Development of a simplified analysis method for deterioration diagnosis of lithium-ion batteries

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Introduction

In recent years, there has been a growing interest in the use of renewable energy such as solar and wind power. Large-scale electric power storage systems are needed to store such a large amount of power, which should contribute to the electric-load leveling. Lithium ion batteries (LIBs) are considered as the most suitable candidate for storage batteries in large-scale applications. Diagnosis methods with low cost and easy operation are required for detecting the state of deterioration of large-scale storage systems under operation. Electrochemical impedance spectroscopy (EIS) is one of the powerful techniques to analyze electrochemical processes occurring in LIBs. It can separate the impedance to that of each component in LIBs [1], and as a result we can estimate the state of deterioration of each component in LIBs. However, EIS cannot be applied to batteries under operation because a steady state is needed for measurements. We are developing an analysis method using Z transformation to estimate the impedance while the LIBs are under operation. Using transient responses, we can know changes in the internal resistance without interrupting operation of LIBs. The Z transformation method needs information of the frequency range that relates to the deterioration of LIBs. Hence, in this study, we investigated changes in impedance before and after repeated charge/discharge cycles using small-sized pouch cells, and evaluated the validity of our analysis method.

Experimental

Pouch cells (5 x 8 cm), in which graphite and lithium manganese oxide (LMO) were used as active materials for negative and positive electrodes, respectively, were used for measurements. The electrochemical properties of the pouch cells were investigated by constant-current/constant-voltage charging/discharging between 3.0 and 4.2 V at a rate of 0.25 C at 30 °C. Ac impedance spectra were measured before cycles and after the 50th and 100th cycle over a frequency range from 100 kHz to 1 mHz at 30 °C at several depths of discharge using a galvanostatic intermittent titration technique. The pouch cells were disassembled in an Ar-filled glove box after the charge/discharge tests, and then both the negative and positive electrodes were investigated by energy dispersive X-ray spectrometer (EDS), and by EIS using three-electrode coin-type half-cells with Li reference and counter electrodes.

Results and discussions

Figure 1 shows variation of discharge capacities and capacity retention with charge/discharge cycles of a LMO/graphite cell. The discharge capacity gradually decreased, and 75% of the initial discharge capacity was obtained after the 100th cycle. The internal resistance increased with a decrease in capacity, as shown in Fig. 2. From the EDS measurements and half-cell tests, the decrease in discharge capacity and the increase in the internal resistance were attributed to formation of surface films and off-balance of the discharge capacity between the positive and negative electrodes. In addition, it was revealed that impedance of pouch cells depends largely on positive electrode. Deterioration diagnosis of this battery was performed using our analysis system, which will be reported in our presentation.

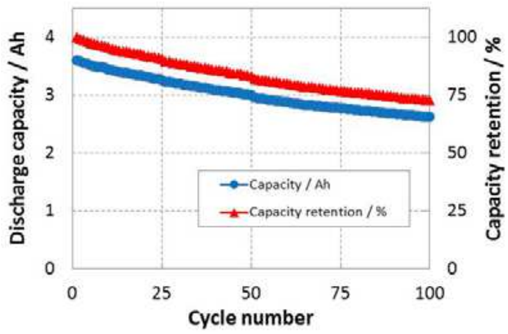

Fig. 1 Variation of discharge capacities and capacity retention with charge/discharge cycles of a LMO/graphite cell.

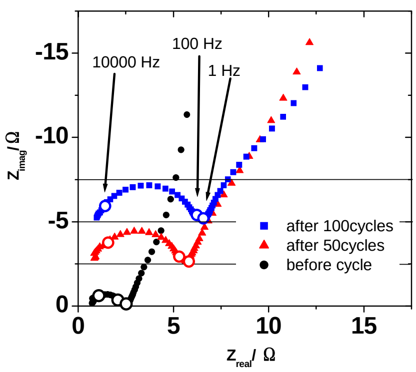

Fig. 2 Nyquist plots of LMO/Graphite cell before and after charge/discharge test.

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[1] M. Itagaki *et al*, *Electrochim. Acta*, **51**, 1629 (2006).
[2] N.Nagaoka *et al*, *13th IEEE COMPEL 2012*, art. no. 6251767(2012).