

Non-destructive analysis of crystal structure of active electrode materials inside cylindrical lithium-ion batteries and consideration of reaction mechanism of self-heating based on the structure change of the materials at elevated temperatures.

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1. Introduction

Lithium-ion batteries (LIB) is attractive batteries for not only mobile tools but also the electric vehicles (EV) and power storage systems, from the high energy density. However, prevention of thermal runaway such as rapture and firing during usage and under accidental conditions such as short-circuit, overcharge, external heating, and so on, is one of the important technical problems. Hence, thermal design is extremely important for LIB. In a corporate work with Hitachi Ltd., we are studying heat generation mechanism of LIB under elevated temperature by using calorimeter. The samples are not the component materials but the whole cells of which size is 18 mm in diameter and 65 mm in length (18650 type cylindrical cell), and we can characterize the onset temperatures, the total heat amounts, and the rate of the exothermal reactions occurring in the sample cells. Unfortunately, we cannot specify the chemistry of the reactions themselves which are origins of the heats from only the calorimetric results. If we can specify the chemical reaction of each exothermic behavior, we can discuss the improvement methods to suppress the heat by changing the material or by adding any kinds of additives. By the result, highly safe LIB is developed. In order to specify the chemical reaction scheme for exothermic behaviors of LIB during heating, we are characterize variation of the component materials such as the electrode materials and the electrolyte which are extracted from the sample cells after heating by calorimetry. We used X-ray diffraction measurement (XRD) for crystal structure analysis of the active electrode materials, and also used liquid chromatography - mass spectroscopy (LC-MS) for the electrolyte. As the result, it was suggested that the main reaction during thermal runaway was combustion of the electrolyte which was originated in oxygen release from the cathode material during thermal decomposition. However, we couldn't obtain any useful information for lithium in the electrode materials by XRD, and the detailed thermal decomposition mechanism was not clear. In addition, we have to consider deterioration of the material during extraction process of the material before the measurement. Since the sample electrode had been washed and dried, surrounding condition of the sample is different with that in the cells, and non-destructive analysis is preferable. By using neutron diffraction measurement, we hope to obtain many important information on thermal decomposition reaction of the component materials of LIB without destruction of the cell, such as crystal structure change depending on heated temperature, and location information of lithium and oxygen.

In this time, the static measurement is planed where the cells are under open-circuit in the room temperature. The main purpose of the measurement is confirmation that the neutron diffraction measurement is useful technique to study of thermal safety for LIB. As the preparation stage, we also prepare heated LIB at the safety temperature range without thermal runaway. In these samples degradation has been progressed with self-heating reaction, and we expect that we can obtain important information on degradation reaction.

2. Experiment

We prepared six sample cells. Those capacities were ca. 1 Ah. For some of them, after setting the state of charge (SOC), we performed calorimetry. During the measurement, the cells were heated to predetermined temperatures, those were 60, 80, 110°C. After cooling to room temperature, we supplied the whole cells themselves to neutron diffraction measurement at BL20 iMATERIA using DF mode. The energy of proton beam was 500 kW. All five detector banks were used. For the crystal structure analysis, we used Z-Code.

3. Results

Figure 1 shows a neutron diffraction pattern of a reference cell where any charging and discharging have not been performed. However lots of strong peaks are originated from the cell case made of stainless steel, we can also observe some peaks which are attributed to the positive electrode material, LiNiMnCoO₂ (NMC), and the negative electrode material (Graphite).

Figure 2 shows the variation of the diffraction peaks of negative electrode materials inside the fully charged cells except one sample which is discharged cell. In the non-heated cell, the material has stage-1 structure. In the heated cells at 60 and 80°C, a small peak of stage-1' appeared suggesting that some lithium ions have been de-intercalated from the material. This variation might be correlated to exothermic self-discharging reaction. It is interesting that the stage-1' known as dilute stage-1 has disappeared for the cell heated at 110°C while the peak of stage-2 is glowing.

4. Conclusion

We confirmed that crystal structure change of the negative electrode material depending on heating temperature without destruction of the cell. For the detailed analysis, the cells of higher capacities with thinner case are preferable. In the next step, we are thinking to develop the system to operando measurement for temperature scanning where the cell become actually thermal runaway in the tenacious sample holder. In addition, we are also planning to operando measurement of LIB during overcharging.

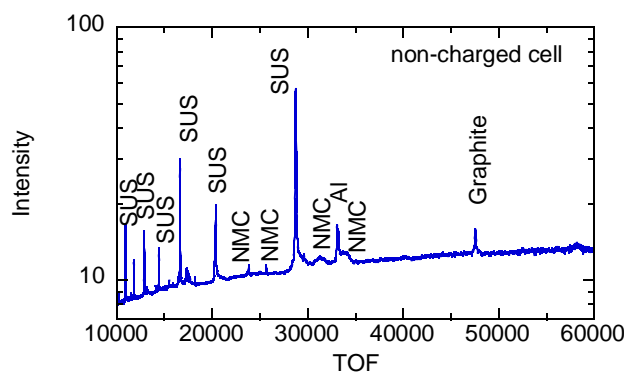


Fig. 1 The neutron diffraction pattern of a fresh cylindrical lithium-ion cell without any charging and discharging history.

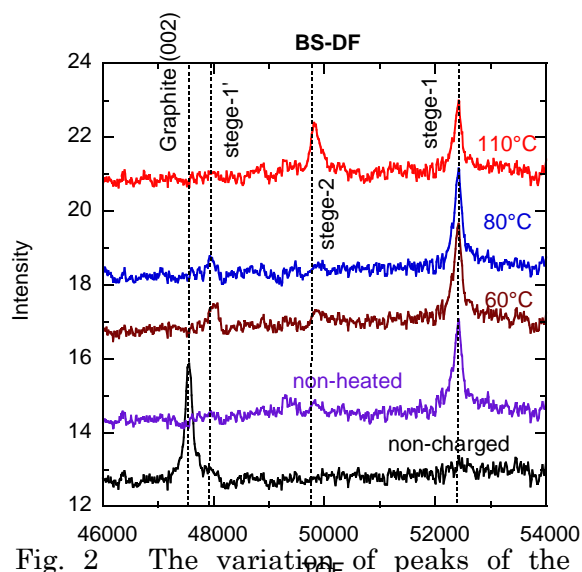


Fig. 2 The variation of peaks of the negative electrode material depending the state of charge and heating temperature.