

Electron Energy Loss Spectroscopic Study on Electronic Structure of Li_xNiO_2

Yukinori Koyama^{1,z}, Teruyasu Mizoguchi^{2,z},
Hidekazu Ikeno³, and Isao Tanaka³

¹ Department of Materials Science and Engineering,
Nagoya University, Furo, Chikusa,
Nagoya 464-8603, Japan

² Institute of Engineering Innovation, The University of
Tokyo, Yayoi, Bunkyo, Tokyo 113-8656, Japan

³ Department of Materials Science and Engineering,
Kyoto University, Yoshida, Sakyo,
Kyoto 606-8501, Japan

Despite importance of understanding redox reactions in battery systems, solid-state redox reactions have not been clear in lithium transition-metal oxides, e.g., LiCoO_2 and LiNiO_2 . In conventional chemical sense, oxygen and lithium species in oxides are regarded to be fully ionized and charge of transition-metal ions is determined to follow charge neutrality. Hence, solid-state redox reaction is ascribed to transition-metal ions. Recently, it has been pointed out by the first-principles calculation that oxygen ions also participate in the solid-state redox reaction. To examine the role of oxygen ions in the solid-state redox reaction for LiNiO_2 , electronic structure of NiO , LiNiO_2 and NiO_2 are studied by electron energy loss spectroscopy (EELS) and the first-principles calculation.

LiNiO_2 was prepared by a solid-state method. A mixture of LiNO_3 and NiCO_3 was heated at 600 °C for 16 hours followed by a reaction at 750 °C for 16 hours. Both reactions were done in an oxygen stream. To prepare NiO_2 , lithium was electrochemically extracted from LiNiO_2 . A pellet of LiNiO_2 was charged up to 5 V in a nonaqueous lithium cell. EELS spectra were recorded using an energy filter (GIF Model 678, Gatan Inc.) attached on a transmission electron microscopy (CM200FEG, FEI Company).

EELS spectra on Ni- $L_{2,3}$ and O-K edge for NiO , LiNiO_2 , and NiO_2 are illustrated in Figs. 1 and 2. Ni- $L_{2,3}$ edge spectrum is a result of electron transition from Ni-2p core levels to unoccupied Ni-3d orbitals. Consequently, Ni- $L_{2,3}$ edge spectrum gives direct information on electronic structure of Ni-3d orbitals that is most interesting to understand solid-state redox reaction in LiNiO_2 . Clear difference in both shape and energy of peaks can be seen among the three samples, indicating different oxidation state of Ni ions. Peak energy is in order of NiO , LiNiO_2 and NiO_2 , and this suggests that Ni is divalent in NiO , trivalent in LiNiO_2 , and tetravalent in NiO_2 .

O-K edge spectrum corresponds to electron transition from O-1s core levels. In the formal sense, O-2p orbitals are completely filled in oxides, and there is no state for the transition. In reality, transition can happen via hybridization between oxygen and metal ions. Intensity of the first peak in O-K edge spectrum gets greater in order of NiO , LiNiO_2 , and NiO_2 . This indicates greater

hybridization between O-2p and Ni-3d orbitals. The first-principles calculation has predicted that lithium extraction causes greater hybridization and this leads to decrease in electron density at oxygen ions. Peaks at 540 to 560 eV shifted between LiNiO_2 and NiO_2 , while they did not between NiO and LiNiO_2 . These changes in O-K edge spectrum are evidence that oxygen ions play an important role in solid-state redox reaction as has been predicted by the first-principles calculation.

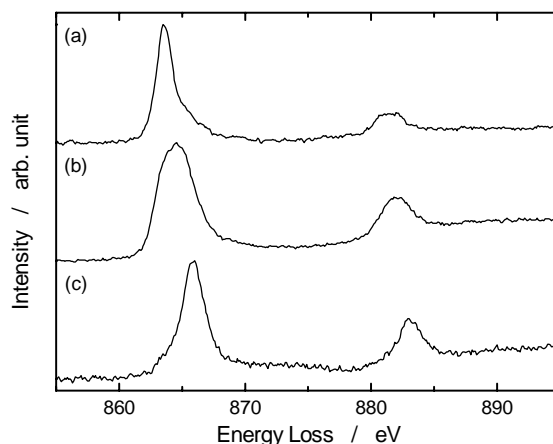


Fig. 1 Ni- $L_{2,3}$ edge EELS spectra of (a) NiO , (b) LiNiO_2 , and (c) NiO_2 . Intensity is normalized by the maximum value of each spectrum.

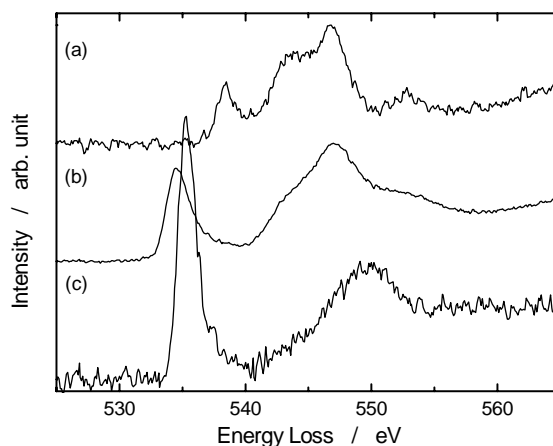


Fig. 2 O-K edge EELS spectra of (a) NiO , (b) LiNiO_2 , and (c) NiO_2 . Intensity is normalized by the maximum value in the range of 540 - 560 eV in each spectrum.

^z Research Fellow of the Japan Society for the Promotion of Science