Revealing the Reaction Mechanisms of Tin-Based Anodes by In Situ X-ray Absorption Spectroscopy (BL-01C)

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To obtain the in-situ XAS data of the Sn-P-O/graphite composite anode, derived powders was mixed with PVDF binder and coated on Cu foils and then assemble to be get a 2032 two-electrode test cell consisted of the Sn-P-O/graphite electrode. The XAS analysis was performed at the beam line BL01C of NSRRC in Taiwan. Fig. 1 shows the voltage profile of the cell adopted in this study and the corresponding voltage and capacity of every taken spectra.

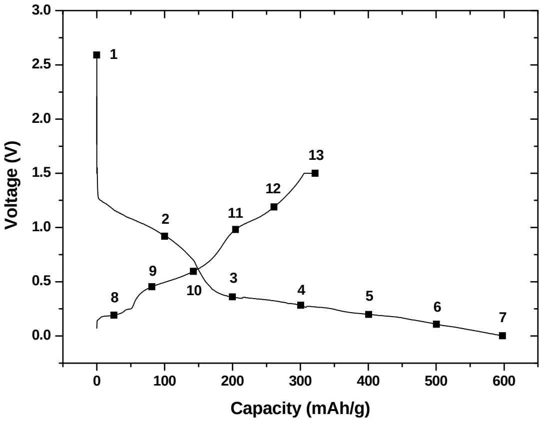

Figure 1. The first charge and discharge curves of the Li/composite cells from 3 to 4.5 V at a C/5 rate.

The valence evolution of Sn during the 1st cycle

Figure 2 shows Sn K-edge EXANES spectra of the Sn-P-O/graphite composite powders during lithiation and the standards. Comparing the spectrum of Sn-P-O/graphite electrode before cycling (#01) with the three standards, it reveals that the valence of Sn is closer to 4+.

Because of the relative low content of Sn exist in the Sn-P-O/graphite composite anodes, the resolution of derived XAS spectra is restricted in this study (jump is lower than 0.3). However, the spectrum shift at the edge position during charge and discharge is still obvious. As Li ions being inserted into the composite, the spectrum shifts toward low energy region (spectrum #01 to #07), which indicates that the average valence of Sn decreases and the composite has undergone a reduction process during discharge. This energy shift occurs continuously even after the cell was lithiated to nearly 0V. This discloses that Sn^{4+} was gradually reduced during the entire lithiation process.

When the cell is charged (Li ions are extracted from the composite), the spectrum shifts in the reverse direction. This shows that the average Sn valence is raised, and the composite experiences an "re-oxidation"process during charge.

According to Courtney's report [1], the removal of lithium from the Li_2O derived from alloying of tin oxides with lithium contributed to the capacity above 0.9 V during discharge. Subsequently, the liberated oxygen would "back react" with Sn atoms released from the Li-Sn alloys and form Sn−O bonds. Hence, the charge profile above 0.9 V was caused by the re-oxidation of Sn. In this study, the voltage plateau above 0.85V shown in Fig. 1 was testified to be partially contributed by the re-oxidation of Sn clusters in this composite anode.

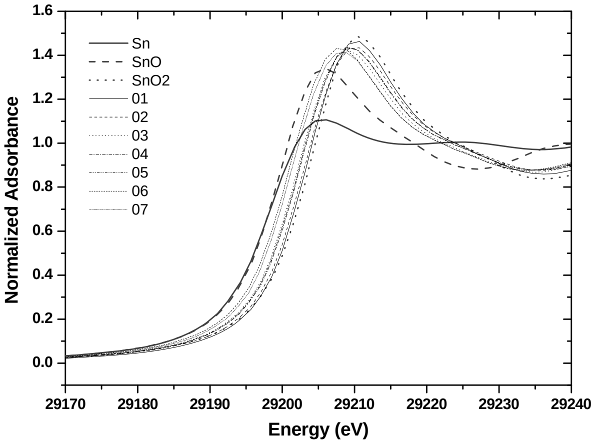

Figure 2. Sn K-edge EXANES spectra of the assembled cell during lithiation.

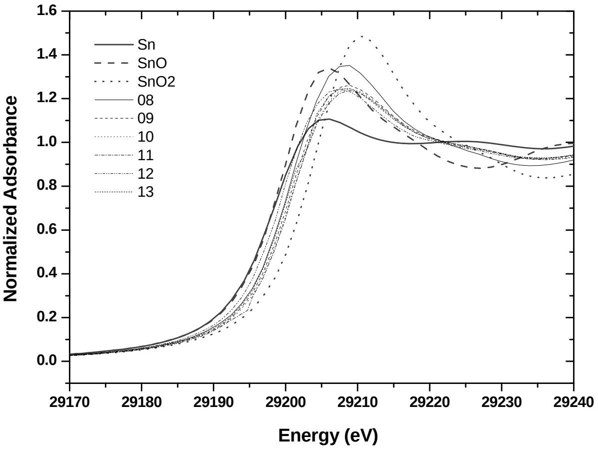

Figure 3. Sn K-edge EXANES spectra of the assembled cell during delithiation.

Reference

[1] Courtney, I. A.; Dahn, J. R. J. electrochem. Soc. **144**, 2943 (1997).