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Degradation diagnosis of lithium-ion batteries with a $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ and $LiMn_2O_4$ blended cathode using dV/dQ curve analysis[☆]

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HIGHLIGHTS

- The degradation factors were investigated using nondestructive analytical method.
- Clear differences were observed in the degree of contribution of degradation factors.
- The degree of contribution of degradation factors on cycle conditions were clarified.
- The cathode and anode degradation and the SEI formation were quantitatively analyzed.

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ABSTRACT

Understanding the degradation factors (cathode and anode degradation and solid electrolyte interface (SEI) formation) of lithium-ion batteries (LIBs) with a blended cathode is necessary to improve their durability because battery drive vehicles often use LIBs with a blended cathode due to advantages of power and cost. We developed a dV/dQ curve analysis adapted for through a dQ/dV curve analysis to elucidate the relations between cycle test conditions and degradation factors. To compare said factors, cycle tests were conducted under different conditions: one charge/discharge rate (C/3), two state-of-charge (SoC) ranges (100%–0% and 100%–70%), and three temperatures (0 °C, 25 °C, and 45 °C). We confirmed that there are clear differences in the degree of contribution of each degradation factor depending on conditions. For instance, at 0 °C, although the capacity reduction rate was almost the same regardless of the SoC range, the degradation mechanisms were different, i.e., the cathode degradation and the SEI formation occurred at the same time, resulting in the reduced capacity for the 100%–0% SoC range, while capacity reduction was mainly due to SEI formation for the 100%–70% SoC range.

1. Introduction

The widespread use of electric drive vehicles (xEVs) with low environmental impacts is crucial for the development of sustainable societies. Among the various types of xEVs, the use of battery electric vehicles (BEVs) with lithium-ion batteries is expected to significantly increase in the upcoming years. However, the limited cruising range (capacity of batteries), battery safety, and performance degradation (battery life) hamper the normalization of BEVs. Since BEVs are subjected to various environments which cause batteries degradation, such as acceleration and deceleration, quick charge, and wide temperature range (from −40 °C to 80 °C), an improvement in batteries durability is needed.

A thorough understanding of the degradation factors of lithium-ion batteries would allow enhancing their durability. These factors are divided into three main categories: (1) cathode degradation, (2) anode degradation, and (3) solid electrolyte interface (SEI) formation. Causes of cathode and anode degradation include deactivation of active materials due to changes in the surface structure of particles [1,2] and the electronic disconnection between the active materials and a conductive carbon network or a current collector [3–7]. SEI formation probably occurs because side reactions such as decomposition of electrolyte solution [8] or lithium-metal deposition [9,10] result in an irreversible lithium-ion form. To date, there are few reports concerning the understanding of the influence of these degrading factors from a quantitative perspective, even though this is a fundamental issue. An example of quantitative analytical methods to assess the anode and cathode degradation is the dV/dQ curve analysis, which is obtained from the

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[☆] In this paper we use the term “cathode” to refer to the positive electrode and the term “anode” to refer to the negative electrode during discharge.

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Table 1
Cycle test conditions.

C rate	C/3
Charge/discharge	CCCV (C/20 or 30 min cut off)/CC
SoC range	100%–0%, 100%–70%
Temperature	0 °C, 25 °C, and 45 °C

differentiation of the charge/discharge curve (voltage–capacity curve). The analysis of battery degradation using dV/dQ curves has been reported for $LiNi_{1\text{-}x\text{-}y}Co_xAl_yO_2$/graphite [11], $LiNi_{1\text{-}x\text{-}y}Co_xMn_yO_2$/hard carbon [12], and $LiCoO_2$/graphite batteries [13]. On the other hand, the half-cell technique of the cathode and anode of the disassembled battery can also be used for degradation analysis [14]. Contrary to the battery disassembling method, the dV/dQ curve analysis is nondestructive. Moreover, the dV/dQ curve analysis has the average information of the degradation over a whole battery, while the half-cell estimates have the local information due to the electrode sampling.

Lithium-ion batteries for BEVs and plug-in hybrid electric vehicles often use a blended cathode (layered-materials and spinel-material) [15,16]. However, investigation on the degradation using dV/dQ curves is scarce for lithium-ion batteries with blended cathodes because conventional dV/dQ analysis is difficult to separate the cathode materials simultaneously reacting in the blend. In a previous report, we studied the specific storage degradation at middle state-of-charge (SoC) and the causes of the degradation rate changes via dV/dQ analysis of lithium-ion batteries with a blended cathode and a graphite anode [17]. In this study, we developed a dV/dQ curve analysis for lithium-ion batteries with blended cathodes employing a separation technique for the materials of the cathode. Using the dV/dQ analysis, we were able to quantitatively and nondestructively analyze the cathode and anode degradation and the SEI formation. Furthermore, by comparing the degradation of lithium-ion batteries under different cycle test conditions, the relation between the conditions and degradation factors was elucidated.

2. Experimental

2.1. Battery

A commercially available lithium-ion cell with a blended cathode (18650-type, 1.4 Ah) was used for the cycle tests. The cell was opened, and the electrode and electrolyte solution were analyzed. The cross section of the cathode, manipulated with an ion-milling system E-3500 (Hitachi High-Technologies), was observed using a field emission-scanning electron microscope (FE-SEM, S8020 model, Hitachi High-Technologies) with energy-dispersive X-ray spectroscopy (EDX, X-Max 80 model Horiba). The mixed state maps and compositions of the two active materials in the cathode were analyzed by EDX. The crystal structures of the cathode and anode were analyzed using an X-ray diffractometer (XRD, SmartLab, Rigaku) with Cu-Kα radiation at 40 kV and 30 mA. The XRD pattern was recorded at a scan rate of 5°/min in the 2θ range of 10°–120°. The ratio of the compounds in the cathode was quantitatively estimated by Rietveld analysis using the Rietan-FP software [18]. The electrolyte solution, which was collected from centrifugation, was analyzed by gas chromatography-mass spectrometry (GC/MS, HP6890 and HP5973, Agilent Technologies) and

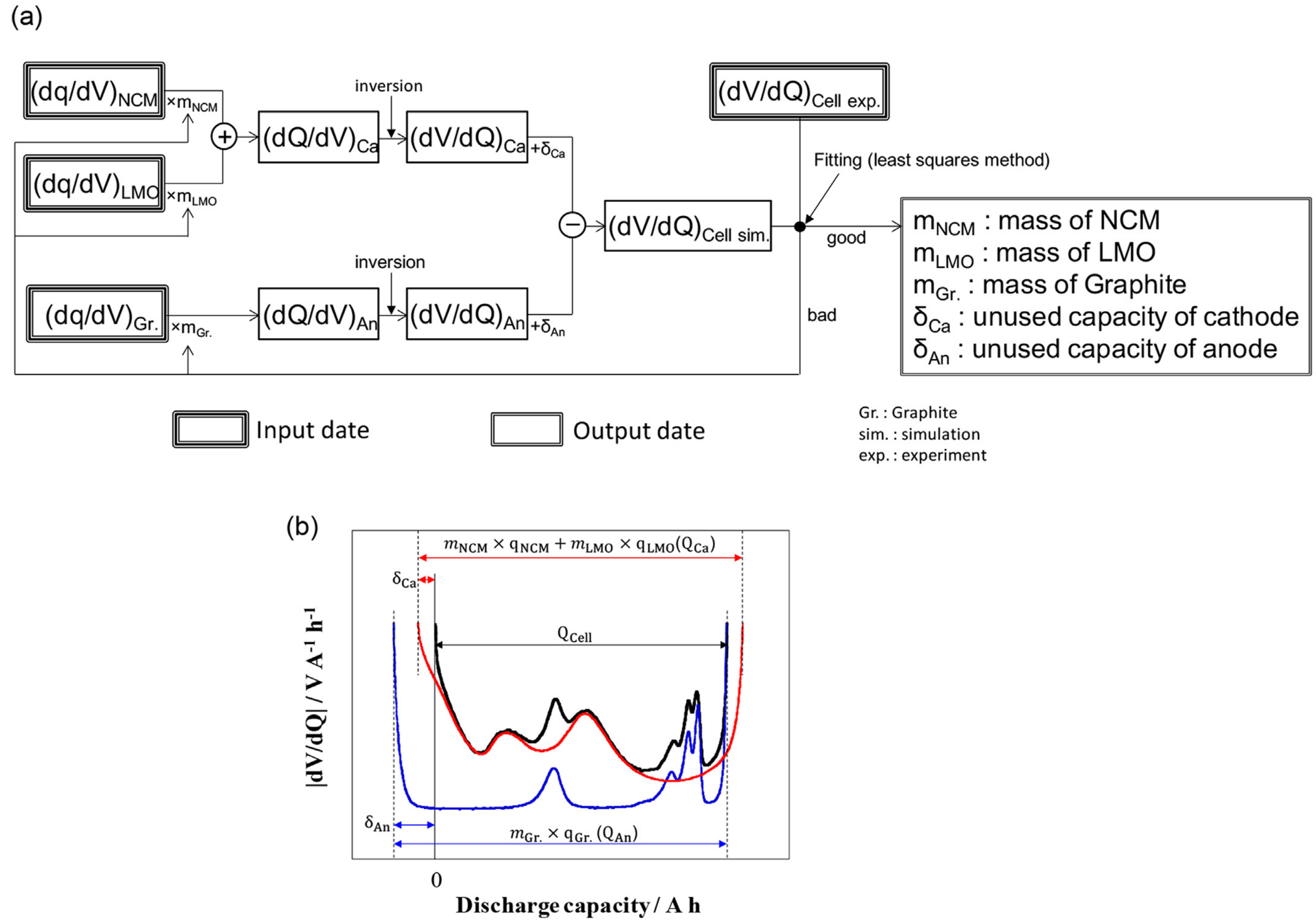

Fig. 1. dV/dQ curve analysis flow chart adapted for the blended cathode (a) and an example of fitting results of the discharge curve (b).