Research paper

Enhancing the stability of silicon nanosheets electrodes by fluoroethylene carbonate

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A B S T R A C T

Stabilization of the SEI layer that is formed by consuming active lithium in electrolytes is a critical issue for improving the cyclability of lithium ion batteries. We used SiNSs as anodes and investigated the effect of fluoroethylene carbonate (FEC) additives on the SEI layer. Our XPS, EIS and TEM analysis of C=O and C@O bonds, interfacial resistance and thickness of SEl layer, respectively, shows that the FEC produces electrochemically and mechanically stable SEI layer. The SiNSs with FEC showed the capacity of over 1500 mA h g⁻¹ with 95% efficiency after 200 cycles.

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1. Introduction

Lithium ion batteries (LIBs) have been used as energy storage systems in many electronics and vehicles. It is well known that the high performance LIBs requires electrodes with a high energy density and durable structures [1,2]. Regarding high energy density, silicon (Si) is the most attractive anode materials by a large theoretical capacity of 4200 mA h g⁻¹, which is a much larger capacity density than that of the commonly used carbon (372 mA h g⁻¹) [3,4]. However, it has not been commercialized yet as an anode material for LIBs because of the poor cyclic retention.

Two critical issues are involved in the cyclic retention of Si, mechanical integrity (physical stability) and formation of a solid electrolyte interphase (SEI) layer (chemical stability) [5,6]. Si electrodes experience a large volume expansion and stresses during Li ion insertion (lithiation) which leads to pulverization. Nanomaterials have been suggested as an alternative because of the stress relaxation mechanism due to their nanoscale effect. For example, 1-D nanowires can expand along the longitudinal and lateral axis and relaxing the stress during expansion/shrinkage [7,8]. Meanwhile, the nanomaterials have an adverse effect on chemical stability in terms of SEI. The SEI layers is formed on the electrode surface by a reaction of Si with electrolytes and experienced severe volume changes and stresses. The layer is therefore pulverized by the volumetric expansion that occurs during lithiation/delithiation and resulted in a growing of the layer, by continuous electrolyte consumption and loss of active lithium with cycles [9–13]. It also creates a large resistance at the interface and adversely affects the properties.

Two-dimensional (2D) nanomaterials are also considered as materials that can address the problems of Si electrodes. It can provide a stress relief mechanism to prevent mechanical integrity during cycling [14]. It can also provide efficient charge and discharge by shorter lithium ion diffusion distance than any other nano electrodes. Accordingly, 2D silicon nanomaterials, that is, Si nanosheets, have been studied and found to have better mechanical properties in charge and discharge processes [15–18] and thus demonstrate the potential as anodes for LIBs. However, SEI-related issues that are expected to be caused by the large surface area of 2D Si electrodes have not been studied thus far. In this study, Si nanosheets were synthesized by chemical vapor deposition (CVD) and their electrochemical properties were investigated. Particularly, the effect of SEI layer on electrochemical properties and the additives that can prevent the adverse effects of SEI layer was studied.

2. Experimental

2.1. Synthesis of Si nanosheets

The SiNSs were directly grown on Grafoil as current collector by CVD process in a high-flux H₂ environment with flow rate of
3000 sccm. The growth was carried out for 5 min at 1020 °C with bubbling of Si chloride (SiCl₄, 99.999%, Aldrich) into the quartz tube reactor using H₂ as carrier gas at a flow rate of 20 sccm. The electrochemical properties were investigated by half-cell tests.

2.2. Characterization of Si nanosheets electrodes

The morphology of SiNSs were investigated by scanning electron microscope (FESEM, Hitachi 3000) and tunneling electron microscope (TEM, JEOL-ARM 200F). The surface state of SiNSs and the compositions of surface derived from SEI layer were analyzed by electrochemical impedance spectroscopy (EIS, Reference 600TM, Gamry Instruments) and X-ray photoelectron spectroscopy (XPS, Thermo VG K-alpha). The EIS measurement was carried out after each cycle in the range from 10 mHz to 1 MHz at each cycle. For XPS analysis, the cycling cells were disassembled and sampling was carried out in argon filled box. The XPS spectra was also collected at each cycle.

2.3. Electrochemical testing

Half-cell tests were carried out for investigating electrochemical properties using 2032 coin cell. Si nanosheets grown on the Grafoil was assembled as the positive electrode and Li metal as a reference electrode with no conducting and binding agents. The loading of SiNSs on the Grafoil were about 0.7 mg. The electrolyte were commercially available 1 M lithium hexafluoro phosphate (LiPF₆) dissolved in ethylene carbonate and diethyl carbonate.

Fig. 1. Representative morphology of SiNSs (a) Cross-section image of SiNSs grown on Grafoil. (b) Single ward image of SiNSs grown on Grafoil. (c) Enlarged SEM images of SiNSs grown on Grafoil. (d) Low resolution TEM. (e) High resolution TEM image of individual SiNSs.
The additives were used 1 ~ 4% fluoroethylene carbonate (FEC, Alfa Aesar) of total electrolytes volume. Other additives, lithium bis (oxalate) borate (LiBOB) and propylene carbonate (PC) in ethylene carbonate and diethyl carbonate (EC: DEC/1:1, volume ratio) were also used for comparison. The cells were subjected to galvanostatic cycling using Battery Charging-Discharging system (Maccor, Series 4000) between 0.005 and 2.0 V at C/10 rate.

3. Results and discussion

The SiNSs were directly grown on Grafoil substrates by CVD process. The Grafoil was used as a current collector in the half-cells. Fig. 1a–c shows the scanning electron microscopy (SEM) images of SiNSs electrodes. The SiNSs grew like a wad of cotton wool with a diameter of about 20 μm as shown in Fig. 1b. Upon closer observation, a great number of SiNSs were observed with extremely high surface area (Fig. 1c). The thickness of the individual SiNSs was characterized using atomic force microscopy (AFM) to be as small as 1–100 nm, increasing with growth time as reported in previous studies [19,20]. The average thickness and diameter of SiNSs in this study was 5 ± 2 nm and, diameter of 1–2 μm, respectively (Fig. S1). The individual SiNSs possesses a single-crystalline nature without defects (Fig. 1d and e). Energy dispersive spectroscopy (EDS) results show that the SiNSs are composed of pure Si without any other impurities (Fig. S2).

Fig. 2 shows the electrochemical properties using half-cell tests in a constant current/constant voltage (CC/CV) mode over the range of 0.005~2.0 V at a C/10 rate (10 h per half cycle). The SiNSs cell was assembled without conducting and binding agents to determine the effect of additives. In a preliminary test, we characterized the electrochemical properties using electrolyte solutions with different additives such as lithium bis (oxalate) borate (LiBOB), propylene carbonate (PC) and fluoroethylene carbonate (FEC). It showed that the SiNSs electrode with LiBOB and PC show the lower Coulombic efficiencies and poor electrochemical performances than FEC added samples. It is due to low concentrations of organic species to form the passivation [21].

We then examined the capacity and cyclic performance at different levels of FEC (1–4%). The SiNSs electrodes showed the best performance with 4% FEC additives as shown by Fig. S3. Accordingly, we further investigate and characterize the electrochemical and chemical properties of SiNSs cells with 4% FEC additives, and compare those to the cells without (w/o) additives as follows.

Fig. 3 shows the electrochemical properties of the SiNSs cells with and w/o FEC additive. In Fig. 3a, the first discharge (lithiation) capacity was 4671 mA h g⁻¹, which is comparable to the theoretical capacity, and degraded, however, stably remained to 2350 mA h g⁻¹ for 100th cycles. Meanwhile, the FEC-free electrode showed the worse capacity retention with 545 mA h g⁻¹ for 100th cycles. The Coulombic efficiency was also stable and enhanced in the electrodes with FEC additives. The FEC produce the SEI with lithium-ethenyl and lithium-ethinyl. These lithium-ethenyl and lithium-ethinyl form a lithium ion conductive and elastometric, partially cross-linked polymer (polycarbonates) layer [12,23]. It improves the lithium transport and thus the capacity of SiNSs with FEC at same current density as compare to SiNSs w/o FEC. Additionally, the elastomeric layer makes the electrodes withstand the stress/strain during cycling.

Fig. 3b shows the voltage profiles and dQ/dV results of the SiNSs electrode with and w/o FEC. At initial discharge (lithiation), sloping plateaus are observed at 1.3, 0.8, and 0.28 V. The first slope change at 1.3 V is attributed to the reduction of FEC [23] that was not shown in the w/o FEC-free sample. The peak at 0.8 V in both electrodes indicates the formation of SEI, as reported previously [24]. The peaks at 1.3 V and 0.8 V indicates that the reductive decomposition of FEC occurs before the formation of SEI layer is formed. It is known that the decomposition stabilize the SEI layer and in turn ascribe to the better cyclability [24]. The phase transition from Si to Li₄Si occurs after 0.28 V, with a long plateau. During the first charge (delithiation), the delithiation peaks are observed at 0.3 and 0.5 V, which indicates the phase transition to Si. The second discharge and charge profile is similar to the first cycle; the same sloping plateaus are observed except for the first reduction peak of FEC, and the profile was maintained during the subsequent cycles.

The long cyclic charge-discharge capacity and Coulombic efficiency of SiNSs with FEC are shown in Fig. 3c. The SiNSs electrode
with FEC demonstrates significantly improved efficiency, with a capacity of over 1500 mA h g\(^{-1}\) during 200 cycles with 98% Coulombic efficiency. It clearly shows that the FEC makes possible to achieve stable long cycles with good capacity retention.

The SEI layers are vulnerable to the mechanical stress. The layers are thus pulverized during the cycle and resulted in the large resistances at the electrodes. We performed the electrochemical impedance spectroscopy (EIS) to investigate the behavior of electrode/solution interfaces. The EIS is a standard analytical method used to provide information on surface reaction through the SEI. The Nyquist plots consist of regions at high-\(\sigma\), intermediate frequencies, which attributed to the resistance of electrolyte and electrode, \(R_e\), the formation of solid-electrolyte interphases (\(R_{sei}\)) and charge transfer resistance (\(R_{ct}\)). The region with linear slope at low frequency is known as the Warburg impedance, which attributed to the mass transfer of Li ions (\(R_{diff}\)). Therefore, the resistances from EIS between the electrodes with and w/o FEC will be attributed to the effect of FEC on the formation of solid-electrolyte interphases and/or charge transfer. The EIS spectra are fitted with equivalent circuit, as shown in inset of Fig. 4 and the calculated values are listed in Table 1.

**Fig. 4.** Electrochemical impedance spectroscopy results of SiNSs electrodes at each cycle (a) without FEC, (b) with FEC.
Rsei values of the electrode with FEC are lower than those of w/o FEC. Whereas, the Rct values of the electrode with FEC are similar. It indicates that the electrode with FEC produced a dense LiF-dominant layer at the first cycle. At the 2nd cycle, both electrodes showed decreasing Rsei and Rct values. With increasing number of cycles, the Rsei and Rct values of the w/o FEC- SiNSs significant increased and total impedance values increase 4.24 times (164.2 Ω) compared to the initial cycle (38.7 Ω). These increase are much larger than nanoparticles and, nanowires (Table 2). It is presumably due to the larger surface area of SiNS than nanoparticles or nanowires, and thus the significant effect of the formation of SEI layer on the resistance at the electrodes. On the other hand, when the FEC was added, the resistance remained constant. This shows that FEC is very effective in stabilizing SEI formation and interfacial resistance in SiNSs electrodes.

It is noted that the Rsei values are tending to rise together with Rct in our system. It may due to that the Rct, which represents charge-transfer, is affected by the surface condition. The Rct can be calculated by the following equation:

$$R_{ct} = \frac{RT}{nF_i} \tag{1}$$

### Table 1
Impedance parameters for w/o and with FEC- SiNSs calculated using an equivalent circuit with increasing cycles.

<table>
<thead>
<tr>
<th>Values</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>5th</th>
<th>10th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare (w/o FEC)</td>
<td>8.89</td>
<td>8.71</td>
<td>10.73</td>
<td>22.38</td>
<td>53.27</td>
</tr>
<tr>
<td>Rsei (Ω)</td>
<td>31.54</td>
<td>9.05</td>
<td>15.25</td>
<td>38.55</td>
<td>88.63</td>
</tr>
<tr>
<td>Rct (Ω)</td>
<td>35.24</td>
<td>18.71</td>
<td>20.51</td>
<td>24.22</td>
<td>33.64</td>
</tr>
<tr>
<td>With FEC</td>
<td>24.22</td>
<td>11.53</td>
<td>13.07</td>
<td>14.78</td>
<td>23.57</td>
</tr>
</tbody>
</table>

### Table 2
The resistance of 0-, 1-, 2- dimensional Si nanostructure electrodes with increasing number of cycles increasing.

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Material</th>
<th>1st (Ω)/(R1st/R10th)</th>
<th>5th (Ω)/(R5th/R10th)</th>
<th>10th (Ω)/(R10th/R1st)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0D</td>
<td>Si nanoparticle</td>
<td>55/1</td>
<td>–</td>
<td>155/2.81</td>
</tr>
<tr>
<td></td>
<td>Si nanoparticle</td>
<td>130/1</td>
<td>–</td>
<td>350/2.69</td>
</tr>
<tr>
<td></td>
<td>Si nanoparticle</td>
<td>90.6/1</td>
<td>108.9/1.2</td>
<td>141.4/1.56</td>
</tr>
<tr>
<td></td>
<td>Si nanoparticle</td>
<td>70.9/1</td>
<td>96.2/1.35</td>
<td>120.2/1.69</td>
</tr>
<tr>
<td></td>
<td>Si nanoparticle</td>
<td>73.6/1</td>
<td>95.7/1.3</td>
<td>111.8/1.32</td>
</tr>
<tr>
<td></td>
<td>Si nanoparticle</td>
<td>46.1/1</td>
<td>65/1.40</td>
<td>110/2.38</td>
</tr>
<tr>
<td>1D</td>
<td>Si NW</td>
<td>155/1</td>
<td>372/2.4</td>
<td>–</td>
</tr>
<tr>
<td>2D</td>
<td>Si NSs</td>
<td>38.7/1</td>
<td>53.7/1.39</td>
<td>164.2/4.24</td>
</tr>
</tbody>
</table>

Fig. 5. C 1s XPS spectra of surface layer formed on SiNSs electrode without/with FEC at initial, 10th cycle.
here, \( R \) is the gas constant, \( T \) is the absolute temperature, \( n \) is the number of electron involved in charge-transfer, \( F \) is the Faraday constant, \( i_0 \) is the exchange current density. The \( i_0 \) depends on the electrode composition/surface and the unstable SEI layer can decrease the exchange current density due to C–O bonds on the surface [25–27]. The growth of SEI layer can also decrease the exchange current density since it is produced by consuming electrons and electrolytic bonds, and thus decreasing the exchange current density by reducing the number of electrons involved in charge transfer.

It is known that the compositions in SEI layer that are resulted by the reduction of FEC additives are important in the cycle performance [13,22,26–28]. Figs. 5 and 6 show the X-ray photoelectron spectroscopy (XPS) results of the electrodes with and w/o FEC additive. The SiNSs electrodes were removed from the cells cycled with/without FEC at the 2nd and, 10th cycle. Fig. 5 shows the C 1s XPS spectra of the SEI layers on the SiNSs electrodes formed with and w/o FEC. The C 1s peak at 285 eV is attributed to the C–H bond. The peaks at 286.5 and, 290 eV were consistent with the presence of species containing C–O and C–F, respectively. During the initial cycle, in both the SiNSs electrodes with FEC and w/o FEC, strong peaks at 286.5 and, 290 eV were observed, while the peak characteristic of C–O containing species is weaker for the electrode w/o FEC. The peak at 290 eV showed strong peaks for both electrodes with and w/o FEC. This is consistent with previous studies using EC electrolytes [21,26–29]. After the 10th cycle, the peak of the C–O bond appeared in SiNSs with FEC, while the SiNSs w/o FEC did not show a significant change. However, the C–O bonds significantly increased for the electrode w/o FEC. The C–O bond is due to the decomposition from solvent in electrolyte. The results thus indicate that the electrolytes in SiNSs electrodes with FEC were less decomposed.

The C–O bonded components around 286–287 eV (i.e. (CH2O-COLi)2) are chemically unstable and can produce continuous electrolyte consumption and generate growth of SEI. Meanwhile, C–O bonded components around 288–290 eV (i.e. Li2CO3, RCO2Li) are the one of constituents of SEI and stabilizing SEI [30–32]. In XPS results, the SiNSs with FEC show the lower intensity of C–O bonding compared to that without FEC. Meanwhile, the intensity of C–O bonds of SiNSs with FEC have the higher intensity. Therefore, it demonstrates that FEC makes SEI more stable.

Fig. 6 shows the F 1s XPS spectra of SiNSs electrode with/without FEC. The peak at 687 eV corresponding to the C–F bond dominated the SiNSs electrodes with and without FEC. During the initial cycle, the peak of LiF at 695 eV was strong for the electrode w/o FEC. Upon cycling, the SiNSs electrodes with FEC showed a consistently lower intensity of LiF, while the SiNSs electrode w/o FEC showed significant increasing in the intensity of LiF. The strong peak of LiF indicates that the more lithium is consumed to produce SEI layers. The thickness of SEI on SiNSs with FEC was generally thinner than that of SiNSs w/o FEC (Fig. 54). It can support the stabilization of SEI by FEC which are same results from XPS and EIS.

We investigated the EIS results for Si nanostructures including 0-D (nano particles) and 1-D (nanowires) and compared with 2-D SiNSs in this study (Table 2). The 2-D SiNSs electrode without FEC shows that the total resistances from EIS increased rapidly with cycling compared to 0-, 1-dimensional nanostructures that may due to large surface area for the formation of SEI layer. However, addition of FEC can stabilize the SEI layer and thus suppress the total resistance quite low. Furthermore, Aurbach et al. reported that the FEC can provided flexible SEI layers which are physically stable [9,27]. The transformation of FEC to vinylene carbonate (VC) followed by polymerization to form poly(carbonates) can form flexible surfaces. Consequently, the flexible surface layers...
provide physically stable passivation layers, which lead to improve electrochemical performances and capacity retention.

4. Conclusions

We characterized 2-D SiNSs as anode materials for LIBs. The SiNSs synthesized by the CVD process using SiCl4 and H2 have a high crystallinity with a thickness of 5 nm. The SiNSs electrodes have large surface area and thus the effect of SEI layer on the cyclability was significant as compare to the other Si electrodes such as nano particles and nanowires. However, addition of FEC in the electrolytes produced chemically- and mechanically stable SEI layer and prevent the growth of SEI and improve the capacity retention of SiNSs electrodes.

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Appendix A. Supplementary material

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