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Changes in electronic structure by Li ion deintercalation in $LiNiO_2$ from nickel *L*-edge and O *K*-edge XANES

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Abstract

Change in electronic structure by lithium ion deintercalation in $LiNiO_2$ was investigated by Ni *L*-edge and O *K*-edge X-ray absorption near edge structure (XANES). The Ni *L*-edge XANES for $LiNiO_2$ indicated the Ni occurs in $LiNiO_2$ as Ni^{2+} ions. The Ni *L*-edge XANES for Li_xNiO_2 showed no chemical shift to indicate that the Ni ion in Li_xNiO_2 is still Ni^{2+}, even at low x value. The O *K*-edge XANES for Li_xNiO_2 also indicated that the holes compensating the lithium ion deintercalation are located primarily in oxygen 2p states rather than in Ni 3d states.

Keywords: Nickel L-edge; O K-edge; $LiNiO_2$

1. Introduction

The $LiNiO_2$ oxide with a layered α-$NaFeO_2$ structure is one of the most promising cathode materials used in 4 V-type lithium ion batteries because its low cost and high theoretical energy density [1–3]. It is important to clarify the change of electronic structure during charge and discharge process in order to understand the electrochemical properties. Recently, first-principle molecular orbital calculations of the electronic structure of the $Li_{1-x}NiO_2$ have indicated that lithium ion deintercalation increases the covalent interaction between Ni and oxygen, and that the oxidation associated with the deintercalation mainly takes place on oxygen [4–6]. However, experimental studies of the electronic structure change during the lithium ion deintercalation are insufficient.

In this study, Ni L_{23}-edge and O *K*-edge X-ray absorption near edge structure (XANES) was determined the electronic structure of $LiNiO_2$ during lithium ion deintercalation.

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2. Experimental

The $LiNiO_2$ powder was prepared by conventional solid state reaction starting with lithium hydroxide (Wako Chemical Co. Inc., 99.9%) and nickel hydroxide (Wako Chemical Co. Inc., 99.9%). A mixture of Li(OH) and $Ni(OH)_2$ in a mole ratio of 1:1 was heated at 770°C for 30 h in an oxygen atmosphere. The crystal structure of the product was determined by XRD using Mo $K\overline{\alpha}$ radiation. The Li_xNiO_2 was prepared by electrochemical lithium deintercalation. A mixture of 82.5 wt.% LiNiO2, 15 wt.% acetylene black, and 2.5 wt.% polytetrafluoropropylene binder was used as working electrode. The electrolyte was a 1 M $LiClO_4$ in PC solution.

The Ni L_{23}-edge XANES spectra were measured on the BL-7A beam line and O *K*-edge XANES were measured on the BL-8B1 beam line at UVSOR (Okazaki, Japan) with a ring energy of 750 MeV in a mode of total electron yield at room temperature.

3. Results and discussion

The XRD pattern for $LiNiO_2$ was indexed in a rhombohedral $R\bar{3}m$ space group [1]. The first-cycle discharge capacity is 140 mAh g^{-1}.

Fig. 1 shows the Ni *L*-edge XANES of Li_xNiO_2 for various x values. The Ni *L*-edge XANES shows two strong

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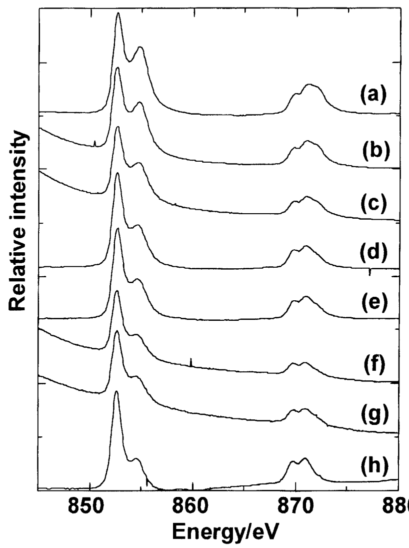

Fig. 1. Ni 2p absorption spectra for Li_xNiO_2: (a) 0.2, (b) 0.4, (c) 0.5, (d) 0.6, (e) 0.7, (f) 0.8, (g) 0.9, (h) 1.0.

absorption features of the spin-orbit splitting of the Ni 2p core hole [7]. The absorption near 852–856 eV is the $2p_{3/2}$ (L3) edge and that near 868–872 eV is the $2p_{1/2}$ (L2) edge. The Ni *L*-edge XANES for $LiNiO_2$ is in good agreement with that reported by Montoro et al. [8]. The XANES for $LiNiO_2$ is similar to that for NiO, which shows the Ni ions in $LiNiO_2$ to be Ni^{2+} ions in a high-spin state [7,8]. The spectra for Li_xNiO_2 ($x = 0.2$, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0) do not exhibit chemical shift and the change in shape are small, indicating the Ni ion in the Li_xNiO_2 is still Ni^{2+} even at as low an x value as 0.2.

Fig. 2 shows the O *K*-edge XANES for Li_xNiO_2 for various x values. The peak at about 532 eV (•) is attributed to oxygen in the substrate. A peak at about 533 eV is attributed to the band derived from the mixing of the Ni 3d states with O 2p states. The broad structure near 535–550 eV is attributed to a Ni band with 4sp character. The peak at near 528 eV increased with decreasing lithium content. This result shows that oxidation influences the oxygen 2p orbital and the ground state of Li_xNiO_2 ($x < 1.0$) is $Ni^{2+}L$, where L represents a ligand hole state [9]. This indicates that the lithium deintercalation reaction does not involve Ni but oxygen. This is in good agreement with the result of first-principles calculations for the Li_xNiO_2 system [4–6].

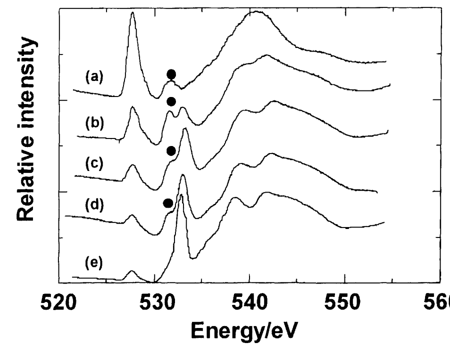

Fig. 2. O 1s absorption spectra for Li_xNiO_2: (a) 0.2, (b) 0.5, (c) 0.6, (d) 0.8, (e) 1.0.

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