Study on the Li de-intercalate mechanism of the $LiNi_{1/2}Mn_{1/2}O_2$-based materials

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INTRODUCTION

$LiNi_{1/2}Mn_{1/2}O_2$-based materials are one of the promising cathode materials of lithium secondary battery. $LiNi_{1/2}Mn_{1/2}O_2$-based materials adopt hexagonal unit cells like $LiCoO_2$ and $LiNiO_2$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ displays a reversible capacity of 170 mAh/g in the voltage range 2.5 to 4.5 V [1]. In addition, these materials show the superior characteristics of a larger capacity than $LiMn_2O_4$ and better thermal stability than $LiNiO_2$. On the other hand, the structure and physical properties of the $Li_{1-y}Ni_{1/2}Mn_{1/2}O_2$-based materials are still ambiguous. Detailed information on the structure and the valence state of the cations in $Li_{1-y}Ni_{1/2}Mn_{1/2}O_2$-based one is very important in order to improve the electrochemical properties of $LiNi_{1/2}Mn_{1/2}O_2$-based material and, therefore, the relationships between the chemical composition, the structure, and electrochemical properties were studied in this study.

EXPERIMENTAL

$Li_{1-y}Ni_{1/2}Mn_{1/2}O_2$-based materials were synthesized in air at 1223-1273 K for 12-24 h and de-lithiated samples were electrochemically prepared using coin-type cells with Li/1M $LiPF_6$ in EC:DEC(1:1)/samples. The *M* (*M* = Ni, Co, Mn, Ti) valence states of samples were determined by the *M K*-edge XANES spectra. Structure and physical property changes were investigated by synchrotron X-ray diffraction (λ = 0.5 Å), neutron diffraction, *M K*-edge EXAFS measurements.

RESULTS AND DISCUSSION

$LiNi_{1/2}Mn_{1/2}O_2$ was a single-phase and adopted the α-$NaFeO_2$ structure. Structural analysis using synchrotron and neutron diffraction data demonstrated that the lattice parameters of $LiNi_{0.5}Mn_{0.5}O_2$ are a = 2.892 Å and c = 14.302 Å and that the chemical composition can be expressed referring to the Wyckoff positions 3*a* and 3*b* as $[Li_{0.91}Ni_{0.09}]_{3a}[Li_{0.09}Mn_{0.5}Ni_{0.41}]_{3b}O_2$. In charging process, the structure of charged $Li_{1-y}Mn_{0.5}Ni_{0.5}O_2$ (y = 0.5) was determined, corresponding to the composition for showing rechargeable capacity of ca. 140 mAh/g. The results show that divalent nickel metal is oxidized to trivalent after charging, in association with the phase transition from hexagonal (*R3m*) to monoclinic (*C2/m*) symmetry [2]. The crystal structures and electron density distributions of the layered oxide $Li_{1-y}Ni_{0.5}Mn_{0.5}O_2$ (y = 0.5) was studied using a combination of Rietveld analysis of high-resolution synchrotron powder X-ray diffraction data and the maximum entropy method (MEM). Structural analysis revealed that $Li_{1-y}Ni_{0.5}Mn_{0.5}O_2$ (y = 0.5) has the lattice parameters a = 4.934 Å, b = 2.852 Å, c = 5.090 Å, β = 108.8° and adopts the space group *C*2/*m*. The chemical formula can be expressed as $[Ni_{0.0815}]_{2a}\{Li_{0.5}Ni_{0.0115}\}_{4i}[Mn_{0.5}Ni_{0.407}\square_{0.093}]_{2d}O_2$ [3]. The electron density map obtained using MEM clearly shows that most of the Li ions migrate from the octahedral 2*a* site to the tetrahedral 4*i* site during Li de-intercalation.

$LiNi_{1/2}Mn_{2/5}Ti_{1/10}O_2$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ were also single-phase and adopted the α-$NaFeO_2$ structure. Structural analysis using synchrotron and neutron diffraction data demonstrated that the lattice parameters of $LiNi_{1/2}Mn_{2/5}Ti_{1/10}O_2$ are a = 2.895 Å and c = 14.317 Å and that the chemical composition can be expressed referring to the Wyckoff positions 3*a* and 3*b* as $[Li_{0.88}Ni_{0.09}Ti_{0.03}]_{3a}[Li_{0.12}Ni_{0.41}Mn_{0.40}Ti_{0.07}]_{3b}O_2$ and that the lattice parameters of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ are a = 2.860 Å and c = 14.22 Å and that the chemical composition can be expressed referring to the Wyckoff positions 3*a* and 3*b* with space group *R3m* as $[Li_{0.97}Ni_{0.03}]_{3a}[Li_{0.03}Mn_{0.33}Ni_{0.30}Co_{0.33}]_{3b}O_2$ [4]. The Li de-intercalate mechanism of these materials will be compared with $LiNi_{0.5}Mn_{0.5}O_2$ and, furthermore, the relationships between the structure changes and their electrochemical properties will be discussed.

References

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