In Situ DRIFTS Analysis of Solid Electrolyte Interphase of Si-Based Anode with and without Fluoroethylene Carbonate Additive

Yonas Beyene Yohannes,a,∗ Shawn D. Lin,a,∗z and Nae-Lih Wub,**

aDepartment of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, 10607 Taiwan
bDepartment of Chemical Engineering, National Taiwan University, Taipei, 10617 Taiwan

The effect of fluoroethylene carbonate (FEC) additive has been studied in the formation of solid electrolyte interphase (SEI) over Si-based anode using in-situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy). SEI species were observed in the first lithiation cycle at an onset potential of 1.4 V in electrolyte containing 2 wt% vinylene carbonate (VC) + 10 wt% FEC and at 1.1 V in electrolyte without FEC additive. With blended VC and FEC, high carbon containing species including poly (FEC), poly (VC), and polycarbonates were identified, while poly (VC) and polycarbonates formed in the absence of FEC. The FEC additive also led to a higher content of organic phosphorous fluorides as compared to the electrolyte containing no FEC. Electrochemical analyses indicated that the combination of 2 wt% VC and 10 wt% FEC resulted in lower impedances and improved the stability of the Si-electrode through cycling as compared to that without FEC. DRIFTS provided evidence that similar SEI species formed after the initiation in the first cycle, and this formation was recorded for five cycles. Finally, possible reactions related to the reduction decomposition of FEC and VC are discussed.

© The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.068171jes] All rights reserved.

Experimental

Silicon based electrodes, Si-SiC-Ni-C, were prepared following a previously reported procedure.37 They consisted of 70 wt% Si-containing active material, 12 wt% sodium alginate (Acros) as a binder, and 3 wt% super P (TIMCAL) and 15 wt% KS6 (TIMCAL) as conductive additives. The prepared slurry was cast on a Cu-foil current collector and then vacuum dried at 150 °C for 12 h. The electrodes were punched into discs of 13 mm diameter. The active material loading of the working electrode was 1.7 mg/cm² with a theoretical capacity of ~600 mAh/g. Typical CR2032 coin cells were assembled.© The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.068171jes] All rights reserved.

∗∗Electrochemical Society Student Member.
∗∗∗Electrochemical Society Member.
*E-mail: sdlin@mail.ntust.edu.tw

With the increasing demand for battery systems with high energy density and high power for applications such as hybrid and electric vehicles, the development of Li-ion batteries has attracted much attention in recent years.1–2 This self-supporting energy storage system3 works based on the principle of redox reactions that can reversibly convert chemical energy into electrical energy. In Li-ion battery operation, the negative electrodes function without FEC additive. With blended VC and FEC, high carbon containing species including poly (FEC), poly (VC), and polycarbonates were identified, while poly (VC) and polycarbonates formed in the absence of FEC. The FEC additive also led to a higher content of organic phosphorous fluorides as compared to the electrolyte containing no FEC. Electrochemical analyses indicated that the combination of 2 wt% VC and 10 wt% FEC resulted in lower impedances and improved the stability of the Si-electrode through cycling as compared to that without FEC. DRIFTS provided evidence that similar SEI species formed after the initiation in the first cycle, and this formation was recorded for five cycles. Finally, possible reactions related to the reduction decomposition of FEC and VC are discussed.

Haregewoin et al. and Teshager et al.30,31 demonstrated that in-situ DRIFTS is an effective tool for investigating the evolving surface film on electrodes. In situ FTIR analysis over Si-based, tin (Sn), and mesocarbon microbead (MCMB) electrodes using alkyl carbonate electrolyte has been carried out.25–24 Surface species such as lithium carbonates, alkyl carbonates, polycarbonates, and also organic phosphorus fluorides have been identified. The role of VC and FEC electrolyte additives in the SEI layer over Si-based anodes has been discussed by means of in-situ24,35 and ex-situ10,36 FTIR measurements. Corte et al.34 used in-situ FTIR measurement to show the dynamic behavior of the SEI film thickness, where the thickness increases during silicon lithiation and partially decreases upon silicon delithiation. Nguyen and Lucht10 also showed the comparative effect of the VC and FEC additives on the cycling performance and SEI composition of Si nanoparticles by using ex-situ measurements. Using infrared spectra with attenuated total reflectance (IR-ATR), they reported an SEI-film consisting of poly (FEC), LiF and Li2CO3 as primary reduction products of FEC additives. Nevertheless, real-time investigation has not been performed on the direct comparison between VC and FEC additives in the formation of the SEI-film, and the reduction mechanism of these two important additives upon cycling is still not clear.

In this paper, in-situ DRIFTS measurements were used to examine the SEI formation over Si-based anode with and without 10 wt% FEC additive in a VC-containing LiPF6-electrolyte up to the fifth cycle. In the presence of FEC additive, we observed the simultaneous formation of poly (FEC) and poly (VC) starting from the first cycle, when FEC was reduced, and similar species continuously formed in later cycles. The reactions leading to SEI formation are discussed, and the findings of this study may provide insights for improving the cycling stability of Si-based anodes.

With the increasing demand for battery systems with high energy density and high power for applications such as hybrid and electric vehicles, the development of Li-ion batteries has attracted much attention in recent years.1–2 This self-supporting energy storage system3 works based on the principle of redox reactions that can reversibly convert chemical energy into electrical energy. In Li-ion battery operation, the negative electrodes function without FEC additive. With blended VC and FEC, high carbon containing species including poly (FEC), poly (VC), and polycarbonates were identified, while poly (VC) and polycarbonates formed in the absence of FEC. The FEC additive also led to a higher content of organic phosphorous fluorides as compared to the electrolyte containing no FEC. Electrochemical analyses indicated that the combination of 2 wt% VC and 10 wt% FEC resulted in lower impedances and improved the stability of the Si-electrode through cycling as compared to that without FEC. DRIFTS provided evidence that similar SEI species formed after the initiation in the first cycle, and this formation was recorded for five cycles. Finally, possible reactions related to the reduction decomposition of FEC and VC are discussed.

© The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.068171jes] All rights reserved.

Experimental

Silicon based electrodes, Si-SiC-Ni-C, were prepared following a previously reported procedure.37 They consisted of 70 wt% Si-containing active material, 12 wt% sodium alginate (Acros) as a binder, and 3 wt% super P (TIMCAL) and 15 wt% KS6 (TIMCAL) as conductive additives. The prepared slurry was cast on a Cu-foil current collector and then vacuum dried at 150 °C for 12 h. The electrodes were punched into discs of 13 mm diameter. The active material loading of the working electrode was 1.7 mg/cm² with a theoretical capacity of ~600 mAh/g. Typical CR2032 coin cells were assembled.© The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.068171jes] All rights reserved.
in an argon-filled glove box (O₂ and H₂O < 1 ppm). Each coin cell consisted of a Si-based working electrode and a lithium foil counter electrode, with electrolyte (0.05 mL) and a Celgard 2320 separator to separate the two electrodes. High purity battery grade electrolyte comprised of 1 M LiPF₆ in a 1:2 (v/v) mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with 2 wt% vinylene carbonate (VC) (Dongguan Shanshan Battery Material Co., LTD, H₂O ≤ 20 ppm, HF ≤ 50 ppm) with or without 10 wt% fluoroethylene carbonate (FEC) (TCI, 98%) additive was used as received. The electrolyte composition of 1 M LiPF₆ in EC:EMC (1:2, v/v); 2 wt% (VC) was labeled as STD + 2% VC, and the 1 M LiPF₆ in EC:EMC (1:2, v/v); 2 wt% (VC) + 10 wt% FEC was labeled as STD + 2% VC + 10% FEC. A VMP3 multichannel battery tester was used for lithiation-delithiation tests in the range of 0.05–1.5 V at a 0.1 C rate. Electrochemical impedance spectroscopy (EIS) measurements were also performed before and after cycling discharge to 0.05 V using a VMP3 multichannel potentiostat. The frequency range used for the impedance measurement was from 100 kHz to 10 mHz with an AC perturbation of 10 mV. For cyclic voltammetry (CV), the same group of cells was analyzed using an Autolab potentiostat/Galvanostat response analyzer (Autolab, Eco Chenie PGSTAT30) with a scan rate of 0.1 mV/s from open circuit potential (OCP ~ 3.0 V vs. Li/Li⁺) to 0.005 V.

To characterize SEI formation during cycling of the Si-based electrodes, a Nicolet 6700 FTIR spectrometer equipped with a DRIFTS sampling accessory and a mercury–cadmium–telluride (MCT/A) detector was used. For the in-situ DRIFTS analysis, a home-made Teflon cell equipped with a ZnSe window was used. After careful assembly inside the argon-filled glove box, the cell was inserted for the FTIR measurement, for which a maximum beam intensity was tuned before feeding of the electrolyte. DRIFTS spectra were acquired after circulating the electrolyte at a resolution of 4 cm⁻¹ and an accumulation of 100 scans with a bare electrode as the background. To examine the potential dependence, the Si-based electrodes were polarized to 0.01 V starting from its OCP, typically at ~3.0 V, and potentiostatically held at selected potentials within a 5 min holding period. The electrolyte contribution was first identified at OCP after filling the in-situ DRIFTS cell, and then the species at the interface during the potential scan were resolved based on the difference spectra between the adjacent FTIR spectra. For instance, the difference spectra ‘1.0–1.3 V’ indicates the spectrum recorded at 1.3 V is subtracted from the spectrum recorded at 1.0 V. The DRIFTS setup used in this study adopted electrolyte circulation to circumvent the compositional change in thin layer electrolyte due to the electrochemical reaction. This allowed a nearly constant IR absorption background for the thin-layer electrode, which was important for the elimination of the electrolyte absorbance via spectrum subtraction.

Results and Discussion

Electrochemical behavior.—Our silicon composite electrode was used to record the voltage profiles during the first lithiation-delithiation cycle, and the cyclic performances of STD + 2%VC and STD + 2% VC + 10% FEC electrolytes are displayed in Figure 1. The first Li intercalation and deintercalation of the Si-based anodes were similar for these two different electrolytes (Figure 1a). In both cases, the intercalation of Li started at low potential (~0.2 V), consistent with previous works,27,38,39 reflecting that the Si-based electrodes during the first electrochemical cycle were not significantly influenced by the presence of 10% FEC additive.

The cycling performance of Si-based electrodes with both electrolytes showed a similar initial drop in capacity, which can be attributed to the formation of SEI film due to the decomposition of electrolyte components. The cells containing electrolyte with STD + 2% VC and STD + 2% VC + 10% FEC had a first cycle efficiency of 74%. Starting from the 2nd cycle, the efficiencies of both cells were constantly higher than 95%, as shown in Figure 1b. The cell containing FEC additive demonstrated a better cycling stability than the electrolyte containing STD + 2% VC, whose cell performance declined after 5 cycles.

Impedance measurements before and after cycling were recorded with the corresponding Nyquist plots shown in Figure 2. The Nyquist plots are all composed of semicircles in the high frequency region, and a sloping line in the low frequency region. Such Nyquist plots can be modeled by an equivalent circuit, shown in Figure 2c.27,28 As shown in Table I, the fitting results indicated that ohmic resistance R₀ had an insignificant change up to the 10th cycle, but the Rₑ value after the 30th cycle showed a 3 in STD + 2% VC + 10% FEC and 6 in STD + 2% VC times increment. The obvious decrease in the resistance of SEI (Rₛₑi) and the charge transfer resistance (Rₜₑ) after the 1st cycle is attributable to the formation of SEI. For both cases, cycled with VC only and with both VC and FEC, Rₛₑi and Rₜₑ decreased with increased cycling, but an obvious increase in both impedances was found from the 10th to 30th cycles. The cell with VC and FEC additive had lower impedances than that without FEC, especially after long cycles. The Nyquist plots in Figure 2 reflect a remarkable difference after 30 cycles between the Si-based electrodes in the two electrolyte solutions. The impedance spectrum of the Si-based electrode with 2 wt% VC and 10 wt% FEC at low frequency was almost capacitive, whereas the electrode without FEC was typical of a highly resistive electrode.4 These results verify that the electrolyte containing both VC and FEC additive critically influenced the charge transfer process of the Si-based electrodes by SEI formation. These EIS results establish that the improved cycling stability with 2 wt% VC and 10 wt% FEC at low frequency was almost capacitive, whereas the electrode without FEC was typical of a highly resistive electrode.4 These results verify that the electrolyte containing both VC and FEC additive critically influenced the charge transfer process of the Si-based electrodes by SEI formation. These EIS results establish that the improved cycling stability with 2 wt% VC and 10 wt% FEC can be ascribed to a higher conductivity at the electrode interface, as compared to that without FEC additive.4

In the literature, debate continues regarding whether the impedance results come from the Li-metal, the graphite/silicon anode, or the metal oxide cathode. For instance, Song et al.40 and Solchenbach
et al.\textsuperscript{41} reported that the higher impedance value for Li-ion batteries resulted from the lithium anode. However, counter-arguments stating that silicon may be the source of the dominant impedance of a Si-Li half-cell have been also reported in many papers.\textsuperscript{10,36} With this disagreement in mind, we confirmed our impedance result using a symmetric Si-Si cell type. Our results showed that the dominance in the impedance of the Si-Li half-cell came from the Si-electrodes.

### Table I. Fitting results of the impedance of Si-based electrode with different electrolyte before and after cycling using 2032-type coin cells.

| Electrolyte       | STD + 2%VC | STD + 2%VC + 10%FEC |
|-------------------|-------------|----------------------|
|                   | $R_e$ (Ω)   | $R_{SEI}$ (Ω)        | $R_{ct}$ (Ω)   | $R_e$ (Ω)   | $R_{SEI}$ (Ω) | $R_{ct}$ (Ω)   |
| At OCP            | 1.01        | 16.01                | 120.10         | 2.01        | 17.01         | 134.30         |
| 1\textsuperscript{st} cycle | 1.11        | 13.40                | 69.33          | 1.31        | 5.04          | 42.01          |
| 10\textsuperscript{th} cycle | 2.05        | 14.21                | 45.05          | 1.81        | 4.00          | 35.11          |
| 30\textsuperscript{th} cycle | 12.30       | 42.31                | 123.10         | 6.74        | 23.14         | 74.03          |

Figures 3a and 3b illustrate the first four cycles of a cyclic voltammogram of Si-based anodes using the two electrolytes. The voltammogram indicated a reversible lithiation and delithiation process. In the 1\textsuperscript{st} negative going potential scan, a cathodic peak with an onset of $\sim$0.2 V conformed to lithiation, while the reduction onset potential shifted to $\sim$0.4 V during the second cycle lithiation. In the positive going potential scans, the two anodic peaks at $\sim$0.3 and $\sim$0.5 V indicate delithiation from the silicon anode. The presence of FEC in the electrolyte solution over Si-based anodes gave a stabilized cyclic voltammetry lithiation/delithiation response as compared with the electrolyte containing STD + 2%VC. After 1\textsuperscript{st}-cycle, the 10 wt% FEC additive also improve the polarization of the electrodes compared...
to the electrolyte containing STD + VC. In Figure 3c, the reduction of electrolyte components (EC, VC, and EC) was observed in the first cycle, but no reduction of component was noticed in CV after the 1st cycle. With use of the electrolyte containing STD+VC the reduction current peak at ~1.1 V vs. Li/Li⁺ can be attributed to the reduction of VC.42 With electrolyte containing STD+VC+FECA reduction peak was observed at ~1.4 V vs. Li/Li⁺ in the first cycle due to the reduction of FEC.38 and the reduction peak of VC was suppressed. A good electrolyte additive for the anode is typically expected to be reduced to a higher potential than the other electrolyte components.43–45

**DRIFTS at open circuit potential (OCP).—** The DRIFTS spectra of the electrolyte solutions over Si-based anodes at OCP are presented in Figure 4. Table II presents the assignments. The three spectra revealed nearly the same absorbance bands, indicating that EC and EMC solvents dominated the electrolyte solution signals. The peaks at 2994 and 2937 cm⁻¹ were related to the C−H stretching of the CH2 and CH3 groups of EC and EMC,30 and the matching bending vibrations of EMC were observed at 1738, 1711, 1304/1259, and 999 cm⁻¹, respectively. Also observed were the C=O stretching of FEC and VC at 1830 cm⁻¹, and the C−F stretching of FEC at 1107 cm⁻¹. The strong band observed at 838 cm⁻¹ is attributed to the νP−F stretching of LiPF6. The FTIR spectra features associated with each electrolyte component are in good agreement with Haregewoin et al.40 and Profatilova et al.47. The presence of 10% FEC seemed to cause decreased peak broadening at ~1150, ~1300 and ~1700 cm⁻¹.

**DRIFTS during electrochemical cycling.**—Figure 5a shows the DRIFTS difference spectra during the 1st cycle lithiation of the Si-based anode with STD + 2% VC. Consistent with the cyclic voltammetry measurement, no absorbance bands other than 1776 and 1281 cm⁻¹ induced by νC−O and νC=O of polarized EC,31 respectively, were observed in the potential scan range between 2.5 V-OCP and 1.3–2.5 V. In the absence of FEC additive, obvious absorbance bands indicating SEI formation started in the potential range 1.0–1.3 V, consistent with CV with an onset potential of 1.1 V for the reduction of VC. The DRIFTS difference spectrum at 1.0–1.3 V showed peaks at 1803 and 1776 cm⁻¹ (νC−O) and at 1075 cm⁻¹ (νC=O), attributable to the formation of poly (VC).36,42 and peaks at 1747 cm⁻¹ (νC=O), 1311 cm⁻¹ (νC=O), 1269 cm⁻¹ (νC-O, C), and 1162 cm⁻¹ (νC=O) for the formation of polycarbonates. Another major species of the SEI layer is Li2CO3, which has peaks at 1481, 1443 (νC=O) and at 876 cm⁻¹ (δC-O).48,49 Alkyl phosphorous fluorides were also witnessed, with absorbance bands at 972 cm⁻¹ (νP=O, C), 729 cm⁻¹ (νP=O, C) and 846 cm⁻¹ (νP=O).48 It was found that major peaks observed at 1.0–1.3 V were continuously formed when the potential was scanned further to 0.8 V, indicating the same SEI species formed in the potential range of 0.8–1.0 V. The DRIFTS difference spectrum for 0.6–0.8 V showed peak shifts in most of the observed bands, e.g., from 1107 to 1796 cm⁻¹ (νC=O); and 1271 to 1260 cm⁻¹ (νC=O, C). This red peak shift may be ascribed to a polarization effect that may be assumed to result from the barrier at the interface between electrode and electrolyte. The DRIFTS difference spectrum through the 2nd lithiation cycle without FEC (Figure 5b) displayed absorbance bands similar to those in the 1st lithiation cycle, except that additional bands at 1724 (νC−O), 1408 (νCH₂), 1309 (νC=O, C) and 1200 cm⁻¹ (νC=O) were observed near OCP. They gradually diminished with the lithiation potential scan. These bands were also found in the 1st delithiation cycle when approaching OCP and they can be attributed to polyethylene carbonate. Similarly, Shi et al.48 showed the formation of this species using EC-based electrolyte over Ni-electrodes. This suggests that SEI film formation in the absence of FEC is somewhat potential-dependent. The absence of an onset potential of SEI formation in the 2nd cycle indicates a non-electrochemical process for SEI formation. In addition, DRIFTS difference spectra during the 2nd cycle lithiation showed no peak around 729 cm⁻¹, and the peak at 846 cm⁻¹ (νP=O) decreased with the anodic scan, indicating that the formation of alkyl phosphorous fluorides decreased.

The in-situ DRIFTS difference spectra on the Si-based electrode during 1st cycle lithiation with electrolyte containing STD + 2% VC + 10% FEC are shown in Figure 6a. Only small changes in polarized EC

---

**Table II.** Comparison of DRIFT vibrational spectra of Si-based electrode at the OCP.

| STD + 2% VC | STD + 2% VC + 10% FEC | Assignment |
|---|---|---|
| 2994, 2937 | 2989, 2937, 2930 | νC-H, CH₂ and CH₃ groups |
| 1799, 1767 | 1799, 1770 | νC=O (VC, FEC) |
| 1738, 1711 | 1738, 1711 | νC=O (EC) |
| 1479, 1441, 1384, 1365 | 1479, 1443, 1388, 1367 | νC=O (EMC) |
| 1261 | 1304, 1259 | δC-H + ν(CH₂) + ν(CH₃) + vs (-CO₂) + ω O=CH₂, EC and EMC |
| 1190, 1149/1068 | 1220, 1151/1072 | νC-O, C=O, O-C-C-O, and C=C stretching vibrations (νC=O, νC=O-C-C-O, and νC=C) of EC were observed at 1799, 1770, 1151/1072, and 793 cm⁻¹, respectively, whereas the C=O, C−O−C−C−O, and C=C stretching vibrations of EMC were observed at 1738, 1711, 1304/1259, and 999 cm⁻¹, respectively. Also observed were the C=O stretching of FEC and VC at 1830 cm⁻¹, and the C−F stretching of FEC at 1107 cm⁻¹. The strong band observed at 838 cm⁻¹ is attributed to the νP−F stretching of LiPF₆. The FTIR spectra features associated with each electrolyte component are in good agreement with Haregewoin et al.40 and Profatilova et al.47. The presence of 10% FEC seemed to cause decreased peak broadening at ~1150, ~1300 and ~1700 cm⁻¹. |
| 999, 968 | 1001, 972 | νC=O (VC, FEC) |
| 868 | 867 | νC=O (EC) |
| 837 | 838 | νC=O (EMC) |
| 771 | 775, 729 | δC-H + ν(CH₂) + ν(CH₃) + vs (-CO₂) + ω O=CH₂, EC and EMC |

---

**Figure 4.** In situ DRIFTS spectra on Si-based electrodes using 1 M LiPF₆ in: (a) EC/EMC (1:2)/STD, (b) STD/VC (2 wt%), and (c) STD/VC (2 wt%) + FEC (10 wt%) at OCP.
Figure 5. In-situ DRIFTS difference spectra of 1 M LiPF$_6$/EC:EMC (1:2):VC (2 wt%) during (a) the first and (b) the second lithiation cycle.

Figure 6. In-situ DRIFTS difference spectra of 1 M LiPF$_6$/EC:EMC (1:2):VC (2 wt%) + FEC (10 wt%) during (a) the first and (b) the second lithiation cycle.

absorbance were observed at 2.5 V–OCP. Obvious changes were found in the potential window from 1.3–2.5 V, indicating SEI formation. The difference spectrum between 1.3 and 2.5 V revealed the formation of poly (FEC) and poly (VC), which have absorbance bands at 1832 cm$^{-1}$ ($\nu$C=O) and 1108 cm$^{-1}$ ($\nu$C-F), and at 1801 cm$^{-1}$ ($\nu$asC=O) and 1070 cm$^{-1}$ ($\nu$vsC-O), respectively. The absorbance bands at 1740 cm$^{-1}$ ($\nu$C=C-O), 1305 cm$^{-1}$ ($\nu$C=C-O) and 1263 cm$^{-1}$ ($\nu$C=O) indicated the formation of polycarbonates.\(^\text{10,49,50}\) Another major SEI component is lithium carbonate, which has peaks at 1482, 1444 cm$^{-1}$ ($\nu$-CO$_3$) and 876 cm$^{-1}$ ($\delta$-CO$_3$).\(^\text{27}\) Also observed were alkoxy species at 1193 and 1150 cm$^{-1}$.$\text{27,32}$ Also observed were absorbance bands at 1002 cm$^{-1}$ ($\nu$asP-O-C), 842 cm$^{-1}$ ($\nu$P-F) and 730 cm$^{-1}$ ($\nu$vsP-O-C) suggesting the formation of alkyl phosphorous fluorides.\(^\text{23,32,47}\) The same SEI species were detected during stepwise potential scanning down to 0.6 V. The presence of 10 wt% FEC additive also enhanced LiPF$_6$ residual (having a relatively higher intensity of P-F stretching) as compared to that without FEC (Figure 5a). This may indicate that the poly (FEC) that formed from FEC decomposition could bind or trap more PF$_6$ anions.\(^\text{31}\) The FEC additive also led to a higher content of organic phosphorous fluorides as compared to the electrolyte containing no FEC. These fluoride species may cause changes in the impedance of SEI.\(^\text{27}\)

DRIFTS difference spectra from the 2nd lithiation cycle in the presence of FEC (Figure 6b) showed nearly the same bands, except for a new broad band at 1587 cm$^{-1}$ that was not present in the 1st cycle DRIFTS difference spectra. This band at 1587 cm$^{-1}$ can be assigned to $\nu$CO$_2$ of carboxylate salt (COO$^-$Li$^+$),\(^\text{23,42}\) but its intensity is relatively weak. Again, SEI formation was noted without an onset potential in the 2nd cycle. Unlike the case with an electrolyte containing STD + VC, the presence of 10 wt% FEC displayed similar absorbance bands throughout the 2nd lithiation cycle, and the formation of organic phosphorous fluoride continued throughout the 2nd cycle. DRIFTS spectra in the presence of 10 wt% FEC additive were recorded for five cycles, and the difference spectra are presented in Figure 7. No onset potential for the formation of SEI was found in that obvious absorbance bands occurred in the potential window 1.3–2.5 V during all cycles. The DRIFTS difference spectra displayed absorbance bands steadily repeated themselves in each cycle, indicating that similar species formed and the SEI grew upon cycling. After the 2nd cycle, the new peak around 1880 cm$^{-1}$ also indicated the further formation of polycarbonates.\(^\text{52}\) The continuous growth of SEI film with similar species was also found in delithiation cycles, indicating that surface species gradually grew upon cycling.
We observed an onset potential of SEI formation corresponding to the reduction potential of FEC in the 1st lithiation cycle, and similar SEI species continuously formed without onset potential in subsequent cycles. This suggests that although charge-transfer initiation occurs in the first cycle, chain transfer reactions are responsible for continuous SEI formation. This seems consistent with the radical polymerization frequently proposed in the literature.\(^{45,51,57}\) However, we observed poly (FEC) formation and simultaneous formation of poly (VC) and polycarbonates. This observation suggests that free radicals formed from FEC reduction can initiate the polymerization, leading to all these polymeric species. Similarly, Etacheri et al. also proposed the formation of poly (VC) in their mechanism as the reduction product, using FEC as a co-solvent electrolyte.\(^{27}\) Yang et al. reported that polycarbonates were formed over Si anode with the use of an electrolyte containing LiPF\(_6\)/EC+DME.\(^{52}\) That report suggests that the radical may also attack EC, leading to the formation of polycarbonates.

Based on the collected works and our in-situ DRIFTS analysis, we propose a possible mechanism, shown in Schemes 1 and 2. We assume, based on the recent work by Jung et al.,\(^{28}\) that FEC is reduced with 1-electron initiation reaction at the carbonyl oxygen. Following the elimination of CO\(_2\) and fluoride, the radical anion ring will be opened and a vinyl radical species will form. We did not observe CO\(_2\) in DRIFTS which implies that CO\(_2\) may be involved in the formation of Li\(_2\)CO\(_3\), as proposed by Yang et al.\(^{52}\) Since the formation of polycarbonates, poly (VC), and poly (FEC) were observed simultaneously in our DRIFTS measurement, we believe that the vinyl radical will abstract a hydrogen from FEC, leading to the formation of an FEC radical and a carbonyl (Scheme 1 path i). As shown in Scheme 1, the FEC radical can undergo radical polymerization with VC, shown as route ii in Scheme 1, leading to the formation of a polycarbonate radical. This radical species can abstract a hydrogen from FEC to form polycarbonate species and also return an FEC radical. The FEC radical may also undergo a chain transfer reaction with a non-radical species such as FEC to produce a neutral polymer chain and a new radical.\(^{59}\) The propagating radical species is capable of initiating another polymer chain.

In route iii in Scheme 1, the FEC radical may react with a neutral FEC to produce a neutral polymer chain species and a hydrogen radical. This new hydrogen radical (H\(^\bullet\)) is reactive and can reinitiate the FEC radical, which can polymerize with FEC further to form the poly (FEC) and H\(_2\). Jung et al. also reported the formation of H\(_2\) as one new reductive decomposition product of FEC.\(^{28}\) In addition, H\(^\bullet\) may transfer with EC in the solvent to form an EC radical and H\(_2\). This new EC radical may react with VC and propagate to another radical polymer chain. Furthermore, this radical chain may recombine with EC to reinitiate the hydrogen radical and form the poly (VC) species.

For the electrolyte containing no FEC, the SEI formation started at the onset potential of ~1.1 V, initiating with 1-electron reduction of VC. The formation of poly (VC) can be explained with reaction shown in Scheme 2. The radical polymerization can lead to the simultaneous formation of the observed polycarbonates, as proposed in Scheme 1.

In contrast to previous works in the literature,\(^{24,27,56}\) our in-situ DRIFTS was able to identify distinctly such SEI components as poly (VC), poly (FEC) and polycarbonates. However, the proposed mechanism in Scheme 1 shows some structural resemblance to the formation of polycarbonates and poly (VC). Similarly with other works, the assignment of the IR spectrum for poly (VC) can be encompassed with polycarbonate species.\(^{24,27}\)

It is generally supposed that the formation of SEI-film on Si-based anodes increases upon cycling, and that the surface film may peel off because of the volume expansion of Si electrodes.\(^{26,60}\) Our DRIFTS analyses indicated the continuous formation of similar polycarbonate species over Si-based anodes through cycling after being triggered in the 1\(^{st}\) cycle delithiation, with and without FEC. The cell with STD/2\%VC+10%FEC exhibited better stability (Figure 1b) and lower impedances (Figure 2b) through cycling than that without FEC. With FEC additive, the low frequency impedance after cycling
Scheme 1. Possible surface reduction of FEC and subsequent chain transfer reactions on Si-based electrodes.

Scheme 2. Possible surface reaction of VC reduction without FEC on Si-based electrodes.

Conclusions

A direct comparison of the SEI formation on silicon-based anode using electrolyte containing 1 M LiPF6/EC/EMC (1:2)/VC (2 wt%) with and without FEC (10 wt%) electrolyte additive was conducted using in-situ DRIFTS measurements. A schematic illustration of the SEI formation with and without FEC is provided in Figure 8. During the 1st lithiation cycle, SEI species were found at the onset of 1.4 and 1.1 V with and without FEC additive, respectively, corresponding to the reduction of FEC and VC. Poly (VC), polycarbonates, and Li2CO3 were identified as SEI species when 1 M LiPF6/EC/EMC (1:2)/VC (2 wt%) was used. Incorporation of 10 wt% FEC additive resulted in the simultaneous formation of the above mentioned SEI species, poly (FEC), alkoxy species, and a relatively high content of alkyl phosphorous fluorides.

Similar SEI species were observed after the initiation in the 1st lithiation cycle, with or without FEC. These similar SEI species were also noted in the delithiation cycle, and no onset potential was observed in the 2nd lithiation cycle. In-situ DRIFTS analyses indicated similar SEI-film buildup for up to five cycles, recorded in the presence
of FEC. This suggests an ongoing SEI formation via an initiation in the 1st li- 
itation cycle and subsequent chain transfer reactions. The ef-
fects of FEC additive on the Si-based anode include lower imped-
ance and improved stability with cycling, as compared to the electrolyte containing STD + 2% VC. This may be related to the inc-
clusion of conductive species during SEI formation in the presence of FEC.

Acknowledgment

The authors gratefully acknowledge funding from the Min-
istry of Economic Affairs of Taiwan, ROC, under contact num-
er 104-EC-17-A-08-S1-183.

References

1. L. Batteries, Eds Nazi G.-A., Pistoia G. Boston: Kluwer Academic, 1 (2004).
2. C. K. Chan, R. Ruffo, S. Hong, and Y. Cui, Journal of Power Sources, 189, 1132
(2009).
3. D. Guyomard and J. M. Tarascon, Adv. Mater., 6, 408 (1994).
4. P. Lu, C. Li, E. W. Schneider, and S. J. Harris, The Journal of Physical Chemistry C, 118, 806 (2014).
5. D. Aurbach, B. Markovsky, J. Weissman, E. Levi, and Y. Ein-Eli, Electrochim. Acta, 45, 67 (1999).
6. J. S. Gnanaraj, R. W. Thompson, J. F. DiCarlo, and K. M. Abraham, Journal of The Electrochemical Society, 154, A185 (2007).
7. M. Green, E. Fielder, B. Scrosati, M. Wachtler, and J. S. Moreno, Electrochemical and Solid-State Letters, 6, A75 (2003).
8. B. Boukamp, G. Lesh, and R. Huggins, Journal of the Electrochemical Society, 128, 725 (1981).
9. J. H. Ryu, J. W. Kim, Y.-E. Sung, and S. M. Oh, Electrochemical and Solid-State Letters, 7, A306 (2004).
10. B. Boukamp, G. Lesh, and R. Huggins, Journal of the Electrochemical Society, 128, 725 (1981).
11. C. S. Nguyen and B. L. Lucht, Journal of the Electrochemical Society, 161, 141 (2014).
12. H. Wu, G. Chan, J. Choi, I. Rya, Y. Yao, M. T. McDowell, S. Lee, A. Jackson, Y. Yang, L. Hu, and Y. Cui, Nature nanotechnology, 7, 310 (2012).
13. C. K. Chan, H. Peng, G. Liu, K. McEwen, X. Zhang, R. A. Huggins, and Y. Cui, Nature nanotechnology, 3, 31 (2008).
14. H. Kim, B. Han, J. Cho, and J. Cho, Angewandte Chemie International Edition, 47, 10151 (2008).
15. M.-H. Park, M. Kim, J. Oo, K. Kim, J. Kim, S. Ahn, Y. Cui, and J. Cho, Nano Letters, 9, 3844 (2009).
16. A. Magasinski, P. Dixon, B. Hertzberg, A. Kvit, J. Alya, and G. Yushin, Nat Mater, 9, 353 (2010).
17. M. Yoshito, H. Wang, K. Fukuda, T. Umenos, N. Dimov, and Z. Oguni, Journal of The Electrochemical Society, 149 (2002).
18. J. Maranchi, A. Hepp, and P. Kumta, Electrochem. Solid-State Lett., 6, A198 (2003).
19. S. Bourdeau, T. Brousse, and D. M. Schleich, J. Power Sources, 81, 233 (1999).
20. J. Graetz, C. C. Ahn, R. Yazami, and B. Fultz, Electrochemical and Solid-State Letters, 6 (2003).
21. A. Magasinski, B. Zdyrko, I. Kovalenko, B. Hertzberg, R. Burtovyy, C. F. Huebner, T. F. Fuller, I. Luzinov, and G. Yushin, ACS applied materials & interfaces, 2, 3004 (2010).
22. S. Xun, B. Xiang, A. Minor, V. Battaglia, and G. Liu, Journal of The Electrochemical Society, 160 (2013).
23. B. Koo, H. Kim, Y. Cho, J. Lee, N. S. Choi, and J. Cho, Angewandte Chemie International Edition, 51, 8762 (2012).
24. H. Jo, J. Kim, D.-T. Nguyen, K. Kang, D.-M. Jeon, A. R. Yang, and S.-W. Song, The Journal of Physical Chemistry C, (2016).
25. A. Cortez, G. Caillon, C. Jeyi, J. N. Chazalviel, M. Rosso, and F. Ozanam, Advanced Energy Materials, 6, 1501768 (2016).
26. K. Schroder, J. Alvarado, T. A. Yersak, J. Li, N. Dudney, L. J. Webb, Y. Meng, and K. J. Stevenson, Chemistry of Materials, 27, 5351 (2015).
27. X. Fu, F. Lindgren, B. Philippe, M. Gomgi, F. Bjorrefors, K. Edstrom, and T. Gustafsson, Chem. Mater., 27, 2591 (2015).
28. V. Etachere, O. Haik, Y. Golfer, G. A. Roberts, I. C. Stefan, R. Fasching, and D. Aurbach, Langmuir: the ACS journal of surfaces and colloids, 28, 9651 (2011).
29. Y. Fung, M. Mitgerz, D. Haering, S. Solchenbach, C. Marino, N. Tsiovouras, C. Sinus, and H. A. Gasteiger, Journal of The Electrochemical Society, 163 (2016).
30. R. Petibon, V. Chevrier, C. Aiken, D. S. Hall, R. R. Hyatt, R. Shnumugasundaram, and J. R. Dahn, Journal of The Electrochemical Societ (2016).