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Chemistry of Electrolyte Reduction on Lithium Silicide

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ABSTRACT: Silicon anodes are promising for next-generation lithium-ion batteries due to high theoretical capacity. However, their performance and lifetime are currently limited by continuous electrolyte reduction and solid-electrolyte interphase (SEI) formation. Thus, SEI studies are important, but often complicated due to the rough morphology of samples, buried interfaces, and presence of binders. Here, we demonstrate the chemical origin of SEI formation by electrolyte reduction on lithium

silicide thin films, synthesized by diffusion of pure evaporated lithium into smooth sputtered silicon. These model samples allowed for accurate estimation of irreversible capacity loss due to electrolyte reduction and for precise characterization of the resulting SEI by vibrational and photoelectron spectroscopies. Spectroscopic characterizations showed clear evidence that lithium silicide reduced electrolyte directly upon contact. Negligible first-cycle irreversible capacity loss was observed for the lithium silicide compared to silicon, indicating that the decomposition product of electrolyte on lithium silicide is able to stop further electrolyte reduction to a large extent. Fluoro-ethylene carbonate (FEC) was shown to significantly affect the chemistry of electrolyte reduction on lithium silicide and subsequent cycling performance. The results of this basic study reveal the chemistry occurring at the interface of the lithium silicide and electrolyte and help in understanding the limited calendar lifetime of Li-ion batteries with Si anodes.

Introduction

Silicon is one of the most promising alternatives to graphite anodes in rechargeable lithium-ion batteries due to its high theoretical capacity of 4,200 mAh/g.[1] If realized, such high capacity would be in great demand for consumer electronics and electric vehicles. Despite this attractive feature, to date, Si anodes have not been commercialized because of several technological problems.[2] In the first cycle, active Li ions are consumed due to 1) the solid-electrolyte interphase (SEI) film formation, which leads to irreversible

capacity loss, and 2) much lower first-cycle coulombic efficiency compared to graphite. Even more importantly, as shown in Figure 1, continuous electrolyte consumption occurs in subsequent cycles, when cracks form and fresh surfaces are exposed to the electrolyte. This continuous consumption of electrolyte ultimately leads to battery degradation. Overall, these challenges compromise the application of Si anodes in batteries.

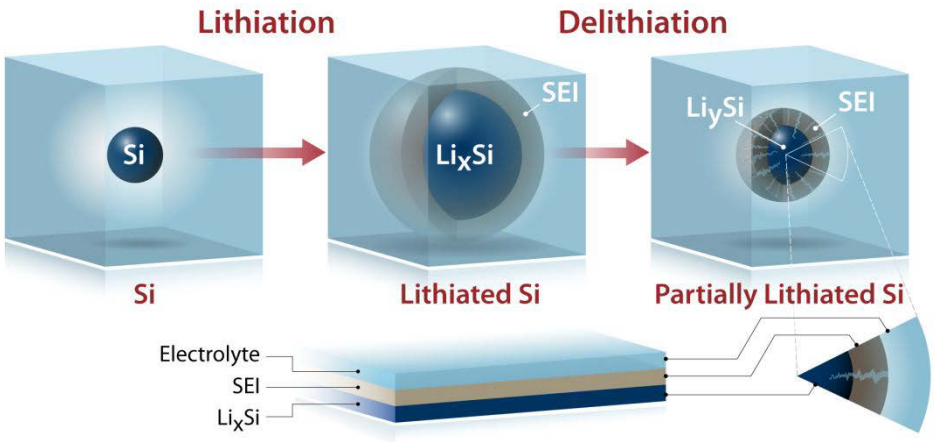

Figure 1. Schematic illustration of crack formation on Si anode upon cycling, and fresh Li_xSi surface exposure to electrolyte when cracks form. A thin-film model is used to study the interface and interphase between lithium silicide and electrolyte.

To address these applied technological problems, a basic scientific understanding of SEI formation is crucial. To this end, numerous studies of SEI formation on electrochemically lithiated silicon have been conducted using X-ray photoelectron spectroscopy (XPS),[3] nuclear magnetic resonance (NMR),[4] X-ray diffraction (XRD),[5] neutron reflectometry (NR),[6] Fourier-transform infrared spectroscopy (FTIR),[7-8] atomic-force microscopy (AFM),[9] and more. Despite significant progress in understanding, such

electrochemical studies are often complicated by the rough sample morphology, buried nature of the Li_xSi/electrolyte interface, presence of binders used for electrochemical lithiation of silicon, and other factors (Figure 1). Thus, what forms at the Li_xSi/electrolyte interface and what these interphases do to the anode performance are still largely unknown.[10-11] Answering these questions may have important implications for improving the limited calendar and cycle lifetimes of Li-ion batteries with Si anodes.

An alternative approach to understanding what happens to fresh exposed lithium silicide at cracks is to expose chemically synthesized lithium silicide to the electrolyte and study the chemical reaction products. All common electrolyte components—such as ethylene carbonate (EC), dimethyl carbonate (DMC),[12,13] and fluoro-ethylene carbonate (FEC) additive[14,15]—have reduction potentials of 0.7–1.3 V, which is much higher than that of lithium silicide. Thus, all these electrolyte components should be possible to reduce by this simple chemical reaction. Despite considerable experimental work on the electrochemical electrolyte decomposition on Si,[16-19] no experimental studies on chemical electrolyte reduction have been reported. Several computational papers are available on chemical reduction of electrolyte components on the lithium silicide surface,[20] [21] but similar experimental studies are missing from the literature. One major challenge in synthesis and characterization of lithium silicide is the strong reactivity of these materials with oxygen. In particular, Li is a very electropositive element with an electronegativity of 1. Thus, significant contamination (e.g., 20% from XPS depth profile[22]) can occur even

if very little oxygen is present in the synthesis or characterization equipment, or during the sample transfer.

Here, we report on the experimental study of the chemistry of electrolyte reduction on lithium silicide. For this purpose, nearly oxygen-free lithium silicide samples with planar geometry were prepared by diffusion of evaporated lithium into sputtered silicon thin film. The smooth surface of these samples enabled accurate spectroscopic characterization of the SEI to elucidate the effect of electrolyte composition on the reduction products. These model system samples also enabled quantitative electrochemical evaluation of irreversible capacity and estimation of electrolyte consumption in the first cycle, found to be negligible for lithium silicide compared to silicon. The results of these studies indicate that electrolyte reduction on lithium silicide occurs by a purely chemical reaction and suggests a possibility of forming SEI on prelithiated silicon for improved cell cycling performance.

Experimental Section

Lithium silicide thin films were synthesized in a two-step process. First, a 50-nm silicon thin film was deposited by RF magnetron sputtering at 4.5 W/cm^2 from a 99.999%-pure, 2-inch Si target positioned 8 cm away from the Cu foil and Pt/Si substrates in 5×10^{-3} torr of Ar. Second, a 200-nm lithium thin film was thermally evaporated onto the silicon thin film at a rate of 2 Å/s and monitored by a quartz-crystal microbalance. Both depositions were performed in a vacuum chamber with a base pressure of 3×10^{-8} torr coupled to a

glovebox (0.1 ppm of O_2). Following the depositions steps, lithium silicide was formed by inter-diffusion of lithium into silicon at ambient conditions driven by the high chemical potential of lithium on the silicon surface.

Two types of electrolytes were used in this study. The first electrolyte was composed of $LiPF_6$ (1.2M) dissolved in EC+DMC (volume ratio = 3:7). The second electrolyte also contained FEC (10 wt.%). For galvano-charge and discharge cycling measurements in coin cells, lithium silicide thin films on Cu foil with 15-mm diameter were assembled with lithium foil as a reference electrode. These half-cells were discharged to 50 mV and charged to 1 V at a C/5 rate. In addition, these two electrolytes were dropped on the surface of the lithium silicide thin film deposited on a Pt-coated silicon wafer for the attenuated total reflection – Fourier-transform infrared spectroscopy (ATR-FTIR) measurements. After 20 min of exposure, DMC solvent was used to gently wash the sample. The ATR-FTIR was performed with a Bruker Alpha spectrometer in a glovebox under argon atmosphere. Peak analysis was based on previous ATR-FTIR studies[6, 23] of SEI formation on lithium and silicon.

The XPS measurements were performed using a glovebox-integrated Phi 5600 XPS system. Glovebox conditions were better than <10 ppm H_2O and O_2. Base pressures for the XPS system were below 7×10^{-10} torr. Photoelectrons were generated using monochromatic Al Kα X-ray excitation (1,486.7 eV). The spectrometer binding-energy (BE) scale was calibrated by measuring valence-band and core-level spectra from sputter-

cleaned Au, Ag, and Cu foils (E_F = 0.00 eV, Au 4f7/2 = 83.96 eV, Ag 3d5/2 = 368.26 eV, and Cu 2p3/2 = 932.62 eV). Ar^+ sputtering (incident energy 3 keV) was used for depth profiling. Curve fitting and data processing were performed using Igor Pro with a custom program adapted from Schmid et al.[24]

Results and Discussions

Table 1. Comparison of oxygen contamination and lithium content determined from XPS measurements for two different lithium silicide deposition techniques

Deposition Technique	Pressure (torr)	Li rate (Å/s)	O (at%)	Li (at%)	Si (at%)
Li / Si co-sputtering	5×10^{-3}	0.5	40	20	40
Si sputtering / Li evaporation	4×10^{-8}	2	1	~50	~50

As shown in Table 1, a combined sputtering/thermal evaporation technique resulted in lithium silicide thin films with much lower oxygen levels (~1% in the bulk) compared to our previous work[25] on Li_xSiO_y thin films obtained by a Li/Si co-sputtering method. One possible reason for lower oxygen content is the high vacuum environment of the Li evaporation process (4×10^{-8} torr base pressure, mostly water vapor) compared to Li sputtering (5×10^{-3} torr of Ar). Another likely reason is that Li evaporation lacks the presence of Ar plasma that is used for sputtering, which can make oxygen (resulting from

the water-vapor base pressure in the chamber) more reactive. Finally, the Li deposition rate in thermal evaporation was four times higher than that in sputtering due to an upper limit of power that can be applied to the Li sputtering target before causing it to melt. The higher vacuum environment, higher deposition rate, and absence of plasma during Li evaporation all helped to reduce oxygen contamination in the lithium silicide thin films reported here. In addition to reducing the oxygen contamination, the combined sputtering/evaporation technique also led to thin-film samples with higher lithium content, as shown in Table 1.

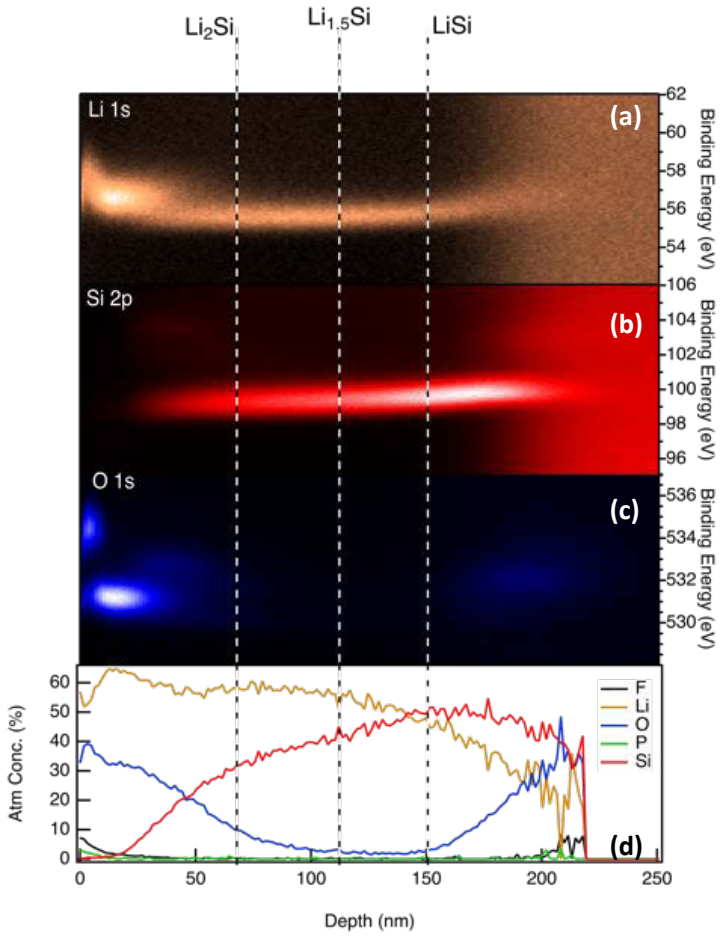

Figure 2. XPS color-intensity maps showing the signal intensity and binding energy of (a) Li 1s, (b) Si 2p, and (c) O 1s as a function of distance from the surface of the sample. Bottom figure shows the changes in composition gradient along the depth direction. Dashed lines in the images indicate the LiSi ratio at each depth.

To measure the chemical composition of the samples summarized above, an XPS depth profile was collected and is shown in Figure 2. This sample shows a gradient of lithium/silicon with depth: the lithium concentration gradually decreases while the silicon concentration gradually increases from surface to bulk. The resulting lithium-silicon ratio ranges from Li_2Si to LiSi. In the future, it would be interesting to study Li_xSi with a more homogeneous composition depth profile formed from inter-diffusion of multilayered Li/Si samples. At the depth of ~50–150 nm, the Si 2p XPS peak has a low BE of ~98 eV and the Li 1s peak has a metallic BE of 55 eV. This result, combined with the negligible O 1s content, indicates the formation of lithium silicide. The XPS depth profile also suggests that the lithium silicide thin film expanded compared to the original 50-nm Si thin film, which is similar to the electrochemically lithiated silicon. Even though the sample was stored in a glovebox for only 3 days before the XPS measurement, surface oxygen contamination was inevitable. We also found that the surface of the lithium silicide was contaminated with P and F due to electrolyte-related activities performed in the same glovebox.

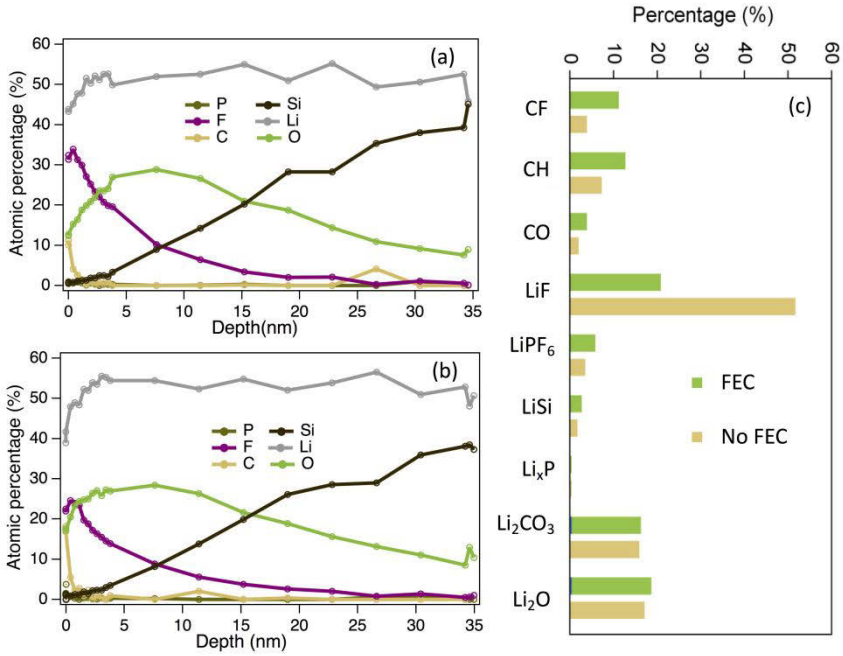

Figure 3. Composition depth profile of two Li_xSi samples treated by EC/DMC electrolyte (a) with FEC; (b) without FEC; (c) Composition analysis at the surface for EC/DMC electrolyte with FEC and without FEC.

To reveal the chemistry at the interface of the lithium silicide and electrolyte, lithium silicide film was exposed to two electrolytes (with and without FEC) immediately after deposition. The film was then gently washed with DMC before spectroscopic characterization. XPS spectra are shown in Figure S1. The XPS atomic percentage depth profiles are shown in Figure 3 for thin-film samples treated by electrolytes both with and without FEC. Large differences in F and O concentration were observed between the pristine and electrolyte-treated sample. F concentration increased and O concentration decreased after being treated with electrolyte. Generally, for both types of samples, the decomposition product layer has a composition that varies from the surface to bulk, with

the surface enriched in LiF, Li_2O, Li_2CO_3, and organic species. The F signal and C signal decrease from the surface to bulk.

Significant differences are observed between decomposition products of the two electrolytes at the near-surface layer. Electrolyte with FEC resulted in two times less F-containing species at the surface (Figure 3c). Also, more C-containing species were observed at the surface of the FEC decomposition products. One possible decomposition mechanism is that FEC quickly breaks down on the surface of lithium silicide, generating carbon monoxide or its precursor, F^- anion, and negatively charged C- and O-containing fragments.[26] These fragments may undergo further reactions and affect the subsequent decomposition of other solvents and salts. The SEI layer that grows on lithium silicide can be described by the near-shore mechanism—where the SEI components aggregate in the near-shore region—rather than by the "surface-growth mechanism," which describes the SEI formation on silicon where the SEI components progress until the SEI layer is thick enough to prevent further electrolyte reduction.[27-28] Note that even with the Li_2O at the surface, the electrolyte was reduced by Li_xSi. Despite the difference in the depth profile, these two samples (with and without FEC) share a similar thickness of SEI layer (20–30 nm), defined as the depth at which the F signal disappears. As a reference, XPS was also collected on an electrolyte-treated silicon wafer (Figure S2). We found that the Si wafer surface was covered by a very thin (1-nm) residue, indicating that no chemical reduction of electrolyte occurred at the silicon surface.

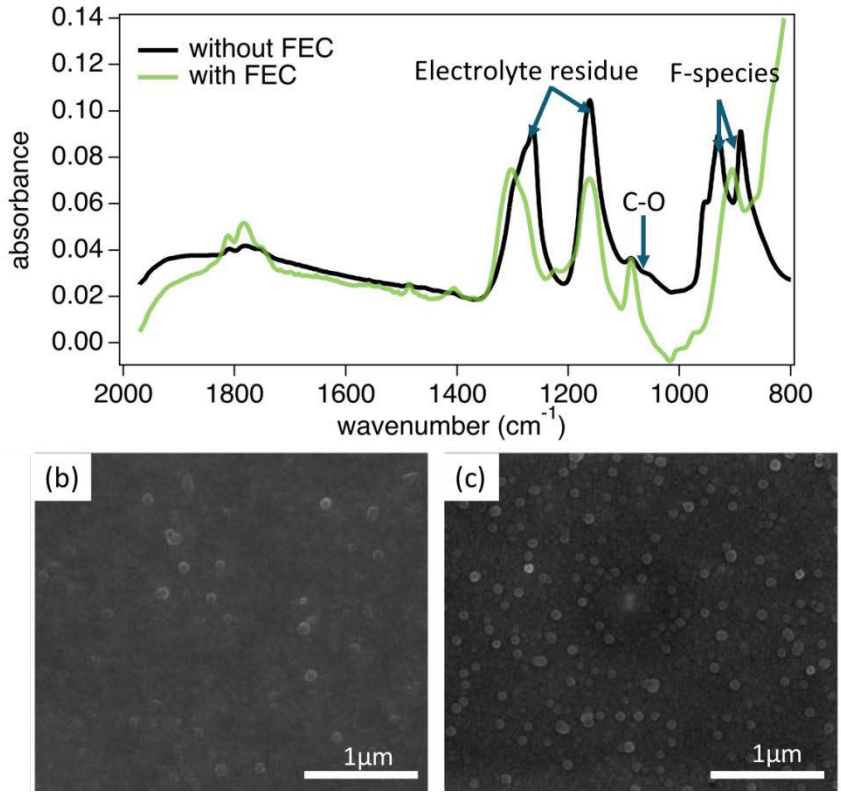

Figure 4. (a) ATR-FTIR spectra of the lithium silicide surface treated by EC/DMC electrolyte with and without FEC. Signals were normalized by signal strength of electrolyte residue. Scanning electron microscopy images of the electrode surface after EC/DMC electrolyte treatments (b) with FEC and (c) without FEC. Scale bar is 1 µm.

To gain additional insight into the chemistry of electrolyte reduction on lithium silicide, we measured ATR-FTIR spectra of the lithium silicide samples treated with two different electrolytes (Figure 4). We found that more F-containing species (P-F and LiF) are observed in the spectrum between 800 and 900 cm^{-1} for electrolyte with FEC, indicating that it helps to suppress the decomposition of $LiPF_6$ on lithium-rich surfaces. The

presence of FEC also increases the C-O signal at 1,084 cm^{-1}, indicating that more organic species are formed. These differences in F species and carbonate species measured by ATR-FTIR are consistent with XPS data. Overall, this ATR-FTIR measurement combined with XPS results support the fact that electrolyte can be chemically reduced by lithium silicide. Scanning electron microscope images in Figures 4b and 4c show that the presence of the FEC electrolyte component led to a smoother surface compared to the electrolyte without FEC.

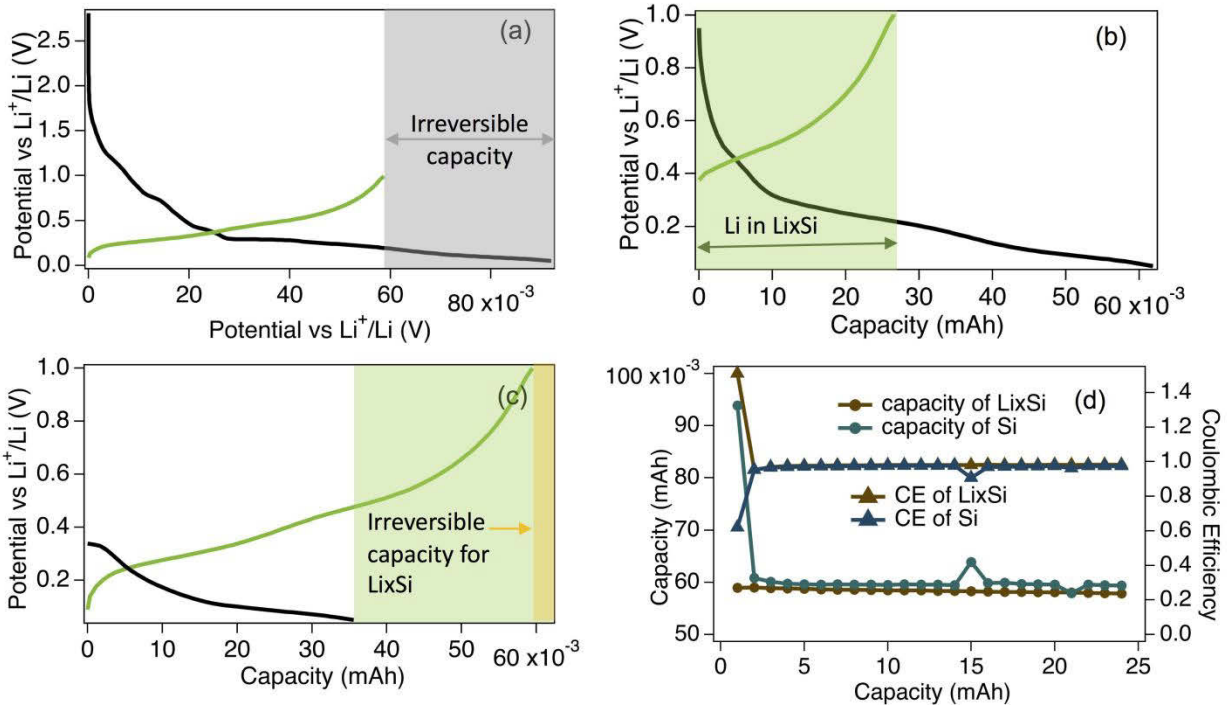

Figure 5. (a) Voltage profiles of Si thin film; (b) Voltage profiles of Li_xSi thin film; cell was discharged first; (c) Voltage profiles of Li_xSi; cell was charged first; (d) cycling performance of Si and Li_xSi half-cell.

The first-cycle irreversible capacity was used to estimate how the surface lithium potential would affect the SEI formation by comparing the planar amorphous silicon (50 nm) and lithium silicide thin films, both of which are expected to show no cracking during the cycling. This methodology has also been used in previous studies.[29-30] For this purpose, the as-deposited Si and Li_xSi thin films were assembled into half cells in EC/DMC electrolyte with FEC additive. The resulting first-cycle voltage profiles of the reference silicon thin film and lithium silicide thin films are shown in Figure 5. Irreversible capacity for silicon is usually calculated by subtracting the charge capacity from discharge capacity (0.032 mAh in Figure 5a). To evaluate the irreversible capacity of lithium silicide, two separate cells with the same electrode areas were prepared. First, we determine how much lithium could be extracted from lithium silicide by charging the first half-cell (Figure 5b). Second, we determine how much lithium could be added to lithium silicide by discharging the second half-cell (Figure 5c). By adding how much lithium could be extracted from the lithium silicide film from Figure 5b and how much lithium could be added to lithium silicide from Figure 5c, we can deduce how much total lithium is in the film after the first discharge. Then, irreversible capacity can be calculated by subtracting the first charge capacity from the total lithium in the film, with the result shown in the green rectangular in Figure 5c. The irreversible capacity (0.003 mAh, yellow rectangle in Figure 5c) is negligible compared to silicon. This indicates that very little

irreversible capacity was lost due to SEI formation. The decomposition products on the lithium silicide surface prevent further electrolyte reduction.

To put the results from our lithium silicide study into the context of more common silicon studies, cycling performance measurements were compared for these samples, with both cells discharged (lithiated) first. As shown in Figure 5d, lithium silicide showed almost exactly the same cycling performance and columbic efficiency as silicon, with the exception of the first cycle. This indicates that the SEI formed electrochemically on silicon at the first cycle is as stable as the SEI formed chemically on lithium silicide. To understand the role of different electrolyte components in this process, lithium silicide cycling performance was evaluated with and without FEC (Figure S3). Little difference could be seen from the first-cycle voltage profiles (Figure S3a), but a large difference was observed in the cycling performance of thin films (Figure S3b). After 100 cycles, 93% of the initial capacity was retained with the FEC component, whereas only 30% of capacity was retained without the FEC component. These differences in cycling performance are strongly correlated with the observation that the FEC results in less inorganic and more organic phase formation on the surface (Figure 3), and this leads to a smoother and more uniform surface (Figure 4). Correlation of these electrochemical and spectroscopic results underscores the importance of FEC in the electrolyte reduction process during silicon anode cycling.

Conclusions

In summary, we showed the chemical origin of SEI formation by electrolyte reduction on lithium silicide. Lithium silicide thin films were synthesized by thermal evaporation of lithium onto sputtered silicon thin film, with subsequent inter-diffusion between these two layers. ATR-FTIR and XPS analyses of the surface of lithium silicide that was soaked in electrolyte reveal the products of chemical reaction between lithium silicide and electrolyte. The electrolyte composition affects the chemistry of electrolyte reduction and results in more organic phases and fewer particulates when FEC is added. Lithium silicide thin films exhibited negligible irreversible capacity loss compared to that of the silicon anode. The negligible capacity loss due to SEI formation also suggests that the decomposition product of electrolyte on lithium silicide prevented electrolyte reduction during the first cycle. Furthermore, these two samples showed comparable cycling performance: decomposition product on lithium silicide before the first cycle is comparable to that SEI on Si formed after first discharge. Overall, these results reveal the chemical origin of electrolyte reduction on lithium silicide, which is an important insight for improving the calendar lifetime of Si-based Li-ion batteries. The results of this study also suggest that developing an artificial SEI for silicon, as well as application of prelithiated silicon anodes, can be viable routes for increasing the performance of such batteries.

Supporting Information

Supporting information including XPS of electrolyte-treated silicon wafer, depth profile of the silicon surface, electrochemical cycling of lithium silicide with different electrolyte (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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