Abstract #148, 223rd ECS Meeting, © 2013 The Electrochemical Society

Quantitative analysis of capacity fading mechanism in Mn-based cathode/graphite anode lithium-ion battery

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Introduction

The estimation of the battery life is a critical issue for large scale system such as electric vehicle (EV) and load leveling (LL) use. The degradation mechanism of lithium-ion batteries has been investigated in $LiFePO_4$/graphite1), $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$/graphite2), and $LiMn_2O_4$/graphite systems3). Among them, as $LiFePO_4$ showed excellent reversibility itself, an irreversible loss of lithium ion at the graphite became pronounced so that the correlation between the capacity fading and the loss of lithium ion at the graphite has been reported. However, the quantitative analysis, for example, the correlation between the capacity fading of the cell and the chemical analysis of lithium ion in the solid electrolyte interface (SEI), has not been reported. In addition, $LiMn_2O_4$ based cathode is now the predominant material in EV. However, as Mn-based cathode exhibited the degradation of cathode capacity itself, the determination of the contribution ratio about the capacity fading of the cell is more complicated than the $LiFePO_4$ system. Here, we report the analysis of the capacity fading in Mn-based cathode/graphite anode system by the quantitative determination of cathode/anode capacities, the irreversible loss of lithium ion at the anode and so on.

Experimental

Tested cells were the commercially available Al-laminated type (5 Ah). Before and after degradation, cell capacities were measured at C/20 to estimate the cell capacities of the low rate to minimize the contribution of the capacity decrease due to the increase in internal impedance. All cells were discharged at 3.0 V and held for over 10 h before disassembly. The obtained OCV of the tested cells before disassembly was within 3.0 ±0.01 V owing to the constant voltage. Discharged cells were transferred to an Ar-filled glove box (Miwa FMG. Ltd.,). After disassembling each electrode, electrodes with active material on one side were cut out with 16 mmϕ, and each electrode capacity was determined using an Al-laminate cell with a lithium counter electrode.

Results and Discussion

The cathode potential of the cycled cell (3.87 V) was higher than that of as prepared cell (3.67 V) at 3.0 V cell disassembled conditions. Here, as prepared cell were already completed initial formation cycles. In general, the cathode potential at the end of discharge was higher than that of the initial state just after assembling (3.0 – 3.3 V) because some lithium ions were consumed at the graphite anode due to the formation of SEI. However, the cycled cell showed further higher potential than that of as prepared cell. It suggested that the continuous irreversible reaction due to the SEI formation was occurred at the anode during cycle operations. The estimated SOC of the cathode at 3.0 V cell disassembling (6 %) was shifted to 17 % after the cycle operation. On the other hand, the capacity decrease of cathode was 17%. The capacity retention of the cell (73%) could be explained by the shift of the SOC (9%) + the decrease of the cathode capacity (17%). We also determined the loss of the lithium ion at the graphite anode by inductively-coupled plasma (ICP) and glow discharge optical emission spectroscopy (GD-OES). In both chemical analyses, the shift of SOC at the cathode was quantitatively explained by the accumulation of irreversible lithium ion at the graphite. On the other hand, the consumption of lithium ions due to the compensation of Mn^{2+} to Mn4) was the minor factor of the total irreversible lithium ions at the graphite. We also compared the degradation mechanism of cycle operation at 298 K and 313 K. and found that the SOC shift of the cathode was a dominant factor of the capacity decrease for the cell operated at 298 K whereas the degradation of the cathode was a primary factor for the cell operated at 313 K.

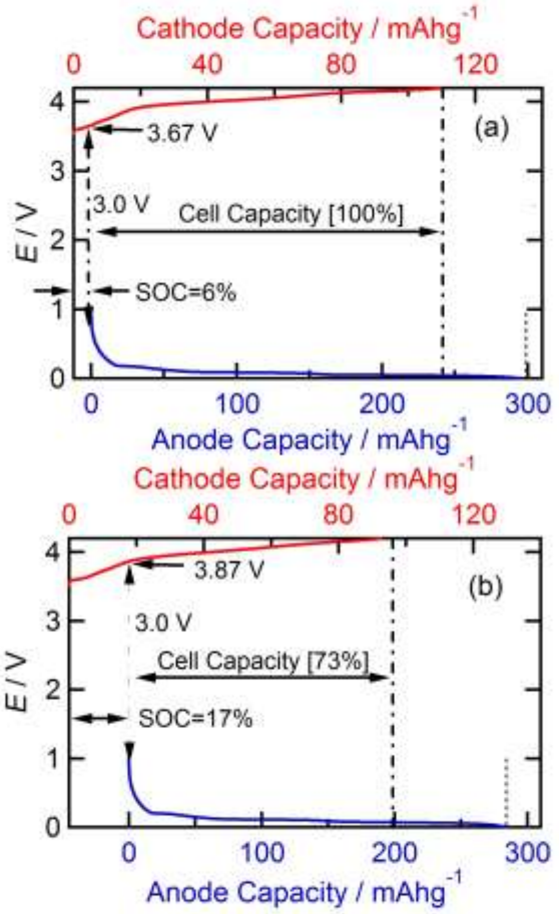

Figure 1 Voltage profiles of cathode and anode during charging from 3.0 V disassembled conditions. (a):As prepared cell (b): After 600 cycles at 313K.

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