

Degradation factor analysis for the storage aging test of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2/\text{Graphite}$ cells

Daichi Imamura, Masao Myojin, Keisuke Shimada
Japan Automobile Research Institute

2530 Karima, Tsukuba, Ibaraki, 305-0822 JAPAN

Introduction

Lithium-ion batteries (LIBs) are promising power sources for electric vehicles (EVs). Extended durability of LIBs is a highly significant requirement for the promotion of widespread use of EVs. To increase the durability of LIBs, understanding the detailed degradation mechanisms of LIBs is essential. Differential voltage (dV/dQ) analysis is an effective tool to investigate the degradation mechanism, and several groups have adopted dV/dQ to analyze cycle life degradation [1-3]. In this study, degradation factors of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2/\text{graphite}$ cells in long-term storage aging were investigated by dV/dQ analysis, and post-test analysis of electrolyte and electrode materials was performed.

Experimental

Commercial 18650 type cells were used for this study. The cell consists of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathode and graphite anode, and has initial capacity of 2.1 Ah. After the initial performance tests, the cells were charged to 4.0, 4.1, and 4.2 V and then stored in constant temperature baths at 25 and 50 °C. During the storage test, the discharge capacity (1 C and 0.05 C) and the internal DC resistance were periodically measured at 25 °C. The cut of voltages for the capacity measurement were set at 4.2 and 2.75 V. The dV/dQ analysis was conducted using low rate (0.05 C) discharge curves.

Results and discussion

Storage aging tests were conducted for over 700 days. Discharge capacity retention of the cells stored at different voltage and temperature is shown in Fig. 1. Higher temperature and higher voltage caused faster capacity deterioration. Measurement of the cell stored at 4.2 V and 50 °C was aborted because of a possible internal short circuit.

The initial discharge curve measured at 0.05 C and its dV/dQ curve are shown in Fig. 2. Two main peaks correspond to the graphite stage change in the dV/dQ curve. The cell capacity was divided into three regions, Q-1, Q-2, and Q-3, as shown in Fig. 2. In addition to overall capacity, Q-all, change was also monitored for Q-1, Q-2, and Q-3.

Figure 3 shows capacity change for Q-1, Q-2, Q-3, and Q-all for the cell stored at 4.1 V and 50 °C. Though Q-2 and Q-3 were nearly constant, Q-1 and Q-all showed same decreasing tendency. Similar results were obtained in all other conditions. These results indicate that electrode capacity slippage was the dominant reason for the decrease in capacity [3]. Electrode capacity slippage can occur by lithium consumption during solid electrolyte interface formation or electrolyte oxidation.

The relationship between relative internal resistance and capacity decrease measured at 1 C is shown in Fig. 4. The plots were divided into two parts with each part having the same temperature condition, suggesting that degradation factors vary with temperature. After the storage test, the degraded cell materials (electrode and electrolyte) were analyzed, and the results will be reported at the conference.

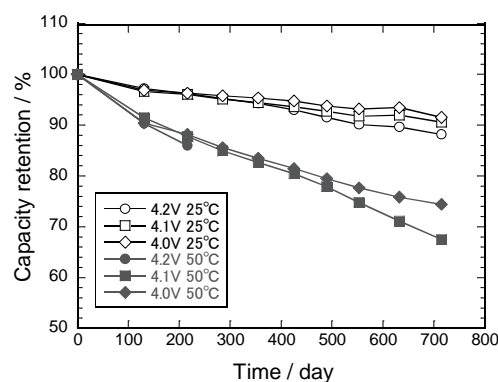


Fig. 1 Discharge capacity retention (0.05 C) at different temperature and voltage.

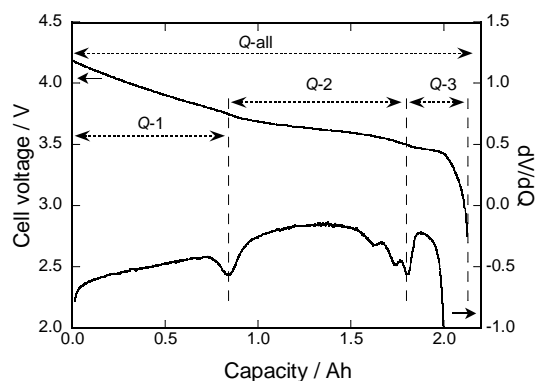


Fig. 2 Initial discharge curve (0.05 C) and differential voltage (dV/dQ) versus capacity.

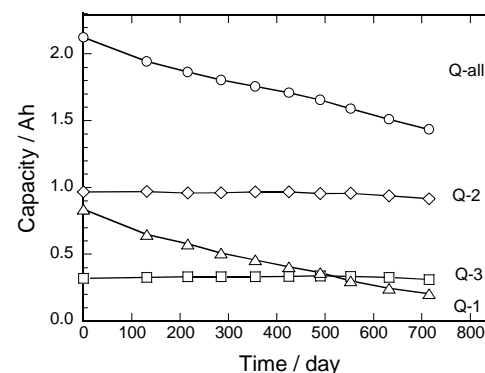


Fig. 3 Discharge capacity change of whole voltage region (Q-all) and three divided voltage regions (Q-1, 2, and 3) for the cell stored at 4.1 V and 50 °C.

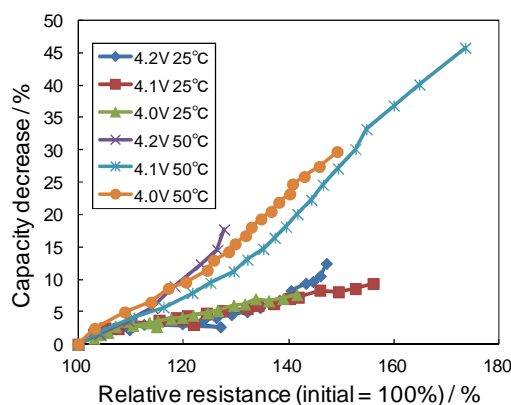


Fig. 4 Relationship between relative resistance and capacity decrease (1 C) for the stored cells.

References

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