Tin-based as Anode Materials for Li-ion Batteries: Structure Analysis during Charge-discharge via In-situ XRD Measurements

Sung-Chieh Chao (趙崧傑)[1], Yu-Chan Yen (嚴佑展)[1], Nae-Lih Wu (吳乃立)[1], and Hwo-Shuenn Sheu (許火順)[2]

[1]Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan
[2]National Synchrotron Radiation Research Center, Hsinchu, Taiwan

Li-ion secondary batteries are foreseen to play a very important role in energy storage for the next decade. Research for advanced Li-ion secondary batteries has followed the direction toward higher energy and power densities. While the theoretical background for Li-ion secondary battery is straightforward and well established, the performance of a practical battery depends largely several material and electrode architectural issues of the electrodes, and the interplays among these issues are not fully understood. One important issue that has profound effect on the cycle life of Li-ion battery is the architecture of the electrode over-layer, which determines the distributions of the stress and strain arising from the volumetric variations. While quite extensive studies have been conducted to characterize the microstructures of individual active materials, most in powder form, it remains almost impossible to link between the architecture of the over-layer and the microstructures of its constituents. Technique in characterizing the architecture, i.e., the microstructures of the electrode over-layer is lacking.

In this study, various anode electrodes containing the advanced high-energy active materials with high atomic number, i. e. Sn-based materials will be prepared, and the architectures of the electrode over-layers will be revealed by the X-ray tomography. Correlation is to be established between the Li-Sn phases from *in-situ* XRD and electrode architecture from *in-situ* TXM of the high-energy Li-ion batteries.

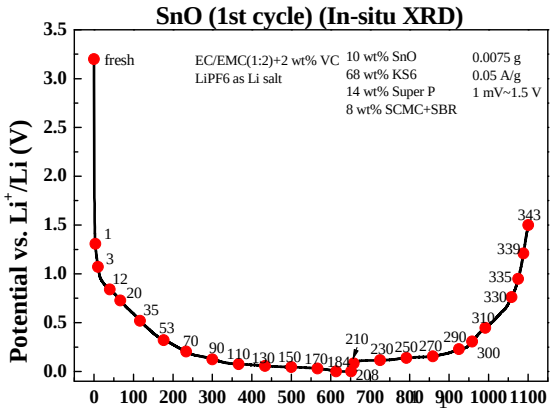

Fig. 1: *In-situ* synchrotron XRD patterns of SiO anode electrode during charge/discharge cycling.

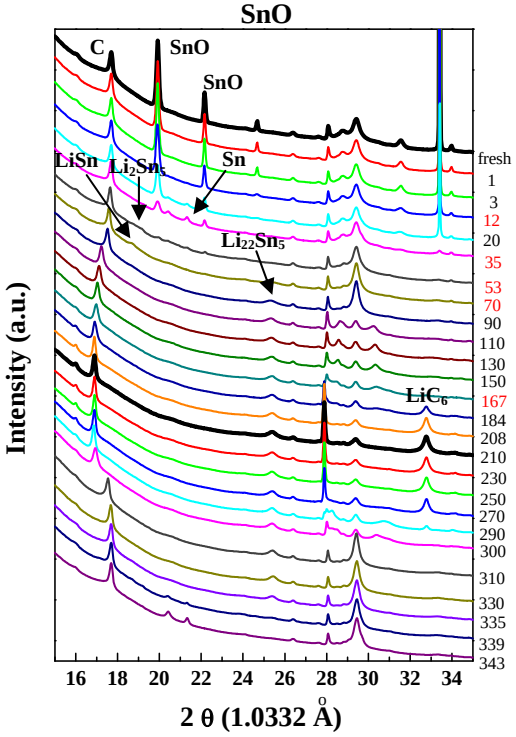

Fig. 2: The charge/discharge voltage profiles are taken during the XRD measurements. The solid symbols index the XRD patterns.

The XRD patterns acquired *in situ* during discharge and charge are shown in Fig. 1, while the corresponding discharging and charging voltage curves marked with the locations where spectra were acquired are shown in Fig. 2.

From the synchrotron XRD data as shown in Fig. 1, the reflection peaks of graphite shifted to lower angles, suggesting lattice expansion due to Li intercalation. Moreover, the Sn peak starts to appears when voltage reaches 0.84V which suggesting the SnO is reduced to form Sn and Li_2O. Futhermore, lithium tin compounds such as Li_2Sn_5, LiSn and $Li_{22}Sn_5$, start to appear when the voltage reach 0.52V, 0.32V and 0.2V in sequence. The corresponding TXM images which are not shown here exhibit the nature of SnO material when subjecting to charging/discharging process. The irreversibility of structure of SnO particle mainly comes from the formation of Li_2O at hign voltage. The shape of SnO remains after first cycle which is very different from Sn may indicating the role of oxide phase or the particle size of Sn in SnO structure. The combination of *in-situ* XRD and *in-situ* TXM is powerful to explore the fundamental behavior of materials as cathode or anode materials for lithium ion batteries.