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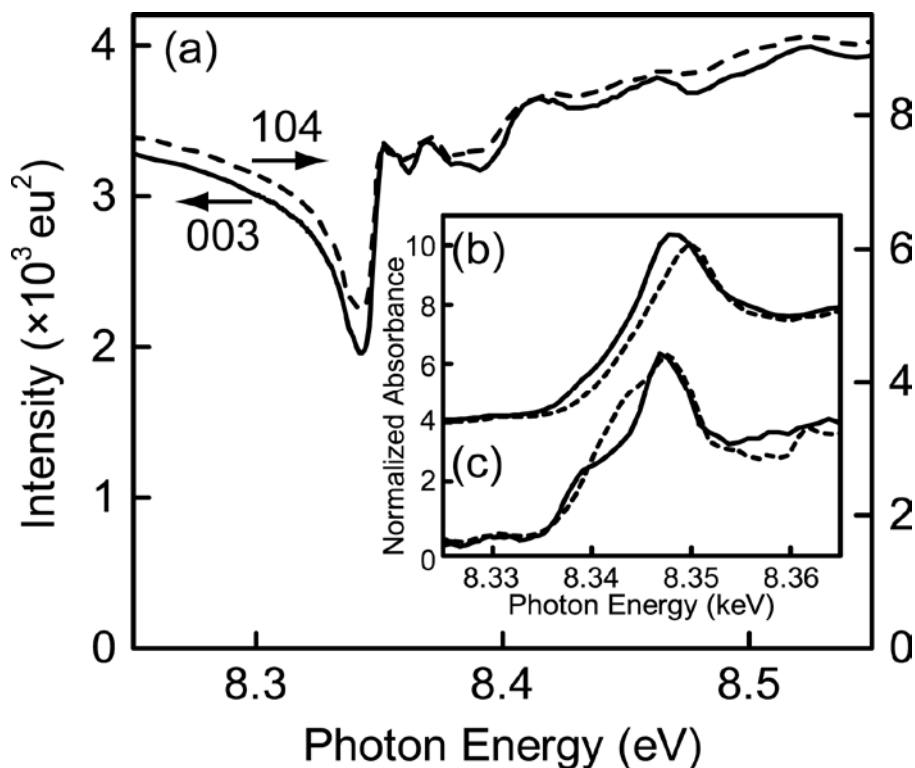
Site-selective analyses of battery reactivities in $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ by powder DAFS

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Deep understanding of a battery reactivity of transition metals in a positive electrode is essential for further development of lithium ion batteries (LIBs). $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ (LNO, $0 < x < 1$) is one of the typical positive-electrodes with a layered rock-salt structure. LNO often contains significant antisite defects of Ni at Li site, i.e., interlayer gallery, in addition to Ni site in the host layer. Though a relationship between such structural disorder and capacity fading of the battery has been reported[1], its degradation mechanism is still unclear presumably because of insufficient insight into electrochemical behavior of Ni at each site in LNO. In the present work, powder diffraction anomalous fine structure (P-DAFS)[2] has been applied to LNO to analyze the valence and local structure of Ni at both different symmetric sites for tackling this degradation issue. We prepared pellets of as-synthesized and charged LNOs for P-DAFS measurements. The composition of the samples is $[\text{Li}_y\text{Ni}_{0.11}]_{3a}[\text{Ni}]_{3b}[\text{O}_2]_{6c}$ ($y = 0.89, 0.40$) in R-3m space group. DAFS measurements were carried out at undulator beamline BL28XU, SPring-8 in Japan. The DAFS spectra were measured with use of 003 and 104 diffractions in ~ 1 keV energy range around Ni K-edge (8.331 keV). The XAFS-like spectra were extracted from DAFS spectra with a priori structural information from Rietveld analyses. Figure 1 shows (a) the DAFS spectra of the as-synthesized sample, XAFS-like spectra of Ni occupying the Ni site (b) and the Li site (c) in the as-synthesized (solid line) and the charged (broken line) samples. The spectrum at the Ni site shows a shift to the higher energy with charging, indicating the oxidation of Ni accompanied with Li extraction. In contrast, Ni at the Li site shows no significant shift with charging. Thus, Ni at the Li site hardly compensates the charge for delithiation, which indicates that the electrochemically inactive Ni occupying the Li sites would cause irreversibility in this system.

[1] J. P. Peres, C. Delmas, A. Rougier et al., *J. Phys. Chem. Solids*, 1996, 57, 1057-1060., [2] I. J. Pickering, M. Sansone, J. Mars et al., *J. Am. Chem. Soc.* 1993, 115, 6302-6311.



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