

In-Situ 2-Dimensional XAFS Imaging of Lithium Nickel Oxide Cathode in Operating Lithium Ion Battery

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1 Introduction

The improvement of the lithium ion battery (LIB) performance is an urgent mission for the modern society. In addition to the capacity increase, the enhancement of the rate property is also important to apply the LIB for a motive power source of vehicles. For the safe utilization of the large current, an inhomogeneity of the electrode reaction during the charge/discharge process becomes a serious problem because of the locally produced high current density at the reacting area. Such inhomogeneous progress of the electrode reaction is also a disadvantage for the effective use of the active species leading to a decline in the battery capacity.

The 2-dimensional (2D) XAFS imaging technique is a powerful tool to observe the progress of redox reactions occurred in the electrode sheet because the XANES spectrum is sensitive to the valence state of the active metal center [1]. The spatially resolved detection using a 2D detector to monitor the transmitted X-ray can reveal the inhomogeneity of the valence state, which is directly related to the local progress of the electrode reaction. In this study, the 2D XAFS imaging has applied to the charge/discharge processes of the lithium nickel oxide (LNO, LiNiO_2) cathode of LIB. The spatial distribution will be compared with that of the lithium iron phosphate (LFP, LiFePO_4) cathode reported previously [2].

2 Experiment

The cathode sheet composed of LNO, the carbon additive, and the binder polymer was prepared, and the LIB cell was compiled using the cathode sheet, the separator sheet, the Li anode, and the 1 M LiPF_6 electrolyte solution. All parts were sealed in a gas-barrier laminated bag. The LIB capacity was 86 mA h g^{-1} , and was charged/discharged with the rate of 0.2 C. The XAFS imaging measurement was performed during the charge/discharge process.

The XAFS imaging was carried out at NW2A of PF-AR (KEK). The Si(111) double-crystal monochromator was used without any focusing optics. This higher-order harmonics was removed by the Rh-coated double-mirror system. The incident X-ray intensity was monitored by an ionization chamber, and a CMOS image sensor (ORCA Flash 2.8) coupled with the $\text{Gd}_2\text{O}_2\text{S:Tb}$ phosphor was used as the transmitted X-ray detector. The measurement area was $4 \times 3 \text{ mm}$. The XANES measurement was carried out at the Ni K edge, and the total measurement time for one XAFS image was 10 min.

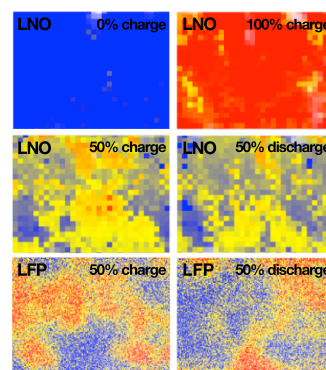


Fig. 1: Chemical state map of LNO and LFP cathode at 0, 50, and 100 % state during the charge process and at 50 % state during the discharge process. The blue and red pixel denotes the oxidized (uncharged) and reduced (charged) state of the active material, respectively. The image size is $0.24 \times 0.18 \text{ mm}$ for LNO and $2.8 \times 2.1 \text{ mm}$ for LFP.

3 Results and Discussion

The measured chemical state maps of the LNO cathode were shown in Fig. 1 at the 0, 50, and 100 % state during the charge process. The E_0 value of a XANES spectrum observed at each detector element was used to judge the chemical state of LNO between the oxidized (uncharged, LiNiO_2) and reduced (charged, $\text{Li}_{1-x}\text{NiO}_2$) states. In Fig. 1, the blue and red pixel represents LiNiO_2 and $\text{Li}_{1-x}\text{NiO}_2$, respectively. Similar to the reported LFP cathode [2], the inhomogeneous reaction distribution was observed also in the case of the LNO cathode. The size of the inhomogeneous reacting spots of LNO was much smaller than that of LFP.

The most impressive difference between LNO and LFP is appeared when the images are compared between the charge and discharge process. The reverse pattern is observed in the maps of LFP, suggesting that the electronic conductance due to the carbon network controls spatially inhomogeneous reaction. In contrast, the maps of LNO shows very similar pattern. This indicates the existence of the gateway for the lithium-ion insertion/desertion on the LNO cathode sheet, maybe caused by the accumulation of organic materials formed by the decomposition of organic solvent.

References

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