Priority Subjects — **Development of a Supply/Demand Infrastructure for Next-Generation Electric Power**

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 photovoltaic and wind power generators. It is thus important to establish technologies which contribute to exact evaluation of secondary battery remaining life time and to keep improving “safety” technologies for their long-period operations.

We will elucidate the degradation mechanism of lithium-ion batteries (LIB), which is excellent in its energy density and energy efficiency, as an accurate understanding of the degradation mechanism makes precise life-time evaluation possible. We will also establish comprehensive analysis methods of LIB for extending life and improving safety.

Main results

1 Evaluation of cell capacity changes during charge-discharge cycle tests

Charge-discharge cycle tests of cells with lithium titanate (LTO) anode* selected as a practical stationary use lithium-ion battery (LIB) were examined at a constant electric current (Fig. 1). Charge-discharge cycle tests were examined at 45°C to accelerate the degradation of the cells, and the discharge capacities were periodically checked at 25°C for evaluation of cell life (Q14009). As a result of the charge-discharge tests for a maximum of 5,000 cycles over approx. 1 year, the cells were found to have capacities of more than 98.9% of the initial capacities, even in the case of the most degraded cell. Therefore, the cells used in this study were expected to have long life (Fig. 2, open symbols).

2 Quantitative evaluation method of cell capacity changes

The degradation of the cell includes various factors, therefore, in order to clarify the degradation characters of the cell, it is important to divide the capacity change into each factor and understand their characters. It is considered that the cell capacity fading can be divided into fading during storage without electric current (storage fading factor, ΔQ_t) and fading by repeating charge-discharge reactions (cycle fading factor, ΔQ_e).

The capacity change of charge-discharge cycle tests includes both of the above fading factors, therefore, in order to distinguish the cycle fading factor, an evaluation method of the capacity based only on charge-discharge reactions (Q_e) was suggested by obtaining the storage fading factor from the results of the storage tests without electrical current (Fig. 2). This method enabled quantification of the cycle fading factor as the difference between the initial capacity and degraded only charge-discharge reactions.

Furthermore, it was elucidated that the cycle fading factor could be divided into the fading with (ΔQ_{eR}) and without (ΔQ_{eC}) the influence of internal resistance of the cell by examining the capacity checks at multiple currents (Fig. 3(a)). Capacity fading by internal resistance (ΔQ_{eR}) was found to increase with the square root of operation time, which may be due to the growth of a coating layer at the electrode surface as was generally considered (Fig. 3(b)).

From the proposed evaluating method in this study, the capacity fading of the cell was able to be quantitatively divided into three parts, the storage fading factor and the cycle fading factor with and without the influence of internal resistance (Fig. 4). The quantitative evaluation of cell degradation will be utilized for the planning of long-term operation through the clarification of the degradation mechanisms of each factor.

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* SCiB™ Manufactured by Toshiba, rating capacity: 20 Ah.

Fig. 1: Lithium-ion cell and charge-discharge test equipment used in this study

The single cell (pictured lower right: provided by Toshiba) was set into the thermostatic chamber (pictured upper right), and the charge-discharge test was examined with a power device (pictured left).

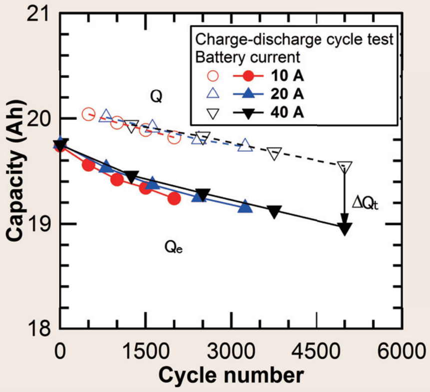

Fig. 2: The dependence of the discharge capacity after the cycle test (Q) and the degraded capacity (Q_e) extracting storage fading factor (ΔQ_t) with cycle numbers

The capacity degraded only the charge-discharge reactions (Q_e) was obtained by extracting the storage fading factor (ΔQ_t) from the discharge capacity after the cycle test (Q). ΔQ_t was the difference between the initial capacity and the capacity after the storage test. Each plot was the averaged value of three samples.

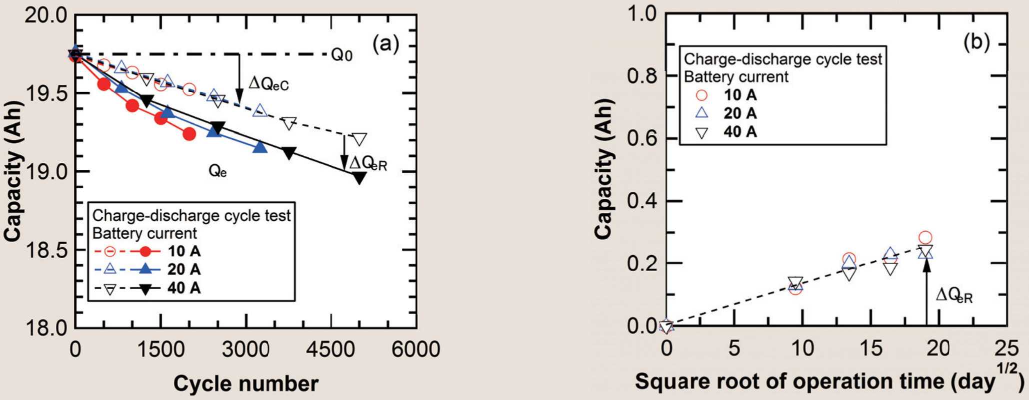

Fig. 3: The dependence of the capacity fading other than the internal resistance of the cell (ΔQ_{eC}) and that due to the internal resistance of the cell (ΔQ_{eR}) with cycle numbers and operation time during the charge-discharge cycle tests

The discharge capacities at currents of 10 A and 20 A in the capacity checks were plotted, and a line was drawn between them and extrapolated to the current of 0 A. This capacity was defined as the virtual 0 C rate capacity. The difference of the virtual 0 C rate capacity between the initial value and the capacity after the test was defined as ΔQ_{eC}. ΔQ_{eR} was defined as the remainder obtained by subtracting ΔQ_{eC} from the cycle fading factor (ΔQ_e: ($Q_0 - Q_e$)). Each plot was the averaged value of three samples.

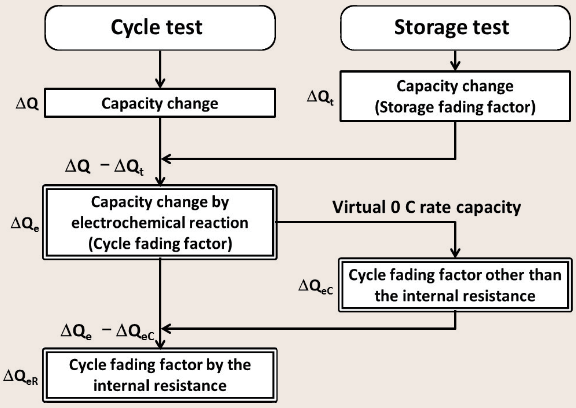

Fig. 4: Flow chart of the quantitative evaluating method for the discharge capacity change in this study

The cycle fading factor (ΔQ_e) was obtained by subtracting the storage fading factor (ΔQ_t) from the discharge capacity during the charge-discharge cycle test (Q). Furthermore, the cycle fading factor was divided into the capacity fading by the internal resistance (ΔQ_{eR}) and that other than the internal resistance (ΔQ_{eC}).