Effect of Surface Termination on Electrochemical Performance of Silicon Thin Films

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Manuscript submitted July 31, 2015; revised manuscript received October 27, 2015. Published November 5, 2015. This was Paper 956 presented at the San Francisco, California, Meeting of the Society, October 27–November 1, 2013.

The surface termination layer of silicon-based lithium-ion anodes is a complex mixture of silicon oxides, hydroxides, and hydrides. The species present reflect the history of the electrode and combine to make each silicon electrode different in its electrochemical performance and reactivity with the electrolyte. This variability creates challenges for silicon-based anodes as it affects SEI formation and stability, columbic efficiency, and irreversible capacity. To elucidate some of the parameters that control surface functionality we used non-aqueous electrodeposition to produce silicon thin films on copper foams. These porous electrodes were studied using $^{29}$Si MAS NMR to correlate the synthetic process and surface functionality with electrochemical performance. We found that the supporting electrolyte salt used has a significant effect on the electrodedeposited silicon thin films electrochemical properties. Films deposited using tetrabutylammonium chloride (TBACl) were found to be more crystalline with much higher surface concentration of hydrides, hydroxides and oxides, have lower capacity, and much higher irreversible capacity than films deposited using tetraethylammonium chloride (TEACl). The role of supporting electrolyte salt is hypothesized to be related to the amount of free solvent in the reaction mixture as the TBACl salt has been reported to tie up significantly more solvent due its larger size.

For many new LIB applications, the space available for the energy storage component in the end device is at a premium. This need is driving the search for new couples that can be designed, modified, or optimized to meet these volumetric goals. Among the materials under study, silicon is a promising alternative anode material to replace graphitic carbon in Li-ion batteries. Its attributes, including high specific capacity, both gravimetric (>3500 mAh/g) and volumetric (>2194 mAh/cm$^3$), and a low charge/discharge insertion/de-insertion voltage at room temperature make it desirable for many applications, however its large volume expansion (>300%) on cycling, poor capacity retention, and Coulombic inefficiencies have limited its use to date. 1,2 While many possible solutions have been proposed, including electrode surface modification, silicon dilution via creation of a composite anode, e.g. (Si-C), identifying new binders that control the expansion, or new electrode designs that contain the expansion, none alone have met the challenge. 3,4 While several studies have focused on the properties of silicon, its morphology, or its fabrication into an electrode, aspects of its electrochemical cycling, such as Coulombic inefficiencies, are related in part to the system level problem of how the silicon interface interacts with the electrolyte. Edström et al., utilizing Soft X-Ray Photoelectron Spectroscopy, was able to not only track SEI and surface changes within an electrochemical cell but was able to differentiate interfacial reaction products forming on the surface of underlying electrode materials. 5 Philippe et al., further investigated the interfacial reactions occurring on silicon-containing anodes and reported that during the first lithiation, various lithium salts formed from the reduction of electrolyte on first discharge react with the native silicon oxide layer leading to the irreversible formation of the lithium silicate $\text{Li}_2\text{SiO}_3$. 6 The lithium cations in this compound are associated (structurally) with the highly charged molecular silicates, which solvate when exposed to polar electrolytes. This process gradually leads to polymerization of the isolated silicate tetrahedra via a condensation reaction and formation of the condensed silicate species $\text{Li}_2\text{SiO}_3$ from what was initially a silica passivation layer at the electrode-electrolyte interface.

While bulk silicon generally has a silica passivation layer, the surface of thin film silicon electrodes are terminated by species that are dependent on the environment the film was produced. The presence of air or water will produce a film passivated by silicon oxides, whereas a film formed using silane (SiH$_4$) would typically be hydride terminated.

In the present study, we utilized films produced by electrodeposition of silicon from a non-aqueous electrolytic bath in the presence of solvents and non-coordinating salts commonly used in electrochemical cells. This process yielded silicon electrodes that had a wider variety of silicon surface species that changed the decomposition pathways and had a significant effect on the resulting electrochemical properties of the materials. Local structure of the silicon species formed was studied by $^1$H and $^{29}$Si MAS NMR, a sensitive tool to study the local environments in both ordered and disordered materials.

**Experimental**

Electrode films were created by electrodeposition of silicon from a bath containing 1 M SiCl$_4$ (Aldrich, 99%), 0.5 M (TEA)Cl (or (TBA)Cl)) (Aldrich, 98%) in propylene carbonate (PC, anhydrous, Aldrich, >99.7%). The materials were used as received. The films were deposited onto a porous copper foam substrate at a constant voltage of −3.4 V vs Pt, based on cyclic voltammetry studies of the same bath. Platinum referenced carbon counter electrodes were used for electrodeposition and all the experiments were carried out under an argon atmosphere at room temperature. The electrodeposition was performed within Cu foam matrix as opposed to traditional Cu foil to mitigate poor cyclability of Si films in order to establish a better method for cycling performance. 7 The copper foam substrate was provided by Circuit Foil Luxembourg. It had an initial thickness 2 mm and was subsequently calendared to various thicknesses (0.1, 0.25 and 0.5 mm) to better fit in cell hardware.

Solid State NMR studies of the powder materials were performed at Bruker Avance III 500 MHz spectrometer (11.7 T superconducting magnet), with a 4 mm MAS probe operating at 14 kHz spinning speed for the single pulse and 8 kHz for $^{29}$Si($^1$H) CP experiments. The $^{29}$Si and $^1$H 90° pulses were 4 and 3.75 μs, respectively. The RF field strengths for $^1$H-$^{29}$Si CP experiments are ~51 and ~57 kHz for $^{29}$Si and $^1$H, respectively. Contact time of 4 ms and pulse delay of 1 s were used in the CP experiments. Pulse delays of 30 s were used for the $^{29}$Si MAS NMR experiments. The $^{29}$Si chemical shifts were referenced to tetramethylsilane (TMS) at 0 ppm and all the experiments were performed on samples with natural abundance silicon.

Electrochemical cells (Hohsen, 2032) were constructed using the electrodeposited silicon films as the cathode and lithium metal as...
The increase of cathodic current around carbonate (EC): ethyl methyl carbonate (EMC) (wt%) using Celgard has been attributed to decomposition of PC and supporting electrolyte electrodes.\(^\text{10,11}\) In that study controlling the distribution of interfacial and a Cu binder were merged to create a series of high power silicon 1.5 V and 100 \(\mu\text{A/cm}^2\) needed for in situ experiments.\(^\text{8,9}\) Previously we examined a series nanostructured materials (e.g. VLS Si nanowires), porous electrodes allowing for different electrode designs to be evaluated that have strong connectivity between the active material and the current collector. This attribute has been taken advantage of to test designs based on understanding various electrode processes, surface reactions, and the effect of cycling on specific physical characteristics of the active material. In addition, depending on the deposition process used, the electrode substrate or current collector for the electrodes can also be varied, allowing for different electrode designs to be evaluated that have strong connectivity between the active material and the current collector. This attribute has been taken advantage of to test designs based on nanostructured materials (e.g. VLS Si nanowires), porous electrodes (e.g. 3DOM or metal foam-based electrodes) or transparent electrodes needed for in situ experiments.\(^\text{8,9}\) Previously we examined a series of ‘inverse design’ porous electrodes where the Cu current collector and a Cu binder were merged to create a series of high power silicon electrodes.\(^\text{10,11}\) In that study controlling the distribution of interfacial phases was a key variable in electrode performance. However, our desire to identify how the surface functionality of silicon was related to the electrochemical performance led us to examine non-aqueous electrolyte deposition as a synthetic tool. Taking advantage of the solubility of silicon tetrachloride in certain non-aqueous solvents, conformal Si anode films can be created that demonstrate good power and capacity retention. Experimentally, silicon tetrachloride is dissolved in a solvent, supporting electrolyte salt is added, and electrodes are placed so as to deposit silicon on the working electrode with evolution of chlorine on the counter electrode. Cyclic voltammetry with a Pt quasi-reference electrode (QRE) cell is used to study silicon electrodeposition on copper foil in a 0.5 M TBACl (or TEACl)/PC electrolyte mixture with SiCl\(_4\) as silicon precursor. Figure 1 shows comparison of voltammograms for solutions with and without silicon precursor. The data suggests that silicon electrodeposition occurs with a cathodic peak around \(-3.4\) V. The increase of cathodic current around \(-4.2\) V (\(-0.1\) V vs Li/Li\(^+\)) has been attributed to decomposition of PC and supporting electrolyte cations. The chronoamperogram at constant potential of \(-3.4\) V with actual cell design shows a constant current density plateau of 10 mA/cm\(^2\) for deposition time of two hours (Figure 1 inset). Cyclic voltammetry data suggest that following reactions are taking place on working and counter electrodes;

\[
\text{SiCl}_4 + 4e^- \rightarrow \text{Si} + 4\text{Cl}^- \quad \text{(working electrode)} \quad [1]
\]

\[
4\text{Cl}^- \rightarrow 2\text{Cl}_2 + 4e^- \quad \text{(counter electrode)} \quad [2]
\]

A comparison of the number of Coulombs passed during thin film deposition for the potentiostatic electrodeposition using Faraday’s law, to amount of lithium stored in the silicon on the first electrochemical lithiation gives an average efficiency for the electrochemical silicon deposition in the SiCl\(_4\)/PC solution of around 35\%, consistent with the reported value.\(^\text{12}\) This low silicon deposition efficiency has been correlated in the literature with electrolyte decomposition and side reactions related to the reactivity of SiCl\(_4\).\(^\text{13,14}\) When the loading levels are calculated via weight difference of the bare copper foam and electrodeposited foam using conventional balance, the values obtained are \(\sim\%\)50 (by weight) higher in comparison to active silicon mass calculations via electrochemistry. This can be explained by the presence of decomposition and side reaction products and residual solvent trapped in foam structure.

Scanning Electron Microscopy images of the silicon thin films deposited on copper foam (Figures 2a and 2b) show non-uniform silicon deposits with plate-like structures with silicon thicknesses varying between 1.5–4 \(\mu\text{m}\). Comparing films from studies produced using different electrolyte counter-ions, we determined that the cation size of the supporting electrolyte has an effect on deposition rate and quality of the deposit. With potentiostatic electrodeposition, the current densities observed for TBACl solution is between \(-10\) to \(-15\) mA/cm\(^2\) whereas with a TEACl supporting electrolyte lower currents of \(-5\) mA/cm\(^2\) are obtained with same precursor concentrations. As seen in Figure 2a, SEM images for silicon thin films electrodeposited with TEACl supporting electrolyte indicate smaller particle sizes and overall thinner silicon films whereas films electrodeposited with TBACl supporting electrolyte show larger and thicker deposits (Figure 2b). By X-Ray diffraction methods, all electrodeposited silicon films prepared show semi-crystalline/amorphous structure. EDX analyses on the thin films indicate that silicon is the main component with minor amounts of chloride, oxygen, and carbon (Figures 2c and 2d). The oxygen in the films is probably due to side reactions between the SiCl\(_4\) and any residual moisture in the system (contaminants, Figure 1. Cyclic Voltammograms for silicon electrodeposition solutions, dashed line shows supporting electrolyte and solvent, solid line shows silicon chloride, supporting electrolyte and solvent (scan rate of 5 mV/s). The inset shows the chronoamperogram for the electrodeposition of silicon on copper foam at a voltage of \(-3.4\) V (1 M SiCl\(_4\), 0.5 M TBACl in PC).

![Figure 1](image1.png)

![Figure 2](image2.png)
Figure 3. a) 1st cycle voltage profile for electrodeposited silicon with TEACl as supporting electrolyte. The inset shows the differential capacity curve for the 1st cycle. b) Cycle performance and columbic efficiency for electrodeposited silicon with TEACl as supporting electrolyte.

Solvent decomposition products) as given with reaction 3 below, while the carbon is attributed to residual solvent trapped in the electrode microstructure and solvent decomposition products.

$$\text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow [\text{Si}_x\text{O}_y\text{Cl}_z + \text{HCl}] \rightarrow \text{SiO}_2 + 4\text{HCl} \quad [3]$$

Figure 3 shows first cycle voltage profile and electrochemical performance for the first 100 cycles for silicon thin films prepared by electrodeposition in a TEACl supporting electrolyte. The electrochemical profile is reminiscent of Si films with poor crystallinity or amorphous-like character especially on the first lithiation with a broad peak close to 0.2 V in the differential capacity plot (Figure 3, inset). A second reaction is observed around $\sim 0.08$ V as a possible signature of small amount of crystalline silicon component. The loading levels are in the range of 0.5–1.0 mg/cm$^2$ (1–2 mAh/cm$^2$) calculated from full lithiation to Li$_3$Si$_4$ composition. Irreversible capacity losses (ICL) for the first cycle vary between 40–55% depending on the silicon loading level. A reversible capacity of $\sim 1970$ mAh g$^{-1}$ is obtained for the first 20 cycles with columbic efficiency of $\sim 99.2\%$. The capacity declines after 20 cycles and a capacity of $\sim 1100$ mAh g$^{-1}$ after 100 cycles with a stable columbic efficiency of $\sim 99.4\%$, in agreement with a previous study.$^{15}$

For silicon thin films electrodeposited in TBACl supporting electrolyte, the electrochemical profile is typical for samples with more crystalline silicon character with a sharper first lithiation peak close to 0.14 V, as seen in the differential capacity plot (Figure 4).$^{2,16-17}$ Irreversible capacity loss (ICL) for the first cycle varies between 65–80%. The loading levels are higher than the films created using TEACl and are in the range of 1–1.5 mg (1–1.5 mAh/cm$^2$) but show approximately the same real capacities. A reversible capacity of $\sim 980$ mAh g$^{-1}$ is obtained for 60 cycles and the columbic efficiency varies from 93 to 98% from the 2nd to 8th cycle, after which is improved and remains close to 99.5% for the rest of the evaluation.

Figure 4. a) 1$^{\text{st}}$ cycle voltage profile for electrodeposited silicon with TBACl as supporting electrolyte. The inset shows the differential capacity curve for the 1$^{\text{st}}$ cycle. b) Cycle performance and columbic efficiency for electrodeposited silicon with TBACl as supporting electrolyte.

Figure 5. Cycling performance of electrodeposited silicon at various rates after 15 cycles.
Rate capability tests were conducted on silicon thin films electrodeposited with TEACl supporting electrolyte cycled at C/8 to 2C rates (Figure 5). At the highest rate the capacity drops almost half which may be related to the poor conductive nature of amorphous silicon, its poor exchange current density, and the absence of electrolyte additives, e.g. FEC, that have become standard for bulk silicon electrodes.

The comparisons of the electrochemical performance of the samples show clear differences in capacity fade rate and overall capacity. The thin films prepared with TEACl were thinner, with smaller particle sizes and lower silicon loadings providing higher specific capacities. However the small particle sizes still suffer from volume expansion and loss of particle-particle contact. On the other hand, silicon films with larger particles and thicker films (prepared with TBACl) show more stable electrochemical performance. In addition, surface species present on thin films prepared by the two different supporting electrolytes are expected to have an effect on electrochemical performance and is explored below.

In order to investigate the surface functionality of silicon thin films deposited and correlate the silicon local environments formed with the supporting electrolyte used, a combination of \( ^1 \text{H} \) and \( ^{29} \text{Si} \) solid state NMR has been used. Solid State NMR is a very sensitive structural characterization tool and it allows us to identify each silicon and proton local environment formed with silicon electrodeposition. \( ^{29} \text{Si} \) NMR chemical shift is mostly influenced by coordination number of silicon and nature of the nuclei in the first coordination sphere. The chemical shift for crystalline bulk silicon is at \( \sim -80 \) ppm which is usually a sharp peak. Increasing the disorder and distribution of chemical shifts, peaks broaden. Amorphous silicon and silicon hydrides show chemical shift distribution between \( -40 \) and \( -90 \) ppm varying with hydrogen content. Silicon oxides/hydroxides give rise to silicon peaks within \( -85 \) to \( -110 \) ppm regions.\(^ {18-23} \) Figure 6 shows single pulse \( ^{29} \text{Si} \) solid state NMR data comparison of commercial silicon, air exposed (oxidized) electrodeposited silicon with thin films electrodeposited in TEACl and TBACl. In addition to the crystalline silicon peak at \( -80 \) ppm, silicon-29 solid state NMR data shows peaks for amorphous silicon, silicon hydrides as well as silicon oxide and silicon hydroxides for films electrodeposited with TEACl. With NMR peaks in similar chemical shift region samples prepared with TBACl shows less amorphous silicon and more silicon oxide character. In an effort to selectively detect the \( ^{29} \text{Si} \) NMR resonances of silicon environments that are in close proximity to protons (i.e. the surface silicon atoms) \( ^1 \text{H}^{^{29} \text{Si}} \) cross polarization solid state experiments were also performed on the thin films prepared. The comparison of the single pulse and cross polarization data shows that, peaks within \( -40 \) to \( -70 \) ppm region for the sample prepared with TEACl are mostly due to amorphous silicon with different particle sizes rather than silicon hydrides (Figure 7). On the other hand, silicon thin film prepared with TBACl shows more crystalline character with distribution of silicon environments of silicon, silicon oxides and hydroxides. This is also consistent with first cycle lithiation plateau where first lithiation was seen at \( \sim 200 \) mV for TEACl sample and \( \sim 150 \) mV for sample prepared in TBACl. \( ^1 \text{H} \) solid state NMR experiments on the same samples show that both thin films have considerable amount of hydrogen (surface and bulk). Peaks in 0.5–1.5 ppm region are usually due to isolated SiOH/SiH groups whereas higher frequency proton peaks represent hydrogen bonded proton species. \( ^1 \text{H} \) NMR data for silicon film prepared with TBACl shows additional proton resonances around 0.4 ppm due to presence of silicon hydride environments (Figure 7). The presence of these concentrated proton environments can be correlated with the higher irreversible capacity loss within first lithiation.

While small changes in the electrochemical performance of an electrode can usually be attributed to its history or small changes in its fabrication, this study has revealed that even secondary variables...
such as the size of the supporting electrolytes salt counterion appear to have a significant effect on the quality of the film and notably its surface termination and composition of the bulk. Apart from the difference in particle size and thickness of the deposited silicon films, the differences in electrochemical performance can be correlated with presence of silicon oxide and surface hydrogen species for samples prepared with TBACI. While it possibly participates in the deposition quality as a source of impurities from its low voltage decomposition, their similar composition would most likely cause them to contribute at about the same level. Another effect relates to solvation sphere. In various electrochemical studies of free versus coordinated solvent, the key defining variable is size. In PC, the Stokes radii of TBA+ has been measured to be about 50% larger than the TEA+ in the same solvent system.24 The larger size of the TBA cation would coordinate more solvent than the TEA cation resulting in a “drier” solvent in the case of TBACI. The lack of free uncoordinated solvent may be having an effect on the transport or changing the structure of various reaction intermediates.

Conclusions

The chemical environment and methodology used to create a porous thin film Si electrode have been investigated. Deposited from a solution of SiCl4 in PC, SEM images show non-uniform silicon deposits with plate-like morphology on the Cu-foam substrate with silicon thicknesses of 1.5–4 μm and up to 2.5 mg/cm2 active silicon (by first cycle capacity). Whereas the films by powder X-Ray diffraction appear to have subtle differences in crystallinity, they have very different electrochemical properties. A variable we have identified that appear to be contributing to this difference is the size of supporting electrolyte cation as its identity appears to strongly affect the long range order of the electro deposited silicon – from semi-crystalline to amorphous. These differences have significant implications for the first cycle irreversible capacity losses and cycling capacity over the first 100 cycles. TBACI as the supporting electrolyte salt was found to yield films with a crystalline silicon character as evidenced by the discharge profile on the first discharge and a first cycle irreversible capacity loss between 65–80%. Conversely, films deposited in the presence of a TEACI supporting electrolyte salt, appeared more similar to reports for amorphous silicon electrodes. These films gave first discharges with a first cycle irreversible capacity loss of about half of the films deposited using TBACI salts. After the first cycle, these silicon films showed cycling efficiencies of 99.8%.

One of the main differences in these electrodes was found to be in their surface functionalization. 1H and 29Si MAS NMR was used to show that the counterion in the supporting electrolyte salt has a tremendous effect on the electrodeposited silicon surface functionality. Films deposited in TBACI tended to be more oxygen and proton rich, while those deposited in TEACI appeared to have more amorphous silicon character. This difference can be attributed to the effect of the large TBA+ cation on the amount of free solvent available when compared to the smaller TEA+ cations.

Acknowledgments

Support to conduct this work came from the Office of Vehicle Technologies (Batteries for Advanced Transportation Technologies (BATT) Program) of the U.S. Department of Energy under Contract No. DE-AC02- 06CH11357 and is gratefully acknowledged.

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