



Differential voltage curve analysis of a lithium-ion battery during discharge

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HIGHLIGHTS

- Correlation between dV/dQ peak and capacity fade of Li-ion battery was compared.
- The peak sharpening of dV/dQ at LiC_{12} is not related to the anode degradation.
- The shape change of dV/dQ is related to the intercalation content in the anode.
- Charging voltage is recommended for non-destructive analysis with graphite anode.

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ABSTRACT

Differential voltage (dV/dQ) curve is examined to analyze the degradation of 30 Ah commercial lithium-ion batteries consisting of a Mn-based cathode and graphite anode during discharge. It is observed that the dV/dQ peak became sharper after the capacity faded. The corresponding peak change is confirmed by analysis of the electrode potential separation analysis using pseudo reference electrode and attributed to graphite voltage step at LiC_{12} single phase. In addition, the change in peak shape is not related to the degradation of lithium distribution in the electrode but is strongly related to the intercalation content in the graphite anode. Because the change in peak shape is observed only during discharge, charge voltage is recommended for the non-destructive analysis of lithium-ion batteries with graphite anode.

1. Introduction

Lithium-ion batteries have been developed and are applied as power sources for mobile and stationary applications [1]. The prediction of the battery life is very important, especially for stationary applications, because it is expected to contribute to improve the operation efficiency and optimize the maintenance plan considering the lifetime. The careful observation of changes in voltage [2], temperature [3], and thickness [4] during charge and discharge may indicate levels of battery degradation, and it leads the prediction of the battery lifetime.

Among them, analyses using a differential voltage (dV/dQ) curve, obtained by differentiating the charge/discharge voltage with respect to capacity, have been reported as an indicator of the degradation of electrodes [2], [5]. The peak shift of dV/dQ and the change in the peak-to-peak capacity were usable indicators to understand the capacity fade of electrodes inside the cell. For example, the shift in the dV/dQ peak was derived from the change in the cathode/anode operating region, which was called as “slippage” or “misalignment” [2], [5]. Moreover, the change in peak-to-peak capacity attributed to either electrode was a

good indicator to estimate the electrode capacity retention [6].

In this study, we applied dV/dQ analysis to estimate the degradation of a commercially available 30 Ah cell. In general, dV/dQ peaks exhibit a broader character after cycle operation because the electrode degradation normally occurs inhomogeneous reaction. However, the dV/dQ peak unexpectedly became sharper only during the discharge after cycling and storage. Then, we determined the origin of the anomalous character by (i) assigning the peaks using the pseudo-reference electrode (section 3.2), (ii) changing the operated state of charge and the electrode loading weight (section 3.3), and (iii) confirming the correlation between the dV/dQ profiles and the stage structure of graphite using *in situ* XRD (section 3.4).

2. Experimental

2.1. Cycling and storage test

The tested cell was a commercially available Al-laminated cell (30 Ah) consisting of a Mn-based cathode and graphite anode. One cell was

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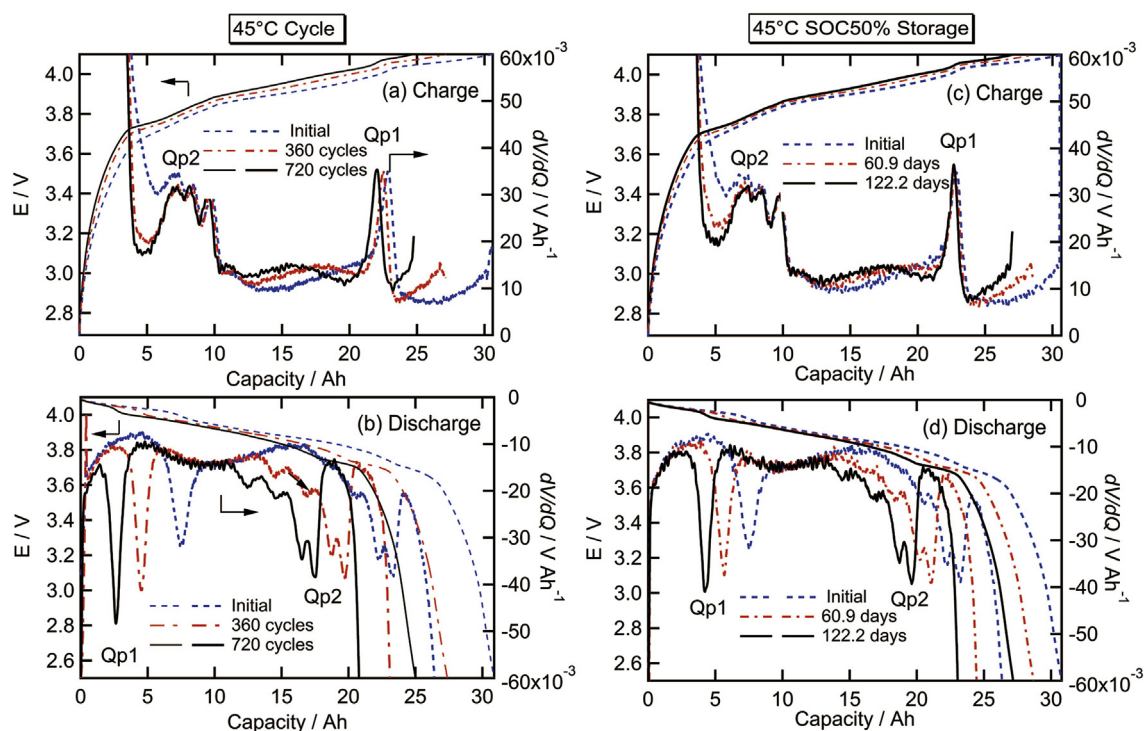


Fig. 1. Cell voltage and dV/dQ vs. cell capacity at C/2 (a), (b) or storage SOC of 50% (c), (d) at 45 °C. dV/dQ curves were obtained from the capacity test operated at a C/20 rate at 25 °C.

cycled at 45 °C in a range of 10–90% State-of-Charge (SOC) at a C/2 rate. The other cell was stored at 45 °C and an SOC of 50%. The relaxation time between the charge and discharge was 30 min. Before and after degradation, the cell capacities were measured at C/20 at 25 °C to minimize the contribution of the increase in internal impedance.

2.2. Cell disassembly/reassembly and assignment of peaks in the dV/dQ curve

The cell disassembly was carried out as previously reported [6]. The disassembled cells were non-degraded cell, degraded cells cycled at 45 °C and stored at 50% SOC conditions. The capacity retention of the degraded cells cycled at 45 °C and at stored at 50% SOC are 80% and 90%, respectively. Before disassembly, each cell was held at 3.0 V for 10 h. The discharged cells were transferred to an Ar-filled glove box (Miwa FMG, Ltd., $H_2O < 0.1$ ppm, $O_2 < 0.2$ ppm).

After disassembling the electrodes, they were rinsed using dimethyl carbonate (DMC), and then, one side of the active material was gently removed using N-methyl pyrrolidone (NMP). After the treatment, the electrodes with active material on one side were cut to a size of 16 mm ϕ , rinsed twice using DMC, and dried in vacuum for 1 h without heating. To assign the dV/dQ curve, the charge and discharge was carried out using a pseudo-reference electrode (Nico-Ichi-type cells [7]) combining two half-cells consisting of a cathode/Li and an anode/Li. The cathode or anode was placed facing the lithium metal (Honjo Metal, 0.3 mm t, 16 mm ϕ) through the separator. The electrolyte composition was 1 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC)/DMC with a 1/1 vol ratio (Kishida). The Nico-Ichi-type cell was operated between 2.5 and 4.1 V, which was similar to those of the 30 Ah cells. The prepared cells were operated at C/20 for three cycles at 298 K. In the case of the Nico-Ichi-type cell, each lithium electrode was connected through the current collector and used as a pseudo-reference electrode [7].

2.3. Half-cell tests

We prepared thick and thin anodes to determine the correlation between electrode thickness and the voltage profile. For the anode, by disassembling a commercial 30 Ah cell, a side of the anode was peeled off in the same way as described in section 2.2 and was labeled (A). The reversible capacity of the anode (A) was approximately 3 mAh cm $^{-2}$ (thick electrode). Since the tested electrodes were commercial ones, the actual active material ratio was not given. We thus estimated the active material weight as 90% of the total electrode weight (not including the current collector). The other anode consisted of 91% artificial graphite MAGD20 (Hitachi Chemical), 5% PVDF, and 4% VGCF and was labeled (B). The reversible capacity of anode (B) was approximately 1 mAh cm $^{-2}$ (thin electrode). The 2032 coin-type cells with a lithium counter electrode was prepared. Charge/discharge tests were carried out using Bio-Logic VMP-3 at a C/20 rate at 25 °C. The rest time between charge and discharge was 15 min.

2.4. In situ X-ray diffraction measurement

In situ XRD of the electrochemical cells was performed using a Rigaku SmartLab-MoK α 1 diffractometer in the transmission geometry and molybdenum K α 1 radiation ($\lambda = 0.70926$ Å). To understand the change in the stage structure of the graphite anode during charge and discharge, we carried out *in situ* XRD measurements in a laminate pouch cell using electrochemical measurements. A Bio-Logic SP-150 was used under constant current corresponding to a rate of C/20. Furthermore, 2θ scans from 10.5° to 12.5° were performed, and the XRD pattern was measured every 15 min, which was equivalent to a 1% SOC during charge and discharge.

3. Results and discussion

3.1. dV/dQ peak profiles after cycle and storage

Fig. 1 shows the shifts in the charge and discharge curves and the

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