



Utilization of ^{29}Si MAS-NMR to Understand Solid State Diffusion in Energy Storage Materials

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The properties of many solid-state materials arise from critical interfaces tied to the structure, morphology, and composition of the materials under study. For many materials, identifying components that may be invisible to diffraction techniques or other bulk sensitive techniques (i.e. inductively coupled plasma (ICP)), may cause important information to be overlooked. These can include grain boundary phases, nanoscale coatings, amorphous layers, or second phases that influence the materials environment. In this short review, the use of ^{29}Si MAS NMR as a local probe to detect silicon-containing phases in complex energy storage systems is explored with a focus is on silicon-containing materials and silicon electrodes. Examples highlighting the utility of ^{29}Si MAS NMR include 1) examining copper diffusion into silicon as a method to create 3 dimensional electrodes, 2) using Mg(II) electrolyte additives to create *in-situ* nanoscale silicide coatings to inhibit low voltage parasitic side reactions and extend calendar life, and 3) studying the lithiation reactions of passivated silicon on different time scales.

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INTRODUCTION

Understanding solid-state diffusion is critical to understanding the role of syntheses in areas ranging from materials processing to the creation of protective coatings (van der Ven et al., 2013). While optimizing solid state diffusion is the desired result of many materials studies, i.e. Li^+ conduction in $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ or O^{2-} diffusion in $(\text{Y,Zr})\text{O}_{2-x}$, understanding its role in the synthetic pathway can help form specific structures or change the rate of reaction (Descemond et al., 1993; Kuhn et al., 2011). As an example, the commercial lithium-ion battery (LIB) cathode LiCoO_2 exists in two forms depending on the synthesis route chosen (Gummow et al., 1993a). Using a conventional solid-state synthesis heated to high temperature ($\sim 900^\circ\text{C}$), a hexagonal layered phase is isolated. However, it was noted by Gummow, et al., that if the mixture is heated to only 400°C for an extended period and cooled to room temperature, a three-dimensional cubic spinel structure with a distinct electrochemical cycling profile is seen rather than the high temperature hexagonal layered oxide (Gummow et al., 1993a; Gummow et al., 1993b). Later studies by Kan et al., showed that samples annealed for shorter time lengths, intermediate intergrowths in the samples were observed (Kan et al., 2014; Shi et al., 2021). Mechanistic studies highlighted that the spinel-phase is the dominant product below 620°C followed by conversion to the layered LiCoO_2 . In these examples, the spinel cation ordering was identified by diffraction methods, *in-situ* spectroscopic techniques, thermal properties, and electrochemical properties to correlate the structural differences to the electrochemical properties. In this report, the use of local-probe ^{29}Si Solid State Magic Angle Spinning (MAS) NMR spectroscopy is reviewed for its uses as a tool to better understand the role of annealing temperature, precursor, and sample

history on the properties of energy storage materials (Blanc et al., 2013; Delpuech et al., 2016; Dogan and Vaughey, 2016; Michan et al., 2016). Specific examples from the literature in the fields of solid-state electrolytes, electrode formation, and silicon-based anode materials will be used to create a better understanding of the synthetic processes involved.

²⁹Si NMR Studies of Silicon-Based LIB Electrodes

²⁹Si Solid State Magic Angle Spinning (MAS) NMR spectroscopy is a local structural probe that can identify the different local silicon environments in a sample and correlate them with compositions. In a study of the copper/silicon deposition process used to create an all-inorganic electrode, the local environments and phases formed after processing the copper-coated silicon powder at various temperatures were identified by ²⁹Si MAS NMR (Dogan et al., 2013). This study, part of an effort to understand the interface between nanoscale copper and silicon, was performed in the temperature range (450–650°C) to study intermetallic formation and copper diffusion in silicon. Previous diffraction studies showed formation of the electrochemically inactive phase Cu₃Si for samples heated above 700°C but the isolation of disordered (lacking long-range order) or amorphous species (i.e., nanoscale silicon oxides, surface silicon hydrides/hydroxides) was not possible using XRD methods (Joyce et al., 2012). Identifying these interfacial phases is important in understanding the electrode properties as many silicon oxides are insulating and electrochemically inactive. Globally, their presence on the particle surface has an effect on the cell impedance, irreversible capacity, and SEI stability.

Since ²⁹Si MAS NMR spectroscopy is sensitive to the local environment of silicon, it can be used to study the formation of both ordered (crystalline) and disordered materials within the electrode at various processing temperatures. To focus the study on surface species, ²⁹Si single pulse (SP) and ²⁹Si{¹H} cross-polarization (CP) techniques were combined so that both bulk and protonated surface silicon sites can be identified. Using ²⁹Si {¹H} CP MAS NMR allowed the selective investigation and detection of the ²⁹Si NMR resonances from silicon atoms in close proximity to protons and surface silicon atoms.

Background

The silicon isotope ²⁹Si has a spin $I = \frac{1}{2}$ and a low natural abundance of 4.7%. Despite its low natural abundance, it is commonly used as structural characterization tool for silicon oxides and zeolite-based catalysts and more recently silicon based energy storage materials. The locations of the ²⁹Si NMR peak shift values, reported relative to a tetramethylsilane (TMS) standard, are directly related to the shielding of the ²⁹Si nucleus by the electronic structure in its immediate environment. Therefore, ²⁹Si MAS NMR spectroscopy provides direct information about the structure of silicon compounds *via* measurements of the isotropic chemical shifts (Blanc et al., 2013; Delpuech et al., 2016; Dogan and Vaughey, 2016; Michan et al., 2016). The observed silicon chemical shift is influenced by: 1) the coordination number of the Si, 2) the nature of the nuclei in

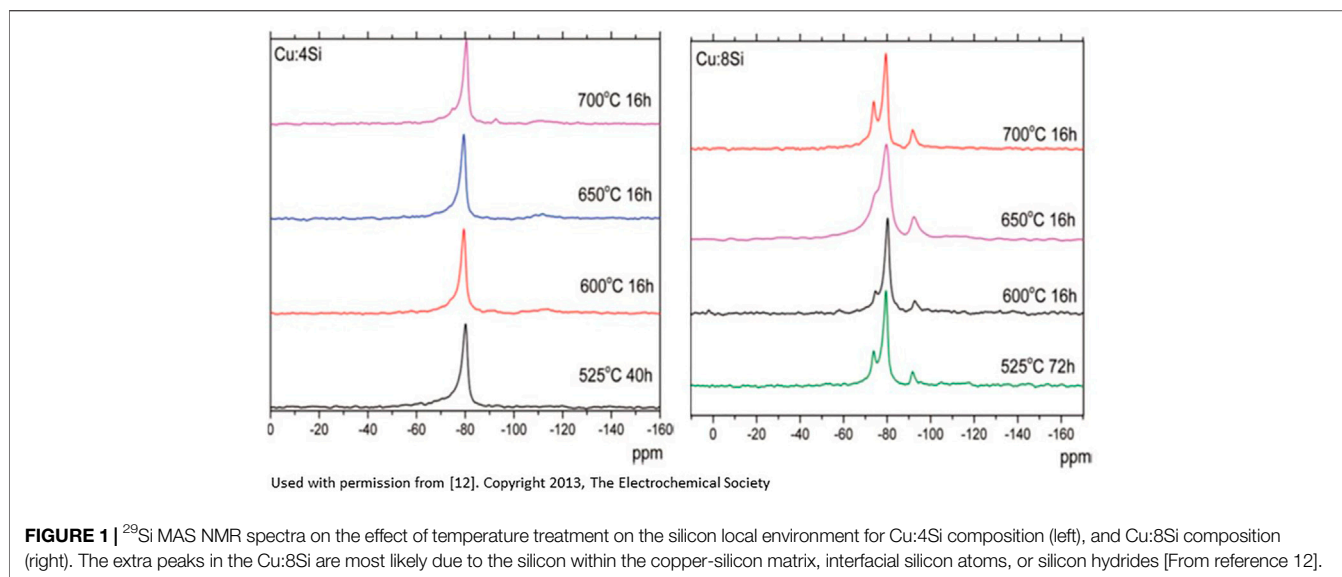
the first coordination sphere, and 3) the local symmetry of the silicon's environment. Based on literature studies, the ²⁹Si chemical shift of bulk silicon is a sharp resonance at –80 ppm. While the linewidth increases with increasing local environment disorder, by utilizing the Magic Angle Spinning (MAS) technique, the averaging of dipole-dipole interactions and chemical shift anisotropy, reduces the peak width (Chang et al., 1996). Since the silicon linewidth in powder samples is dominated by these interactions, using MAS to examine these different silicon local environments can greatly improve the data resolution. Literature studies report a typical chemical shift value of –40 ppm for amorphous silicon which changes depending on the hydrogen content up to an experimental value of –92.5 ppm for silane (SiH₄) (Pietraß et al., 1996). Silicon oxide environments typically give rise to ²⁹Si peaks in the range –90 to –110 ppm, depending on the local environment and coordination and are often referred to with a Qⁿ to indicate the number of bridging bonds (–O–Si) tied to the central silicon atoms (Mackenzie and Smith, 2002; Petit et al., 1063).

For the annealed inorganic electrodes, samples were prepared using electroless Cu deposition. The literature method operates by the reduction of soluble copper cations (as CuSO₄) dissolved in 70°C water at pH ≈ 12 by slow addition of formaldehyde. The samples were processed as reported in reference 12. Analysis of the data for the unannealed copper coated silicon powders showed a similar ²⁹Si NMR spectrum to elemental bulk silicon supporting the conclusion that the local silicon environment remains for the most part unchanged after the copper deposition process and that formation of any silicon oxide/hydroxide/hydride species is minor and cannot be detected by MAS NMR. For comparison, X-ray powder diffraction data showed only elemental copper and silicon with small amounts of copper oxide (Cu_xO) for the most copper rich samples (Joyce et al., 2012; Dogan et al., 2013).

Data Analysis

After annealing under an argon atmosphere at various temperatures, several new silicon environments emerged during the ²⁹Si NMR experiments that provided information about various silicon compounds present, notably for the high silicon content materials. The formation of these new silicon environments identified by MAS-NMR may arise from 1) higher population of copper-free silicon particles in silicon rich samples, 2) silicon being reactive (silicon oxides, hydroxides, or silicon hydrides) in the storage environment, 3) charge disproportionation of the copper cations, or 4) interfacial copper-containing grain boundary phases.

Various species identified in the study, such as the formation of silicon hydrides, are consistent with the third scenario where the deposition of copper onto a silica support and surface silicon is linked to a hydrogen spillover reaction (protons from water associated with the copper ions). Data analysis indicates that the electrode materials prepared with the lowest silicon (highest copper) content (Cu:4Si) and post treated below 600°C show only pure silicon environments, indicative of no Cu-Si reactivity, and the most stable cycling performance. Cu-Si electrode materials with higher silicon contents (Cu:6Si and Cu:8Si) but annealed at high temperatures near 700°C showed formation of



multiple silicon local environments originating from both bulk and surface sites. These sites had a significant impact on the electrochemical performance of the materials as these new environments are at the critical interface in the system between the active electrode and the electrolyte. **Figure 1** highlights the differences in the spectra. Analyzing the data collected, Cu-Si samples with lower amounts of silicon surface defects had superior electrochemical performance than those with more defects implying it is possible to improve the system electrochemical performance by minimizing the undesirable interfacial silicon local structures that may lead to more surface reactivity (i.e. thicker SEI formation). Analyzing the ^{29}Si MAS NMR data and XRD data, the silicon-rich Cu:8Si compositions show formation of the phase Cu_3Si , an electrochemically inactive phase, and the expected performance drop. While XRD data showed mainly crystalline phases, the MAS-NMR techniques identified several new Si environments that are assigned to various silicon oxides/hydrides as well as interfacial silicon atoms near and influenced by the copper (Joyce et al., 2012; Dogan et al., 2013).

^{29}Si and ^7Li NMR Studies of Silicon-Based Electrodes Containing $\text{Li}_{14}\text{MgSi}_4$

In the previous section, ^{29}Si MAS-NMR was used to identify poorly crystalline surface species that formed on annealing. The most common crystalline species, identified using X-ray diffraction, were elemental copper, silicon, and the bulk intermetallic phase Cu_3Si . Intermediate phases, identified by MAS-NMR, included various silicon oxide, hydroxide, and hydride species that effected the cycling performance due to increased surface reactivity with the electrolyte as a function of charge. Building on the ability to study amorphous and nanoscale surface coatings, it was used to evaluate the products of an *in-situ* synthesis method that selectively coats the surface of an active silicon particle (BH Han et al., 2019a; BH Han et al., 2021; Li et al., 2021).

Background

For an LIB silicon electrode, a fully charged anode mainly contains the Zintl phase $\text{Li}_{15}\text{Si}_4$. Using Zintl-Klemm rules, the stoichiometry and properties of this phase can be understood as being composed of a combination of fully reduced four Si^{-4} anions, surrounded by 15 lithium cations per unit cell (Heider and Scheschkewitz, 2021). Using these rules, the phase is formally electron rich (exact charge balance would be 16 lithium cations) and is metastable at room temperature at this defect stoichiometry. On exposure to the constituents of an electrochemical cell, these electron rich phases are observed to react (formally oxidize) with the solvent and electrode binder to form various insoluble and electrolyte-soluble organic species (BH Han et al., 2019b). The exact oxidized silicon species (i.e. $\text{Li}_{13}\text{Si}_4$) depend on sample history and conditions. When considering the degradation mechanisms associated with full cell calendar life, this reactivity results in a parasitic current that effects the Coulombic efficiency of the cell. Under calendar life conditions that involve maintaining a specific cell voltage for extended time, the slightly oxidized silicon is reduced formally back to the electron non-precise $\text{Li}_{15}\text{Si}_4$ creating a redox cycle that degrades the electrolyte. To counter this cell reactivity and add stability, Mg^{+2} ions were added to the electrolyte. These ions move into the charged phase at low cell voltage formally to make the electrode surface electron precise by forming $\text{Li}_{14}\text{MgSi}_4$. The material, by Zintl-Klemm electron counting rules, is stoichiometric and (ideally) has a closed (electron) shell due to the extra electrons brought in by the Mg ions (Heider and Scheschkewitz, 2021). Creating these phases at the silicon/electrolyte interface adds stability to the cell and extends electrochemical cell cycle and calendar life (Zeilinger et al., 2013).

In a recent proof-of-concept study, Han et al., evaluated the stoichiometric Zintl phase Li_2MgSi (an isostructural Mg-rich endmember of the solid solution with $\text{Li}_{14}\text{MgSi}_4$) against common organic cell materials (binder, solvents, salt) and observed the Si^{-4} anion was not obviously oxidized (as they were in the $\text{Li}_{15}\text{Si}_4$ study) and the enhanced stability was obtained

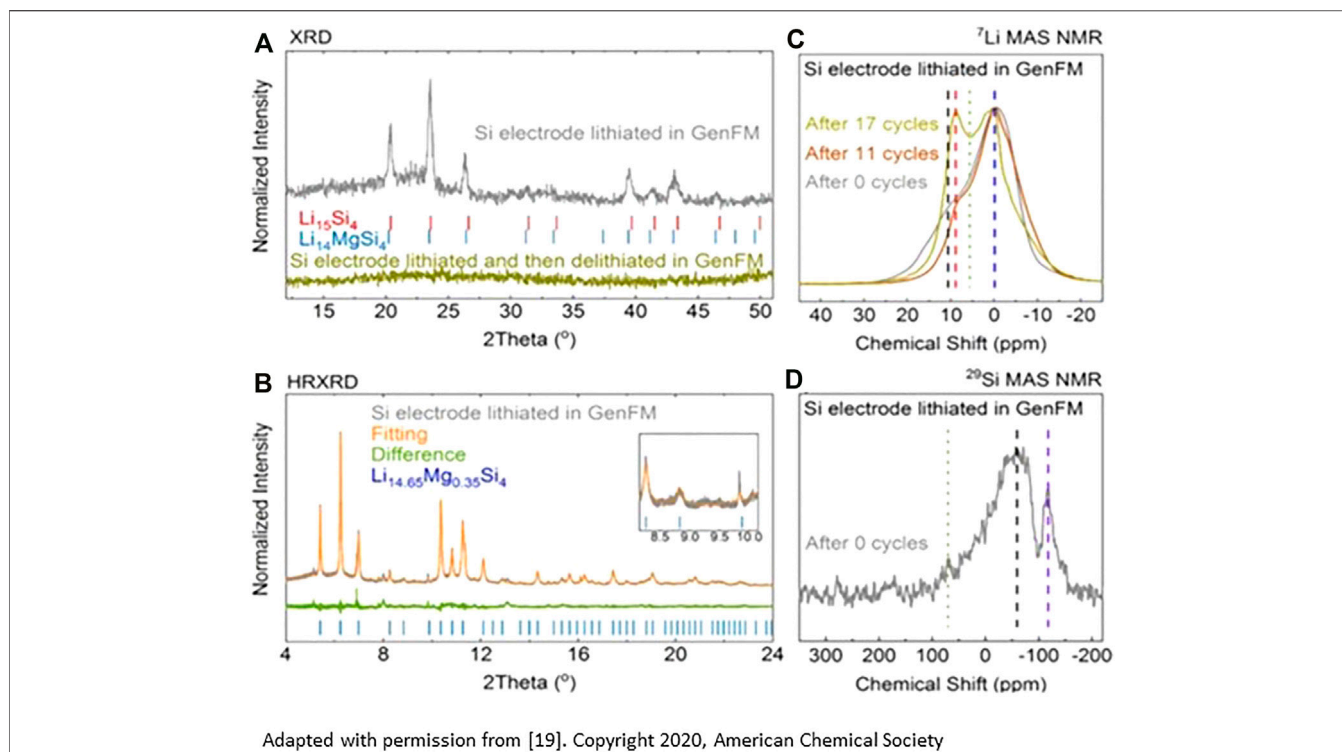


FIGURE 2 | (A) Rietveld analysis from XRD data of the phases formed, (B) high resolution XRD of the cycled materials with stoichiometric refinement; (C) ^7Li NMR study on cycled materials showing the growth of a second phase (Li-Mg-Si) on cycling; (D) ^{29}Si MAS NMR study highlighting formation of a second reduced silicon phase. Both spectra are consistent with gradual formation of a ternary Li-Mg-Si phase(s) on cycling in the Mg-containing electrolyte. [from reference 18]

(BH Han et al., 2021). This lack of reactivity, compared to the pure lithium silicide phases, diminishes the parasitic currents by a mechanism consistent with removing Si^{-3} , Si^{-2} , or Si^{-1} phases (as seen in the Li-Si binary system) from the reaction pathway. From the ternary Li-Mg-Si phase diagram, no equivalent intermediately charged cluster species exist as in the Li-Si system. Since elemental silicon is the next phase in the diagram, the transition requires a four-electron oxidation, which may represent a high kinetic barrier making the electrode surface more stable against the organic species in the electrochemical cell.

Data Analysis

To form a coating of these phases on the silicon in an electrochemical cell, small amounts of the salt $\text{Mg}(\text{TFSI})_2$ were added to the standard Gen2 electrolyte (1.2M LiPF_6 EMC/EC 3:7). After cycling, TEM, EDX, MAS-NMR, and XPS studies showed surface Mg^{+2} at the approximate stoichiometric ratio of $\text{Li}_{14.5}\text{Mg}_{0.5}\text{Si}_4$, a point in the solid solution between Li_4MgSi_4 and $\text{Li}_{15}\text{Si}_4$ that may represent a limit based on magnesium diffusion under the conditions used for the study (BH Han et al., 2019a; BH Han et al., 2021; Li et al., 2021). Spectroscopic evidence for interfacial phase formation is shown in **Figure 2**. With *in-situ* ternary salt formation at the surface, baseline Si electrode samples have extended cycle and calendar life compared to electrolytes without the additive.

The mechanism of ternary Zintl phase formation and its dynamics upon lithiation/delithiation were also studied with ^{29}Si MAS NMR on Si electrodes harvested from cycled coin

and pouch cells at various states of (de)lithiation, see **Figure 3** (Li et al., 2021). The NMR data, along with other complimentary characterization techniques, reveal that lithiation of Si starts from the Si-O surface layer and progresses with heterogeneous silicon clustering with Si^{-4} anions at high states of lithiation. At a fully lithiated state, formation of an overlithiated Si species was also detected. At a low-voltage region (below 100 mV) and/or high lithiation levels, direct evidence for Mg-ion insertion is found, postulated by two possible mechanisms: ion exchange with fully or overlithiated binary domains ($\text{Li}_{3.75+x}\text{Si}$) and/or a co-insertion into slightly underlithiated domains ($\sim\text{Li}_{3.55}\text{Si}$).

For silicon based systems, calendar life is an important performance issue as it reduces the cycle life and utility of lithium-ion cells. The use of ^{29}Si MAS NMR was critical to identify the mechanism of Mg insertion, the role of time and diffusion, and the growth of the phase at that critical interface. Extending the calendar life of the silicon cell, by reducing the redox activity of the electrode surface, was difficult to characterize due to the nature of the coating. However the local probe aspect of MAS-NMR is capable of yielding insights many other techniques are incapable of providing to the researcher.

Silicate Reactivity

Although it does not have any appreciable redox reactivity in an electrochemical cell, the silica layer on silicon is chemically reactive with other SEI components and forms a variety of lithium silicates, ranging from the molecular species Li_4SiO_4 to

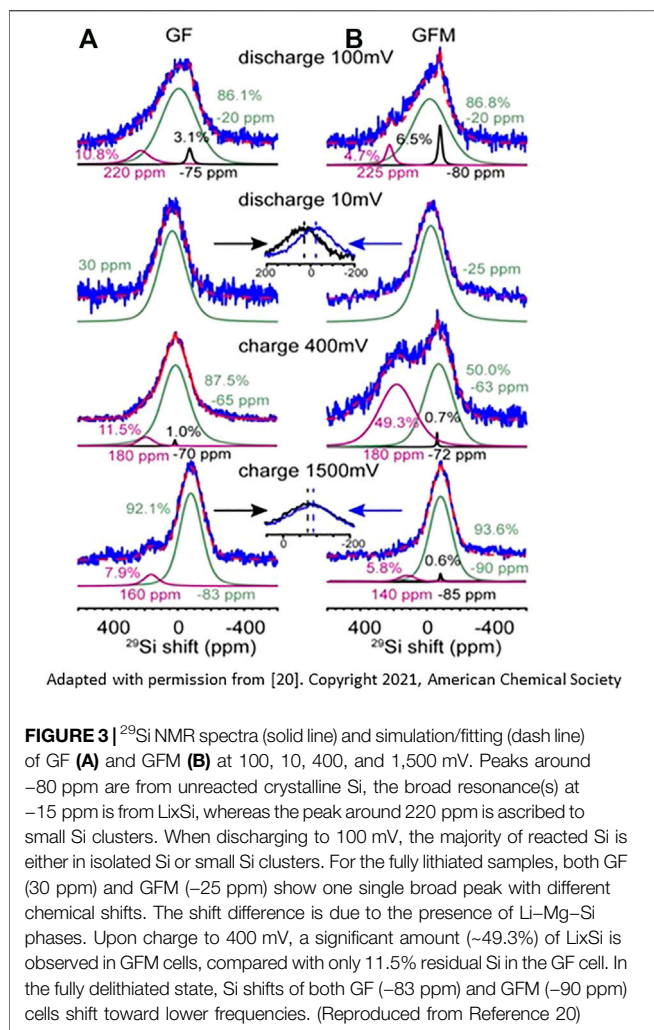


FIGURE 3 | ²⁹Si NMR spectra (solid line) and simulation/fitting (dash line) of GF (A) and GFM (B) at 100, 10, 400, and 1,500 mV. Peaks around -80 ppm are from unreacted crystalline Si, the broad resonance(s) at -15 ppm is from Li_xSi, whereas the peak around 220 ppm is ascribed to small Si clusters. When discharging to 100 mV, the majority of reacted Si is either in isolated Si or small Si clusters. For the fully lithiated samples, both GF (30 ppm) and GFM (-25 ppm) show one single broad peak with different chemical shifts. The shift difference is due to the presence of Li-Mg-Si phases. Upon charge to 400 mV, a significant amount (~49.3%) of Li_xSi is observed in GFM cells, compared with only 11.5% residual Si in the GF cell. In the fully delithiated state, Si shifts of both GF (-83 ppm) and GFM (-90 ppm) cells shift toward lower frequencies. (Reproduced from Reference 20)

the condensed material Li₂SiO₃. This chemical reaction is notable when evaluating the nanoscale Si/SiO₂ composite “SiO_x” as lithiation of the silica is a sink for active lithium and produces high irreversible capacity on the first cycle. Various approaches to overcome this reaction require pre-lithiation of the electrode to retain active lithium on cycling, however the active matrix produced is a relatively good lithium-ion conductor and produces an electrode with a stable cycling performance.

Background

Silicon is passivated quickly on exposure to air, water, or other oxygen containing species, to form a relatively dense silica coating that has a typical depth of 5 nm. This layer, difficult to detect with common lab XRD methods, acts to block additional reactions with an oxygen source and allows silicon to be handled and processed in air (Kale et al., 2019). Uses that require silica free materials require more stringent handling due to this oxyphilic nature of the silicon surfaces (Jiang et al., 2019; Schulze et al., 2021). In an electrochemical cell, it was noted by Edström et al., that this natural silica-based coating on silicon is lithiated early in the process forming a variety of lithium silicates, notably Li₄SiO₄

(Philippe et al., 2012; Philippe et al., 2013a). While no redox reactions occur, the lithiation is thought to occur as a reaction between the nanoscale silica and various species produced at the interface during the electrochemical silicon reduction (Hubaud et al., 2015). On long term cycling, these phases are not readily identifiable at the interface which may indicate reactions occur with SEI materials that form a soluble species or loss of interfacial cohesion in the cell.

Data Analysis

The Li₄SiO₄ was a commercially sourced powder from Alfa Aesar[®]. Lab XRD revealed a broad-peaked Li₄SiO₄ material. Small amounts of Li₂SiO₃ often seen in lab preps (from the oxides) could not be eliminated as a possible contaminant (i.e. from lithia loss on heating) due to similarities in the XRD spectra. NMR analysis of the as-received powder revealed a multiphase mixture, consistent with similar powders created in the lab. This sample analysis found the commercial material was a mixture of at least two silicate phases, one being relatively amorphous and thus difficult to detect in XRD experiments. Based on a mechanistic understanding of the formation of the second phase (probably Li₂SiO₃) it was probably nucleated on the surface phase of a crystalline Li₄SiO₄ (Philippe et al., 2012; Philippe et al., 2013a) Previous work has reported both Li₂O and Li₄SiO₄ form initially when Li⁺ is inserted through a SiO₂ native oxide on Si (Philippe et al., 2013b).

The commercial Li₄SiO₄ was stirred in a salt free mixture of ethylene carbonate and ethyl methyl carbonate (EC:EMC, 3:7 weight%) at room temperature for 48 h to test for solubility and reactivity. ²⁹Si and ⁷Li solution NMR were performed to look for Si and Li species in the solvent after samples were filtered and spectra revealed the presence of lithium but no solubilized silicon in the electrolyte. Solid-state ²⁹Si NMR was performed, on the as-received powder and powder that was in contact with the solvent for 2 days. The data are consistent with a decrease in the amount of Li₄SiO₄ and a corresponding increase in Li₆Si₂O₇ and in Li₂SiO₃, indicating that the dissolving species from the electrode into the electrolyte may formally be Li₂O or related (reaction product) species. The reaction mechanism is thought to be dimerization of the [SiO₄]⁴⁻ tetrahedra to form pyrosilicate [Si₂O₇]⁶⁻, then eventually the fully condensed Li₂SiO₃ linear chain material. Given longer exposure to the electrolyte, it is anticipated that expulsion of lithium oxide would continue depending on diffusion to the active surface, and possibly other intermediate or oligomeric species might be detected (Hubaud et al., 2015).

CONCLUSION

While diffusion is an important aspect of many commercial systems, methods to understand these properties at a mechanistic level are often limited to an understanding of crystalline pathways available to the diffusing species. In the examples noted, ²⁹Si MAS NMR has been used to understand the role of amorphous or poorly crystalline species in reaction mechanisms and their evolution of these phases over time. In the examples of the active surface coatings, the diffusion of Mg⁺²

into Li₁₅Si₄ was critical in understanding the formation cycling issues associated with the emergence of Li₁₄MgSi₄-boundary coatings, the mechanism of Mg insertion into the bulk forming ternary Zintl phases, as well as the long-term advantages to important properties like calendar life. For the compound Li₄SiO₄, initially formed during the first charge for silicon containing anodes, these phases condense and eventually move into the cell environment by reaction, formally releasing lithia. Changes at this critical interface have an important role in an energy storage system, be it stabilizing the long cycle life anode SiO_x, releasing of silicates gradually into the SEI layer, or tracking copper diffusion in silicon and understanding the role of minority surface species. Local probe techniques such as ²⁹Si MAS NMR are critical tools to understand these differences in reactivity and the relationship with the electrodes performance.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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