



Degradation analysis of 18650-type lithium-ion cells by *operando* neutron diffraction



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HIGHLIGHTS

- Analysis of Li-ion cell degradation by *in-situ* and *operando* neutron diffraction.
- Capacity loss mainly caused by loss of active Li-ions due to side reactions.
- The cathode active material deteriorated due to phase transitions.

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ABSTRACT

In-situ and *operando* neutron diffraction are used to analyze the degradation of 18650-type Li-ion cells. Structural characterization of the electrode materials is performed by applying the Rietveld refinement technique to the *in-situ* data. The structural refinement of both electrodes in the degraded cells indicates that the amount of active Li-ions is reduced by 14.4% and 13.7% in the cathode and anode, respectively. This reduction is good in agreement with the capacity loss determined electrochemically. The results suggest that capacity loss might be mainly caused by loss of active Li-ions due to side reactions such as solid electrolyte interface (SEI) growth. Furthermore, *operando* measurements are performed to examine the deterioration of the electrode and active materials. Because the structural evolution depending on capacity is increased in the cathode of degraded cells, it is presumed that the cathode active material has deteriorated due to phase transitions.

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1. Introduction

Further performance improvements of Li-ion batteries, such as life and power performance, are desired for their use in HVs, PHVs, and EVs. Service life improvement is very important for batteries used as power sources in vehicles due to long service periods and the need to be able to maintain performance over long distances [1].

Li-ion batteries are known to degrade with use, and there are two kinds of degradation: power fade and capacity fade. Power fade will lead to a decrease in driving performance (e.g. acceleration) of

HVs. On the other hand, capacity fade will lead to shorten service life of HVs, PHVs, and EVs. Therefore, the improvement of capacity fade is crucial for use of the Li-ion batteries in vehicles. The features of capacity fade are described as follows [2–4]:

- Capacity fade accompanied by power fade which is caused by an impedance rise due to electrolyte decomposition and solid electrolyte interface (SEI) formation.
- Unbalancing of active Li-ions in the electrodes caused by side reactions.
- Structural changes of electrodes and active materials. Loss of electric contact between particles, and particles and the current collector in the electrodes, as well as the formation of

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transition phases due to deterioration in the active materials also falls under this category.

Generally, analysis of degradation factors is conducted by the disassembling method which is a powerful tool [5,6]. However, it has some disadvantages, such as induction of chemical changes in the active and electrode materials due to air exposure and the inability to analyze during degradation. To overcome these issues, the development and application of a non-disassembling method become necessary. Neutron diffraction is considered to be the most effective non-disassembling method for the analysis of practical batteries because of the remarkable features of neutrons, e.g. sensitivity to light atoms (lithium and oxygen) and high penetration depth. Thus, recent studies have demonstrated the successful usage of neutron diffraction for studying commercial Li-ion batteries [7–20]. However, few reports are available on the study in Li-ion battery by combining the *in-situ* and *operando* techniques. Therefore, we focused on degradation of in Li-ion battery and employed the combination of both *in-situ* and *operando* techniques.

In this paper, the neutron diffraction technique was used to analyze the degradation of 18650-type Li-ion cells. Neutron measurements were conducted for cells before and after degradation tests, either in the charged and discharged state (*in-situ*) or during discharge (*operando*). The degradation factors are discussed based on the obtained data.

2. Experimental

18650-type Li-ion cells with a nominal capacity of 1800 mAh were fabricated using $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and graphite as the cathode and anode materials, respectively. Ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7 v/v) containing 1 M LiPF_6 was used as the electrolyte.

The cells were degraded by carrying out cycle and storage tests. In the cycle tests, the cells were charged in CC/CV mode (rate: 0.5C (900 mA), cutoff: 90 mA) and discharged in CC mode (rate: 1C (1800 mA)) between 4.2 and 2.7 V using a multi-channel potentiostat/galvanostat 1470E (Solartron). Between the charge and discharge, a 30 min rest was included. Cells were cycled 200 times at 50 °C, 400 times at 25 °C, and 400 times at 0 °C. The number of cycle in each test was adjusted to uniform the capacity loss of the cells. In the storage tests, the cells were stored at 50 °C for 1000 h at 4.2 V. Before and after the degradation tests, the cells (“fresh” and “degraded”, respectively) were charged in CC/CV mode (rate: 0.1C (180 mA), cutoff: 90 mA) and discharged in CC mode (rate: 0.1C (180 mA)) at ambient temperature to measure the capacity using a potentiostat/galvanostat VSP-300 (Bio-Logic).

The neutron diffraction experiments either in the charged and discharged state (*in-situ*) or during the discharge process (*operando*) were performed using the special environment neutron powder diffractometer, SPICA [21], in MLF/J-PARC. Diffraction measurements, whether by angle dispersive or time of flights (TOF) method, are governed by Bragg’s law.

$$\lambda = 2d\sin\theta \quad (1)$$

At the TOF method, neutrons with different wavelengths may be discriminated by their time of reach at a detector and thus different d spacing may be measured at a fixed scattering angle.

$$\lambda_{hkl} = 2d_{hkl} \sin \theta_{\text{fixed angle}} \quad (2)$$

The linear relationship between the wavelength of a neutron and its time of flight may be obtained from de Broglie’s law.

$$p = mv = m\left(\frac{L}{t}\right) = h/\lambda \quad (3)$$

$$\lambda = ht/mL \quad (4)$$

where L is the total combined flight path from neutron source to sample and sample to detector, and t is the TOF of the neutron over this distance. These equations become

$$d[\text{Å}] = \left(\frac{ht}{2mL\sin\theta}\right) = \frac{t[\mu \text{ sec.}]}{(505.555[\mu \text{ sec.}/\text{Åm}]L[m]\sin\theta)} \quad (5)$$

In SPICA, L is 54 m and the range of the wavelength λ which can be used for analysis is 0.5–9.8 Å. All diffraction patterns were collected using all detectors in the range $10^\circ < 2\theta < 175^\circ$. For the purpose of observation of the Bragg reflection (003) of $\text{Li}_x\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ whose d space is near 4.8 Å, data from the 90° bank ($70^\circ < 2\theta < 110^\circ$) which covered the d space range from 0.3 to 5.8 Å were used for the analysis. The collection time for *in-situ* data was about 3 h. *Operando* data were collected during the all-time of electrochemical process. Obtained data were sliced by the time of 20 min after the measurements. All experiments were performed at ambient temperature.

In-situ data for fresh and degraded cells were acquired at state of charge (SOC) 100% (i.e., charged to 4.2 V) and 0% (i.e., discharged to 2.7 V). Cell voltage for *in-situ* measurements was controlled by CC/CV mode (rate: 0.1C (180 mA), cutoff: 90 mA) for charging to SOC 100%, and by CC mode (rate: 0.1C (180 mA)) for discharging to SOC 0%. *Operando* data for fresh and degraded cells were taken during discharge at the rate of 0.1C (180 mA). The all electrochemical experiments during *in-situ* and *operando* measurements were performed by using a potentiostat/galvanostat VSP-300 (Bio-Logic).

By using the Z-Rietveld program [22], the data acquired from *in-situ* measurements were analyzed by the Rietveld method to refine the crystal structures of both electrodes. The diffraction data were fitted in the range from 5.3 to 0.75 Å in d space. Crystal structure models of $\text{Li}_x\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [23] for the cathode and LiC_6 and LiC_{12} [24] for the anode were used to analyze the diffraction patterns at SOC 100%. The crystal structure model of graphite [24] for the anode was used to analyze the diffraction patterns at SOC 0%. Furthermore, the crystal structure models of the current collector materials Al and Cu, and the steel housing (SUS304) material represented by iron were used for multi-phase Rietveld refinement.

The data collected from *operando* measurements were analyzed by the profile fitting technique. Single profile fitting was applied to the Bragg reflection (003) of $\text{Li}_x\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ because of non-overlapping with other materials (anode, Al, Cu, and Fe). Assuming a Gaussian peak shape, the parameters for position, intensity, and full width half maximum were optimized. A d space of the reflection was evaluated from the peak position.

3. Results and discussion

The discharge capacity (capacity loss in %) of fresh and degraded cells are listed in Table 1. Regardless of the degradation conditions,

Table 1
Capacity and capacity loss of fresh and degraded cells.

Cell	Capacity, mAh	Capacity loss, %
Fresh	1891	0
Cycled at 50 °C (200 cycles)	1584	16.3
Cycled at 25 °C (400 cycles)	1604	15.2
Cycled at 0 °C (400 cycles)	1614	14.7
Stored at 50 °C	1625	14.1

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