The Mechanism of SEI Formation on a Single Crystal Si(100) Electrode

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A fundamental study of interfacial phenomena on a Si(100) single crystal electrode in organic carbonate-based electrolytes was carried out. The SEI formation on the Si(100) single crystal electrode was investigated as a function of the electrolyte composition, electrode potential and Li$_x$Si lithiation degree. Fourier transform infrared spectroscopy (FTIR) and X-ray photon spectroscopy (XPS) studies of the SEI layer during early stages of SEI formation indicate a strong dependence of the SEI composition on the electrolyte composition. However, the influence of the electrolyte composition becomes negligible at low potentials, when lithium alloys with Si and forms amorphous Li$_x$Si. The effect of vinylene carbonate (VC) and fluoroethylene carbonate (FEC) electrolyte additives on the composition of the SEI layer was evaluated.

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Currently, graphite is the most common negative electrode material in commercial lithium ion batteries for portable electronics.1–3 However, lithium ion batteries for large-scale transportation applications require new inexpensive electrode materials with higher specific capacity. For decades, silicon has been considered as a promising negative electrode material, mainly because of its high specific capacity of ca. 3500 mAh/g4 and its abundance in the earth crust.4–6 The key problems that prevent its widespread use are large, up to 300 % volume changes during lithiation/delithiation processes and interfacial instability of lithium silicides in organic solvent based electrolytes.7–12 The resultant poor electrochemical performance and large irreversible capacities during formation and operation of the Si negative electrode contribute to rapid degradation and failure of the battery.8,13

The solid electrolyte interphase (SEI) layer, which forms at the electrode/electrolyte interface during the initial charge/discharge cycles, is the key component that determines the long-term stability and cycling behavior of carbonaceous and intermetallic negative Li-ion battery electrodes.14–16 Electrolyte reduction and SEI layer formation on a Si electrode usually take place at potentials below 1.8 V vs. Li/Li$^+$ and accompany the formation of Li-Si phases, the so-called “Si-Li alloying” process at E ≤0.4 V vs. Li/Li$^+$.17 The exact mechanism of the SEI formation processes on Si, the SEI composition and the effect on the Si electrode electrochemical cycling performance is not well understood.18 On the other hand, SEI-forming electrolyte additives such as vinylene carbonate (VC) and fluoroethylene carbonate (FEC) are known to alter the composition and properties of the SEI on Si and improve the electrode electrochemical performance.19–21

Interestingly, recent model studies on Sn single crystal electrodes in organic carbonate electrolytes revealed a strong correlation between the crystal surface orientation and the SEI composition.22,23 A similar study of the composition of the SEI on a silicon monocrystal electrode showed strong effects of different SEI formation protocols, presence/absence of intrinsic SiO$_2$, electrolyte composition and impurities e.g., HF.24–26 Also graphite exhibits different SEI layer compositions on plane and edge sites.16,27,28 In this study, the mechanism of SEI formation on a model binder- and conductive additive-free Si(100) wafer electrode is studied as a function of the electrode potential and electrolyte composition.

Experimental

Commercial single crystal Si(100), n-type (∼10 Ω-cm resistivity), 500 μm thick wafers were obtained from Silicon Quest International (San Jose, USA). The wafers were cut into 1×1 cm pieces and heated at 195°C under vacuum for 48 h to remove adsorbed water.29 The baseline electrolyte 1M LiPF$_6$, EC:DEC [3:7 wt] was prepared by dissolving lithium hexafluorophosphate (LiPF$_6$) (Sigma Aldrich, battery grade) in a mixture of ethylene carbonate (EC) and diethylene carbonate (DEC) (Sigma Aldrich, battery grade) and fluoroethylene carbonate (FEC) (Solvay S.A., battery grade) and vinylene carbonate (VC, Sigma Aldrich, battery grade) additives were used to prepare 1 M LiPF$_6$, FEC:EC:DEC [10:27:63] and 1M LiPF$_6$, VC:EC:DEC [2:29:4:68.6] electrolytes. Electrochemical experiments were carried out in a three-electrode test cell with Li-foil counter and reference electrodes (Figure 1), using a Reference 600 Potentiostat/Galvanostat/ZRA (Gamry Instruments). Linear sweep voltammetry scans were performed at a 0.025 mV/s scan rate. Prior to spectroscopic and microscopic measurements, the Si(100) electrodes were removed from the electrochemical cell, soaked in DEC three times and dried under vacuum for 5 min. All materials and sample handling were conducted in a He-filled glove box (VAC Nexus one, O$_2$ and H$_2$O < 1 ppm). All potentials are referred vs. the Li/Li$^+$ electrode. Transmission FTIR spectra were recorded in a N$_2$-filled environmental chamber using a MB102 (Bomem) spectrometer equipped with CsI windows. The Si electrodes were transferred from the glove

Figure 1. Schematic diagram of the three-electrode test cell.
Figure 2. Linear sweep voltammograms of the Si(100) electrode in 1M LiPF₆, EC:DEC [3:7], 1M LiPF₆, VC:EC:DEC [2:29.4:68.6], and 1M LiPF₆, FEC:EC:DEC [10:27:63].

Table I. Current-charge characteristics of cathodic linear sweep voltammograms (Figure 2) of the Si(100) electrode in 1M LiPF₆, EC:DEC [3:7], 1M LiPF₆, VC:EC:DEC [2:29.4:68.6] and 1M LiPF₆, FEC:EC:DEC [10:27:63].

| Electrolyte         | Peak current density (µA cm⁻²) | Total consumed charge (C) | On-set potential of electrolyte decomposition (V) |
|---------------------|-------------------------------|---------------------------|-----------------------------------------------|
| 1M LiPF₆, EC:DEC [3:7] | 330 (at 1.4 V)                | 4.38                      | 1.8                                           |
| 1M LiPF₆, VC:EC:DEC [2:29.4:68.6] | 480 (at 0.9 V)                | 5.52                      | 1.6                                           |
| 1M LiPF₆, FEC:EC:DEC [10:27:63] | 920 (at 0.5 V)                | 11.88                     | 2.1                                           |

Results and Discussion

Figure 2 depicts linear sweep voltammetric profiles of the Si (100) electrode in 1M LiPF₆, EC:DEC [3:7], 1M LiPF₆, VC:EC:DEC [2:29.4:68.6] and 1M LiPF₆, FEC:EC:DEC [10:27:63] electrolytes. The cathodic current threshold, the current peaks potentials and the total charge consumed (Table I) vary significantly with the electrolyte composition, which may indicate different interfacial reaction pathways and rates. The current response in the 1M LiPF₆, EC:DEC [3:7] baseline electrolyte shows a peak at 1.5 V followed by a broad and featureless current tail. In the presence of FEC the current shows a broad maximum at -0.5 V, whereas the VC-containing electrolyte displays two strong cathodic peaks at 0.8 and 0.6 V and a broad shoulder centered around 1.3 V similar to the current features observed in the baseline electrolyte. The on-set potential of electrolyte decomposition in the baseline electrolyte is located at 1.8 V, which is consistent with literature. It is shifted by 0.2 V to lower potentials in the presence of VC, but in the 1M LiPF₆, FEC:EC:DEC [10:27:63] electrolyte it is observed at higher potentials, at ca. 2.1 V (Table I). The total charge consumed by the electrolyte reduction reactions during the initial potential scans increases slightly in the presence of VC but nearly triples in 1M LiPF₆, FEC:EC:DEC [10:27:63].

The presence of VC and FEC induces different SEI formation pathways at different potentials (Figure 2), which usually results in an improvement of the cycling performance of Si in lithium ion batteries. To unveil processes, which occur during the early stages of SEI formation, two series of control experiments were carried out. One set of electrode samples was obtained from electrochemical experiments on an unlithiated Si(100), where the linear voltammetric scan was stopped at 0.5 V i.e., before the Li-Si alloying. The other set of electrodes was removed from the cell after scanning the potential to 0.01 V, i.e., when the surface of the Si wafer electrode becomes fully lithiated and amorphous LiₓSiₓ. SEM images of the Si(100) electrodes removed at 0.5 V are shown in Figure 3. The morphology of the SEI layer formed in the additive-free baseline electrolyte is rough, highly inhomogeneous and consists of particles and agglomerates of various sizes. The SEI layers obtained in the VC- and FEC-containing electrolytes appear more uniform and homogenous. The elongated cracks and channels observed in Figure 3b most likely originate from the drying process prior to the SEM investigation.

EDX elemental analysis of the surface films (Table II) shows signals for carbon, oxygen, fluorine, phosphorus and silicon. The Si background signal doubles for the electrode from the VC-containing electrolyte and it becomes huge for the electrode stemming from the FEC-containing electrolyte. The intensity of the silicon signal from the Si(100) substrate depends on the SEI composition and is proportional to the thickness of the SEI, which presents a quite opposite trend to the observed pattern of consumed cathodic charge (Table I), assuming that the majority of the reduction products formed in the 1M LiPF₆, VC:EC:DEC [2:29.4:68.6] and 1M LiPF₆, FEC:EC:DEC [10:27:63] electrolytes.
LiPF₆, FEC-EC:DEC [10:27:63] electrolytes are soluble and diffuse away in the electrolyte immediately after formation. Another possibility is that the deposition mechanism of the electrolyte with FEC follows multi-electron pathways and thus more charge is consumed per solvent/salt molecule.

Figure 4 shows FTIR spectra for the SEI layers formed at 0.5 V in the three electrolytes. The spectra display different characteristics clearly indicating variations of chemical composition in the corresponding SEI layers. Similarly to the studies of Tsubouchi et al.31 and Profatilova et al.,17 the FTIR spectra consist of features associated with each electrolyte component. LiPF₆ decomposition products appear as a broad peak at 500 cm⁻¹ for ν(Li-F) in LiF, a peak at 842 cm⁻¹ for ν(P-F) in PF₃, and peaks at 982, 905 and 730 cm⁻¹ represent the the ν(p(O-C)) stretching modes in P(OR)₃. The triplet at 1775 cm⁻¹ corresponds to the ν(C=O) stretch modes of DEC and EC decomposition products.32 The asymmetric stretching mode ν(C=O) at 1484 cm⁻¹ can be attributed to decomposition products of EC whereas the symmetric mode ν(C=O) at 1300 cm⁻¹ originates from products of DEC reduction. The two peaks at 1200 and 1086 cm⁻¹ are characteristic for carbonate ring stretching modes ν(C-O) of EC decomposition products. The peak at 1410 cm⁻¹ is attributed to bending modes of the CH₃/CH₂/CH groups. The FTIR spectrum of the SEI layer formed at 0.5 V vs. Li/Li⁺ in 1M LiPF₆ in VC:EC:DEC [2:29.4:68.6] shows similar bands at 1200 and 1086 cm⁻¹ of the EC decomposition products and a strong band from LiF at 500 cm⁻¹ in comparison to the baseline electrolyte.

The FTIR spectrum of the SEI layer grown in the presence of FEC is somewhat similar to the spectrum of the SEI formed in the baseline electrolyte. The peak distribution pattern between 600 and 1500 cm⁻¹ is comparable to the spectrum from the baseline electrolyte. However, the ν(ILI-F) peak at 500 cm⁻¹ and bands representing the DEC decomposition products at 1300 and 1775 cm⁻¹ appear to be more intense in relation to the other bands. The additional broad spectral features at 1980 and 1860 cm⁻¹ may indicate a wider variety of decomposition products at the Si(100) electrode in the baseline electrolyte. The FTIR spectrum of the Si(100) electrode in the VC-containing electrolyte shows a radically different peak distribution pattern. Especially, the high profile of the peaks at 1300 cm⁻¹ and in between 500 and 1000 cm⁻¹ deviates from the observed spectra of the Si(100) electrode in the baseline and FEC-containing electrolytes.

Figure 5 shows C 1s XPS spectra of the SEI layers on Si(100) electrode formed during the linear voltammetric scan to 0.5 V. The spectra are dominated by the C-H bond at 285.0 eV, C-O bond at 286.3 eV, O-C-O/R-C=O bonds at 287.7 eV and C≡O bonds from ketones/esters at 289 eV. The relative C-H/C-O band intensities vary significantly between the samples and are the highest for the SEI from the FEC-containing electrolyte and the lowest for the VC-containing electrolyte. The VC-containing electrolyte appears to favor formation of Si compounds with C-O and O-C-O functional groups, possibly originating from VC polymerization products.

Table II. Relative elemental composition of the SEI on Si(100) at 0.5 V in 1M LiPF₆, EC:DEC [3:7], 1M LiPF₆, VC:EC:DEC [2:29.4:68.6] and 1M LiPF₆, FEC:EC:DEC [10:27:63].

| Electrolyte | C [%] | O [%] | F [%] | Si [%] | P [%] |
|-------------|-------|-------|-------|--------|-------|
| 1M LiPF₆, EC:DEC [3:7] | 10.13 | 16.00 | 66.19 | 1.17 | 06.51 |
| 1M LiPF₆, VC:EC:DEC [2:29.4:68.6] | 10.52 | 10.44 | 76.05 | 2.37 | 00.62 |
| 1M LiPF₆, FEC:EC:DEC [10:27:63] | 28.43 | 06.70 | 18.10 | 46.60 | 00.18 |

Figure 4. Ex situ FTIR spectra of the Si(100) electrode removed at 0.5 V from 1M LiPF₆, EC:DEC [3:7], 1M LiPF₆, VC:EC:DEC [2:29.4:68.6] and 1M LiPF₆, FEC:EC:DEC [10:27:63].
Figure 6. F 1s XPS spectra of SEI on the Si(100) removed at 0.5 V from 1M LiPF$_6$, EC:DEC [3:7], 1M LiPF$_6$, VC:EC:DEC [2:29.4:68.6] and 1M LiPF$_6$, FEC:EC:DEC [10:27:63].

Figure 7. Si 2p XPS spectra of SEI on the Si(100) removed at 0.5 V from 1M LiPF$_6$, EC:DEC [3:7], 1M LiPF$_6$, VC:EC:DEC [2:29.4:68.6] and 1M LiPF$_6$, FEC:EC:DEC [10:27:63].

Figure 8. Normalized FTIR spectra of the Si(100) electrode scanned to 0.01 V in 1M LiPF$_6$ in EC:DEC [3:7], 1M LiPF$_6$, VC:EC:DEC [2:29.4:68.6] and 1M LiPF$_6$, FEC:EC:DEC [10:27:63].
ferences in the chemical composition of the SEI layer as compared to the electrode scanned to 0.5 V. The spectra of the Si(100) electrode in the baseline electrolyte recorded at 0.01 V (Figure 8) reveal a slight increase of the Li-F peak at 500 cm$^{-1}$ and the $\nu_{V(P)}$ and $\nu_{P(O-C)}$ modes at 842, 982, 905 and 730 cm$^{-1}$, respectively. This effect may indicate increased content of inorganic electrolyte decomposition products in the SEI at 0.01 V as compared to 0.5 V (Figure 4).

A closer look at the shape of the broad peak at 1775 cm$^{-1}$, originating from the symmetric $\nu_{V(C-O)}$ mode, reveals that the right shoulder is less intense in the SEI produced at 0.5 V. Additionally, the (as)symmetric mode $\nu_{V(C-O)}$ at 1300 cm$^{-1}$ is less pronounced, as well. The lower intensity of these bands, which are attributed to the decomposition products of DEC suggests their lower concentration in the SEI at 0.5 V. This leads to the overall conclusion that at early stages of SEI formation (E>0.5V) the formation mechanism is mainly driven by the decomposition of the organic carbones, preferably the linear ones, whereas at lower potentials the salt and cyclic carbonates decomposition rates tend to increase significantly.

A similar spectral response is seen in all the three electrolytes, which is quite unexpected, considering the observed very different electrochemical behavior (Figure 2) and the remarkable differences in the SEI composition at 0.5 V. It appears that the SEI that forms on pristine Si(100) at E>0.5 V undergoes further growth and transformation during silicon alloying with lithium at lower potentials. This produces a fairly consistent SEI on the fully lithiated/amorphous LixSi as reported.41–43 This concept has also been expanded to a thermal process is accompanied by a substantial volume expansion,6,8,9 it is undergoing further growth and transformation during silicon alloying with lithium at lower potentials. This produces a fairly consistent SEI on the fully lithiated/amorphous LixSi as reported.41–43 This concept has also been expanded to a thermal process is accompanied by a substantial volume expansion,6,8,9 it is

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