

Inhomogeneous distribution of chemical species in lithium nickel oxide cathode of lithium ion battery

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Abstract. The spatial distribution of the oxidation state for the nickel species in the LiNiO_2 cathode was analyzed by means of the *in-situ* XAFS imaging technique during the charging and discharging processes. The inhomogeneous reaction for the LiNiO_2 cathode was observed under the operating condition. The pattern in the 2-dimensional map of the oxidation state of the active material in the discharging process was similar to that in the charging process. It means that the areas preceding the discharging reaction agree with the areas delaying the charging reaction. It was suggested that the diffusion of Li^+ was restricted by the surface product of the LiNiO_2 electrode, and the concentration gradient of Li^+ delayed the charging reaction at the reaction channel of the discharging reaction.

1. Introduction

The inhomogeneous distribution of the chemical state for the active material in the electrode of lithium ion secondary battery (LIB) should be understood to prevent unexpected accidents, because it causes the local excess current and the local deactivation of the electrode. The control of such inhomogeneous distribution contributes to improve the battery performance for the stabilized utilization. The LIB electrodes are generally made as a composite of the active material, the conductive additive, and the binder. In such composite electrodes, the pathway of electrons and Li^+ ions for the electrochemical reaction include various interfaces. If the interfacial resistance differs by each position in the electrode, the inhomogeneous reaction may be caused during the charging and discharging processes. The analysis of the spatial distribution of the state of charge in the operating condition is essential to understand the spatial distribution of the resistance in the electrode. X-Ray absorption fine structure (XAFS) is the most powerful technique to observe the electrochemical reaction in operating battery cells. In the LIB cathode, the charging and discharging process involves the redox reaction of the transition metal species in the active material. The oxidation state of such metal species can be determined by the XANES spectrum. The full field XAFS imaging technique using a 2-dimensional detector was developed by Grunwaldt *et al.* in the investigation on $\text{Rh}/\text{Al}_2\text{O}_3$ catalyst [1]. We applied the XAFS imaging to analyze the progress of the electrode reaction with the spatial resolution in the order of $10\ \mu\text{m}$ [2].

Lithium nickel oxide (LiNiO_2) has been expected as a promising active material of the next generation LIB [3]. However, the practical use of LiNiO_2 is not achieved due to the synthetic difficulty and the structural instability [4]. The partial substitution of Ni is thus attempted to improve the cycle performance [5,6] and the stability [7]. The knowledge of the spatial distribution for the charging/discharging reaction in the LiNiO_2 cathode is fundamental to understand the reaction of the partially substituted LiNiO_2 electrodes. In this research, we clarified the inhomogeneous reaction of the LiNiO_2 cathode under the operating conditions by means of the 2-dimensional XAFS imaging technique.



2. Experimental

Lithium nickel oxide (LiNiO_2) was synthesized by the sol-gel method [8]. The adipic acid solution was added to an aqueous solution of nickel acetate and lithium acetate ($\text{Li:Ni} = 1:1$) at 333 K and was evaporated to form the sol at 363 K in air. It was further dried at 363 K in vacuum for 24 h and was calcined at 973 K for 14 h under the O_2/He gas flow. The obtained material was identified as LiNiO_2 by the X-ray diffraction pattern. A cathode sheet was made as the composite of LiNiO_2 , acetylene black, and a polymer binder applied on an aluminum foil as a current collector. The test LIB cell was assembled with the cathode sheet, two sheets of polypropylene as the separator, Li foil as the anode, and 1 mol dm^{-3} LiPF_6 solution as the electrolyte solution. The solvent of the electrolyte solution was the 3:7 mixture of ethylene carbonate and ethyl methyl carbonate. An Al-laminated polymer bag was used as the outer shell of the battery for the *in-situ* XAFS experiments. The battery capacity was 86 mA h g^{-1} , and the charging/discharging processes were performed with the constant current of 39 mA g^{-1} .

The 2-dimensional XAFS imaging measurements were performed during the charging/discharging processes at the NW2A station of Photon Factory Advanced Ring (KEK, Japan). The Si(111) double-crystal monochromator was used without the focusing optics. The higher-order harmonics were removed by the Rh-coated double-mirror system. The incident X-ray intensity was monitored by an ionization chamber. 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 $4 \text{ mm} \times 3 \text{ mm}$. The XANES measurement was carried out at the photon energy from 8300 eV to 8400 eV around the Ni K edge, and the total measurement time for one XANES image was 10 min. The energy difference caused by the vertical dispersion of the beam and its incident angle to the monochromator was corrected by the previously reported procedure [2]. A chemical state map was drawn by judging the X-ray energy of the white line peak at each detector element.

3. Results and discussion

The chemical state maps of the LiNiO_2 cathode were shown in figure 1 together with the charging and discharging curves. The XAFS image shown in figure 1 were obtained for the third charging/discharging cycle. The similar patterns were observed for the further cycles. The chemical state of the nickel species in figure 1(a) and (k) shows the uncharged LiNiO_2 and charged $\text{Li}_{1-x}\text{NiO}_2$ state, respectively. Similar to the reported LiFePO_4 cathode [9], the inhomogeneous distribution was observed also in the case of the LiNiO_2 cathode, although the LiFePO_4 cathode consists of only two phases of LiFePO_4 and FePO_4 .

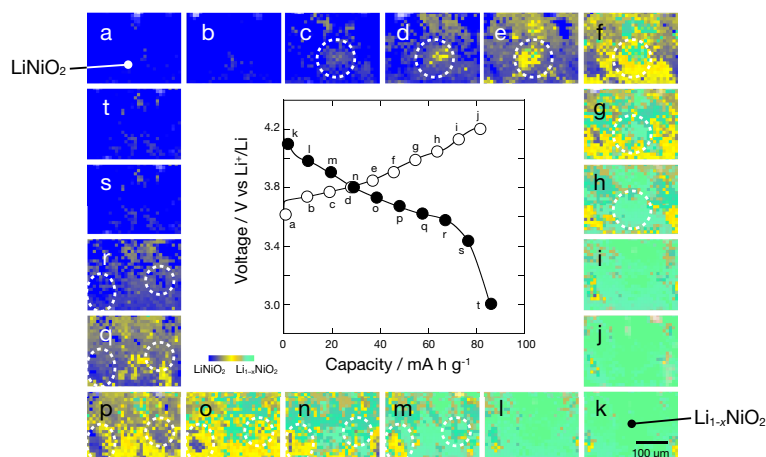


Figure 1. The chemical state maps of the LiNiO_2 cathode for the charging (from a to j) and discharging (from k to t) processes. The dashed circle shows the preceding area for the chemical state change of the Ni species during the electrode reactions.

during the charging process in contrast to the non-stoichiometric $\text{Li}_{1-x}\text{NiO}_2$ phase. The preceding area during the charging process was observed at almost the center in the presented maps (dashed circle in figure 1(c)-(h)). In the discharging process, the preceding area (dashed circle in figure 1(m)-(r)) was not identical to that in the charging process.

The images at the 50 % charged and discharged states are compared in figure 2 between the LiNiO_2 and LiFePO_4 cathodes. The scale of images is different between figure 2(a,b) and (c,d) according as the scale of inhomogeneity. The size of the distribution for the LiNiO_2 cathode is close to the spatial resolution of the present XAFS imaging analysis. The size of the preceding area of LiNiO_2 was *ca.* 100 μm , while that of LiFePO_4 was the order of 1 mm. The different scale of the spatial distribution indicates that the formation mechanism of the inhomogeneous distribution differs between two active materials. The reverse pattern was observed in the maps of LiFePO_4 between the charging and discharging processes (figure 2(c) and (d)), which means that the common reaction channel exists in both processes. The inhomogeneous distribution of LiFePO_4 becomes more uniform with increasing the carbon content in the cathode composite [9]. It has been suggested that the electronic conductance due to the carbon network controls the spatially inhomogeneous electrode reaction. In contrast, the maps of LiNiO_2 (figure 2(a) and (b)) show a similar pattern between both processes. It means that the charging reaction is delayed at the preceding area for the discharging process in the case of the LiNiO_2 electrode.

The disagreement of the preceding area at each process is explained in considering the accumulation of surface products, such as the polycarbonate species [10], on the LiNiO_2 cathode. The SEM images of the LiNiO_2 cathode were shown in figure 3 before and after the fifteen charging/discharging cycles. The porous shape of the pristine electrode, which can supply a lot of pathways for the Li^+ diffusion, disappeared after the redox cycles as shown in figure 3(b). This surface products formed during the aging process can restrict the Li^+ diffusion between the inside of the electrode composite and the bulk electrolyte solution. Because some cracks are found in the surface product, it is considered that the Li^+ diffusion occur mainly through such remaining pathways.

The observed inhomogeneous distribution of LiNiO_2 is thus ascribed by the restricted pathway for the Li^+ diffusion. At the discharging process, the pathway of Li^+ becomes the reaction channel, because the Li^+ supply from the bulk electrolyte solution is necessary to progress the electrode reaction. On the other hand, the following change of the Li^+ concentration is expected during the charging process. The charging reaction increases the Li^+ concentration in the cathode composite. The diffusion of the Li^+ ion occurs from the inside of the cathode composite to the bulk solution through the reaction channel. As

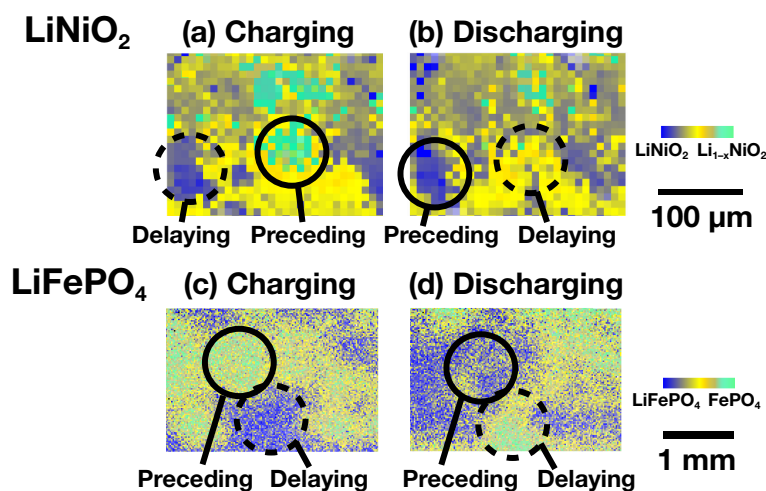


Figure 2. The comparison of the spatial distribution of the chemical state of active materials at the 50 % charged and discharged states between the LiNiO_2 and LiFePO_4 cathodes.

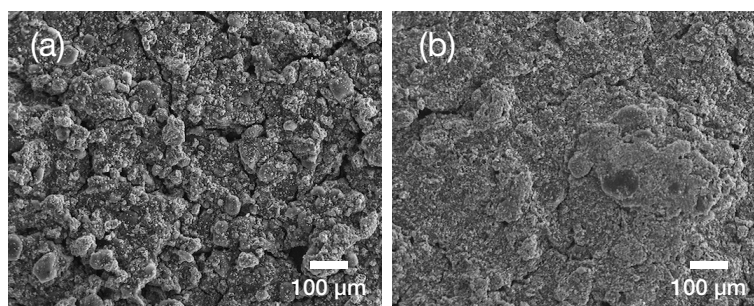


Figure 3. The SEM images of the LiNiO₂ cathode (a) before and (b) after the fifteen charging/discharging cycles.

the result, the concentration gradient forms from the reaction channel to the covered area in the LiNiO₂ cathode. The increase in the Li⁺ concentration at the reaction channel causes the delay of the charging reaction.

4. Conclusions

The spatial distribution of the oxidation state of the Ni species in the LiNiO₂ cathode during the charging and discharging processes was analyzed using the 2-dimensional XAFS imaging technique. The inhomogeneous distribution was observed in the scale of 100 μm. The disagreement of the preceding area between the charging and discharging processes is explained in considering the Li⁺ diffusion inside the cathode sheet. It has been clarified that the surface products on the LiNiO₂ cathode cause the inhomogeneous reaction by restricting the Li⁺ diffusion.

Acknowledgement

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