

Short communication

Changes in electronic structure of the electrochemically Li-ion deintercalated LiNiO_2 system investigated by soft X-ray absorption spectroscopy

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Abstract

The electronic structures of $\text{Li}_{1-x}\text{NiO}_2$ system after electrochemically deintercalated to various “ x ” values have been investigated using soft X-ray absorption spectroscopy (XAS) for oxygen K-edge and Ni $L_{\text{II,III}}$ -edge. By comparing the O K-edge XAS spectra of $\text{Li}_{1-x}\text{NiO}_2$ electrode collected simultaneously by the partial electron yield (PEY) mode and fluorescence mode (FY), it was found that the surface electronic structure of $\text{Li}_{1-x}\text{NiO}_2$ electrode is different from the bulk. Therefore, if the PEY mode, which is a surface-sensitive technique, is used alone, the reliability of the results is limited to the surface structures only. Ni $L_{\text{II,III}}$ -edge XAS results of $\text{Li}_{1-x}\text{NiO}_2$ electrode at different charge states, in both the FY and PEY modes, show that Ni^{2+} ions at the surface are mostly oxidized to Ni^{3+} ions during Li deintercalation, whereas the process in the bulk is the oxidation of Ni ions from Ni^{3+} to Ni^{4+} .

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1. Introduction

Extensive research on the electronic structure of the Li-ion intercalated cathode material has been carried out. The local structure of the transition metal ion of the cathode has been investigated using X-ray absorption spectroscopy (XAS) [1–5]. The XAS studies for the Li-ion intercalation–deintercalation have been mainly focused on the transition metal K-edges using hard X-ray. Although the metal K-edge spectra can provide important structural information such as oxidation state of chemical species, their site symmetries, and covalent bond strength, they could not give any direct information of the role of oxygen in the charge compensation process. The contribution of oxygen atom could only be indirectly inferred from the peak intensity for electronic transition of 1s electron to 4p orbital with shake-down process. Recently, soft XAS, using synchrotron radiation,

has been applied in the investigation of the electronic structure of electrode materials for Li rechargeable batteries [6–13]. In the case of soft XAS, the electric dipole-allowed $1s \rightarrow 2p$ transition in the O K-edge XAS can provide a direct probe of the oxygen charge state and the metal–oxygen bonding interactions since the 2p orbitals of oxygen are involved in the bonding with metal ions. In addition, information about the unoccupied molecular levels can be obtained from the absorption peaks of metal $L_{\text{II,III}}$ -edges. These intense XAS peaks represent the main electric dipole-allowed $2p \rightarrow 3d$ transitions and give information on the unoccupied 3d states. At the transition metal K-edges the quadrupole-allowed $1s \rightarrow 3d$ transitions are much weaker. Therefore, soft XAS can be used as a powerful tool to elucidate the charge compensation mechanism in the Li-ion intercalation–deintercalation process of cathode materials for Li rechargeable batteries.

Soft XAS spectra can be obtained in both the electron yield and fluorescence yield modes. The electron yield mode is surface sensitive (within $\sim 50 \text{ \AA}$) while the fluorescence yield mode is suitable for bulk studies (more than $\sim 2000 \text{ \AA}$) [14,15]. Unfor-

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tunately, most of the soft XAS results reported in the literature on lithium battery materials have been obtained by the electron yield method [6–11]. Although soft XAS, using electron yield method, gives useful information about the electronic structure of the transition metal and oxygen ions, the results are limited only to probing the surface, which may not reflect what is happening in the bulk. In this work, therefore, we applied soft XAS, both in the fluorescence yield (FY) and the partial electron yield (PEY) modes simultaneously, at the O K-edge and the Ni L_{II,III}-edges, to investigate changes in the electronic structure of a LiNiO₂ electrode during charge. By doing this, a more complete picture of the electronic structure, both at the surface and in the bulk, was obtained for the electrochemically deintercalated Li_{1-x}NiO₂.

2. Experimental

The LiNiO₂ samples were provided by FMC Corp. LiNiO₂ powders were heated at 700 °C for 5 h in O₂ to clean surface contamination of the powders before the electrochemical experiment was conducted. The electrochemical deintercalation process was performed as follows; cathode specimens were prepared by mixing the LiNiO₂ powders with 10 wt.% acetylene black and 10 wt.% poly-vinylidene fluoride (PVDF) in *n*-methyl pyrrolidone (NMP) solution. One molar LiPF₆ in a 1:1 ethyl carbonate:dimethyl carbonate (EC:DMC) solution was used as the electrolyte. The cell was assembled in an argon-filled glove box. The cells were first charged to the desired value of deintercalated Li-ion content (*x* value) at a C/50 rate and then relaxed for a day. The electrochemical cells were disassembled in an argon-

filled glove box, and the LiNiO₂ electrodes were taken out from the cell. The electrodes were then washed with tetrahydrofuran (THF) and dried thoroughly in vacuum. All XAS sample preparations were carried out in an inert atmosphere, except during the insertion in the experimental XAS chamber, where the samples are exposed to air in a short period of time (for a few minutes).

Soft-XAS measurements were performed at Beam Line U7A of the National Synchrotron Light Source (NSLS). The beam size was 1 mm in diameter. The estimated incident X-ray energy resolution was ~0.2 eV. Data were obtained both in PEY and FY modes. The PEY mode collects more of the Auger electrons and less of the inelastic secondary electrons than the total electron yield (TEY) mode. Therefore, the surface sensitivity of PEY is higher than TEY. The PEY data were recorded using a channel electron multiplier while the FY data were recorded using a windowless energy dispersive Si (Li) detector. A linear background fit to the pre-edge region was subtracted from the spectra. The O K-edge spectra are normalized between 585 and 630 eV.

3. Results and discussion

The O K-edge XAS spectra of electrochemically Li-ion deintercalated Li_{1-x}NiO₂ system is shown in Fig. 1. The O K-edge XAS spectrum collected by the FY mode plotted in Fig. 1(a) is dramatically different from that collected by the PEY mode shown in Fig. 1(b). The most significant differences are in the pre-edge peak features. Pre-edge peaks below ~534 eV in these spectra correspond to the transition of oxygen 1s electron to the hybridized state of the nickel 3d and oxygen 2p orbitals, whereas the broad higher peaks above ~534 eV correspond to the transi-

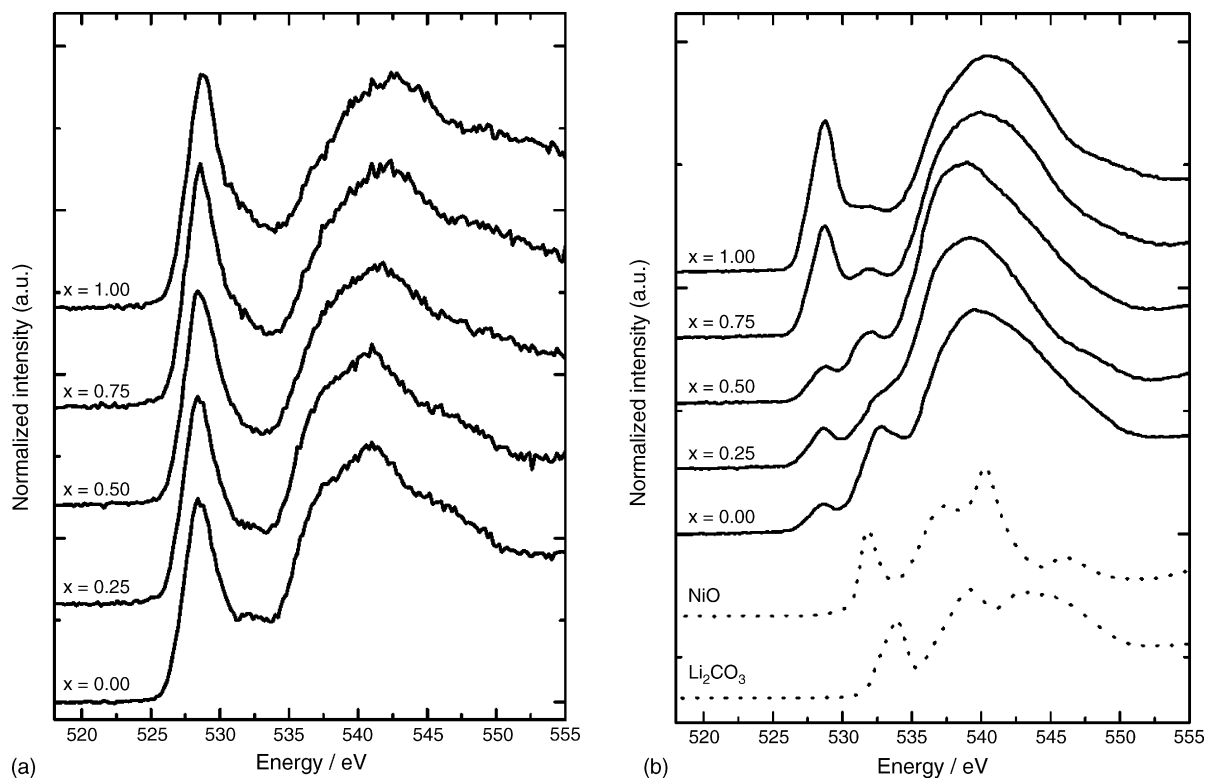


Fig. 1. Normalized O K-edge XAS spectra of Li_{1-x}NiO₂ system at different *x* values using (a) FY method and (b) PEY method.

tions to hybridized states of oxygen 2p and nickel 4sp orbitals. O K-edge XAS spectra of $\text{Li}_{1-x}\text{NiO}_2$ collected by the FY mode in Fig. 1(a) show a single intense absorption peak at ~ 528.5 eV which corresponds to a transition to the hybridized state of $\text{Ni}^{3+,4+}$ 3d–O 2p orbitals. In contrast, in the O K-edge XAS spectra of $\text{Li}_{1-x}\text{NiO}_2$ collected by the PEY mode in Fig. 1(b), an additional pre-edge peak at ~ 532 eV is observed, which corresponds to the hybridized state of Ni^{2+} 3d–O 2p orbitals. The assignment of Ni^{2+} state can be clearly verified by the reference spectrum of NiO plotted in dash line. The observation of this transition tells us that the majority of Ni ions at the surface of LiNiO_2 are in the form of Ni^{2+} . This peak shifted a little to higher energy region in the pristine LiNiO_2 due to the transition originated from Li_2CO_3 on the surface of pristine LiNiO_2 particles. Li_2CO_3 is a common contamination formed at the surface of cathode materials and gradually dissolved in the electrolyte during Li deintercalation. The reference spectrum of Li_2CO_3 is also plotted in dash line as marked in Fig. 1(b). The effects of Li_2CO_3 are basically disappeared in the O K-edge XAS spectrum of $\text{Li}_{0.5}\text{NiO}_2$ in the PEY mode. From $x = 0.5$ in $\text{Li}_{1-x}\text{NiO}_2$ the peak at ~ 532 eV starts to decrease gradually showing Ni^{2+} ions at the surface oxidized to higher oxidation state during Li deintercalation. This will be confirmed and further discussed in our Ni L-edge XAS results during Li deintercalation later in this paper. Now back to the spectra collected by the FY mode in Fig. 1(a), as the degree of electrochemical deintercalation increases (the x value increases), the integrated peak intensity at ~ 528.5 eV increases slightly in O K-edge XAS spectra of $\text{Li}_{1-x}\text{NiO}_2$ in the FY mode. Compared to our earlier O K-edge absorption study

of $\text{Li}_{1-x}\text{CoO}_2$ system [10,12], it is clear that changes in O K-edge XAS of $\text{Li}_{1-x}\text{NiO}_2$ system during the Li deintercalation are relatively small. It is notable that this behavior is dramatically different from that of the electrochemically Li-ion deintercalated $\text{Li}_{1-x}\text{CoO}_2$ system where oxygen site makes large contribution for the charge compensation for the Li-ion deintercalation process, which is reflected in much larger changes in the integrated intensity of the corresponding transition.

Fig. 2 shows the Ni $L_{\text{II,III}}$ -edge XAS spectra of electrochemically Li-ion deintercalated $\text{Li}_{1-x}\text{NiO}_2$ system in the FY mode (a) and PEY mode (b). These spectra correspond to Ni 2p \rightarrow Ni 3d transitions, split by the spin–orbit interaction of the Ni 2p core level. The pristine Ni $L_{\text{II,III}}$ -edge PEY spectrum shows main peaks at ~ 851.0 and ~ 867.6 eV, and weak shoulder peaks at higher energy, respectively, due to Ni 2p–3d electrostatic interaction and crystal field effect of octahedral symmetry. The FY data is distorted by self-absorption effects which diminishes the intensity of peaks/features with high intrinsic intensity. However, the positions of the peaks are not significantly changed. Furthermore, the amount of self-absorption will be largely independent of Li-content. Therefore, relative comparison of FY data obtained at various states of charge can be performed on a quantitative basis. Based on the previous Ni L-edge XAS experimental results and calculations [6], Ni L-edge XAS of pristine LiNiO_2 obtained in PEY mode clearly shows that most of Ni ions at the surface of LiNiO_2 powders exist as Ni^{2+} . As Li deintercalated, Ni^{2+} ions at the surface are oxidized to Ni^{3+} ions. In contrast, Ni L-edge XAS of pristine LiNiO_2 in FY mode shows most of Ni ions in the bulk are in the form of Ni^{3+} . The Ni ions in the

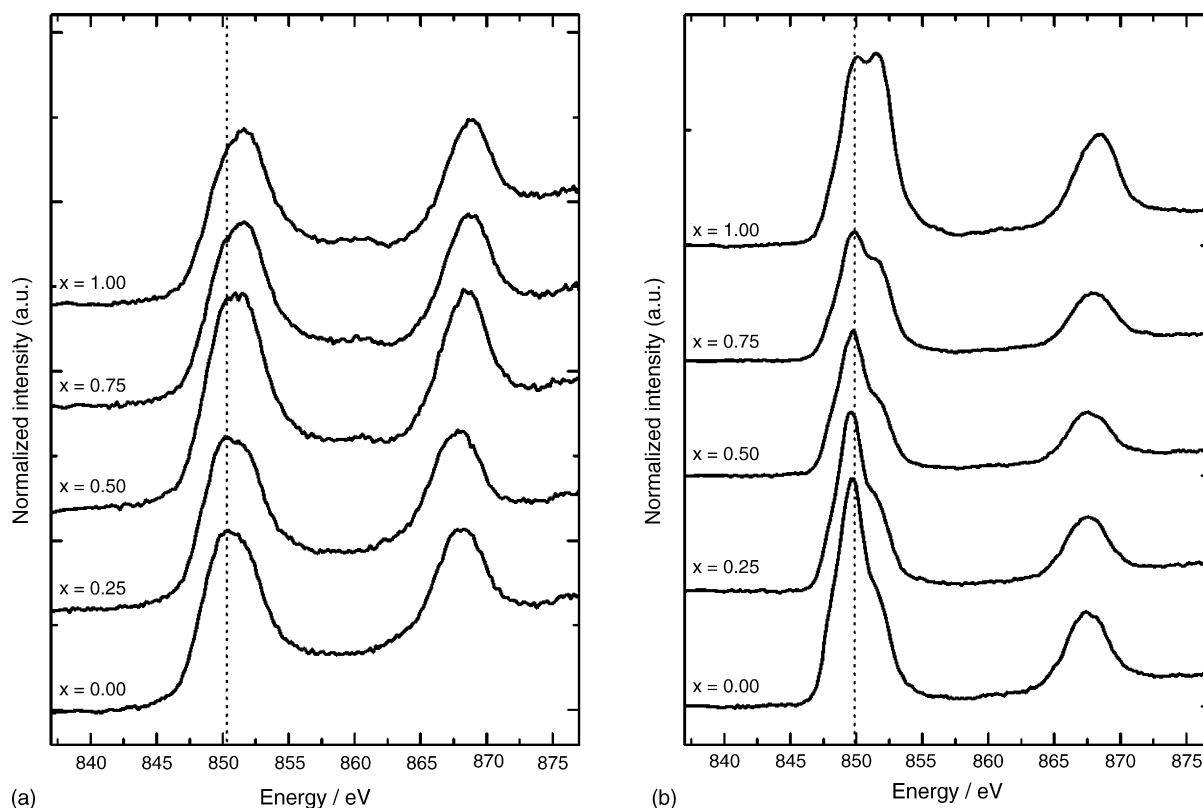


Fig. 2. Normalized Ni $L_{\text{II,III}}$ -edge XAS spectra of $\text{Li}_{1-x}\text{NiO}_2$ system at different x values using (a) FY method and (b) PEY method.

bulk are oxidized from Ni^{3+} to Ni^{4+} during Li deintercalation. Through the discussion of the spectral differences collected by FY and PEY, it is clear that the interpretation of the data should be limited to the surface structure only, if the PEY mode is used alone. In order to get a full picture of both the surface and the bulk, both FY and PEY modes should be used simultaneously.

In conclusion, the electronic structure for an electrochemically deintercalated $\text{Li}_{1-x}\text{NiO}_2$ electrode has been investigated with soft XAS technique, in both the FY and PEY modes. By comparing the O K-edge XAS spectra of $\text{Li}_{1-x}\text{NiO}_2$ electrode collected simultaneously by the FY and PEY modes, it was found that the surface electronic structure of $\text{Li}_{1-x}\text{NiO}_2$ electrode is different from the bulk. Therefore, if the PEY mode, which is a surface-sensitive technique, is used alone, the reliability of the results is limited to the surface structures only. In order to get the full picture of both the surface and the bulk, both the FY mode and PEY mode should be used simultaneously. Ni $\text{L}_{\text{II,III}}$ -edge XAS results of $\text{Li}_{1-x}\text{NiO}_2$ electrode at different charge states, collected in both the FY and PEY modes, show that Ni^{2+} ions at the surface are mostly oxidized to Ni^{3+} ions during Li deintercalation, whereas the process in the bulk is the oxidation of Ni ions from Ni^{3+} to Ni^{4+} .

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