Solid State Nuclear Magnetic Resonance ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Solid State Nuclear Magnetic Resonance

journal homepage: www.elsevier.com/locate/ssnmr

Ionic Pathways in $Li_{13}Si_4$ investigated by ^6Li and ^7Li solid state NMR experiments

Sven Dupke [a], Thorsten Langer [b], Florian Winter [b], Rainer Pöttgen [b], Martin Winter [a], Hellmut Eckert [a,c,*]

[a] Institut für Physikalische Chemie, Universität Münster, Corrensstrasse 30, 48149 Münster, Germany
[b] Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstrasse 30, 48149 Münster, Germany
[c] Institute of Physics in São Carlos, University of São Paulo, Av. Trabalhador Sãocarlense 400, 13590 São Carlos, SP, Brazil

ARTICLE INFO

Article history:
Received 8 August 2014
Received in revised form
11 November 2014
Accepted 18 November 2014

Keywords:
lithium ion conductors
2D-exchange NMR
Spin-lattice relaxation
Li silicides
Li ion batteries

ABSTRACT

Local environments and dynamics of lithium ions in the binary lithium silicide $Li_{13}Si_4$ have been studied by ^6Li MAS-NMR, ^7Li spin-lattice relaxation time and site-resolved ^7Li 2D exchange NMR measurements as a function of mixing time. Variable temperature experiments result in distinct differences in activation energies characterizing the transfer rates between the different lithium sites. Based on this information, a comprehensive picture of the preferred ionic transfer pathways in this silicide has been developed. With respect to local mobility, the results of the present study suggests the ordering Li6/Li7 > Li5 > Li1 > Li4 > Li2/Li3. Mobility within the $z=0.5$ plane is distinctly higher than within the $z=0$ plane, and the ionic transfer between the planes is most facile via Li1/Li5 exchange. The lithium ionic mobility can be rationalized on the basis of the type of the coordinating silicide anions and the lithium-lithium distances within the structure. Lithium ions strongly interacting with the isolated Si^{4-} anions have distinctly lower mobility than those the coordination of which is dominated by Si_2^{6-} dumbbells.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

The binary lithium silicides $Li_{12}Si_7$, Li_7Si_3, $Li_{13}Si_4$, $Li_{15}Si_4$ and $Li_{21}Si_5$ [1–8] have recently attracted considerable interest, as they serve as closely related reference compounds for the amorphous Li_xSi materials formed during the electrochemical lithiation of nano-silicon. Previous solid state NMR studies have shown that the amorphous materials have local lithium environments comparable to those present in crystalline silicides. Their quantitative distribution depends on the extent of the electrochemical charge transfer, illustrating the reference character of the crystalline phases [9–11]. Variable temperature single and double resonance, as well as double quantum solid state NMR studies on the crystalline binary phases have established detailed assignments of the numerous observable resonances in $^{6/7}Li$ and ^{29}Si MAS-NMR spectra to the crystallographically distinct lithium and silicon sites [12–16]. Lithium ion dynamics as one key feature in the understanding of electrochemical processes have been examined as well. In the binary compound $Li_{12}Si_7$ the lithium ion dynamics could be partially quantified by using NMR T_1 and $T_{1\rho}$ relaxometry [12] as well as temperature dependent ^7Li wideline NMR spectra [15], but a clear assignment of the determined activation energies to specific processes or lithium sites could not be established. ^6Li variable temperature 1D MAS- and $^{29}Si\{^7Li\}$ CPMAS-NMR have shown qualitatively that the lithium ion dynamics in the binary phases are influenced by their local coordination with the silicon species and their respective charges present [13–16]. In general, the lithium ion mobility has a tendency to decrease with increasing lithium content of the silicide phases, reflecting the increased Coulombic forces of the anionic Si species acting on the cations [15].

The crystal structure of $Li_{13}Si_4$ (see Fig. 1) has been recently redetermined, confirming the previous structure report [6], yet providing higher accuracy for the different lithium and silicon positions [17] including one lithium split position. It features two distinct types of silicon species, namely Si-Si dimers (Si-1 site) ordered in the $z=0.5$ plane and isolated silicon species (Si-2 site), ordered in the $z=0$ plane. There are seven distinct lithium sites in a 1:2:2:2:2:2:2 ratio. For all of them, Li-Li and Li-Si closest distances are of comparable magnitude. Table 1 lists the closest Li-Si distances involved. The $^{6/7}Li$ MAS-NMR spectra at 200 K (Fig. 2) show four resolved resonances in a 1.5:3:1:1 ratio, and they have been assigned on the basis of advanced dipolar $^6Li/^7Li$ and $^7Li/^{29}Si$ NMR experiments [15] (see Table 2). The assignment is

* Corresponding author at: Institut für Physikalische Chemie, Universität Münster, Corrensstrasse 30, 48149 Münster, Germany.
E-mail address: eckerth@uni-muenster.de (H. Eckert).

http://dx.doi.org/10.1016/j.ssnmr.2014.11.003
0926-2040/© 2014 Elsevier Inc. All rights reserved.

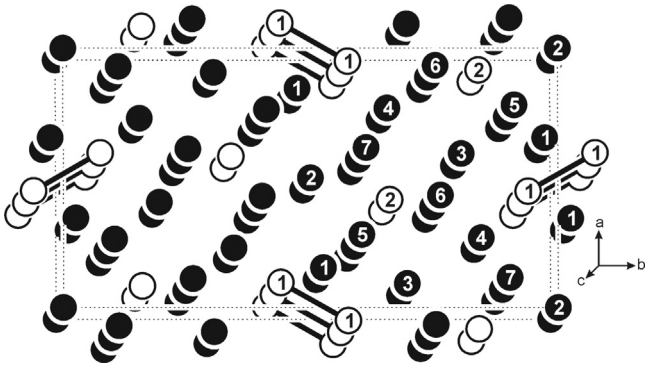

Fig. 1. Crystal Structure of $Li_{13}Si_4$. Crystallographically inequivalent Li and Si sites have been labeled.

Table 1
Silicon-lithium distances (in Å) within the first coordination sphere of silicon (d < 3.0 Å) for $Li_{13}Si_4$. The respective Wyckoff multiplicities of the lithium sites are given in parentheses. Based on reference [17].

Li	Si1	Si2
1 (4*g*)	**2.7374 (2 ×)**	**2.9045**
	2.9244 (2 ×)	
2 (2*c*)		**2.5174 (2x)**
3 (4*g*)		**2.6031**
		2.6099
4 (4*g*)	**2.8561 (2 ×)**	**2.8229**
5 (4*h*)	**2.6762**	**2.7487 (2x)**
	2.8559	
6 (4*h*)*	**2.6628 (A)**	**2.6554 (2x) (A)**
	2.860 (B)	**2.684 (2x) (B)**
7 (4 *h*)	**2.7133**	**2.7638 (2 ×)**

* split position.

based on the fact that Li-1 is exclusively bonded to Si-1, while Li-2 and Li-3 are exclusively bonded to Si-2 sites. The remaining lithium sites have both crystallographic silicon sites in their first coordination spheres. The objective of the present study is to gain insights into the crystallographically resolved ionic mobilities and preferred ionic pathways in this compound. With this objective in mind, variable temperature ^{7}Li 2D exchange NMR studies have been conducted as a function of mixing time. This approach has been previously used for other lithium ion conductors and offers the prospect of measuring site exchange rates and activation barriers involving crystallographically inequivalent lithium sites [18–25]. Based on this information we develop a comprehensive description of ionic motion and pathways in crystalline $Li_{13}Si_4$.

2. Materials and methods

2.1. Sample preparation and characterization.

The preparation and characterization of the samples has been carried out as previously reported [14,15] using sealed tantalum tubes and a water-cooled induction furnace. As a starting material for a 50% ^{6}Li enriched sample an adequate mixture of isotopically enriched (95% ^{6}Li, Aldrich Chemistry) and Li at natural abundance (metal chunks) was used. Synthesis of the ^{29}Si enriched samples was carried out using silicon powder (99.34% ^{29}Si, STB Isotope Germany).

2.2. Solid state NMR

Solid state NMR studies were carried out on a Bruker Avance DSX spectrometer working at 9.4 T using a commercial 4 mm

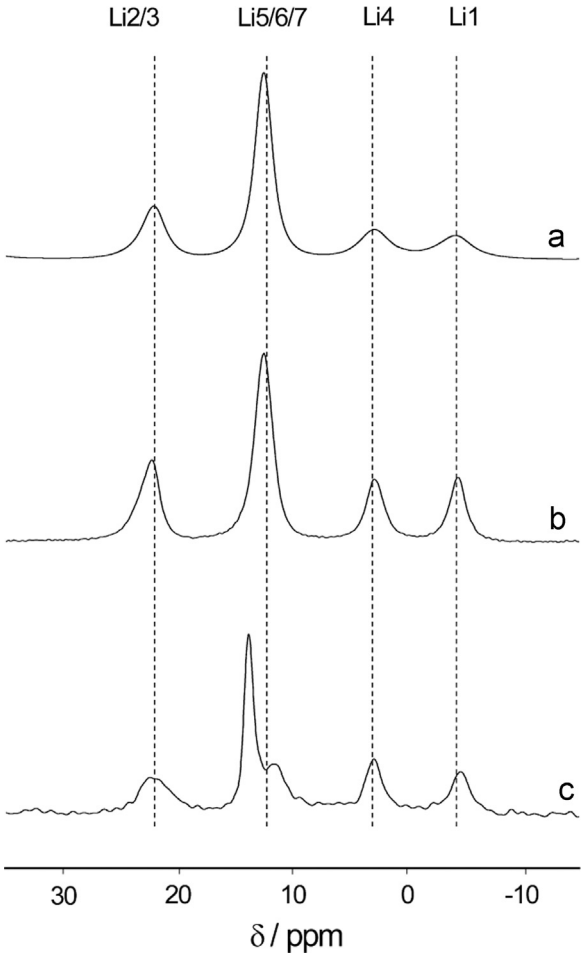

Fig. 2. ^{6}Li and ^{7}Li MAS-NMR spectra of $Li_{13}Si_4$ at 200 K. a) 50% ^{6}Li enriched sample, ^{7}Li MAS-NMR (6.5 kHz spinning speed). b) 50% ^{6}Li enriched sample, ^{6}Li MAS-NMR (6.5 kHz spinning speed). c) 99% ^{29}Si enriched sample, ^{6}Li MAS-NMR (5.0 kHz spinning speed).

Bruker VT MAS triple resonance probe. Samples were powdered and diluted with dried boron nitride in a 1:1 mass ratio to minimize undesirable probe detuning and sample heating effects caused by spinning the metallic samples in the high-field magnet. Dry nitrogen gas was used for MAS experiments with typical spinning speeds of 6.5 kHz. A temperature calibration using the ^{207}Pb NMR signal of lead nitrate was done to remove deviations between set and actual temperatures within an uncertainty of 1 K [26,27]. A 1 M aqueous LiCl solution and tetramethylsilane served as reference compounds (0 ppm) for $^{6/7}$Li and ^{29}Si, respectively. ^{7}Li 2D exchange (EXSY) spectra were measured at 200, 206 and 214 K using ^{7}Li 90° pulse lengths of 5.5–6.5 ms and mixing times of 5, 10, 20, 40, 60 and 80 μs. In order to suppress contributions from spin diffusion, a sample containing 50% ^{7}Li and ^{6}Li was used. Because of the rather long ^{6}Li T_2 relaxation times (on the order of 30 ms), these measurements were done on the ^{7}Li isotope. A NOESY-type sequence preceded by a saturation comb of sixty 90° pulses using the TPPI-scheme for quadrature detection has been used to acquire 86 to 160 experiments with 144 transients per experiment. For the experiment with a 5 ms mixing time a total of 360 transients and 160 experiments were recorded. In all experiments the dwell time and the F1 increment were equally set to yield a spectral window equal to the spinning frequency. ^{7}Li spin-lattice relaxation time (T_1) measurements were done at 200 K using inversion recovery and saturation recovery sequences at 9.4 T. All the spectra were simulated as superpositions of Gauss/Lorentz lineshapes using the DMfit software [28].

Please cite this article as: S. Dupke, et al., Solid State Nucl. Magn. Reson. (2014), http://dx.doi.org/10.1016/j.ssnmr.2014.11.003

Download English Version:

https://daneshyari.com/en/article/5420353

Download Persian Version:

https://daneshyari.com/article/5420353

Daneshyari.com