect of Na\(^+\) on 16c.

Increasing \( x \) from 0.1 to 0.5 changes this situation drastically. The NMR line representing Li\(^+\) on 8a is further narrowed revealing a strong elimination of dipolar interactions through rapid 8a-16c exchange processes. Li\(^+\) ions on 16c give rise to a rather broad, and thus, less intense signal at negative ppm values, as they experience Fermi contact hyperfine interactions with the Ti\(^{3+}\) centres generated. This feature is not shown here as it has been discussed for heavily lithiated LTO elsewhere [23]. Furthermore, we clearly see that significant 16c-16d Li\(^+\) exchange is absent as we still observe an almost untouched 16d NMR signal that is not affected by any coalescence effects. This finding is in excellent agreement with the earlier \(^6\)Li 2D MAS NMR experiments mentioned above [23]. The \(^6\)Li NMR signal of Li\(_2\)Na\(_0.5\)Ti\(_2\)O\(_5\) is almost identical with that of Li\(_{4.3}\)Ti\(_3\)O\(_{12}\) [23], for which extremely fast 8a-16c Li\(^+\) exchange has been probed.

Increasing \( x \) in Li\(_2\)Na\(_x\)Ti\(_4\)O\(_{12}\) further does not change the \(^6\)Li NMR spectrum much. Li in Li\(_2\)Ti\(_3\)O\(_{12}\) produces a broadened signal shifted toward negative ppm values (not shown here for the sake of clarity). The Li\(^+\) ions on 16d remain rather immobile on the NMR time scale. Hence, the \(^6\)Li NMR spectrum referring to a value of \( x = 1.5 \) reflects the rather mobile Li\(^+\) ions in the remaining solid-solution areas. Again, the narrow NMR line belonging to Li on 8a governs the overall signal; this line dominates the line recorded under static conditions (see figures 2(c) and 3). The intensity near 1 ppm might indicate the marginal occupation of a new Li site other than 8a and 16c (see arrows).

### 3.6. Diffusion-induced \(^7\)Li SLR rates

To quantify our results in terms of mean activation energies that the Li\(^+\) ions have to surmount while diffusing, we carried out variable-temperature \(^7\)Li NMR SLR measurements. Such measurements sense the temporal magnetic spin fluctuations to which the ions are subjected to because of self-diffusion processes. These fluctuations are, roughly speaking, characterised by motional correlation rates \( 1/\tau_c \) on the MHz time scale. According to classical relaxation theory [37], the NMR rate \( 1/T_1(1/T) \), which is proportional to \( 1/\tau_c \), passes through a characteristic diffusion-induced rate peak whose flanks entail information on long-range (high temperature regime) and short-range (low-temperature regime) ion dynamics [51, 65, 66]. In the case of ordinary \( 1/T_1 \) NMR measurements, the slope of the so-called low-\( T \) flank is sensitive to local ion dynamics [67]. Here, the coupling of the spins with the paramagnetic Ti\(^{3+}\) centres [22] does, however, govern the rates and masks any diffusion-induced contributions, which results in a weaker-than-activated temperature behaviour (see figure 5(a)). At temperatures below 300 K the longitudinal \(^7\)Li NMR transients show even biexponential behaviour, which could either be a result of longitudinal relaxation driven by electric quadrupolar interactions [68, 69] or, at least for \( x = 0.1 \), originate from fast and slow spin reservoirs, as suggested by the \(^7\)Li NMR lines.

When switching to spin-lock \( 1/T_{1\rho} \) NMR, which is sensitive to spin fluctuations with rates in the kHz range, the diffusion-induced contributions dominate the primary NMR observable \( 1/T_{1\rho} \), now giving access to the so-called low-\( T \) flank of the respective \( 1/T_{1\rho}(1/T) \) peak. At low \( T \), non-diffusive background relaxation due to coupling with parametric centres (Curie–Weiss behaviour [70]) influence the experiments, while the rates \( 1/T_{1\rho} \) pass into the Arrhenius-type regimes at sufficiently high temperature. The lower this crossover temperature, the higher the Li\(^+\) diffusivity in Li\(_2\)Na\(_x\)Ti\(_3\)O\(_{12}\). We clearly see that, as compared to unsodiated LTO (\( x = 0 \)), which has also been milled for 200 min in ethanol, the flank of Li\(_{4.3}\)Ti\(_3\)O\(_{12}\) is shifted towards a much lower crossover temperature. Simultaneously, the activation energy reduces from ca. 0.89 eV in pure LTO to 0.6 eV in the sodiated form. Worth mentioning, is that the spin-lock experiments do not point to two magnetically decoupled spin reservoirs, as might be expected from the two-component line shape of this sample. Hence, we conclude that effective spin-diffusion affects the underlying transversal transients, which can be very well approximated with stretched exponentials. The corresponding stretching factors \( \gamma_\rho \) are shown in the upper graph of figure 5(b).

The \( 1/T_{1\rho} \) NMR flank of the sample characterised by \( x = 0.5 \) reveals a further decrease in slope resulting in an activation energy as low as approximately 0.4 eV. We recognise that the corresponding rates pass through a shallow maximum at \( T_{\text{max}} = 390 \text{ K} \). At this temperature the mean motional correlation rate \( 1/\tau_c \) is given by [66] \( 1/\tau_c \approx 2\omega_1 \) with \( \omega_1/2\pi = 33.3 \text{ kHz} \), thus, resulting in a jump rate \( 1/\tau \approx \pi/\tau_c \) of \( 4.2 \times 10^5 \text{ s}^{-1} \).

The fact that we cannot detect a clear peak maximum in \( 1/T_{1\rho}(x = 0.5) \) could be explained by considering a superposition of several diffusion processes taking place between the available Li sites in LTO. This behaviour is in contrast to that seen for lithiated LTO where the rate \( 1/T_{1\rho} \) passes through a rate peak already at 350 K [22].

Increasing \( x \) to \( x = 1.5 \) slows Li\(^+\) diffusion down again. The corresponding flanks belonging to Li\(_{4.3}\)Ti\(_3\)O\(_{12}\) shift back to higher temperatures. Simultaneously, their temperature behaviour becomes quite complex, likely revealing two temperature regimes pointing to activation energies of 0.29 eV and...
0.37 eV, respectively (see figure 5(b)). This behaviour points to the assumption that at high levels of $x$, the ions increasingly have access to further sites, and thus, diffusion pathways; figure 6(a) shows the connectivities of the (interstitial) octahedral and tetrahedral voids in LTO. Note that a value of 0.29 eV would be in agreement with local Li$^+$ exchange processes [22, 27].

Interpreting the $^7$Li NMR response of this sample is further complicated by the fact that we have to take into account the following heteronuclear spin interaction. The Li spins in this sample, most likely, do not only sense their own spin-fluctuations but also those of the $^{23}$Na spins and vice versa. For $^{23}$Na ($I = \frac{3}{2}$), with its large electric quadrupole moment, we expect strong electric quadrupolar interactions that will also govern NMR relaxation of the $^7$Li nuclei. Indeed, the absolute values of the corresponding $1/T_1$ of $^{23}$Na NMR rates exceed the rates $1/T_1$ of $^7$Li by several orders of magnitude (see figure 6(b)).

3.7. $^{23}$Na NMR: SLR and line shapes

Here, the $^{23}$Na $1/T_1$ NMR transients of Li$_4$Na$_{1.5}$Ti$_5$O$_{12}$ are clearly composed of two contributions, leading to two NMR rates $1/T_{1,fast}$ and $1/T_{1,slow}$ (see figure 6(b)). Fast $^{23}$Na NMR relaxation, characterised by an activation energy of 0.48 eV, likely mirrors Na$^+$ exchange according to the Na$^+$ pathway 16c-8a-16c′. The corresponding $^{23}$Na NMR line shapes are shown in figure S2. They reveal the beginning of motional narrowing at temperatures higher than 300 K (see also figure 3(a)).

The rate $1/T_{1,slow}$, on the other hand, passes through a rate maximum located at $T_{max} \approx 390$ K. We tend to ascribe this feature to a $^{23}$Na NMR relaxation process that is indirectly controlled by fast Li$^+$ jumps that occur in the direct neighbourhood of the Na$^+$ centres. Most likely, this diffusion-induced rate peak is caused by the localised but rapid Li$^+$ 8a-16c forward-backward jump processes in the vicinity to a 16c site that is occupied by Na$^+$. Again, the corresponding activation energy of 0.24 eV is comparable to that probed by $^7$Li spin-lock NMR (0.29 eV, see above) and thus, seems to be a reasonable value for such a rapid Li$^+$ exchange process.
Figure 6. (a) Crystal structure of Li$_4$Ti$_5$O$_{12}$ highlighting possible Na (and Li) diffusion pathways to explain the NMR SLR behaviour which points to multiple Li and Na diffusion pathways in heavily sodiated LTO. As an example, one might think about Na$^+$ exchange not only between 16$c$ (via 8$a$) but also between the 16$c$ and 16$d$ sites using the empty tetrahedral sites (48$f$) as transition states. (b) $^{23}$Na NMR SLR rates of Li$_4$N$_{1.5}$Ti$_5$O$_{12}$ recorded in the laboratory frame of reference at a Larmor frequency of 132 MHz. $^{23}$Na NMR yields two rates, $1/T_{1i}$ ($i =$ fast, slow). Dashed lines serve as guides to the eye, whereas the solid line represents an Arrhenius fit to extract a mean activation energy of 0.48 eV for Na$^+$ self-diffusion, most likely describing the pathway 16$c$-8$a$-16$c'$. The rate $R_{1i\text{slow}}$ is expected to be indirectly controlled by rather rapid $^7$Li spin-fluctuations such as local 8$a$-16$c$ forward-backward jumps nearby a Na$^+$ (16$c$) centre. The upper graph includes the stretching exponents to characterise the $^{23}$Na SLR NMR transients. Above ambient temperature, we need a sum of two stretched exponentials to satisfactorily parameterise the longitudinal recovery of the magnetization. For comparison, the $^7$Li NMR $1/T_{1\rho}$ are also shown. See text for further discussion.

Unfortunately, variable-temperature $^{23}$Na SLR of the samples with rather low amounts of Na do not show clear diffusion-induced contributions (see figure S3). In agreement with these changes, the $^{23}$Na NMR lines do not change much in the temperature range from 60 °C to 140 °C. Therefore, Na$^+$ diffusivity in samples with $x = 0.1$ and $x = 0.5$ are much less mobile than those in the sample with $x = 1.5$. Furthermore, if we compare our $^{23}$Na NMR lines with the situation seen for $^7$Li, at the early stages of sodiation, the Li$^+$ ions turned out to be much more mobile than the Na$^+$ ions. In figure 3(a) we have included the corresponding $^{23}$Na NMR motional narrowing curves; only for $x = 1.5$ are significant motional averaging effects seen. This observation underpins the idea of rapid Li$^+$ 8$a$-16$c$ exchange processes, which are immediately initialised as soon as sodium ions enter the near-surface 16$c$ sites.

4. Conclusion

We studied the influence of chemical Na insertion into the pentatitanate host Li$_4$Na$_x$Ti$_5$O$_{12}$ on Li$^+$ diffusion. While Li$^+$ ion dynamics were studied by $^7$Li NMR spectroscopy, $^{23}$Na NMR helped us to obtain first insights into the Na$^+$ ion dynamics of a sample with $x = 1.5$. The present study is multifaceted, as it attempts to understand ion dynamics in a mixed ion–electron system that additionally provides two mobile cations. We tried to understand ion dynamics with a single, non-destructive, contactless nuclear method that is capable of selectively studying Li$^+$ and Na$^+$ hopping processes from the atomic-scale point of view. Future studies might also include muon spin measurements to underpin the current findings.

Here, Na insertion leads, already at the very early stages of sodiation, to a drastic enhancement of Li$^+$ ion dynamics because of 8$a$-16$c$ Coulomb repulsions, which is accompanied by a significant decrease in activation energy from 0.83 eV ($x = 0.$) to 0.38 eV ($x = 0.5$). Compared to lithiated LTO, the increase does, however, start less pronounced and reaches a maximum diffusivity at values of approximately $x = 0.5$. Two-component $^7$Li NMR line shape measurements point to the initial formation of interfacially located solid solutions that propagate over the whole crystallites with increasing sodiation level $x$. At larger insertions levels, we assume that besides the solid solution areas, Li-rich and Na-rich phases also form. These separate
phases show lower Li\(^+\) diffusivity, respectively, explaining the observed overall decrease in Li\(^+\) ion diffusivity for \(x = 1.5\). However, at low insertion levels, \(\text{Li}_4\text{Na}_x\text{Ti}_3\text{O}_12\) immediately turns into a fast Li\(^+\) ion conductor with the Li\(^+\) performing rapid exchange processes in a solid-solution like environment. At these insertion levels, the Na\(^+\) ions on 1c are less mobile than the smaller Li\(^+\) cations. We think that any foreign ion, be it mobile or immobile, will immediately switch on Coulomb repulsions, forcing the 8\(a\) Li ions to get involved in rapid exchange processes.

These rapid Li\(^+\) ion dynamics in the solid-solution like regions explain the excellent suitability of LTO to act as fast-charging anode material. Hence, the pentatitanate should not be regarded as a material that only provides a two-phase insertion host, as seen in studies investigating its macroscopic electrochemical properties at progressed levels of lithiation or sodiation. Rather, interfacial properties and the existence of solid-solutions in LTO need to be considered, too.

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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**Conflict of interest**

The authors declare no competing interests.

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**References**

[1] Bruce P G, Scrosati B and Tarascon J-M 2008 Nanomaterials for rechargeable lithium batteries Angew. Chem., Int. Ed. 47 2930–46
[2] Dunn B, Kamath H and Tarascon J-M 2011 Electrical energy storage for the grid: a battery of choices Science 334 928–35
[3] Larcher D and Tarascon J M 2015 Towards greener and more sustainable batteries for electrical energy storage Nat. Chem. 7 19–29
[4] Nishide H and Oyairu K 2008 Materials science—toward flexible batteries Science 319 737–8
[5] Armand M and Tarascon J M 2008 Building better batteries Nature 451 652–7
[6] Rawlence M, Garbayo I, Bücheler S and Rupp J L M 2016 On the chemical stability of post-lithiated garnet Al-stabilised Li$_{1.5}$Li$_{4/3}$Ti$_{4/3}$O$_{12}$ solid state electrolyte thin films Nanoscale 8 14746–53
[7] Fotouhi A, Auger D J, Propp K, Lungo S and Wild M 2016 A review on electric vehicle battery modelling: from lithium-ion toward lithium sulphur Renew. Sust. Energy Rev. 56 1008–21
[8] Slater M D, Kim D, Lee E and Johnson C S 2013 Sodium-ion batteries Adv. Funct. Mater. 23 947–58
[9] Nagaura T and Totaowa K 1990 Progress in Batteries and Solar Cells vol 9 (Brunswwick, OH: JEC Press)
[10] Naya P K, Yang I T, Brehn W and Adelhelm P 2018 From lithium-ion to sodium-ion batteries: advantages, challenges, and surprises Angew. Chem., Int. Ed. 57 302–20
[11] Peters J, Buchholz D, Passerini S and Weil M 2016 Life cycle assessment of sodium-ion batteries Progress in Batteries and Solar Cells vol 9 (Brunswick, OH: JEC Press)
[12] Ley L C, Li X, Liu L and Ceder G 2014 Synthesis and stoichiometry of different layered sodium cobalt oxides Chem. Mater. 26 5288–96
[13] Yang J, Han D W, Jo M R, Song K, Kim Y I, Chou S L, Liu H K and Kang Y M 2015 Na$_{53}$Li$_x$Ti$_{52}$O$_{147}$ particles partly embedded in carbon nanofibers for supercapacitors with ultra-high power sodium ion batteries J. Mater. Chem. A 3 1003–9
[14] Stevens D A and Dahn J R 2000 High capacity anode materials for rechargeable sodium-ion batteries J. Electrochem. Soc. 147 1271–3
[15] Pan H L, Lu X, Yu X Q, Hu Y S, Li H, Yang X Q and Chen L Q 2013 Sodium storage and transport properties in layered Na$_{1.5}$Ti$_3$O$_7$ for room-temperature sodium-ion batteries Adv. Energy Mater. 3 1186–94
[16] Li Z F, Jian Z L, Wang X F, Rodriguez-Perez I A, Bommier C and Ji X L 2017 Hard carbon anodes of sodium-ion batteries: undervalued rate capability Chem. Commun. 53 2610–3
[17] Thackeray M M and Amin K 2021 Li$_{1.5}$Ti$_3$O$_7$ spinel anodes Nat. Energy 6 683
[18] Ohzuku T, Ueda A and Yamamoto N 1995 Zero-strain insertion material of Li[Li$_{1/3}$Ti$_2$O$_7$] for rechargeable lithium cells J. Electrochem. Soc. 142 1431–5
[19] Scharner S, Wepner W and Schmid-Beurmann P 1999 Evidence of two-phase formation upon lithium insertion into the Li$_{1.5}$Ti$_3$O$_7$ spinel J. Electrochem. Soc. 146 857–61
[20] Kanamura K, Umeagaki T, Naito H, Takehara Z and Yao T 2001 Structural and electrochemical characteristics of Li$_{45}$Ti$_3$O$_7$ as an anode material for rechargeable lithium batteries J. Appl. Electrochem. 31 73–78
[60] Habasaki J and Ngai K L 2007 The mixed alkali effect in ionically conducting glasses revisited: a study by molecular dynamics simulation Phys. Chem. Chem. Phys. 9 4673–89
[61] Gadermaier B, Hogrefe K, Heitjans P and Wilkening H M R 2021 Broadband impedance spectroscopy of Li$_4$Ti$_5$O$_{12}$: from nearly constant loss effects to long-range ion dynamics Z. Anorg. Allg. Chem. 647 2167–71
[62] Wilkening M, Iwaniak W, Heine J, Epp V, Kleinert A, Behrens M, Nuspl G, Bensch W and Heitjans P 2007 Microscopic Li self-diffusion parameters in the lithiated anode material Li$_{4+x}$Ti$_5$O$_{12}$ Li$_{4+x}$Ti$_5$O$_{12}$ (0 < x < 3) measured by $^7$Li solid state NMR Phys. Chem. Chem. Phys. 9 6199–202
[63] Kartha J P, Tunstall D P and Irvine J T S 2000 An NMR investigation of lithium occupancy of different sites in the oxide superconductor Li$_2$Ti$_3$O$_4$ and related compounds J. Solid State Chem. 152 397–402
[64] Brandstätter H, Wohlmuth D, Bottke P, Pregartner V and Wilkening M 2015 Li ion dynamics in nanocrystalline and structurally disordered Li$_2$TiO$_3$ Phys. Chem. 229 1363–74
[65] Kuhn A, Narayanan S, Spencer L, Goward G, Thangadurai V and Wilkening M 2011 Li self-diffusion in garnet-type Li$_3$La$_2$Zr$_2$O$_{12}$ as probed directly by diffusion-induced $^7$Li spin-lattice relaxation NMR spectroscopy Phys. Rev. B 83 094302
[66] Epp V, Gün O, Deiseroth H J and Wilkening M 2013 Highly mobile ions: low-temperature NMR directly probes extremely fast Li$^+$ hopping in argyrodite-type Li$_6$P$_{5}$S$_5$Br J. Phys. Chem. Lett. 4 2118–23
[67] Epp V, Ma Q L, Hammer E M, Tietz F and Wilkening M 2015 Very fast bulk Li ion diffusivity in crystalline Li$_{1.5}$Al$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$ as seen using NMR relaxometry Phys. Chem. Chem. Phys. 17 32115–21
[68] Hubbard P S 1970 Non-exponential nuclear magnetic relaxation by quadrupole interactions J. Chem. Phys. 53 985–7
[69] Kelly S W and Sholl C A 1992 A relationship between nuclear spin relaxation in the laboratory and rotating frames for dipolar and quadrupolar relaxation J. Phys.: Condens. Matter 4 3317–30
[70] Fujiwara N, Yasuoka H and Ueda Y 1998 Anomalous spin fluctuation in vanadium spinel LiV$_2$O$_4$ studied by $^7$Li NMR Phys. Rev. B 57 3539–42