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The Chemistry of Electrolyte Reduction on Silicon Electrodes Revealed by in Situ ATR-FTIR Spectroscopy

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Supporting Information

ABSTRACT: While silicon is the most promising next-generation anode material for lithium-ion batteries (LIBs), silicon electrodes exhibit significant capacity fade with cycling. A common hypothesis is that the capacity loss is due to the solid electrolyte interphase (SEI) forming in the first cycle and becoming destabilized by large cyclic volume changes. A cell for in situ attenuated total reflection-Fourier transform infrared spectroscopy with controllable penetration depth was used to study the chemistry at the electrode-electrolyte interface. The SEI product precursors at the interface were successfully identified and differentiated from free or solvated solvent molecules in the bulk electrolyte. Intriguingly, for the most common electrolyte consisting of ethylene carbonate and diethyl carbonate, ethylene carbonate was found to directly reduce to lithium ethylene dicarbonate on the lithiated silicon surface and diethyl carbonate to selectively reduce to diethyl 2,5-dioxahexane dicarboxylate on the surface of the native silicon-oxide film. Understanding this surface dependence of the SEI composition is critical to tuning the silicon electrode surface condition and, ultimately, enhancing the performance of future LIBs.

INTRODUCTION

Rechargeable batteries that exhibit high energy density, good cyclability, and minimum capacity decrease after prolonged charging/discharging are of high demand in various industrial applications, including large-scale/long-term energy storage, power supplies for portable electronics, and electric vehicles.1 Because of the high energy capacity, alloy anode materials (e.g., silicon) have attracted significant attention as the most promising next-generation anode materials.2,3 Although silicon anodes can store about 10 times more lithium than graphite anodes, this high energy capacity comes at a cost—the silicon anode undergoes large volume expansion (~300%) when fully charged, inevitably causing the electrode to fracture during repeated lithiation/delithiation.4 In addition, the Coulombic efficiency is typically low in the first cycle and the capacity degrades after extended cycling.5 This capacity loss is believed to initiate with the formation of a passivation layer on the silicon surface, known as the solid electrolyte interphase (SEI), followed by electrode cracking and continued reduction of electrolyte on freshly exposed electrode material. This process increases the interphase resistance, consumes the electrolyte, and, eventually, leads to cell failure.6 Therefore, a chemically and mechanically stable SEI is critical to the durability of silicon anodes.

The chemical composition of the SEI forming on silicon anodes is still under debate, mainly because most of the available information has been derived from ex situ characterization methods, therefore, inevitably compromised by electrolyte residue, operational uncertainty, and SEI air sensitivity.6 Also, the small thickness (~50 nm) and nonuniform surface morphology of the SEI inhibits accurate characterization of its composition.8–10 Moreover, in addition to the small mean free path in traditional electron/photon spectroscopy, the majority of previous surface analyses were performed with dry samples and with or without solvent rinsing, which prevented direct observation of the solid/liquid interface or probing of the SEI composition during cycling.11 In earlier studies, composition depth profiles were mainly obtained with destructive techniques, such as sputter-assisted X-ray photoelectron spectroscopy, Auger electron spectroscopy, and time-of-flight secondary ion mass spectroscopy.11–14 Although these methods provide valuable information about the distribution of organic and inorganic chemical species, they inevitably damage and contaminate the sample and increase the surface roughness, thus complicating the interface definition.15 Therefore, an in situ nondestructive method with adequate depth resolution is essential for characterizing the chemical composition of the SEI.

In this study, the chemical composition of the SEI forming on silicon electrodes was investigated in situ by attenuated total
reflections-Fourier transform infrared (ATR-FTIR) spectroscopy with adjustable penetration depth. By varying the IR incidence angle, the SEI precursors at the silicon electrode surface were probed and successfully distinguished from free or lithium-ion solvated molecules in the bulk electrolyte. Cyclic voltammograms (CV) and chronocoulometry (CA) were used to examine the dependence of the SEI chemical composition on the applied potential and surface condition. When the potential is swept from the open circuit potential (OCP) to the lithiation potential, an electrocatalytic reduction of diethyl carbonate (DEC) occurs on the native silicon-oxide film of the silicon electrode. The final product of this reaction is diethyl 2,5-dioxohexane dicarbamate (DEDHOC), which is produced from the reaction of ethoxide radical anion (CH₂−CH₂O⁻) intermediates with cosolvent molecules of ethylene carbonate (EC). It is also shown that lithium ethylene dicarbamate (LiEDC) forms primarily on lithiated silicon exposed by progressive cracking. The results of this study reveal two primary electrolyte side reactions on silicon anodes and provide insight into the mechanism of SEI formation during long-term cycling.

**EXPERIMENTAL METHODS**

Electrochemical Experiments. The electrolyte used in this study consists of 1 M LiPF₆/EC:DEC (= 1:2 v/v) (Novolyte Technologies, BASF). A high-performance-liquid-chromatography grade dimethyl carbonate (DMC) (99.9±%, Sigma-Aldrich) was used as rinsing solvent. A p-type Si(100) wafer (UniversityWafer) of 5–10 Ω·cm resistivity and 100 μm thickness was cut into 25.4 mm × 25.4 mm pieces, which were double-polished, thoroughly cleaned, and then used both as IR transport window and working electrode. A single-compartment Teflon cell with two electrodes was used in the *ex situ* measurements. A lithium electrode was used as both counter and reference electrode. The potentials reported here are referred to the Li/Li⁺ redox couple. All electrochemical cells were assembled in an Ar-filled glovebox (water and oxygen contents < 1 ppm).

**In Situ and Ex Situ ATR-FTIR Spectroscopy.** The ATR-FTIR spectra were acquired with a Nicolet Nexus 670 FTIR spectrometer equipped with a mercury-cadmium-telluride detector cooled with liquid nitrogen. No polarization discrimination was used, and the spectral resolution was 4 cm⁻¹. Each spectrum was obtained by superimposing a total of 256 interferograms. The spectra are presented in the form of absorbance \( A = \log(1/T) = -\log(R/R_{ref}) \), where \( R \) and \( R_{ref} \) are the single-beam spectrum of the sample and electrode/prism system without the electrolyte, respectively. All spectra were processed with an ATR correction.

A semicylindrical prism of ZnSe crystal (Del Mar Photonics) was used as the primary ATR element in the *in situ* ATR-FTIR setup (Figure 1). A double-polished Si(100) wafer was pressed against the reflecting plane of the ZnSe prism and served as both ATR element and working electrode. The gap distance was controlled to be close to the surface roughness of the ZnSe prism and the Si(100) wafer (rms ≈ 1–10 nm) by tightening the four screws of a clamping apparatus against the Teflon cell with an O-ring that sealed the electrolyte. For this setup, the interference due to silicon absorption in the range of 900–1300 cm⁻¹ has been found to be negligible. This is a critical feature for detecting the LiPF₆ salt in the electrolyte because the stretch frequency of the PF₆⁻ anions is in the same range. The silicon electrode was connected to the potentiostat (Wave-now, Pine Research Instrument) with an ultrathin copper foil.

In the *ex situ* ATR-FTIR experiments, the Si(100) electrode in the Teflon cell was discharged under the same conditions as in the *in situ* experiments. The spectra were obtained in the ATR mode directly from the electrode surface immediately after DMC rinsing. After the evaporation of the volatile DMC electrolyte component in the glovebox and rinsing with DMC to remove the residual electrolyte, the silicon electrode was transferred directly into an Ar-filled spectrometer for ATR-FTIR analysis. Both *in situ* and *ex situ* assembly and rinsing were performed inside the glovebox.

**Surface Morphology Characterization.** After the electrochemical treatment, the silicon electrodes were rinsed with DMC to remove the residual electrolyte and then transferred to a scanning electron microscope (SEM) (JSM-6700F, JEOL) for imaging. The fractured electrodes were cross-sectioned with a Ga⁺ ion beam and observed with an SEM (Nova 600i Dual Beam, FEI).

**RESULTS**

*In Situ* ATR-FTIR Electrochemical Cell and Calibration of Penetration Depth. Figure 1 shows a schematic of the *in situ* ATR-FTIR electrochemical cell in which single-crystal silicon is used as both IR transport window and working electrode. The advantage of using the internal reflection mode in ATR is that the signal from the bulk electrolyte is minimized. However, because silicon strongly absorbs wave energies of less than 1200 cm⁻¹, the structural and mechanistic analysis of SEI formation on silicon electrodes can be compromised because of the loss of important spectral fingerprints in this range. For example, the P–F stretch frequency of PF₆⁻ is in the range of 1300–900 cm⁻¹. To solve this problem, a composite ATR prism consisting of a double-polished Si(100) wafer pressed against a semicylindrical ZnSe prism was constructed. Since the Si(100) wafer is only 100 μm thick, its absorbance is negligibly small. Thus, the Si(100)/ZnSe prism exhibits a wide energy transparency similar to that of the ZnSe prism. Single-beam spectra of different ATR prism materials are shown in the Supporting Information (SI) (Figure S1). Because the penetration of evanescent waves into the sample depends on the incidence angle and IR wavelength, the IR penetration depth was varied by smoothly changing the incidence angle on the semicylindrical prism. With this cell design, it was possible to analyze both near-surface (<65 nm) and diffuse-layer (∼0.5 μm) regions and, hence, determine the SEI composition across the electrode/electrolyte interface over a wide energy range. A low-doped Si wafer (5–10 Ω·cm resistivity) was used to
minimize any dopant effects while maintaining a reasonably good conductivity. More details about the prism material absorbance and IR penetration depth can be found in the SI (Figures S1–S4).

Figure 2a shows reference spectra of DEC, EC/LiPF$_6$, EC/DEC, and EC/DEC/LiPF$_6$ obtained on a 45° cut Ge ATR prism. Electrolyte spectra at OCP for the 40–65° range of incidence angle are shown in Figure 2b. The penetration depth decreases with increasing infrared (IR) incidence angle (see the SI, eq (S1) and Figure S2). In the C–H vibration region (Figure 2a), the characteristic C–H stretch (2986 cm$^{-1}$) is assigned to the methyl groups of DEC molecules and is observed in the spectra of pure DEC, EC/DEC, and EC/DEC/LiPF$_6$. Increasing the incidence angle from 40° to 65° causes the peak at 2986 cm$^{-1}$ to disappear and a new peak at 2918 cm$^{-1}$ to appear (Figure 2b), indicating that the signals from the DEC molecules in the bulk electrolyte vanish and surface adsorbed species emerge. In the C–O vibration region (Figure 2a), the peaks at 1805 and 1770 cm$^{-1}$ are assigned to the C–O bond of solvated EC, while the peaks at 1744 and 1717 cm$^{-1}$ are attributed to free and solvated DEC, respectively. As the incidence angle increases, the C–O absorbance of free DEC (∼1744–1736 cm$^{-1}$) and its solvated shoulder (∼1713 cm$^{-1}$) gradually diminish (Figure 2c), indicating the reconstruction of the double-layer relative to the bulk electrolyte due to DEC chemisorption at the interface. Moreover, in the P–F region (Figure 2b), the PF$_6^-$ anions near the surface (842 cm$^{-1}$) are distinguished from those in the bulk electrolyte (838 cm$^{-1}$). This correlates with the change of Li-ion solvation with varying penetration depth, as evidenced by the shift of the C–O, C=O, and C–H features. Indeed, Figure 2c shows a shift of all DEC peaks to higher energies with decreasing distance from the electrode surface. In the C–O region, the ratio of peak intensities corresponding to DEC (1262 cm$^{-1}$) and its solvation shoulder (1302 cm$^{-1}$) increases with decreasing penetration depth compared with the intensity ratio of peaks assigned to EC (i.e., 1160 and 1200 cm$^{-1}$ in Figure 2c). Importantly, the peak at 1262 cm$^{-1}$ is blue-shifted near the surface, confirming the chemisorption of DEC molecules onto the electrode surface at OCP. A summary of

Figure 2. ATR-FTIR spectra. (a) Reference spectra of DEC, EC/LiPF$_6$, EC/DEC, and EC/DEC/LiPF$_6$ collected on a 45° cut Ge ATR prism surface. (b) Spectra of a Si(100) electrode in 1 M LiPF$_6$/EC/DEC (1:2 v/v) electrolyte obtained at OCP for different incidence angles. (c) Magnified spectra in the range of 1850–1650 and 1350–1100 cm$^{-1}$. For comparison, all spectra were normalized to the main C=O vibration peak of the EC molecule at 1770 cm$^{-1}$. The peaks labeled by sol-EC and sol-DEC are attributed to Li$^+$ solvation peaks of EC and DEC.
the electrolyte peak assignments is given in the SI (Table S1). These peak assignments provide an important reference basis for studying the potential dependence of the SEI composition.

**Potential Dependence of Interfacial Chemistry.** Figure 3a shows characteristic CV curves of a Si(100) electrode in 1 M LiPF₆/EC:DEC (1:2 v/v) electrolyte obtained in situ by sweeping the potential from 2 to 0.005 V at a scan rate of 1 mV/s. In the first cycle, the electrolyte reduction commences at ~1.8 V, while the maximum current occurs at ~1.3 V and decreases continuously until the onset of lithiation at ~0.1 V. Such a reduction wave is usually interpreted as the SEI formation on the silicon electrode surface. The lithiation of silicon is evidenced by the corresponding anodic current in the positive sweep. In the second cycle, the electrolyte reduction process is not apparent, indicating the occurrence of surface passivation in the first sweep. The shift of the onset potential of lithiation to ~0.3 V is due to the crystalline–amorphous silicon transformation in the first cycle. The two anodic peaks at ~0.3 and ~0.5 V are associated with delithiation. In the following in situ ATR-FTIR measurements, the focus is onto the near-surface electrode region (incidence angle = 65°). Figure 3b shows spectra obtained by applying a potential sweep from 1.9 to <0.4 V. The appearance of new features is consistent with the CV results shown in Figure 3a. The intensity and position of the peak at 842 cm⁻¹ (assigned to the absorbance of PF₆⁻ anions) are not affected by the potential sweep. No changes in the spectra were observed after further stepping down to 5 mV and back to OCP (data not shown). On the basis of the spectra of the synthesized reference compounds (see the SI, Figure S5), the new peaks at 2986, 1760, 1274, and 1032 cm⁻¹ are assigned to the DEDOHC components. Both C=O (1760 cm⁻¹) and C–O (1274 cm⁻¹) peaks are slightly shifted compared with the bulk DEDOHC spectra (1744 and 1238 cm⁻¹, respectively), presumably due to the adsorption of DEDOHC at the surface. The C=O feature at 1565 cm⁻¹ is assigned to the Li propionate compound, which is the coproduct of DEDOHC. The formation of DEDOHC occurs via ethoxy radical anions produced by the electrochemical reduction of DEC (Scheme 1). A similar electrolyte chemistry has been observed with tin electrodes. By analogy with the foregoing study of tin and gold electrodes, the selective reduction of DEC is attributed to the catalytic properties of oxide groups on silicon surfaces. None of the DEDOHC features were observed on a silicon electrode subjected to HF-etch treatment.

**Electrolyte Reduction on Lithiated Silicon.** Due to the excessive volume expansion and contraction caused by cyclic lithiation/delithiation, the silicon electrode fractured, exposing

![Scheme 1. Formation Mechanism of DEDOHC](image-url)
fresh lithiated silicon to the electrolyte. It is, therefore, instructive to understand the formation of SEI on freshly exposed lithiated silicon. A constant potential of 5 mV leading to the formation of a metastable phase (Li$_2$Si$_4$) but not Li metal plating was applied in the CA experiments, and the IR incidence angle was varied to obtain the composition depth profile of the SEI. Figure 4 shows that increasing the incidence angle above 45° causes the disappearance of the peak at 2986 cm$^{-1}$ (Figure 2), which corresponds to the C−H signal of bulk electrolyte. The C=O peaks at 1805, 1770, 1736, and 1713 cm$^{-1}$ (Figure 2) vanish with the increase of incidence angle above 60°, and new peaks appear at 3008, 2975, 2961, 2943, 1664, and 1310 cm$^{-1}$, which are assigned to LiEDC. (The reference spectrum of pure LiEDC is included in the SI, Figure S6.) When the IR beam probes deeper into the electrolyte (incidence angle = 40° and 45°), the LiEDC signal diminishes and the electrolyte signal becomes dominant. The broad peak at ~940 cm$^{-1}$ is only visible when the incidence angle is greater than 60°, indicating the formation of Si−F bonding at the silicon electrode surface. This result is consistent with a previous finding that the formation of fluorinated silicon oxide (SiOF$_2$) is due to the reaction of silicon oxide with HF produced from hydrolysis of the LiPF$_6$ salt in the presence of trace amounts of water. Clearly, reactions under a potential step of 5 mV bypass the catalytic effect of the native silicon oxide for DEC reduction, instead favoring the lithiation of silicon oxide, which appears to accelerate the fluorination of silicon oxide compared with long-term aging. As shown by the SEM images presented in the next section, the subsequent lithiation of silicon and outward expansion produces surface cracks in the silicon electrode, facilitating the reduction of EC molecules on the lithiated silicon and resulting in the formation of LiEDC (Scheme 2).

**Evolution of SEI Composition Due to Cycling.** Further evidence of the reduction of LiEDC due to the reaction of EC with exposed lithiated silicon can be obtained by observing the evolution of the spectra with cycling, which causes electrode surface cracking. Figure 4a shows in situ ATR-FTIR spectra of a lithiated silicon electrode for 65° incidence angle obtained after 0, 5, 10, and 10 lithiation/delithiation cycles. The results from successive cyclic voltammetry of the silicon electrode are given in the SI (Figure S7). The increase of the magnitude of the oxidation and reduction peaks with the number of cycles (Figure S7a) is attributed to the continuous increase of the amount of electrochemically active silicon in each cycle. During the first half-cycle, an electrochemical reduction peak is clearly observed, and the electrode surface is covered by DEDOH (peaks at 1760 and 1274 cm$^{-1}$), which appears to passivate the electrode surface for further electrolyte reduction during the first lithiation cycle. In the following 5–10 cycles, LiEDC emerges (peaks at 3008, 2975, 2961, 2943, 1664, and 1310 cm$^{-1}$), while the peaks assigned to DEDOH disappear. (For the former peak assignments, the reader is referred to the ex situ ATR-FTIR spectra of synthesized reference compounds shown in the SI, Figure S6.) Figure 5b–e shows top-view SEM images of the electrode’s surface morphology after 1, 5, 10, and 30 lithiation/delithiation cycles, while Figure 5f,g shows top-view and cross-sectional high-magnification SEM images of the
electrode after 30 cycles, respectively. Before imaging, the electrode was rinsed with DMC to remove the residual electrolyte. After the first cycle, the silicon surface is fairly intact; however, there is evidence of microscopic fissure formation in the silicon-oxide film (Figure 5b). Further cycling causes cracks to initiate at the electrode surface and then grow in the depth direction (Figure 5c–g). The details of cracking of the native silicon-oxide film on the electrode surface differ from those reported in a previous study, where the silicon-oxide film was etched off to match the mathematical simulation of the stress gradients driving crack growth. In the current sample, the silicon-oxide film is lithiated to lithium silicate in the first cycle. This restricts the volume expansion at the electrode surface and results in irregular surface cracking as opposed to the regular crack pattern observed on silicon electrodes free of the native oxide film. Figure 5c shows flaking of the lithium silicate layer due to the volume expansion mismatch between the silicon-oxide film and bulk silicon. The presence of silicon-oxygen species is confirmed by energy dispersive X-ray analysis (see the SI, Figure S8). The accumulation of more cycles causes the oxide flakes to peel off (Figure 5f) and cracks to grow into the electrode bulk (Figure 5g). Surface roughening induced by cycling explains the increase of the signal-to-noise ratio from 0.5 to 10 cycles in Figure 5a. Because of the effect of surface roughness on the estimation of the penetration depth and signal-to-noise ratio, only FTIR spectra for the first 10 cycles are presented. Cross sections of cracked silicon electrodes obtained with a focused ion beam revealed crack penetration into the electrode bulk by several micrometers. The ATR-FTIR results indicate that cycling not only increases the SEI thickness but also leads to a change from DEDOHC-dominant to LiEDC-dominant SEI composition. The SEM studies confirm that the change of the SEI composition is indeed a consequence of electrode fracturing.

**DISCUSSION**

The in situ ATR-FTIR spectra for initial and multiple cycling indicate a strong dependence of the electrolyte reduction products on the surface condition and number of cycles. On the basis of these findings, an electrolyte reduction process on
silicon electrodes can be proposed (Figure 6). Sweeping from the OCP to the lithiation potential drives the selective electrocatalytic reduction of DEC, which leads to the formation of DEDOH on the native silicon-oxide film. Passivation is triggered when the scan potential is below ~1.3 V and is characterized by the accumulation of DEDOH. After the first cycle, the SEI mainly consists of DEDOH on Li$_2$SiO$_3$. The DEDOH has been reported to increase the battery impedance, causing the charge/discharge performance to degrade. The formation of DEDOH consumes extra electrons, whereas the co-product lithium propionate traps the Li ions contributing to the low Coulombic efficiency of silicon-based batteries in the first cycle. Applying a potential of 5 mV results in the simultaneous lithiation of the silicon-oxide film and bulk silicon and bypasses the formation of DEDOH. Under this condition, solvated EC molecules are directly reduced to LiEDC on lithiated silicon, which is exposed through the cracks forming due to the excessive volume expansion mismatch during lithiation. The LiEDC is usually considered to be a beneficial SEI component because it exhibits reasonably good ionic conductivity. Extended cycling leads to electrode cracking, producing LiEDC on the freshly cracked lithiated silicon surface, while the original native silicon-oxide film remains covered with DEDOH. This is consistent with the disappearance of the electrolyte reduction curve after the first half-cycle (Figure S7). The present work suggests that premature failure of silicon electrodes is due to the formation of high-ionic-resistance DEDOH species. After prolonged cycling, the continuous low-rate electrolyte consumption and electrical isolation of active silicon electrode materials are the major factors contributing to capacity fading.

**CONCLUSIONS**

This study represents the first effort to use depth-resolved, in situ ATR-FTIR spectroscopy to analyze the interface chemistry of the SEI produced on silicon electrodes during cycling. The formation mechanism of the SEI under various potentials and surface conditions and the evolution of its composition with cycling were examined in the light of CV, CA, and ATR-FTIR techniques. It was discovered that DEDOH is the main SEI reduction product on the native oxide film of the silicon electrode, contributing to the capacity loss during initial cycling. LiEDC, a typical EC reduction product, was detected on the lithiated silicon electrode, which explains how cracked surfaces consume electrolyte and are passivated during long-term cycling. The electrolyte reduction mechanism reveals a strong dependence of the SEI composition on surface condition and number of cycles. The findings of the present investigation reveal the degradation mechanism of silicon electrodes, which includes both chemical degradation during initial cycling and chemical-mechanical degradation after prolonged cycling.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b04132.

Additional information about single-beam spectra of different ATR prisms materials, evanescent wave penetration depth, reference ATR-FTIR spectra of electrolyte compounds, energy dispersive X-ray spectroscopy of Si(100) electrode, and ATR-FTIR spectra peak assignments (PDF)

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**Notes**

The authors declare no competing financial interest.
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