Abstract #1098, 224th ECS Meeting, © 2013 The Electrochemical Society

Characterization and Average, Local and Erectronic Structures by Charge-Discharge Cycle in $0.6Li_2MnO_3$-$0.4Li(Co_{1/3}Ni_{1/3}Mn_{1/3})O_2$ solid solution of a Cathode Active Material for Li Ion Battery

Ryousuke Kawai, Naoya Ishida,
Yasushi Idemoto
Department of Pure and Applied Chemistry
Faculty of Science & Technology,
Tokyo University of Science,
2641 Yamazaki, Noda-shi, Chiba 278-8510, Japan

INTRODUCTION

Layered type oxides are of interest for the positive electrode materials in lithium-ion batteries. Especially the $LiCoO_2$ is the most commercially used material due to its high electric capacity and excellent cycle life. The high cost and toxicity of cobalt compounds, however, have led to the investigation of alternative materials that intercalate lithium ions. The layered rock-salt type $LiNiO_2$, $LiNi_{0.5}Mn_{0.5}O_2$, $LiMnO_2$, Li_2MnO_3 and xLi_2MnO_3-$(1-x)LiMO_2$ (M: Mn, Co and Ni) [1] have been intensively studied. Especially xLi_2MnO_3-$(1-x)Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ exhibited high discharge capacity of over 200 mAh/g by charging above 4.5 V. Although the transition-metal arrangements were disturbed with the progress of the lithium insertion/extraction reaction, the perturbation of transition metals has not been explained yet [2].

In this study, the lithium of $0.6Li_2MnO_3$-$0.4Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ was electrochemically extracted and inserted for several cycles. The structural changes were explored using the synchrotron radiation and neutron beam. The X-ray absorption fine structure (XAFS), neutron total scattering and pair distribution function (PDF) analyses are precise in determining the local structure that may reflect the lattice disorder.

EXPERIMENTAL

Mixed Ni–Mn–Co precipitates were prepared by standard aqueous co-precipitation method. The alkaline solution of $LiOH•H_2O$ was added to the mixed solutions with stirring. The precipitates were filtered, dried, and then heated at 950 ºC for 15 hours. The samples were identified by X-ray diffraction (XRD) at room temperature on a PANalytical X'Pert PRO X-ray diffractometer using Cu Kα radiation. The sample was analysed for selected cations (Li, Mn, Ni and Co ions) using a Shimadzu ICP E-9000 unit (Kyoto, Japan). Electrochemical cycling experiments were carried out at 20 ºC with Hohsen cells (Hohsen Co., Japan) containing the sample electrode, a Li metal anode, a microporous polyethylene separator, and an electrolyte consisting of 1 M $LiPF_6$ solution in a 1:2 EC:DMC mixture (by volume). For the fabrication of the cathode, the sample powder blended with Acetylene black (to assist with current collection) and with a polyvinylidene fluoride (PVDF) binder in a mass ratio of 8:1:1. The sample and carbon black powders were first added to a solution of PVDF in N-methyl-2-pyrrolidone (NMP) to make slurry with appropriate viscosity. The cathode was then cast onto an Al foil. After the electrode was dried at 100 ºC for 24 h, it was compressed after cutting out the sample electrode for electrochemical evaluation. The cells were assembled in the argon filled glove box. We measured the synchrotron X-ray diffraction (BL19B2, SPring-8) and the powder neutron diffraction (BL20, J-PARC) and neutron total scattering measurement (Nomad, SNS) for the sample. The data was analyzed with the Rietveld technique using Rietan-FP and Z-Rietveld.

RESULTS AND DISCUSSION

All the XRD peaks of the sample were attributed to the layered structure with a space group of *C*2/*m*. The chemical analysis by ICP for the sample confirmed a good agreement with the chemical composition of $0.6Li_2MnO_3$-$0.4Li(Co_{1/3}Ni_{1/3}Mn_{1/3})O_2$. The sample after charge and discharge processes showed the extraction and insertion of lithium ions located at both Li-layer and TM-layer (TM: transition metal). It was found that the lithium ions were preferentially extracted at the 2b site compared with 4g site. From the XAFS results, the several oxygens around Mn site were missing in the host structure during first charge process because of the decrease of Mn-O bonds by EXAFS spectra (Fig. 1). Since the next-nearest neighbors surrounding Co and Ni ions, M-M bonds, differed from the first to the fifth discharge process, the TM arrangements might disturb during the fist five cycles. From the PDF it was found that the short range order became notably different between 5th charge and discharge states as shown in Fig. 2.

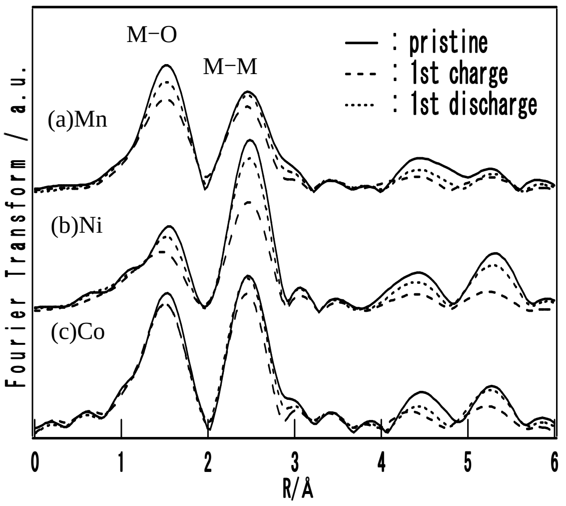

Figure 1. Mn, Ni and Co *K*-edge EXAFS spectra: (a)Mn (b)Ni and (c)Co.

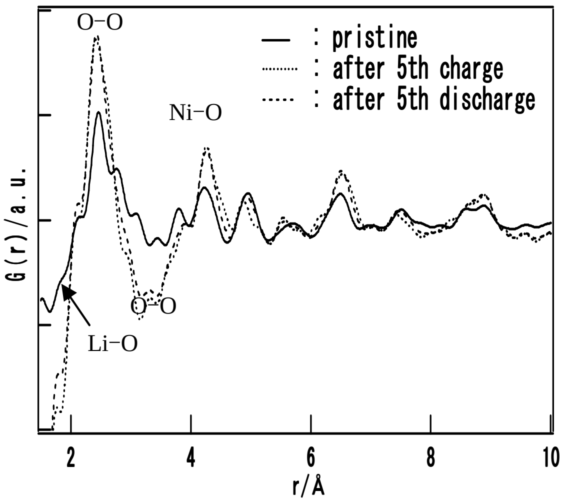

Figure 2. Pair distribution function of cathode active material.

References
1) M. M. Thaсkeray *et al.*, *J. Mater. Chem.*, **17**, 2069 (2007).
2) H. Koga *et al.*, *J. Phys. Chem. C*, **116**, 13497 (2012)