스피넬 리튬망간산화물에 대한 EXAFS 와 XANES 연구
EXAFS an d XANES Studies of Spinel $Li_xMn_2O_4$

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1. Introduction

Spinel phase $Li_xMn_2O_4$ has received considerable attention and is currently the most promising cathode material for use in lithium ion batteries because of its economic and environmental advantages.[1-3] Although capacity fading on charge/discharge is observed, optimum spinel electrode can maintain more than 120 mAh/g over extensive cycling at room temperature.[4] The cyclability is closely related with structural variations evolved during the charge/discharge cycling. Electronic and structural aspects of $Li_xMn_2O_4$ electrode as a function of its state of charge have been investigated by Mn K-edge XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure)[5,6], which allow to describe quantitaively a short-range order in structural analysis.

2. Experimental

Spinel $Li_xMn_2O_4$ was prepared by reacting a stoichiometric mixture of Li_2CO_3 and electrolytically prepared MnO_2 at 750℃ for 24h under air in an alumina crucible. The electrochemical cells consisted of $LiMn_2O_4$ (WE), Li metal (CE, RE) and 1M $LiPF_6$/ EC+DME (1:1) electrolyte. Electrochemical measurement was performed in three-electrode glass cell set up in an Ar-filled glove box. Cells were charged or discharged using Solartron SI 1287 in a galvanostatic mode. Mn 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.[7,8]

3. Results

At a higher voltage of the charge curves, the capacity loss on cycling for the spinel arose, which is

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considered as the main factor that causes capacity loss. This could result from increase in contact resistance at the spinel surface or structural aspects such as Mn dissolution and structural distortion. In analysis of XANES, the main edge features appear to be shifted consistent with the change both length (Mn-O) and in manganese oxidation state. This is in accordance with the fact that mean Mn-O bond length is at minimum in charged state and increases progressively with lithium reinsertion in EXAFS analysis.(Fig. 1)

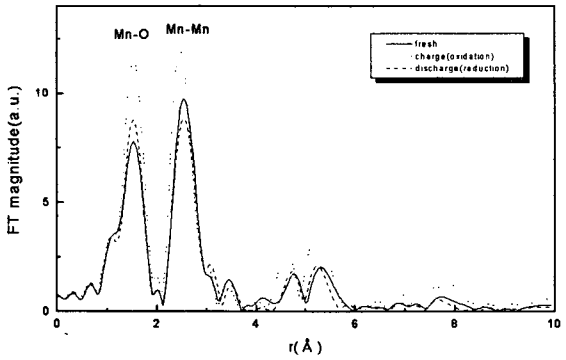

Figure 1. Fourier-transformed EXAFS data for fresh $LiMn_2O_4$ (solid line), charged (dot line) and discharged (dash line).

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