The Studies of Novel Cathode and Anode Materials for Li Secondary Batteries

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Lithium-ion batteries have played an important role in portable electronic device and electric vehicles (EVs) recently. Therefore, higher capacity and better retention are the critical issue for the research. Moreover, the capacity fading is attributed to the irreversible reation during charge and discharge. Furthermore, analysing in situ XRD pattern by synchrotron radiation could realize the phase transformation during lithiation and delithiation. In the study, the X-ray diffraction data were collected using synchrotron radiations at NSRRC BL01C and BL17A beam lines.

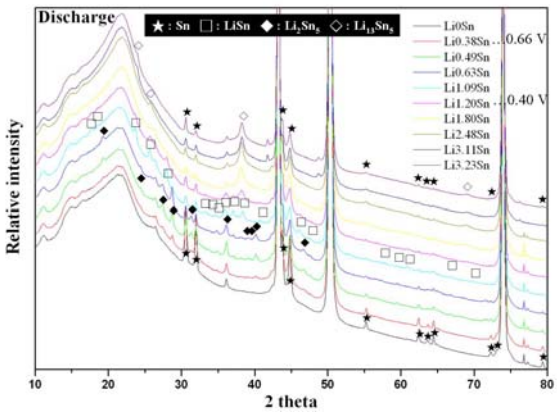

Figure 1. In situ XRD analysis of sample during discharge process.

When the voltage was below 0.66V, the peaks of pure Sn were converted into those of Li_2Sn_5 and LiSn, as shown in Fig.1. Moreover, when the voltage was even below 0.4V, the phases of Li-rich alloys appeared. The results above were identical with those which were done by J. R. Dahn[1]. Furthermore, since Li_2Sn_5 and LiSn alloys were layered and related structures, the reaction with Li was more reversible than if we were to react over the full range of Li-Sn alloys. However, These Li-rich alloy phases Li_5Sn_2, $Li_{13}Sn_5$, Li_7Sn_2, and $Li_{22}Sn_5$ were all based on the BCC unit cell of lithium and showed large volume change during charge / discharge. That is, the appearance of Li-rich alloy phases could cause the irreversible capacity. Therefore, setting lower cutoff voltage to prevent the generation of Li-rich alloys could enhance the cyling performace (Fig 2).

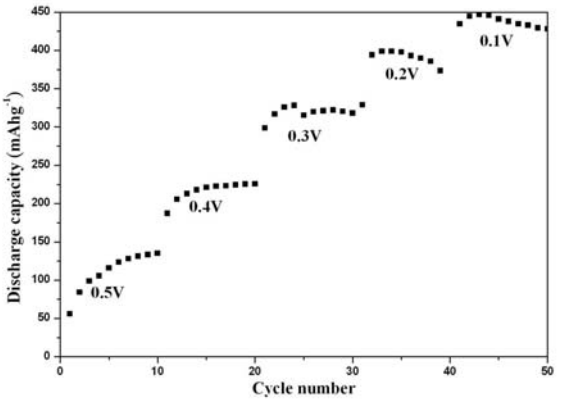

Figure 2. Different lower cutoff voltages of sample during discharge process.

The result of capacity which was derived from various lower cutoff voltages showed in fig. 2. When the voltage was below 0.4V, the capacity fading was revealed, which was attributed to the appearance of Li-rich alloys.

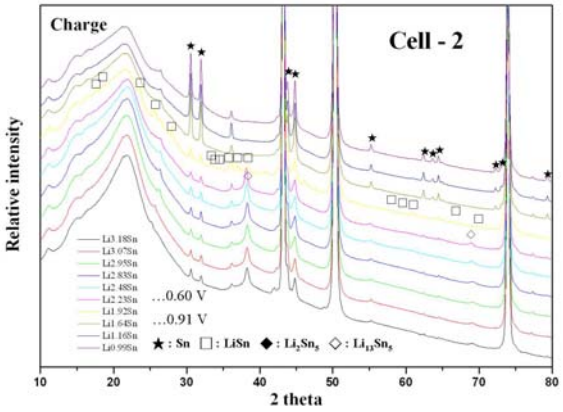

Figure 3. In situ XRD analysis of sample during charge process.

From the figure 3, when the voltage was above 0.60V the peaks of Li-rich alloy became those of LiSn. Moreover, when the voltage was even above 0.91V, the sharp peaks of pure Sn, which resulted from the agglomeration of Sn clusters could encounter severe volume change during lithiation and delithiation.

Reference:
[1] I. A. Courtney and J. R. Dahn, J Electrochem. Soc. **144,** 2045-2052 (1997).