

Site-selective analyses of valence states in LiNiO₂ by resonant X-ray scattering

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Analyses of the relation between valence and structure changes during a battery reaction provide us fundamental understanding of phase transition of active materials. X-ray absorption fine structure (XAFS) is commonly used to investigate a change of valence states of a transition metal (TM) during lithiation/delithiation. Since only average information on valence of a certain element in a sample is obtained by XAFS, we cannot distinguish the valences in different crystalline sites and/or different phases. This is crucial in a study of electrode materials with a complicate crystalline symmetry or a system with mixing of cations during the battery reaction. In the present work, diffraction anomalous fine structure (DAFS)¹⁻³ has been applied to reveal the valence states of Ni at the Li site (Wyckoff 3a site) and the original TM site (Wyckoff 3b site) in layered rock salt LiNiO₂ ($R\bar{3}m$)⁴.

We prepared pellets of as-synthesized and charged Li_xNiO₂ for DAFS measurements. For the as-synthesized sample, a mixture of ~10 mg LiNiO₂ powder (Toshiba Manufacturing Co., Ltd) and ~150 mg BN powder was pelletized into a 10 mm diameter disk. For the charged sample, a cell of a composite electrode was electrochemically charged. The positive electrode was a mixture of 88wt% LiNiO₂ powder, 6wt% carbon black, and 6wt% PVDF. The cell assembled in an Ar-filled glove box was charged by 167 mAh g⁻¹ with HJ-1001SD8 (Hokuto Denko Corporation) at 0.1C up to 4.2 V vs. Li/Li⁺ and maintained at this voltage. The charged electrode was taken out from the cell, washed by dimethyl carbonate, removed from the metal collector and pelletized in the same procedure mentioned above. The pellet samples were sealed with a Kapton film in Ar gas atmosphere. Occupancy of Ni ions at the Li site, determined by Rietveld analysis with RIETAN-FP, was 0.11. Namely, the compositions of as-synthesized and charged samples were [Li_{0.89}Ni_{0.11}]_{3a}[Ni]_{3b}[O₂]_{6c} and [Li_{0.25}Ni_{0.11}]_{3a}[Ni]_{3b}[O₂]_{6c}, respectively. DAFS measurements were carried out at BL28XU in SPring-8, Japan. DAFS spectra of 003 and 104 diffraction peaks were taken at Ni K-edge by a one-dimensional detector Mythen (Dectris Ltd.).

From the DAFS measurements, XAFS-like spectrum can be obtained from each diffraction peak. It is a weighted sum of the imaginary parts of Ni resonant terms at the two sites. Namely,

$$F''(003) = 0.33f''_{\text{Ni}(3a)} - 3f''_{\text{Ni}(3b)} \quad (1)$$

$$F''(104) = 0.33f''_{\text{Ni}(3a)} + 3f''_{\text{Ni}(3b)}, \quad (2)$$

where $F''(hkl)$ is a XAFS-like spectrum taken from hkl diffraction, and f''_j is an imaginary part of resonant terms in an atomic scattering factor of atom j .

Figure 1 shows $-F''(003)$ and $F''(104)$ of (a)

Li_{0.89}Ni_{1.11}O₂ and (b) Li_{0.25}Ni_{1.11}O₂. The heights of the both spectra are normalized at 8.38 keV. In Fig. 1(a) of the as-synthesized sample, the shapes of the two spectra are similar. It indicates that the valence states of Ni ions at 3a and 3b sites resemble each other. In contrast, in Fig. 1(b) of the charged sample, the energies of the absorption edges of 003 and 104 at ~8.345 keV are higher than these in Fig. 1(a), because the Ni ions are oxidized by delithiation. Furthermore, the discrepancy of the absorption edges of 003 and 104 are more significant than that of the charged state. It indicates Ni ion at 3a has a different valence state from that at 3b. The profile of $f''_{\text{Ni}(3a)}$, obtained by subtraction of the two spectra in Fig. 1 (b), clearly shifts to a higher energy. This indicates that the valence of Ni ions at 3a becomes higher than that at 3b.

A space for intercalation of Li ions is reduced because of the presence of Ni ions at the Li site with the higher oxidized state. Consequently, the present work provides the experimental evidence of the degradation in the cation mixed LiNiO₂ as mentioned by Peres et al.⁵

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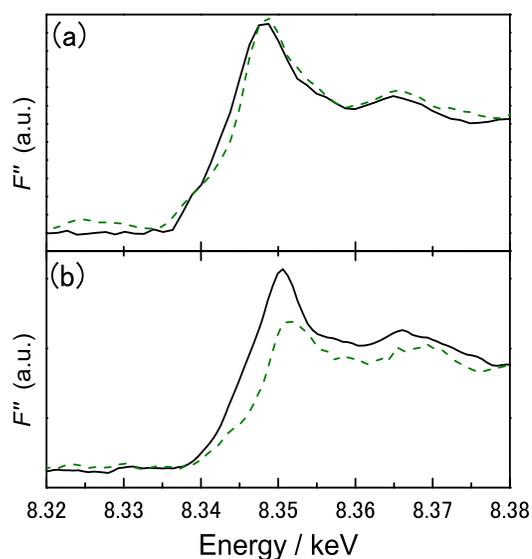


Figure 1. XAFS-like spectra of (a) Li_{0.89}Ni_{1.11}O₂ and (b) Li_{0.25}Ni_{1.11}O₂ taken from 003 ($-F''(003)$: solid lines) and 104 ($F''(104)$: broken lines) diffraction lines.