Simultaneous Measurements of Positive and Negative Electrodes of LIRB by in-situ EIS During Charge-Discharge Cycle

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Lithium-ion rechargeable battery (LIRB) has been used for the electric power rechargeable of various electronic devices. The detailed investigations of elementary processes, i.e., reactions and mass transfers, of LIRB are quite significant to improve performance of LIRB. Several time-constants related to battery structure and reactions can be discriminated by using Electrochemical Impedance Spectroscopy (EIS). Especially, the separation of time-constants of anode and cathode from full cell impedance is desired in the interpretation of impedance spectra of LIRB\textsuperscript{4,5}. However, the precise separation is not easy, because the time-constants related to cathode are close to those of anode. In the present study, we applied in-situ EIS to simultaneous measurements of three impedance spectra, i.e., full cell, anode and cathode, during the charge-discharge cycle. We investigated the influence of charge rate (C-rate) on impedance spectra of both cathode and anode and discussed the possibility of separation of these components from the full cell impedance at a room temperature.

The electrochemical cell was a three-electrode cell equipped by Toyo System co. The cathode was a LiCoO\textsubscript{2} fabricated on aluminum foil. The spherical natural graphite on copper foil was used as the anode (10 mm\textsuperscript{2}, Hosen co.). A lithium wire was used as the reference electrode (RE). A polyethylene separator was sandwiched between cathode and anode. The impedance spectra were measured successively by superimposing the small ac current on the dc current during the measurements of the charge or discharge curves. The impedance measurement was performed in a frequency range from 10 mHz to 10 kHz and started from high frequency toward low frequency in the logarithmic scan. In the present study, the charge is defined as the intercalation of lithium from the cathode, and the discharge is defined as the intercalation of lithium into the cathode. All measurements were performed in a glove box under an argon atmosphere at 25 °C. The measurement of impedance spectra was carried out using a potentiostat (Hokuto Denko, HA501G) and frequency response analyzer (FRA) (Solartron, SI1254) controlled by a personal computer (IBM, ThinkPad A22m) through GP–IB interface. Data fitting was carried out with Zview.

Impedance spectra were measured successively during charge or discharge sequence, and plotted on the three dimensional (3D) complex diagram that has a time axis. The plots were connected by the spline under tension function at each frequency. The cross-section of 3D impedance shell perpendicular to the time axis gives the instantaneous impedance at an arbitrary time\textsuperscript{5}. The impedance and the parameters obtained by the impedance were represented by the values per the surface area (0.785 cm\textsuperscript{2}) of the cathode and anode.

Figure 1 shows the potential-capacity curve and three-dimensional (3D) complex plots of electrochemical impedance of cathode, anode and cell during first charge.


References