

리튬니켈산화물에 대한 XAFS 연구

X-Ray Absorption Spectroscopic Studies of Lithium Nickel Oxide Electrodes

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Introduction

Four volt secondary lithium cells have been of great interest among battery researchers and electrochemists. Possible candidate cathode materials reported so far are LiCoO_2 ,¹⁾ LiMn_2O_4 ,²⁾ LiNiO_2 ,^{3,4)} and $\text{LiNi}_{1/2}\text{Co}_{1/2}\text{O}_2$.⁵⁾ Of these, the research on LiCoO_2 and LiMn_2O_4 is more advanced than for other cathodes because of the simplicity of preparing these materials. LiNiO_2 prepared by high temperature synthesis commonly used for LiCoO_2 preparation, shows poor or no electrochemical reactivity due to the contamination of structural disorder or defects in the LiNiO_2 matrix. The electrochemical performance of LiNiO_2 electrode is closely related with structural variations evolved during the charge/discharge cycling. In this study electronic and structural aspects of LiNiO_2 electrode have been investigated by XRD, Ni K-edge XANES(X-ray Absorption Near Edge Structure) and EXAFS(Extended X-ray Absorption Fine Structure)⁶⁾ to describe quantitatively a short-range order in structural analysis as a function of its state of charge.

Experimental

LiNiO_2 was prepared by reacting a stoichiometric mixture of LiNO_2 and Ni(OH)_2 . The mixture was well-mixed and pressed into pellets(20mm dia. ca. 5mm thick). The pellets were precalcined at 600°C for 12h in a stream of oxygen. The precalcined materials were ground and pressed into pellets, which were reacted at 750°C for 24h under oxygen stream. The reaction product was ground and stored in a desiccator over blue silica-gel.

A cathode mix, which consisted of 88w/o LiNiO_2 , 6w/o denka black, and 6w/o PVDF was used. The electrolyte was 1M LiClO_4 in propylene carbonate (PC) solution. Lithium metal was used as an anode and a reference electrode. Electrochemical measurement was performed in three-electrode glass cell set up in an Ar-filled glove box.

Ni K-edge EXAFS measurements were performed in transmission mode with double crystal monochromator Si(111) at beam line 3C1 of Pohang Light Source(PLS). The analysis of the EXAFS data was performed using UWXAFS 3.0 program package which uses multiple scattering calculations of FEFF.

Reference

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