In-situ neutron diffraction measurements of lithium-rich transition metal oxides with high capacity by oxgen loss and redox

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1. Introduction

Recently, the Novel Prize awarded to three chemists for the development of the lithium ion battery. Lithium ion battery has been used as a power supply for the electronic vehicles, and required to develop into the higher energy density. For the realization, to establish the guideline of new cathode materials is expected based on the crystal structure analysis. However, since many conventional studies dismantled a cathode from battery after charge/discharge experiments, there were many questions about the behavior of the cathode during the battery operation. Therefore, it is to establish a high-precision design guideline for cathode materials. Although many works of in-situ "synchrotron X-ray diffraction" have been conducted by several researchers, the X-ray scattered by electrons is unsuitable for getting insight of the structural information of light elements such as Li in operating lithium ion battery.

From such a background, we proposed the in-situ neutron diffraction measurement about lithium ion battery in battery operation to get knowledge about the crystal structure of the cathode materials in the nonequilibrium states. Although the past in-situ neutron diffraction measurement intended for spinel type oxide or layered rock-salt type oxide mainly [1], we will pay our attentions to lithium rich transition metal oxide indicating the high capacity derived from oxygen desorption or oxidation into peroxide or superoxide. At the beginning, we must estimate the appropriated battery capacity because the capacity depends on the cathode weight per unit area and hence affects the neutron diffraction intensities derived from cathode materials. In this proposal, we measured the layered cathode material of $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ with the extremely close crystal structure [2] to the Li-rich layered materials to reveal the appropriate incident beam angle and cathode material amounts in the electrode for in-situ experiments.

2. Experiment

In this study, as a preliminary experiment before in-situ experiment, we examined the angle of the incident neutron beam and the detector bank suitable for the neutron diffraction measurement for the uncharged laminate cell. The laminate cell used was a 1.5 Ah class in which the active materials of the cathode and anode were $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ and graphite, respectively. The size of the laminate cell was 8 cm × 5 cm, and the neutron diffraction measurement was performed with the laminate cell fixed to an aluminum holder. The neutron diffraction measurement was performed from 0 ° to 60 ° in increments of 10 °, with the incident beam and the cell being perpendicular to 0 °. In each measurement, the same event-count, i.e. proton amounts, was used, and the incident neutrons were controlled to be the same, thereby examining the angle dependence of the diffraction intensity by the cathode active material. Then, in order to obtain data for performing Rietveld analysis at an incident angle at which high intensity data is obtained in each of the backscattered (BS), special environment (SE), and low angle (LA) banks, integration was performed so that the active material intensity became 100,000 counts. We estimated the required cathode material amounts for in-situ experiment at 0.1C by the present diffraction intensities in several conditions.

3. Results

The aluminum holder could seal the present laminate cell by bending the lead tab. The neutron diffractions were performed for several angles for the laminate cell with BS, SE and LA banks as shown in Fig. 1. Most peaks were assigned to the aluminum holder, laminate materials and the Cu current collector for anode. The diffractions derived from cathode active material were few peaks represented by the arrows in Fig. 1. The peak intensity of cathode active material depended on the different incident angles for each BS, SE and LA bank. The highest intensities were obtained at 20 ° in the BS and LA35 banks and at 50 ° in the SE bank. The high intensity data were collected at their angle to obtain 100,000 counts in the cathode active material (Fig. 2). The present laminate cell included 0.25 g/cm^2 as the cathode active material. Since the neutron beam at iMATERIA irradiate the 2 × 2 cm^2 area, the required weight of active material in the cathode can be estimated from 30 to 50 mg/cm^2 for in-situ experiments with 0.1C charge/discharge rate. The present study contributed to the in-situ experiments in the ongoing proposal.

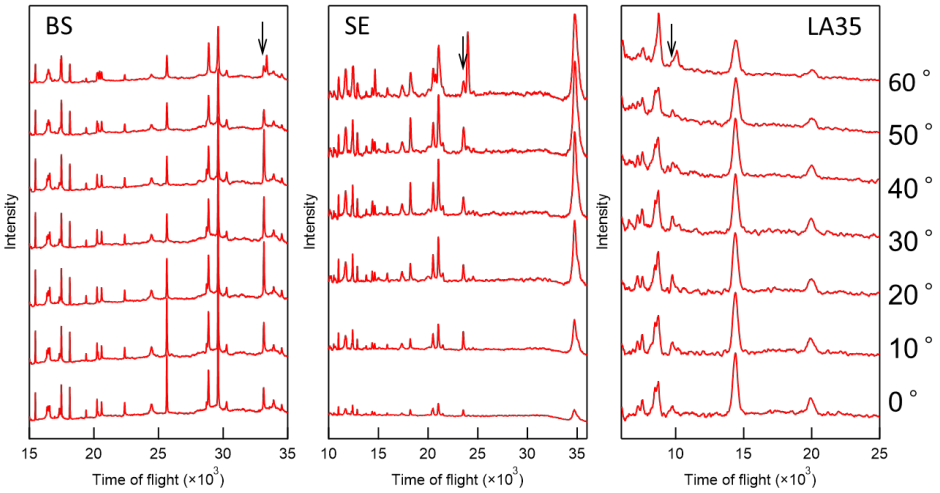

Fig. 1 Neutron diffraction patterns of a laminate cell consisted of $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathode and graphite anode with different incident beam angle. The arrows represent the diffraction peaks derived from $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathode.

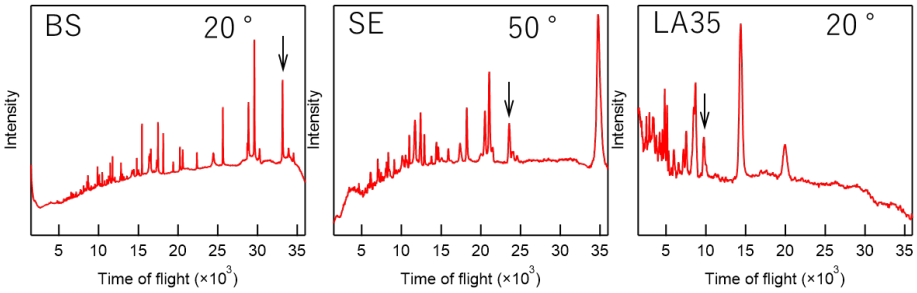

Fig. 2 Neutron diffraction patterns of laminate cell with high intensity of about 100,000 counts for cathode active material represented by the arrows.

4. Conclusion

We succeeded to collect the high intensity data in the laminate cell consisted of $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ cathode active materials and graphite anode. The appropriate incident angles were determined for the BS, SE and LA banks as 20 °, 50 ° and 20 °. The sample weights for in-situ experiments were estimated to be from 30 to 50 mg/cm^2. The next ongoing proposal will conduct the in-situ neutron diffractions for laminate cell with Li-rich cathode materials.

[1] S. Shiotani, T. Naka, M. Morishima, M. Yonemura, T. Kamiyama, Y. Ishikawa, Y. Ukyo, Y. Uchimoto, Z. Ogumi, *J. Power Sources*, **325**, 404-409 (2016), [2] Y. Idemoto, K. Ueki, N. Kitamura, *Electrochem.*, **78**, 475-481 (2010)