

WENDELIB, Teilprojekt 13.1.

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Development and application of new multinuclear solid state NMR strategies for the structural and kinetic characterization of silicon anode materials

Nano-Silicon is one of the most promising potential anode materials for lithium ion batteries, owing to its large theoretical charge capacity (3579 vs 372 mAh/g of graphite). However, the dramatic volume expansion during lithiation (about 300%) encountered with this material poses still a tremendous challenge for its application in lithium ion batteries. The materials science goal, namely developing reliable correlations between anode composition and performance, is being pursued on the basis of the detailed characterization of the structural and dynamic properties of lithiated nano-silicon. The amorphous character of these materials necessitates the use of locally selective spectroscopic approaches, such as solid state NMR. Project 13.1. develops new advanced solid state NMR spectroscopic strategies for the structural and dynamical characterization of anode materials in lithium ion batteries, as well as for model systems, in order to develop an atomic-level understanding of the electrochemical lithiation mechanism.

As shown in Figure, 1, ^7Li chemical shifts measured in various binary lithium silicides show a remarkable sensitivity to the structural motifs present in the silicon frameworks. This fact can be used to monitor the various local environments sampled by the lithium ions at the various stages of electrochemical lithiation.

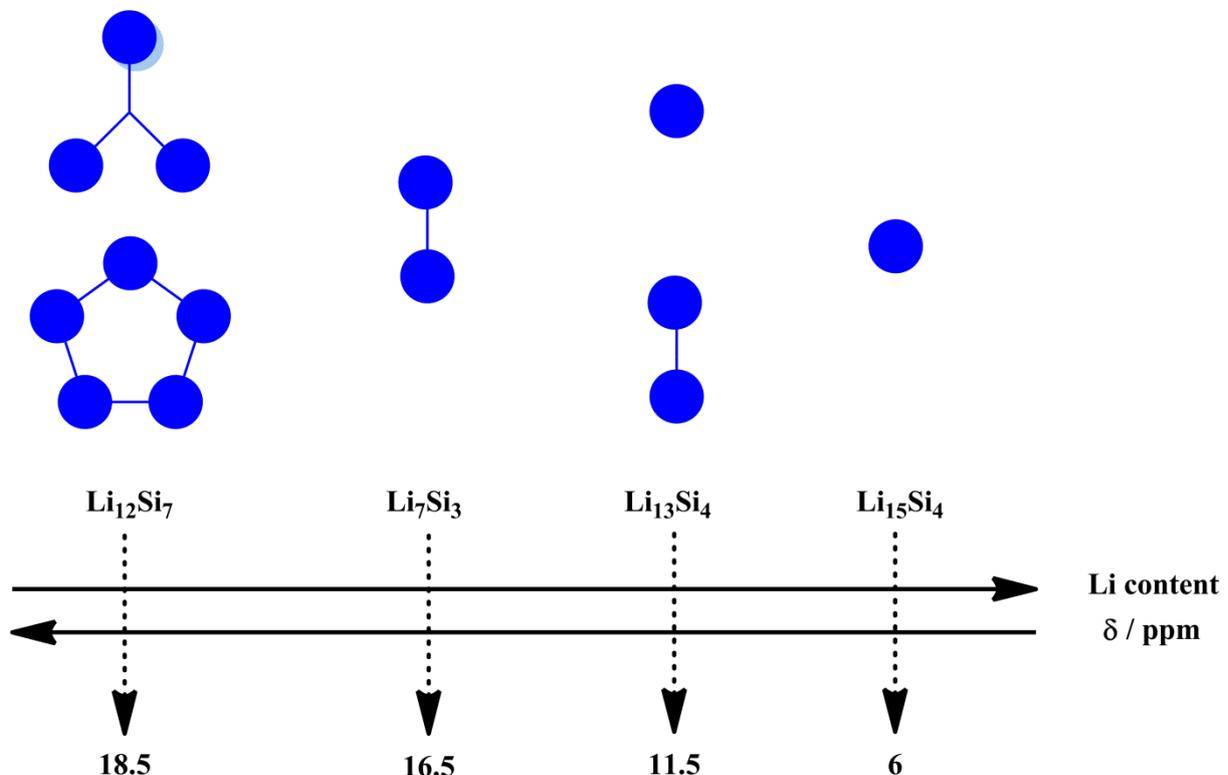


Figure 1: ^6Li chemical shifts and structural motifs present in binary lithium silicides

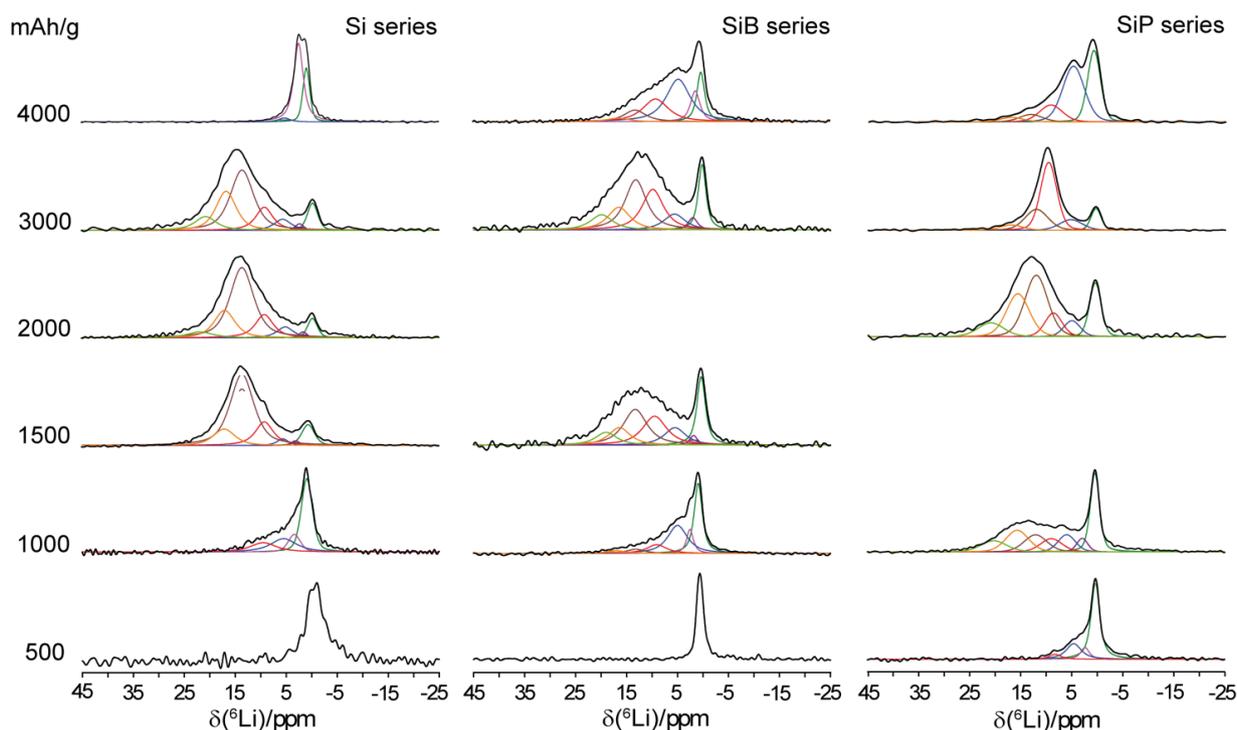


Fig.2 ^6Li MAS NMR spectra recorded at room temperature for the anodes of undoped, boron-doped and phosphorus-doped nano-Si samples lithiated from 500 to 4000 mAh/g. The colored lines are line-shape deconvolution components.

Figure 2 shows, that environments typical for various different binary lithium silicide phases are encountered at different lithiation stages of undoped and doped nano-Silicon samples. A particular result of the work is the early formation of environments resembling the $\text{Li}_{15}\text{Si}_4$ phase, for which the results of the present project indicate a rather low degree of ion mobility and transport rate. A survey of a large number of different samples reveals that high irreversible capacity losses are always observed when $\text{Li}_{15}\text{Si}_4$ -like environments form a major part of the lithium inventory. In addition, the results suggest that P-doped nano-silicon, presumably due to its higher electrical conductivity, favors faster lithiation kinetics.

Advanced solid state NMR techniques are also being applied to characterize the crystalline phases $\text{Li}_{12}\text{Si}_7$, Li_7Si_3 , $\text{Li}_{13}\text{Si}_4$, and $\text{Li}_{15}\text{Si}_4$, which serve as models for the various stages of the electrochemical lithiation process. For example, the crystallographically distinct lithium sites in a $\text{Li}_{12}\text{Si}_7$ can be assigned via two-dimensional $^6\text{Li}/^7\text{Li}$ and $^7\text{Li}/^{29}\text{Si}$ dipolar correlation experiments, and their different degrees of ionic mobility assessed on the basis of variable temperature ^6Li NMR experiments (see Figure 3 for an initial result). Based on this information, preferred ion conduction pathways can be visualized, as shown in Figure 4 for the compound $\text{Li}_{12}\text{Si}_7$. Finally, systematic variable temperature NMR studies also indicate that the lithium ion mobility tends to decrease with increasing extent of the depolymerization of the nano-silicon framework. The lithium ionic mobility is particularly low in $\text{Li}_{15}\text{Si}_4$, which corresponds to the end-composition (3579 mAh/g) reached during the electrochemical lithiation process. The early formation of this phase may also be linked to large irreversible capacity losses during the initial lithiation cycle.

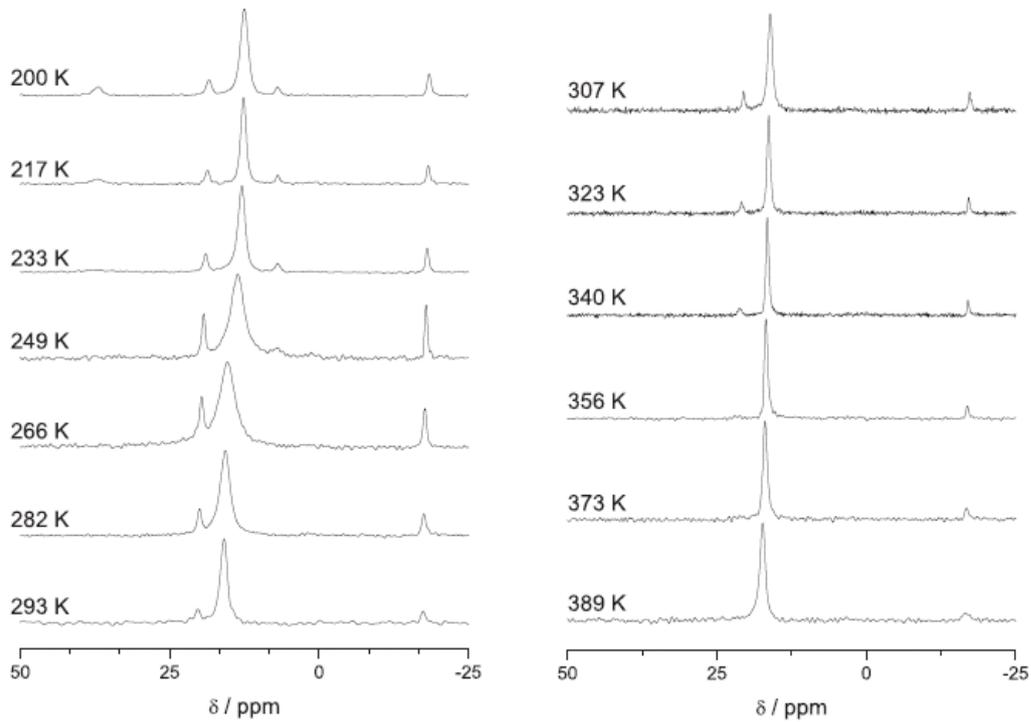


Figure 3: Variable temperature ${}^6\text{Li}$ MAS-NMR spectra of $\text{Li}_{12}\text{Si}_7$, revealing the gradual freezing-out of several lithium ions which become immobile on the NMR timescale at sufficiently low temperatures.

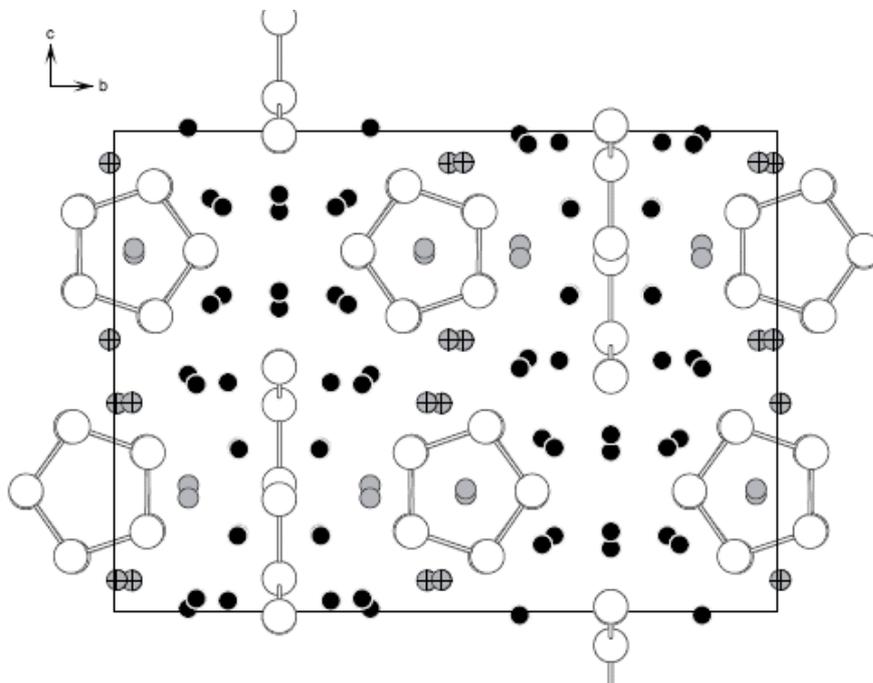


Figure 4: Simplified mobility profiles for the lithium sites in the structure of $\text{Li}_{12}\text{Si}_7$. Light grey circles symbolize less mobile, black circles more highly mobile lithium ions, while crossed circles denote lithium ions with intermediate mobility.