

Study of degradation mechanism of Si alloy anode active material

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Silicon is regarded as one of the candidates for the next generation negative electrode materials for high energy density lithium-ion batteries because the gravimetric theoretical capacity of silicon negative electrode shows ten times higher than the conventional graphite negative electrode. For the development of the Si-based negative electrode, the heavy degradation due to the surface state change including a chemical state of active material and the film formation on the electrode/electrolyte interface (SEI: Solid Electrolyte Interphase) should be overcome. In addition, the bulk structure change due to expansion and shrinkage is also a serious problem. It is reported that the increase of the resistance is caused by the formation and growth of SEI by electrolyte decomposition¹. The transition from Si to silicate phase in the surface layer of the active material has been reported, which decreases the active site for the charge transfer reaction of lithium-ion². However, the kinds of silicate phases formed in the surface layer and their formation mechanisms have not been clarified. In this study, we investigate the bulk structure change of the Si alloy negative electrode, especially the active material surface layer, and discuss the relationship between structural change and the deterioration behavior.

A composite electrode having a Si alloy active material (Si / Sn / Ti = 66: 5: 29 atom%): carbon black: polyimide = 80: 5: 15 (wt%) was used as a working electrode. Coin cells using Li metal as a counter electrode and 1.0 M LiClO₄ (EC/DEC (50:50 vol%)) as an electrolyte were prepared. The charge-discharge voltage range was 0.01 - 2.0 V. After one cycle of charge and discharge at 0.1C as the activation treatment, 50 cycles charge-discharge were performed at 0.3C, and then the capacity was checked at 0.1C charge-discharge. Si K-edge XAS was measured at BL-10 of Ritsumeikan University SR Center. The measured samples were the electrodes before the charge-discharge cycle (Pristine), after the initial charge-discharge (Initial) and after 50 cycles (Cycled). The measurement mode was total electron yield (TEY) mode.

The capacity retention after charge-discharge at 0.3C decreased to about 50% after 50 cycles and the capacity retention at 0.1 C was 83%. This difference is supposed to be due to the increase of

the resistance. In the measured Si K-edge XANES spectra of Pristine, the peaks corresponding to Si and SiO₂ are observed at 1840 eV and 1847 eV, respectively. The surface of the Si alloy active material is considered to be oxidized even before charging and discharging. For Initial and Cycled, the peak intensity from SiO₂ is increased, which indicates the ratio of SiO₂ increases. In addition, the peak broadening at 1847 eV of Cycled is observed, suggesting the formation of silicate.

In the radial distribution function, the peak intensity near 1 Å corresponding to the Si-O bond increases by the charge-discharge cycle and the peak intensity near 2 Å corresponding to the Si-Si bond decreases. This change shows the transition from Si to SiO₂ by charge-discharge cycle, which is consistent with XANES observation. From these results, it is revealed that the Si alloy negative electrode changes by the charge-discharge cycle from the Si phase to the SiO₂ and the silicate phases in the active material surface layer of several tens nm.

It has been reported that Li silicate forms by reaction of SiO₂ with Li³⁻⁵. It is assumed that the Li silicate phase presents in the surface layer of the active materials during charge/discharge. Although the Li silicate is Li-ion conductor, the conductivity is lower than that of electrolyte^{6, 7}. Therefore, it is considered that one of the degradation factors due to the charge-discharge cycle is resistance increase caused by Li silicate phase growth in the surface layer of the active material.

References

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