XAFS Imaging Analysis of LiFePO$_4$ Cathode in Lithium Ion Battery with Graphite Anode

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1. Introduction

Lithium ion secondary battery (LIB) is widely used as an energy source for portable devices. The investigation by using the XAFS imaging technique has been carried out to reveal the actual electrode reaction in the battery cell. The spatial distribution of the chemical state of the active species is visualized by the XAFS imaging technique for the cathode in the operating battery. We have found that the inhomogeneous reaction is observed in the lithium iron phosphate (LiFePO$_4$, LFP) cathode in LIB with a Li anode and that the redox reactions of LFP progress at the reaction channels with a high electrical conductivity [1]. In this study, the chemical state mapping for the LFP cathode has been carried out using the XAFS imaging technique to clarify the spatial distribution of the electrode reaction of LFP for a battery with the graphite anode.

2. Experimental

An LFP cathode (13 mm$\phi$), a separator sheet, and a graphite anode (15 mm$\phi$) were assembled in a battery cell made of stainless steel. Two battery cells were prepared, and the first cell (Battery-0) was discharged to 2.0 V at the rate of 0.1 C after five aging cycles of 0.5 C. A set of the charge at 0.5 C and the discharge at 5 C was repeated 100 times using another cell (Battery-100), and the cell was finally discharged to 2.0 V at 0.1 C. The LFP cathode was then taken out from the battery cell under an Ar gas atmosphere, and it was put in an Al-laminated package. The XAFS imaging measurements at the energy range around the Fe K edge were performed at BL-4 of SR Center (Ritsumeikan University). The chemical state of LFP was evaluated using the XANES spectra of standard samples (LFP and FePO$_4$).
3. Results and Discussion

Figure 1 shows the chemical state maps of the LFP cathode before and after the 100 cycles test. The blue and red pixel indicates the LFP (Fe$^{2+}$) and FePO$_4$ (Fe$^{3+}$) state, respectively, and the yellow pixel means the mixed state of LFP and FePO$_4$. The chemical state map of Battery-0 shows that the cathode is mostly discharged except for the yellow area near the edge of the cathode plate. On the other hand, the cathode of Battery-100 shows the ring-shaped area, where the discharging reaction is not completed. Some reaction channels depicted by the blue spot are appeared in the yellow ring. The ring-shaped distribution shown in Fig. 1(B) is explained by the inhomogeneous distribution of Li in the graphite anode. Because the size of the graphite anode is larger than that of the cathode, the intercalated Li species in the graphite anode can diffuse in the anode plane during the charging process. At the high-rate discharging process, the diffused Li species at the outside area where the cathode is not faced may not participate in the electrochemical reaction, because the longer distance to the cathode causes the electric resistance. Consequently, the inert Li species is accumulated in the graphite anode during the repeated charge/discharge cycles, and thus the discharge reaction of the cathode is not completed due to the lack of the compensating Li species. Because the Li ion insertion into the cathode is considered to be superior at the cathode center in considering the electrode separation, the ring-shaped inhomogeneity is reasonably explained by the Li accumulation in the graphite anode.

Fig. 1. Chemical state map of the LFP cathode at the discharged state before (A) and after (B) the 100 cycles test.

Reference