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Morphological and Chemical Evolution of Silicon Nanocomposite during Cycling

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High-capacity materials are required to further the development of Li-ion batteries. As a result, silicon (Si) has been investigated as a promising anode in Li-ion batteries because of its high theoretical capacity (3579 mAh/g), which is 10 times higher than of the commercial graphite anodes (372 mAh/g). However, Si electrodes undergo sever mechanical degradation due to the volume exaptation (300%) upon lithiation and suffers from an unstable solid electrolyte interphase (SEI) layer. The SEI layer occurs at the electrode/electrolyte interface as a result of the electrolyte decomposition. In this work crystalline Si (60 nm particle size) was used to prevent large strain that occurs from the volume expansion. In order to improve the cycling performance of Si composite electrode, fluoroethylene carbonate (FEC) electrolyte additive was added to the electrolyte [1-4]. For the first time, various TEM/STEM EELS techniques demonstrated the effects of FEC on the morphological and chemical evolution of the SEI on Si composite electrode during electrochemical cycling.

ADF-STEM images of the lithiathed electrodes cycled in EC/DEC and EC/DEC/FEC are shown in Figure 1. The surface of the lithiated electrode cycled in EC/DEC (Figure 1(a)) is unevenly covered with a porous SEI layer. Conversely, adding 10 wt% FEC to the traditional (EC/DEC) electrolyte forms a uniform dense SEI while maintaining particle integrity. (Figure 1(c)). The corresponding EELS spectra (Figure 1(e)) from the lithiated electrodes with and without FEC further confirm the presence of a SEI layer. The EELS spectra results demonstrate that the SEI layer (darker area) does not contain Si. Additionally, the SEI mainly contains Li_2CO_3 for the electrode cycled in EC/DEC, however, it mostly consisting of LiF for the electrode cycled in EC/DEC/FEC. Throughout electrochemical cycling (1, 5 and 100 cycles) the SEI layer on the electrode cycled with EC/DEC thickens unevenly (Figure 1(b)) were the electrode cycled in EC/DEC/FEC formed uniform dense SEI up to 5 cycles. Surprisingly, the electrode cycled with FEC formed a thick inhomogeneous SEI after 100 cycles.

Figure 2 shows the comparison of the EELS spectra from the cycled Si electrode in EC/DEC and EC/DEC/FEC after various cycle numbers. The Si-L varies significantly between bulk and surface of the Si cycled in EC/DEC, which is attributed to the presence amorphous Li_xSi alloy and Li_xSiO_y in the bulk and at the edge of the electrode (Figure 2(a)). After one cycle, only amorphous Li_xSi was detected at the surface and bulk of the Si cycled in EC/DEC/FEC and the Li_xSiO_y was not detected at the edge (Figure 2(b)). However, the Li_xSiO_y was observed after 5 cycles and increased at the interface of the electrode cycled in EC/DEC/FEC with cycle number. Interestingly, the presence of FEC suppresses the formation of Li_xSiO_y layer and also it leads to the formation of uniform and homogenous SEI layer with high LiF content as a result of the initial FEC decomposition. Pushing the boundaries of the STEM/EELS led to further understanding of the effects that FEC has on the SEI formation by directly visualizing and characterizing Si composite electrodes [5].

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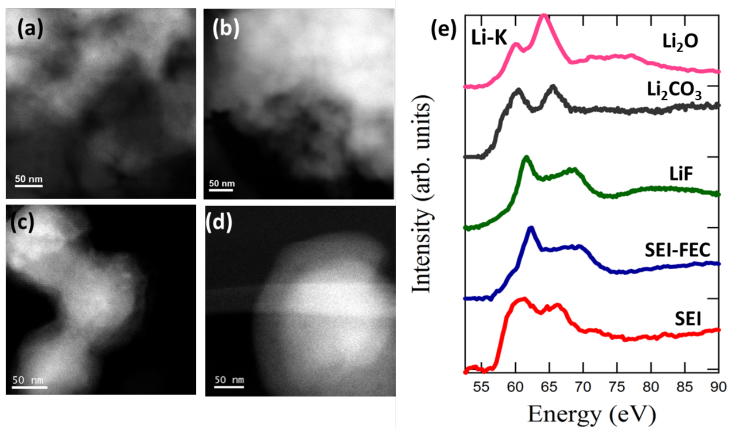

Figure 1. ADF STEM images of the lithiated electrodes cycled with EC/DEC at the (a) first cycle and (b) five cycles. Lithiated Si composite electrodes cycled with EC/DEC/FEC at (c) first cycle and, (d) five cycles. (e) The corresponding Li-K edge EELS spectra taken from SEI layer of the lithiated Si with and without FEC comparing the possible standard phases (LiF, Li_2CO_3, Li_2O).

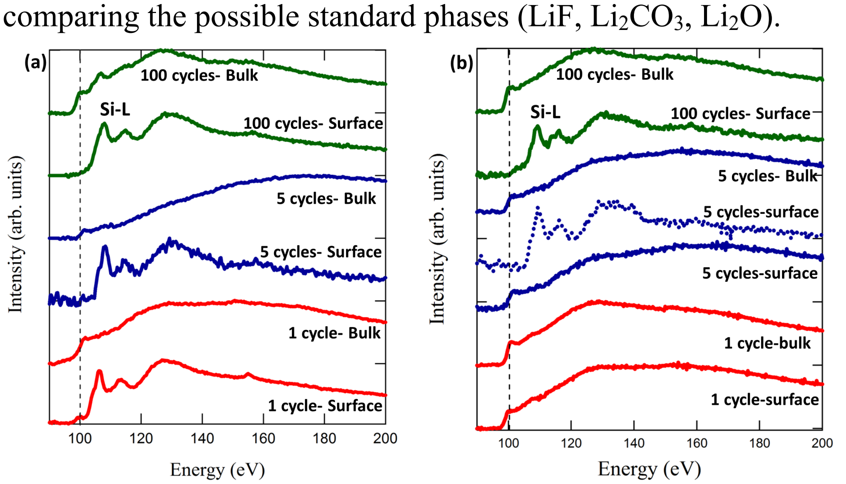

Figure 2. Si-L EELS spectra of the Si electrodes cycled in (a) EC/DEC and (b) EC/DEC/FEC at various cycle numbers.