Electrode Surface Analyses on a LiFePO₄//Li₄Ti₅O₁₂ Lithium-Ion Battery

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Lithium-ion batteries (LIBs) have been widely used as a power source for portable devices. During long-period battery operation, electrolyte decomposition is considered one of the main problems of capacity degradation. The degraded electrode surface is covered by a thin film layer of the decomposition products. In this study, the positive and negative electrode surfaces were analyzed to identify the chemical states of the film using X-ray photoelectron spectroscopy (XPS).

LiFePO₄ (LFP) and Li₄Ti₅O₁₂ (LTO) are used as the positive and negative electrode active materials, respectively. The electrodes consisted of the active material, acetylene black (AB), and polyvinylidene difluoride (PVDF) binder. The electrolyte was 1M LiPF₆ dissolved in anhydrous ethylene carbonate (EC) and ethyl methyl carbonate (EMC) by 3:7 in volume ratio. One-cycle charging test was performed at 25 °C, and the cells were disassembled in a glove box. The XPS measurements were performed using PHI Quantes (ULVAC-PHI) with a monochromatic Al K_a radiation. The pass energy was set to 26 eV. Dual-beam charge neutralization was applied to suppress sample charging. Binding energies were calibrated for the C 1s signal from AB at 284.6 eV.

Figs. 1 (a-c) show the Fe 2*p*, O 1*s*, and F 1*s* spectra of the LFP electrode samples. The Fe valence states of the pristine and charged (1c) samples were 2+ and 3+, respectively (LiFePO₄ \rightarrow FePO₄ + Li⁺ + e^-). The O 1*s* and F 1*s* spectra suggested that the film layer formed after the 1st-charging is negligible [1].

Figs. 1 (d-f) show the Ti 2*p*, O 1*s*, and F 1*s* spectra of the LTO electrode samples. The Ti valence state of Li₄Ti₅O₁₂ is 4+. A shoulder peak was observed at a lower binding energy for the charged sample, attributed to Ti³⁺ (Li₄Ti₅O₁₂ + 3Li⁺ + 3 $e^- \rightarrow$ Li₇Ti₅O₁₂). The decreased Ti 2*p* intensity indicates the formation of a thick film layer on the charged electrode. It is found that the LTO electrode is covered by the decomposition products such as organic carbonates, fluorophosphates, and LiF.

References

[1] K. Shimoda et al., J. Electrochem. Soc., 2014, 161, A1012.



Fig. 1 (a) Fe 2*p*, (b) O 1*s*, and (c) F 1*s* core-level spectra of the LiFePO₄ electrode samples. (d) Ti 2*p*, (e) O 1*s*, and (f) F 1*s* spectra of the Li₄Ti₅O₁₂ electrode samples.