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Silicon Clusters

Resolving the Different Silicon Clusters in $Li_{12}Si_7$ by ^{29}Si and $^{6,7}Li$ Solid-State NMR Spectroscopy**

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Silicon has attracted considerable interest as an anode material for high-energy lithium ion batteries owing to its very high specific capacity. Unfortunately the enormous uptake of lithium ions is accompanied by a drastic volume expansion, causing particle rupture and rapid failing of the electrode.[1] Further and rational progress in this field requires a detailed understanding of the microscopic processes that occur during the (de)lithiation of silicon particles. This electrochemical process involves the formation of several amorphous phases, limiting the information that can be extracted from classical diffraction methods.

The lithium NMR spectroscopy studies performed to date provide only an indirect probe of the silicon structure,[2] and the exact nature of the silicon clusters formed upon charge and discharge of silicon is still unknown. In particular, we do not know, at a given stage of charge or discharge, if the silicon clusters all have the same structure or if several types of clusters coexist. Prior analysis of the silicon substructure by NMR spectroscopy using the direct probe ^{29}Si was hampered by the low signal–noise ratio and the difficulty in interpreting the usually very broad and poorly resolved spectra of lithiated Si particles.[2a,c] Herein, we establish a new ^{29}Si and $^{7,6}Li$ NMR spectroscopy approach to identify and differentiate the different types of clusters formed in lithium silicides. The method involves the detection of Si–Si connectivities and Si–Li proximities in two-dimensional (2D) NMR experiments. The crystalline lithium silicide $Li_{12}Si_7$ represents the most suitable model compound with which to establish the NMR approach since there are two different types of clusters,[3,4] 5-membered Si rings stacked in one-dimensional columns, and 4-membered Si "Y" stars located in the planes between the Si_5 rings, as shown in Figure 1. The results demonstrated here for this material form the basis for the investigation of the anode material silicon and silicon-containing anodes in general. Apart from analyzing these clusters, we show that ^7Li NMR shifts in lithium silicides are relatively complex and cannot be fully rationalized with a simple model that considers only isolated Si atoms versus Si atoms in clusters.

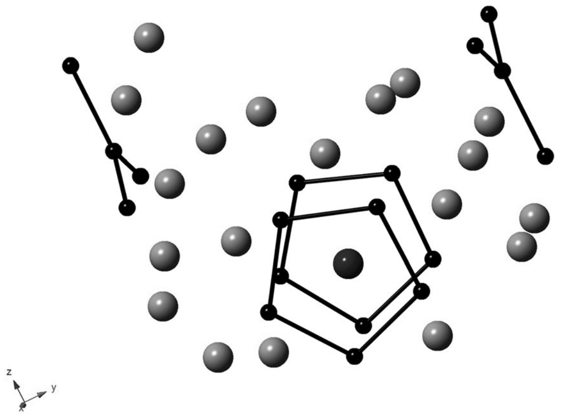

Figure 1. Fragment of the crystal structure of $Li_{12}Si_7$ showing the Si_4 stars and the Si_5 rings. Most of the Li positions surround the stacks of Si_5 rings, whereas one out of 12 Li ions is "sandwiched" between the Si_5 rings.[3a]

The ^{29}Si magic angle spinning (MAS) NMR spectrum of $Li_{12}Si_7$ at 233 K is shown in Figure 2. The sample used in this

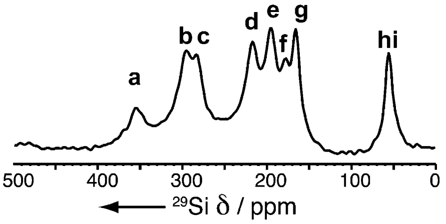

Figure 2. ^{29}Si NMR spectrum of $Li_{12}Si_7$ at 233 K. See text for details.

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study was 99% enriched in ^{29}Si in order to facilitate the ^{29}Si one-dimensional (1D) and 2D experiments. Eight isotropic resonances can be identified in the spectrum: **a** ($\delta = 356$ ppm), **b** ($\delta = 298$ ppm), **c** ($\delta = 284$ ppm), **d** ($\delta = 218$ ppm), **e** ($\delta = 198$ ppm), **f** ($\delta = 181$ ppm), **g** ($\delta = 167$ ppm), **h/i** ($\delta = 57$ ppm, as described below, this signal represents two different Si positions). Interestingly, the shift of **f** shows a strong temperature dependence. At 293 K, the signal is hidden under **e**, and upon decreasing the temperature it shifts to lower frequencies (Supporting Information), with signal **a** shifting to higher frequencies. This behavior is ascribed to the mobility of both the Si clusters and Li ions.

The assignment of the Si resonances to the Si_5 rings and Si_4 stars cannot be completed solely on the 1D spectra. To address this issue, through-bond correlations between the Si spins were analyzed in a 2D refocused INADEQUATE[5] experiment at 233 K (Figure 3). In this spectrum, two spins with resonance frequencies ν_1 and ν_2 result in a correlation at $\nu_1 + \nu_2$ in the indirect dimension of the 2D spectrum if they are coupled through a covalent bond (and thus *J*-coupling). In our case the 2D spectrum shows the existence of two separate spin systems. We find connectivities between peaks **e** and **g**, **g** and **c**, **c** and **b**, **b** and **d**, and **d** and **e**, clearly representing the five-membered ring. Signal **a** is correlated to both **f** and **h/i**. This correlation can be explained by assigning **a** to the central atom in the Si_4 star, and **f** and **h/i** to its terminal atoms. On the basis of the signal intensities, **h/i** arises from two of the terminal Si atoms, whereas **f** is due to one Si position only. Si–Si internuclear distances can also be studied by experiments designed to measure Si homonuclear dipolar coupling, as will be discussed elsewhere.[6]

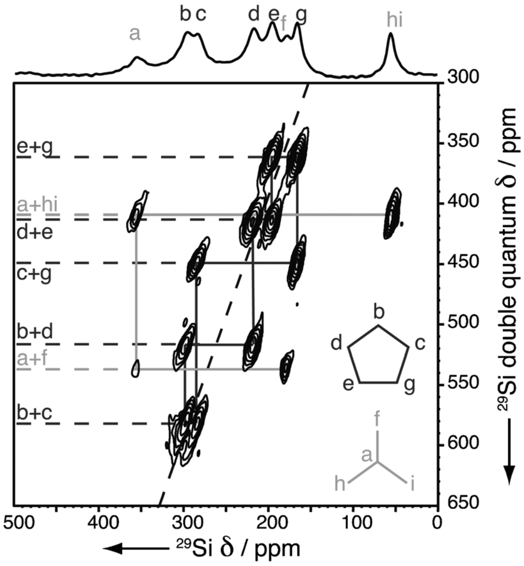

Figure 3. Experimental one-pulse spectrum acquired at a MAS rate of 21 kHz (top axis) and ^{29}Si refocused INADEQUATE NMR spectrum of $Li_{12}Si_7$ at 235 K. The pseudo-diagonal dashed line is the 2ν–ν line. Other lines are a guide to the eye, added so as to follow the Si–Si connectivities in the two kinds of Si clusters.

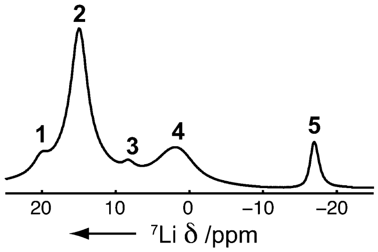

Figure 4. ^{7}Li NMR spectrum of $Li_{12}Si_7$ at 233 K. See text for details.

^{7}Li MAS NMR spectroscopy provides further insights into the material's structure. The spectrum in Figure 4 shows five peaks with chemical shifts of $\delta = 19.8$, 15.0, 8.3, 1.8, and -17.0 ppm, which we refer to as **1**–**5** in the following. The effect of the ion dynamics on the spectra becomes evident on examining the NMR spectra measured between 283 and 213 K. Upon cooling, the line-width of **2** is significantly reduced, and **3** can only be detected at temperatures below 263 K (see Supporting Information). Correlations between all five resonances are observed at both 233 K (Figure 5) and room temperature (see Supporting Information) in the 2D magnetization exchange experiments, demonstrating that all the lithium species are in environments in the same chemical phase. A comparison of ^{7}Li and ^{6}Li 2D exchange spectra showed that at room temperature the ^{7}Li exchange is dominated by spin diffusion rather than chemical exchange (see Supporting Information). At higher temperatures, chemical exchange between the ions located between the Si_5 rings and the other lithium atoms may be expected based on the 3D diffusional process observed by Kuhn et al. in recent ^{7}Li relaxation experiments.[7]

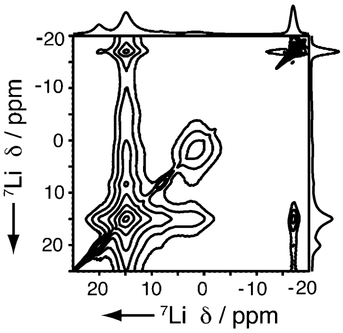

Figure 5. ^{7}Li 2D magnetization exchange at 233 K (mixing time = 8 ms) with spectral projections of the 2D spectra at the top and on the right side. (Differences between these projections and the 1D spectrum of Figure 2 are due the differences in relaxation times of the various resonances).

At a first glance, the upfield shift of signal **5** is surprising, as it appears at frequencies significantly lower than expected for diamagnetic lithium compounds.[8] We can explain this signal by assigning it to the lithium ions that reside between the Si_5 rings. Ring currents in these units will cause an additional shielding of these ^{7}Li nuclei. This aromatic character of the five-membered ring in $Li_{12}Si_7$ was proposed by Liebman and Vincent[9] and by Nesper et al. based on calculations of the band structure,[3b] and was also suggested in recent NMR studies of Kuhn et al.[4] $Li_{12}Si_7$ thus forms part of a group of other compounds with aromatic, homonuclear Si rings.[10] The wide range of ^{7}Li chemical shifts is surprising, and it becomes evident that the previous interpretation of NMR spectra of lithium silicides, assuming approximately identical chemical shifts for all lithium ions close to any Si cluster, is too simplistic. To obtain a more sophisticated understanding of the spectra, progress has to be made in the calculation of chemical shifts for these semiconducting compounds.

Finally, Li–Si correlations were established by performing a 2D Li/Si TEDOR experiment at 233 K (Figure 6). The TEDOR experiment reintroduces the heteronuclear dipolar couplings between Si and Li, that are removed by MAS, connecting the coupled Li–Si nuclei in a 2D experiment.[11] Similar information about spatial Li-Si proximities can in principle also be obtained from cross-polarization (CP) experiments, however owing to concerns about the thermal stability of $Li_{12}Si_7$ under prolonged radio-frequency irradiation, we avoided pulse sequences that involved long pulse durations. We find strong correlations between the lithium signal **5** and the silicon signals of the Si_5 ring, indicating that these nuclei are nearby in space and are rigidly held in the lattice. The lithium spins contributing to **1** and **2** are also correlated with the silicon resonances of the Si_5 ring (**b**, **c**, **g**, **f**), suggesting that these are the Li ions surrounding the ring. No correlations are seen between the lithium ions and the silicon resonances of the star (**a**, **f**, **h/i**), which we ascribe to the high mobility of the lithium ions surrounding these clusters and the dynamics of the clusters themselves, consistent with the ^{29}Si NMR spectra: motion will (partially) average the heteronuclear dipolar couplings necessary for the TEDOR transfer. Clearly even lower temperatures are required in order to obtain all of the Li–Si correlations.

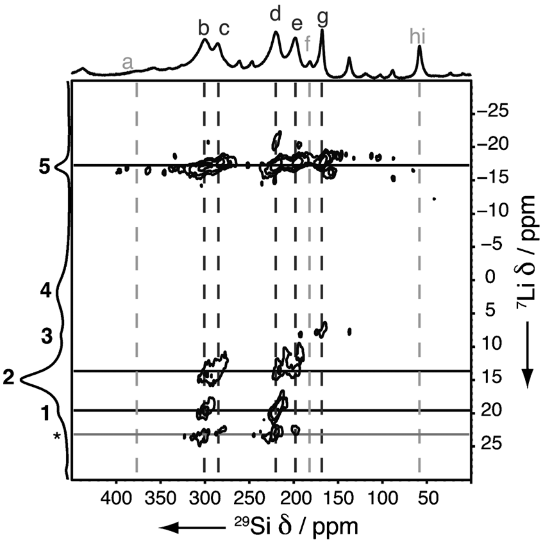

Figure 6. ^{7}Li–^{29}Si TEDOR 2D spectrum of $Li_{12}Si_7$ at 233 K. The asterisk indicates spinning sidebands. The one-pulse spectra obtained at a MAS rate of 10.5 kHz are shown on top (^{29}Si) and left (^{7}Li). A ^{7}Li to ^{29}Si magnetization transfer time of 0.381 ms (corresponding to 4 rotor periods) was used.

In conclusion, we are able to resolve the different Si clusters and analyze their individual connectivities by ^{29}Si correlation NMR spectroscopy. These experiments thus hold much promise for the detailed analysis of structures formed during the (de)lithiation of Si electrodes and are also of high interest for the characterization of other Zintl type compounds. Through-space proximities between the silicon and the lithium atoms can be monitored using dipolar experiments, as long as the experiments are performed at temperatures at which the different ions are rigid. Combining the results from ^{29}Si INADEQUATE and ^{7}Li-^{29}Si TEDOR, particular lithium sites can be identified. In particular, a strongly shielded Li ion located in between Si_5 aromatic rings is clearly identified based on its chemical shift and the Li–Si correlations. The wide range of chemical shifts in the ^{7}Li NMR spectra also shows that it is not straightforward to assign ^{7}Li signals to ions close to Si clusters solely on their chemical shift: the multiple bonding (and aromaticity) clearly result in a large range of shifts for both ^{29}Si and ^{6,7}Li.

Experimental Section

$Li_{12}Si_7$ was prepared as described previously from lithium metal and 99% ^{29}Si enriched silicon.[2a] ^{7}Li MAS and magnetization exchange experiments were performed on a 16.4 T Bruker Avance III 700 spectrometer at a temperature of 233 K, using a spinning speed of 12.5 kHz. Additional ^{7}Li and ^{6}Li magnetization exchange experiments were performed at 293 K. ^{7}Li–^{29}Si TEDOR experiments were performed at 233 K. ^{29}Si INADEQUATE experiments were performed on a 4.7 T Bruker Avance III 200 spectrometer with a spinning speed of 12.5 kHz and at 235 K. ^{29}Si experiments used a repetition delay of 5 s. Samples were handled and stored in an inert atmosphere argon glovebox to avoid contamination with oxygen and humidity. Further details about the NMR experiments can be found in the Supporting Information.

Note added on revision: While this work was under review, papers by Dupke et al.[12a] and Kuhn et al.[12b] on their independent NMR studies of $Li_{12}Si_7$ were published online. Dupke et al. were able to observe the Si–Si ring clusters in an INADEQUATE NMR experiment, but not the Si–Si star correlations. Kuhn et al.'s work focused on the aromaticity of the Si_5 rings.

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[1] a) M. Holzapfel, H. Buqa, L. J. Hardwick, M. Hahn, A. Wursig, W. Scheifele, P. Novak, R. Kötz, C. Veit, F. M. Petrat, *Electrochim. Acta* **2006**, *52*, 973–978; b) N. S. Hochgatterer, M. R. Schweiger, S. Koller, P. R. Raimann, T. Wöhrle, C. Wurm, M. Winter, *Electrochem. Solid-State Lett.* **2008**, *11*, A76–A80; c) J. S. Bridel, T. Azais, M. Morcrette, J. M. Tarascon, D. Larcher, *J. Electrochem. Soc.* **2011**, *158*, A750–759; d) J. S. Bridel, T. Azais, M. Morcrette, J. M. Tarascon, D. Larcher, *Chem. Mater.* **2010**, *22*, 1229–1241.

[2] a) B. Key, R. Bhattacharyya, M. Morcrette, V. Seznéc, J.-M. Tarascon, C. P. Grey, *J. Am. Chem. Soc.* **2009**, *131*, 9239–9249; b) B. Key, M. Morcrette, J.-M. Tarascon, C. P. Grey, *J. Am. Chem. Soc.* **2011**, *133*, 503–512; c) J.-H. Trill, C. Tao, M. Winter,

S. Passerini, H. Eckert, *J. Solid State Electrochem.* **2011**, *15*, 349–356.

[3] a) H. G. von Schnering, R. Nesper, J. Curda, K.-F. Tebbe, *Angew. Chem.* **1980**, *92*, 1070–1070; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 1033–1034; b) R. Nesper, H. G. von Schnering, J. Curda, *Chem. Ber.* **1986**, *119*, 3576–3590; c) M. C. Böhm, R. Ramirez, R. Nesper, H. G. von Schnering, *Phys. Rev. B* **1984**, *30*, 4870–4873.

[4] A. Kuhn, P. Sreeraj, H.-D. Wiemhöfer, P. Heitjans in *SSI-18*, Warsaw, **2011**.

[5] a) A. Lesage, M. Bardet, L. Emsley, *J. Am. Chem. Soc.* **1999**, *121*, 10987–10993; b) S. Cadars, J. Sein, L. Duma, A. Lesage, T. N. Pham, J. H. Baltisberger, S. P. Brown, L. Emsley, *J. Magn. Reson.* **2007**, *188*, 24–34.

[6] E. Salager, A. J. Morris, T. K.-J. Köster, C. J. Pickard, C. P. Grey, unpublished results.

[7] A. Kuhn, P. Sreeraj, R. Pöttgen, H.-D. Wiemhöfer, M. Wilkening, P. Heitjans, *J. Am. Chem. Soc.* **2011**, *133*, 11018–11021.

[8] Z. Xu, J. Stebbins, *Solid State Nucl. Magn. Reson.* **1995**, *5*, 103–112.

[9] J. F. Liebman, J. S. Vincent, *Angew. Chem.* **1982**, *94*, 649–649; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 632–633; *Angew. Chem.* **1982**, *94*, 649.

[10] a) S. Nagase, T. Kudo, M. Aoki, *J. Chem. Soc. Chem. Commun.* **1985**, 1121–1122; b) K. Abersfelder, A. J. P. White, H. S. Rzepa, D. Scheschkewitz, *Science* **2010**, *327*, 564–566; c) I. Fernández, M. Duvall, J. I.-C. Wu, P. v. R. Schleyer, G. Frenking, *Chem. Eur. J.* **2011**, *17*, 2215–2224; d) V. Quéneau, E. Todorov, S. C. Sedov, *J. Am. Chem. Soc.* **1998**, *120*, 3263–3264; e) M. Ichinohe, M. Igarashi, K. Sanuki, A. Sekiguchi, *J. Am. Chem. Soc.* **2005**, *127*, 9978–9979.

[11] A. W. Hing, S. Vega, J. Schaefer, *J. Magn. Reson.* **1992**, *96*, 205–209.

[12] a) S. Dupke, T. Langer, R. Pöttgen, M. Winter, H. Eckert, *Solid State Nucl. Magn. Reson.* **2011**, DOI: 10.1016/j.ssnmr.2011.09.002; b) A. Kuhn, P. Sreeraj, R. Pöttgen, H.-D. Wiemhöfer, M. Wilkening, P. Heitjans, *Angew. Chem.* **2011**, DOI: 10.1002/ange.2011050801; *Angew. Chem. Int. Ed.* **2011**, DOI: 10.1002/anie.2011050801.