Impedance Analysis and Characterization of Electrodes on Degraded Laminated Li-ion Battery with Micro Reference Electrode

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Introduction

To understand the degradation mechanism of lithium-ion batteries (LIBs) is helpful for the development of LIBs. Alternating-current (ac) impedance method is one of powerful techniques to understand an internal state in electrochemical systems. Therefore, the method has been widely applied to investigate LIBs. We have investigated degradation of LIBs by means of ac impedance [1, 2]. We have made a laminated-type cell with micro reference electrode which is considered not to affect the cell operation. As the results, we confirmed the increases of the interfacial resistance of anode and cathode with increasing the number of charge-discharge cycles.

In this study, the internal state of degraded laminated-type cell with micro reference electrode was investigated by ac-impedance method and surface characterization. The impedance changes were discussed on the basis of the changes on the electrode surfaces which were analyzed by Fourier transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS).

Experimental

A laminated-type cells (electrode area: 7 cm x 7 cm) consisting of the graphite anode, $LiCoO_2$ cathode, and micro reference electrode were assembled. The mixture of an ethylene carbonate/diethyl carbonate (EC/DEC 1:1 w/w) with 1M $LiPF_6$ was used as electrolyte. The laminated-type cells were aged by two charge-discharge cycles in the voltage range of 4.2 and 3.0 V at the rate of 0.1 C as pretreatment. The laminated-type cells were degraded by charge-discharge cycles at the rate of 0.5 C with constant current - constant voltage (CC-CV) for charge and constant current (CC) for discharge under various temperatures. The impedance was measured at the depth of discharge (DOD) of 40% in the frequency range between 100 kHz and 1 mHz. After the impedance measurement, these cells were disassembled and rinsed with fresh dimethyl carbonate. The anode and cathode surfaces were analyzed by FT-IR and XPS. These experiments were carried out under a highly pure argon atmosphere (dew point: less than -90°C, oxygen: less than 5 ppm).

Results and Discussion

The impedance spectra of graphite anode and $LiCoO_2$ cathode at DOD of 40% were separately obtained. In both of the anode and the cathode, a small semicircle at high frequency region and a large semicircle at low frequency region were confirmed.

The radius of the semicircle confirmed at the low and high frequency regions increased clearly after 100 cycles compared with those before cycles. In particular, increase of the charge transfer resistance observed at the low frequency region was confirmed in both of the anode and the cathode. About the temperature variation on charge-discharge cycles for degradation, the increase of anode impedance was confirmed when the temperature on charge-discharge cycles for degradation was 60°C compared with the case of 25°C, which was relatively notable compared with the other cases.

Fig. 1 indicates the FT-IR spectra of surface of graphite anodes obtained before cycles and after 100 cycles at the various temperatures at which the cells were cycled for degradation. The spectrum of graphite anode after 100 cycles at 60ºC (Fig. 1c) shows absorptions at ca. 1640, 1320, 1100, 820 cm^{-1} corresponding to lithium alkyl carbonate. These absorptions are attributed to the SEI layer formed by decomposition product of electrolyte.

Fig. 2 shows the XPS spectra of $LiCoO_2$ cathode after 100 cycles at various temperatures for degradation. The LiF peak observed at 684 eV suggests that the inorganic compound was produced by decomposition of $LiPF_6$ salt.

The increase of impedance at the high frequency side after 100 cycles is attributed to the SEI formation.

Therefore, the relationship between composition change on electrode surface and increase in electrode resistance after cycling was suggested for laminated-type cells with reference electrode.

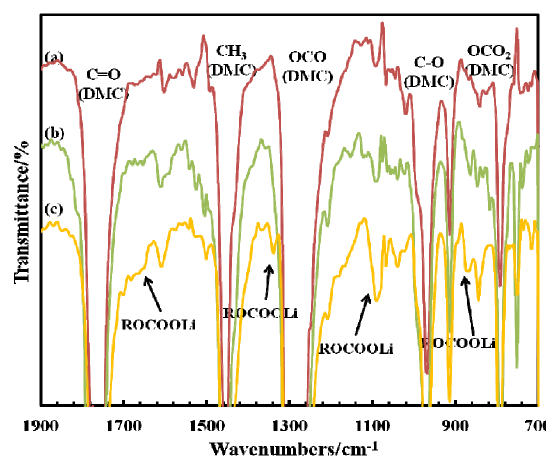

Figure 1. FT-IR spectra of surface of graphite anodes rinsed with DMC (a) before cycles (b) after 100 cycles at 45°C (c) after 100 cycles at 60°C.

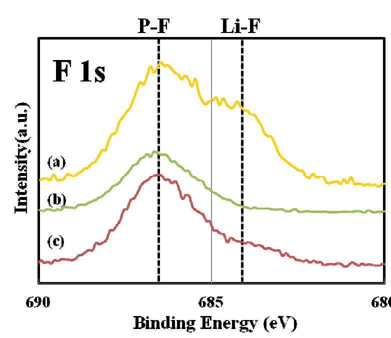

Figure 2. F 1s peaks of surface for $LiCoO_2$ cathodes (a) after 100 cycles at 60°C (b) after 100 cycles at 45°C (c) before cycles.

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References

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[2] D. Mukoyama, T. Momma, H. Nara, T. Osaka, *Chem. Lett.*, **41(4)**, 444 (2012).