

A Study of a High-Capacity Electrode Material for Rechargeable Batteries by X-ray Absorption Spectroscopy, $\text{Li}_2\text{MnO}_3\text{-LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$

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Introduction

The demand for the large-scale rechargeable batteries has grown rapidly over the past few years. In the realm of energy storage, lithium-ion batteries are of great significance as power sources to realize cleaner and energy-efficient automobiles, that is, pure electric vehicles. In this study, a detailed study of the reaction mechanisms of the Li-excess manganese layered oxides in relation to the local and electronic structures by X-ray absorption spectroscopy (XAS) is presented. A one-to-one mixture between Li_2MnO_3 and $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($\text{Li}_{1.2}\text{Co}_{0.13}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{O}_2$) was chosen as a representative material of the Li-excess manganese layered oxides. A study on local and electronic structures allows for a better understanding of the reaction mechanisms of the Li-excess manganese layered oxides before and after initial charging beyond the voltage plateau of 4.5-4.6 V.

Experimental

Composite positive electrodes consisted of 80 wt % active material, 10 wt % acetylene black, and 10 wt % polyvinylidene fluoride (PVdF), pasted on aluminum foil as a current collector. The electrolyte solution used was 1 mol dm^{-3} LiPF_6 dissolved in EC:DMC = 1:1 (Kishida Chem. Corp., Ltd., Japan). Electrochemical testing was conducted using R2032-type coin cells with Li metal as negative electrodes. $\text{Li}_x\text{Co}_{0.13}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{O}_2$ composite samples were prepared by using the coin cells at a current density of 10 mA g^{-1} . The composite electrodes were rinsed with DMC and sealed in a water-resistant polymer film in the argon filled glovebox.

Results and Discussion

X-ray absorption near-edge structures (XANES) spectra, collected at Mn K-edge (6539 eV) and Ni K-edge (8333 eV), are plotted in Figure 1. Figure 1a shows manganese K-edge XANES spectra observed during the charging up to 4.8 V, and points where the spectra were collected in the charge and discharge curves are shown in the inset of the figures. After the charging to the voltage plateau, tetravalent manganese ions were partly reduced to the trivalent state on discharge. Manganese ions became electrochemically active in the subsequent cycles.

The change in the electronic structures of the Ni ions was also examined by XAS. XANES spectra collected at Ni K-edge during the charging up to 4.8 V are shown in Figure 1b. It is found that the spectra shift back toward the lower energy region upon charge. Figure 1c shows

simulated K-edge spectra of the nickel ions locating in different local environments. In the simulation, three different local environments were assumed. By comparing the results between observed and simulated nickel K-edge spectra, it was estimated that the nickel ion partly migrated from the metal to lithium layer during the charging to the voltage plateau. The present XAS study further supported the structural rearrangement observed by Rietveld analysis.¹⁾

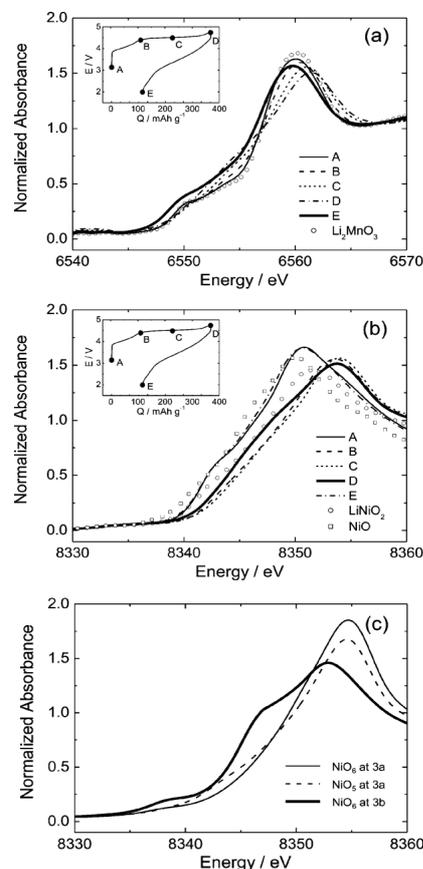


Figure 1. XANES spectra of $\text{Li}_1\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ collected at (a) Mn K-edge and (b) Ni K-edge during the initial charge/discharge cycle in the voltage range of 2.0 and 4.8 V. XANES spectra of Li_2MnO_3 , NiO, and LiNiO_2 as reference samples are also shown. (c) Ni K-edge XANES spectra were simulated to interpret the observed data in the charged state.

Reference

1) N. Yabuuchi, I. Nakai, S. Komaba *et al.*, *J. Am. Chem. Soc.*, **133**, 4404, (2011).

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