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Change in Local Structure of $0.4Li_2MnO_3–0.6LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ During First Discharge Process

Yasushi Idemoto [a,b,*], Ryo Yamamoto [a], Naoya Ishida [a,b], Naoto Kitamura [a,b]

[a] *Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda-shi, Chiba 278-8510, Japan*
[b] *Division of Ecosystem Research, Research Institute for Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda-shi, Chiba 278-8510, Japan*

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ABSTRACT

In the present study, local structural changes in $0.4Li_2MnO_3–0.6LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$, a kind of the layered solid solution, were investigated during initial discharging, in order to clarify the formation mechanism for the stable reversible phase.

A pair distribution function (PDF) analysis was carried out using synchrotron X-ray total scattering data. The results indicated that rearrangement of Mn and Co took place from 3.3 to 4.6 V during the first discharge process. The results suggest that the formation of a stable reversible phase took place around 3.3 V during this process. Fitting to the extended X-ray absorption fine structure at the absorption edges further confirmed the PDF results. The stable reversible phase was then used to examine the origin of the irreversible capacity generated during the first cycles. It was found that a structure is initially formed that can incorporate only about 70% of the Li associated with first charge capacity. However, at around 3.3 V during the first discharge process, a new structure that can incorporate about 83% of the Li is formed.

1. Introduction

The lithium-rich solid solution $Li_2MnO_3–LiMO_2$ (M = Mn, Ni, Co) has attracted considerable attention as a high-energy-density cathode material, since it exhibits a capacity of 200 mAhg^{-1} or higher when charged at 4.6 V or above [1–7]. However, during initial charging at around 4.4 V, loss of oxygen occurs, which leads to an irreversible capacity. Moreover, the complexity of the material's structure has generated considerable debate. $Li_2MnO_3–LiMO_2$ has a layered rock-salt type structure, and the main peaks observed in the powder X-ray diffraction pattern can be attributed to the space group *R-3m*. In the vicinity of $2\theta = 20°$ to $23°$, however, a broad peak associated with Li_2MnO_3 with the space group *C*2/*m* is present. The results of structural simulations, high-resolution transmission electron microscopy, and nuclear magnetic resonance have suggested that excess lithium is present in an orderly arrangement within the transition metal layers in the form of $LiMn_6$ or $LiMn_{6-x}M_x$ (M = Ni, Co), and causes the introduction of stacking faults [8–11].

For the systems $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ and zLi_2MnO_3-$(1-z)LiMO_2$, the authors have used neutron total scattering to investigate differences in the local structure for samples synthesized under different conditions, along with local structural analysis using the pair distribution function (PDF) method using neutron total scattering data [12],[13]. The research presented here focused on zLi_2MnO_3-$(1-z)Li(Mn,Ni,Co)O_2$ (z = 0.4). As described earlier, layered solid-solution cathode materials exhibit peculiar behavior during initial charging, and there has been a considerable amount of research on oxygen loss during this stage. However, there have been no reports on the mechanism involved in the reordering that occurs upon oxygen loss, nor on the formation of a stable reversible phase during the initial discharging process, which allows repeatable, stable charging and discharging to subsequently occur. Elucidation of this mechanism could provide guidance for improving the cycling and rate characteristics, and for mitigating the reduction in discharge potential, all of which remain issues with solid-solution cathode materials. In order to clarify the electrochemical behavior for two cycles and beyond, zLi_2MnO_3-$(1-z)Li(Mn,Ni,Co)O_2$ (z = 0.4) was synthesized and used as an electrode. Structural investigations were performed using neutron and synchrotron X-ray total scattering, and X-ray absorption fine-structure (XAFS) analysis, after initial charging, during the initial discharge process, and during a 2-cycle discharge process. In this study, by analyzing the data obtained during the initial discharge process, the mechanism involved in stable reversible phase formation after initial charging was elucidated from the perspective of the local structure.

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* Corresponding author. Tel.: +81 4 7122 9493; fax: +81 4 7125 7761.
E-mail address: idemoto@rs.noda.tus.ac.jp (Y. Idemoto).

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Table 1
Composition of the $0.4Li_2MnO_3$–$0.6LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ and discharged electrodes measured by the ICP (Total of metal composition is 2).

	Li	Mn	Ni	Co
Pristine	1.153(3)	0.509(2)	0.1695(4)	0.1678(8)
1st discharge 4.6 V	0.1893(9)	0.512(2)	0.1668(3)	0.1674(6)
1st discharge 3.8 V	0.492(1)	0.508(1)	0.1659(5)	0.1721(2)
1st discharge 3.5 V	0.627(2)	0.5092(7)	0.1655(2)	0.1712(4)
1st discharge 3.3 V	0.830(2)	0.5096(9)	0.1652(1)	0.1712(4)
1st discharge 2.0 V	0.907(4)	0.5120(4)	0.1669(4)	0.1678(3)

2. Experimental

2.1. Sample preparation

$0.4Li_2MnO_3$–$0.6LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ [$Li_{7/6}Mn_{3/6}Ni_{1/6}Co_{1/6}O_2$] was synthesized by coprecipitation. Lithium hydroxide monohydrate (98% to 102%, Wako Pure Chemical Industries, Ltd.) was dissolved in twice-distilled water, to which a manganese (II) nitrate (98%, Wako Pure Chemical Industries, Ltd.) solution, a nickel (II) nitrate (98%, Wako Pure Chemical Industries, Ltd.) solution, and a cobalt (II) nitrate (98%, Wako Pure Chemical Industries, Ltd.) solution, each at a concentration of 1 mol/l, were titrated to form a precipitate. The precipitate was dried for 2 days under suction filtration, and subsequently dried in a drier unit (100 °C) for 1 day to obtain the precursor. Based on the results of inductively coupled plasma atomic emission spectroscopy (ICP-AES), the degree of lithium deficiency with regard to the target composition was determined. To compensate for this deficiency, an appropriate quantity of lithium hydroxide monohydrate was added and preliminary firing was carried out in air at 650 °C for 15 h. The product was then pulverized, mixed, and fully fired in air at 900 °C for 15 h to yield the final sample.

2.2. Characterization and local structural analysis

The metallic content of the sample was determined by ICP-AES (ICPS-7500, ICPE-9000, Shimadzu Corporation). The XAFS analysis was performed at BL14B2 at SPring-8, and BL7C and BL9A at KEK, and the analytical programs were REX2000 (ver. 2.3) [14] and Athena (ver. 0.8.057) [15]. Artemis (ver. 0.8.012) [15] was employed for EXAFS fitting. Neutron total scattering analyses were conducted at NOMAD (SNS). We also performed a high-energy X-ray scattering experiment with an incident beam of 61.5 keV by BL04B2 at SPring-8, Japan. The incident X-ray intensity was monitored by an ionization chamber filled with Ar gas, and the scattered beam was detected by a Ge detector. The obtained data was corrected using a standard program [16]. The PDF analysis was performed using PDFgui (release 1.0) [17]. For the initial discharge processes, measurements were carried out at potentials of 4.6, 3.8, 3.5, 3.3, and 2.0 V.

2.3. Electrochemical measurement

A HS cell (Hosen Ltd.) was employed for electrochemical analysis. For the cathode, the prepared sample, acetylene black (AB) as a conductive agent, and polyvinylidene difluoride (PVdF) as a binder were kneaded in a weight ratio of 80:10:10. Using the dispersant N-methyl pyrrolidinone (NMP), the mixture was formed into a slurry, which was applied to Al foil and dried, compressed at approximately 40 MPa, and vacuum deaerated for use. Lithium metal was employed for the anode, a 1 mol/l $LiPF_6$-EC: DMC (volume ratio 1:2) solution (Kishida Chemical, Ltd.) for the electrolyte, and polypropylene (PP) films for separators. The foregoing parts were used to assemble a cell in a glove box under an argon atmosphere. A charge–discharge apparatus (HJR-110 m SM8, Hokuto Denko Corp.) was employed to conduct charge-

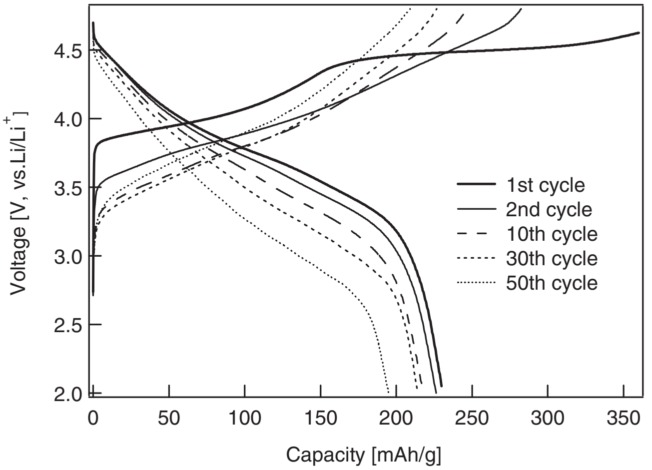

Fig. 1. Charge and discharge curves of 1st, 2nd, 10th, 30th, and 50th cycles of $0.4Li_2MnO_3$–$0.6LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$/Li cells.

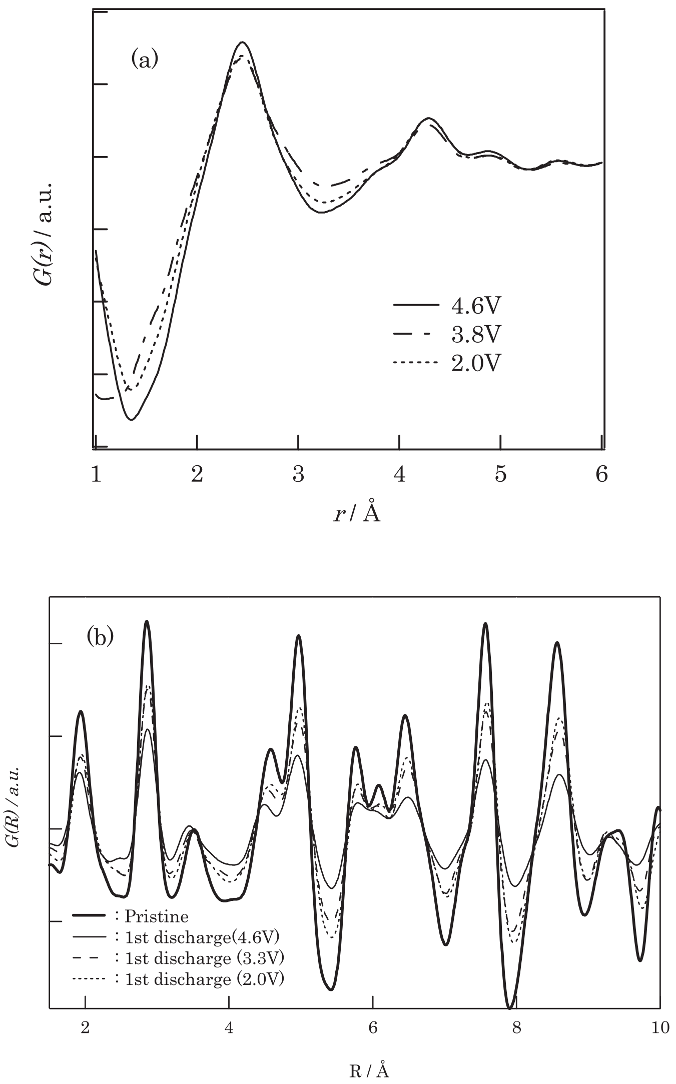

Fig. 2. Observed *G(r)* of total scattering in first discharge process.
(a) Neutron total scattering, (b) Synchrotron total scattering.