

Establishment of Evaluation Technologies for High Performance Secondary Batteries

Background and Objective

Secondary batteries are expected to be utilized not only for load leveling energy storage, but also for stabilization of electric power grid systems connected with renewable power sources such as a photovoltaic and wind power generators. It is thus important to establish the technologies contributing to exact evaluation of their remaining life time and to keep improving the safety technologies for their long-period

operations. We will elucidate the degradation mechanism of lithium-ion batteries (LIB), which have excellent energy density and energy efficiency, as the proper understanding of the degradation mechanism enables exact life-time evaluation. We will also establish comprehensive analysis methods for LIB in order to realize longer life and improve safety.

Main results

1 Elucidating the degradation mechanism of LIB after charge-discharge cycling test

For elucidation of the degradation mechanism, it is important to measure the potential of cathode and anode individually on an operating LIB. The lithium manganese oxide-based cathode and the graphite-based anode were first extracted from a commercially available LIB cell with faded capacity after a long cycling test. Both electrodes were then reassembled into two coin-type half cells with lithium metal as a reference (counter) electrode (Fig. 1), and these two cells were electrically connected at the lithium-metal reference electrodes, which can reproduce the battery performance of the original cell. Next, the test cell was charged and discharged while monitoring the potential

of not only the cathode and the anode, but also the reference electrode. From the analysis, it was revealed that the capacity fading occurred mostly due to less overlapping of individual operation regions (narrowing) for cathode- and anode-side half cells. It was also found that, in addition to the narrowing, the decrease of the reversible capacity caused by inactivation of the active material* at the cathode gives secondary contribution to the capacity degradation of the cell (Fig. 2) (Q13404). We will confirm if this degradation mechanism is applicable to other LIB with different cathode (anode) materials, and propose new materials that realize a prolonged cycle-life.

2 Development of a method to identify the material responsible for the capacity fading in combined cathodes

Certain LIBs use a combination of two active materials as a cathode in order to enhance the performance of capacity and life-time. For proper understanding of the effect of combining on life-time enhancement, it is important to know the individual capacity of each active material in a combined cathode. Through the detailed analysis of capacity-vs-voltage characteristics, we have found that several peaks appear in the differential capacity-vs-voltage curves. Each of them can be assigned to the response from one of the activation

materials, and we can estimate the capacity of each cathode materials by counting the area below each peak (Fig. 3). The result indicates that the mass ratio of the two cathode materials can be estimated simply as the total capacity should be the sum of the capacity attributing to each cathode material. This allows identification of the cathode material mainly contributing to capacity fading^[1]. We will use this method to verify the origin of long-life LIBs with a combination of various cathode materials.

3 Analysis of internal resistance in solid-electrolytes LIBs

An ongoing effort to improve the safety of batteries is required in order to utilize them as an energy storage system connected with power grids. Solid-polymer-electrolytes (SPE) are one of the promising electrolytes for the realization of safer batteries, with more potential than organic solvents normally used in LIB. We constructed the same type of all solid LIBs consisting of a $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathode and a graphite anode as shown in Fig. 1, and

performed AC impedance measurements during a long-period charge-discharge cycling test. From the result, it was revealed that the main reason of the increase of internal impedance was the increase of the interfacial resistance at the cathode-electrolyte interface (Fig. 4), which indicates the importance of externally controlling the interface condition for suppressing capacity fading^[2].

* The materials which take charge-discharge reaction in a battery

[1] T. Kobayashi et al., J. Power Sources, 245, 1-6, 2014

[2] K. Shono et al., J. Power Sources, 247, 1026-1032, 2014.

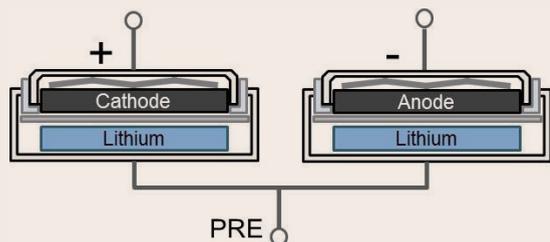


Fig. 1: Simple cell structure within the pseudo reference electrode for measurement of each electrode potential

Instead of special cell construction needed to install reference electrode between the cathode and anode, normal coin-type cell construction is now available by using lithium metal as the pseudo reference electrode (PRE). We disassembled the battery and reconstructed two coin-type cells with a cathode and anode in a glove-box filled with argon gas, and we confirmed cell capacity did not change before and after the disassembly.

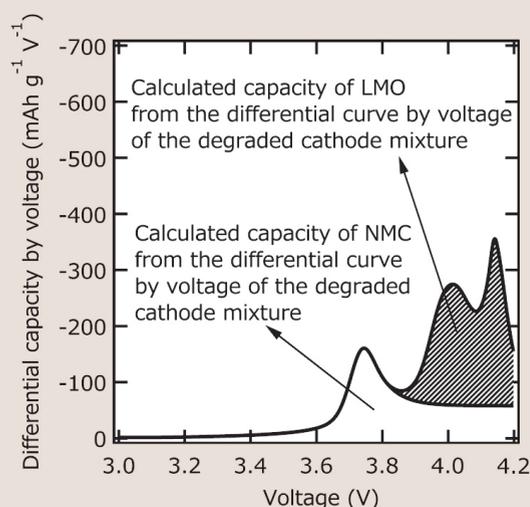


Fig. 3: Evaluation method of individual cathode material in the mixture cathode

In many cases, manganese oxide is used with other cathode materials with different composition. We estimated the capacity of a LiMn_2O_4 [LMO] and a $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ [NMC] in the cathode mixture, by analysis of the voltage derivative curve of the cathode capacity. We separated the area of the derivative curve based on the characteristics of materials as shown in the figure, which shows the capacity of each cathode material.

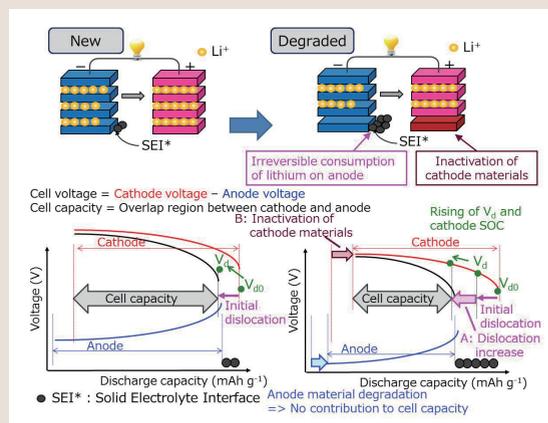


Fig. 2: Capacity fading mechanism evaluated by disassembly and reassembly

A capacity of lithium-ion battery is determined by the size of overlap in the cathode and anode capacity operation area. In a new cell, it is well known that the initial charge-discharge makes film layer on the anode surface by consumption of lithium (• in the figure). We clarified that capacity fading was due to continuous consumption of lithium leading to increasing dislocation of cathode and anode operation regions (A in the figure), and deactivation of the cathode active material (B in the figure) by analysis of discharge end cathode voltage, V_d , and SOC rising.

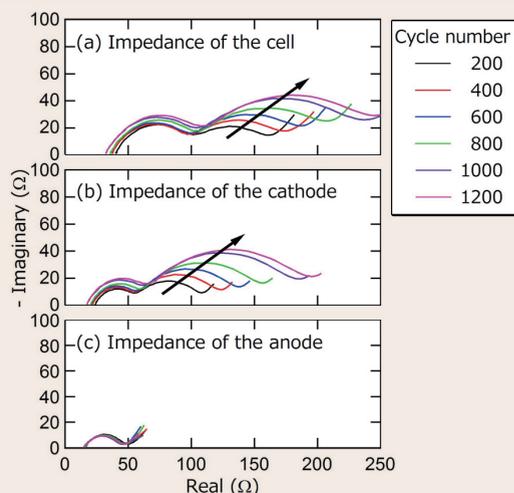


Fig. 4: Analysis of internal impedance of an all-solid lithium-ion battery during long-period operation

We studied the change in internal resistance of a lithium-ion battery consisting of all-solid electrolytes during long charge-discharge operation, using two coin-type cells with the pseudo reference electrode as shown in Fig. 1 by FRA^{*1}. The results showed that the increase of cell impedance (a) is mainly due to the impedance at the interface between the cathode and the electrolyte (b). However, there are almost no changes in the impedance of the interface between the anode and the electrolyte (c).

*1: Frequency Response Analyzer is used to measure AC current response vs. voltage at various frequencies. The impedance data were plotted to the axis with the real number component as x-coordinates and the imaginary number component as y-coordinates.