Principal Research Results

Development of Quantification Analysis Method about Lithium Battery Degradation
− Non-Destructive Analysis of Cathode and Anode Electrode Characteristics by Using Thermal/Electrical Responses −

Background

It is expected that lithium-ion batteries, which are widely used in small power sources of mobile devices, will spread to moving vehicle and stationary energy storage uses. However, it is necessary for commercial use to improve life time performance. Since it is important to identify degraded regions and causes, it is necessary to recognize characteristics of cathode and anode electrodes in a battery cell separately and non-destructive analysis method for degradation quantification.

Objectives

This study aims to propose a method of extracting individual response of cathode and anode electrodes in a lithium-ion battery by using thermal measurement technique and AC impedance measurement technique as non-destructive analysis method;

Principal Results

1. Establishment of experimental technique for verification of non-destructive analysis method

To verify the validity of the non-destructive analysis method, test cells were made, which were coin type cells or flat sheet cells with reference electrode. They were made by disassembly of commercial lithium-ion battery and extracting cathode and anode electrodes individually. They were used for evaluation of cathode and anode electrodes separately by thermal measurement and AC impedance measurement. This will enable us to evaluate characteristics of electrodes with original electrode structures of commercial lithium-ion battery.

2. Thermal measurement data acquisition and its application to non-destructive analysis

Exothermic and endothermic profiles of various cathode/anode electrode materials for lithium-ion battery during charge and discharge were organized and analyzed from relationship with change of reaction entropy, phase transition, etc. The results led to definition of correspondence between heat peaks and concentration of lithium in the electrodes (electrode capacitance (mAh g^{-1})) (Figure 1 left). If heat peaks are fixed to lithium content, these thermal measurement data can be applied to identification of degraded regions and qualification analysis of degradation (Figure 1 right).

3. Separate determination of cathode and anode characteristics by using AC impedance measurement technique

Under some combinations of cathode and anode electrode materials, it was very difficult to separate profiles of cathode/electrolyte and anode/electrolyte interfaces from AC impedance data at 25 ℃ (Figure 2 upper-left). However, each AC impedance profile of cathode and anode electrodes of commercial lithium-ion battery at -5 ℃ shows anode/electrolyte interface has more than four times larger impedance than cathode interface (Figure 2 right). So, we found out that anode/electrolyte interface profile, which has larger impedance than cathode interface, is dominant in AC impedance profile at low temperature (Figure 2 bottom-left). These results show that AC impedance of lithium-ion battery at specified temperature is one of the non-destructive analysis methods for individual impedance of cathode/electrolyte and anode/electrolyte interface, which is a promising parameter for degradation qualification.

Future Developments

To contribute to life time improvement of lithium-ion battery, the method will be applied to lithium-ion battery in the process of capacity degradation, and the degradation factors will be analyzed.

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Reference

Y. Mita, et.al., 2008, “Development of quantification method about lithium battery degradation - Nondestructive analysis of cathode and anode electrodes characteristics by using thermal/electrical responses - ”, CRIEPI Report Q07023 (in Japanese)

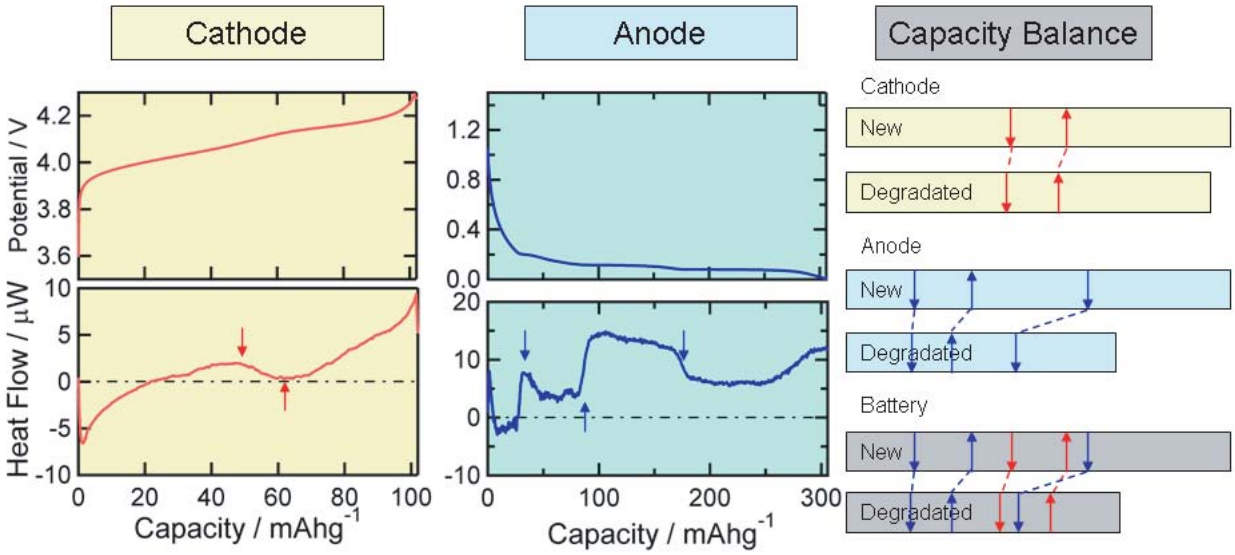

Fig.1 Heat peaks during charge of cathode material (manganese oxide) and anode material (graphite) which are used in lithium-ion batteries, and shifts of heat peaks corresponding to electrode capacity before and after degradation (concept, see note #2).

Note #1: Upper arrows mean exothermic and lower ones mean endothermic.
#2: In this case, anode degradation was mainly caused heat peak shifts of lithium-ion battery.

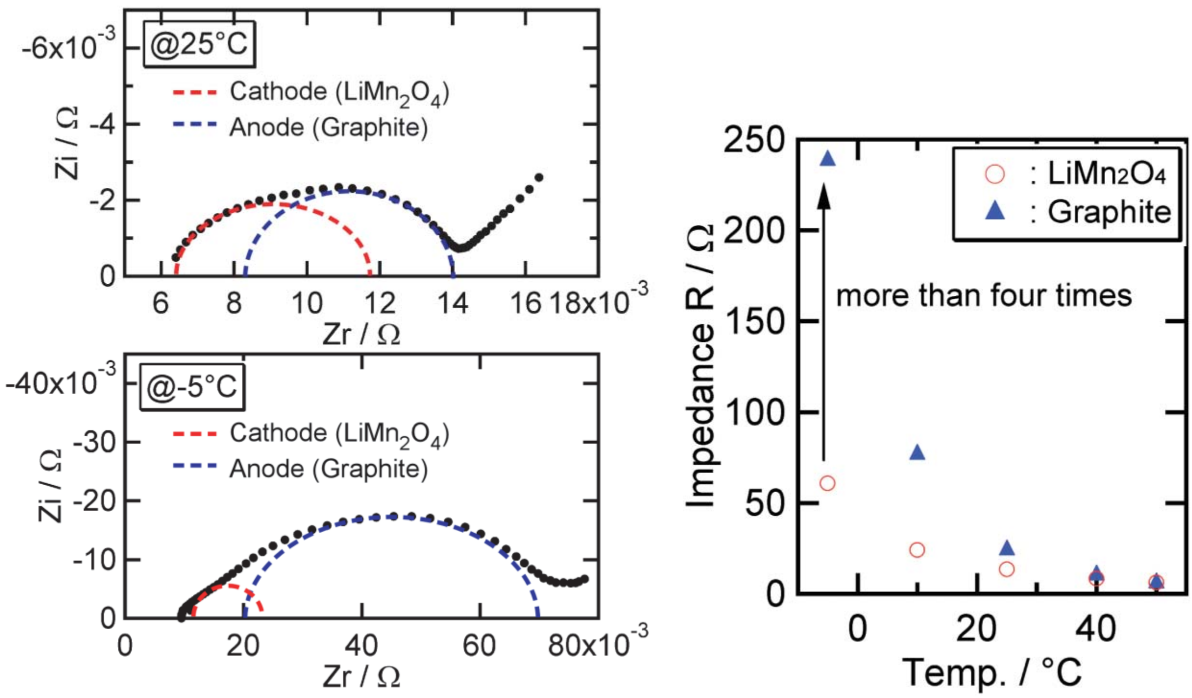

Fig.2 Nyquist plots of commercial lithium-ion battery (see note #3), and interfacial impedances of cathode material (manganese oxide) and anode material (graphite) in the battery at various temperatures calculated from AC impedance characteristics.

Note #3: Dotted semi-circles from fitting calculation shows that it is possible to separate profiles of cathode and anode at -5 ℃ rather than at 25 ℃.