



Short communication

Electronic structures of partially fluorinated lithium manganese spinel oxides and their electrochemical properties

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ABSTRACT

Partially fluorinated lithium manganese spinel oxides (LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{4-x}F_x) were prepared by solid-state reaction. Relationship between the electronic structures of LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{4-x}F_x and their electrochemical properties were investigated. X-ray absorption near-edge structure (XANES) of Mn K-edge showed that the absorption edge shifted to lower energy with increasing F⁻ content, which indicated decrease of the Mn average oxidation state. Discharge capacity at first cycle was increased by decrease of the Mn average oxidation state with increasing F⁻ content.

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1. Introduction

Practical application of lithium-ion batteries to HEV or EV requires higher energy density, safety, and durability. LiMn₂O₄ spinel oxide is one of the candidates for the positive electrode materials for lithium-ion batteries as an alternative to LiCoO₂ because of its low cost, low toxicity, high energy density, and so on. However, capacity fading during charge–discharge cycle is one of problems. It is thought that this phenomenon is caused by disproportional dissolution of Mn³⁺ into the electrolyte, unstable structure at charge state, or local structural distortion of MnO₆ octahedra by Jahn–Teller effect [1,2]. In order to improve the cycle performance, several groups have investigated the electrochemical properties of metal-substituted lithium manganese spinel oxides LiMn_{2-y}M_yO₄ (M: Li or 3d-transition metals such as Ni²⁺) [3–7]. However, this substitution increases the average oxidation state of Mn, leading to the decrease of the reversible capacity. Increase of Mn³⁺ is directly linked with the increase of the reversible capacity. Hence, decrease of the average oxidation state of Mn with remaining of stability of metal-substituted lithium manganese spinel oxides should be effective to improve the electrochemical properties of lithium

manganese spinel oxides. Therefore, the partial substitution of F⁻ for O²⁻ might be one of the solutions for this problem. For example, spinel oxyfluorides such as LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{3.8}F_{0.2} was reported to show superior electrochemical performance compared to LiMn₂O₄ by Choi and Manthiram [8,9]. However, relationships between the electronic structures and their electrochemical properties have not been clarified. Electronic structures of positive electrode materials are important to reveal the electrochemical properties.

The purpose of this study is to reveal relationship between the electronic structures and their electrochemical properties. The electronic structures of the partial fluorinated metal-substituted lithium manganese spinel oxides investigated by X-ray absorption near-edge structure (XANES) technique. In this paper, the relationship between electronic structures and first discharge capacities of LiMn_{1.8}Li_{0.1}Ni_{0.1}O_{4-x}F_x was discussed.

2. Experimental

LiMn_{1.8}Li_{0.1}Ni_{0.1}O₄ was synthesized by solid-state reactions. Reagents Li₂CO₃ (99.99% Kojundo Chemical Lab Industries), NiO (99.9% Furuuchi Chemical Industries), and Mn₂O₃ (preheated MnCO₃ (99.99% Kojundo Chemical Lab Industries) at 600 °C for 48 h) were used as starting materials. Mixtures were heated at 800 °C for 2 days in air, and cooled with a rate of 0.5 °C min⁻¹.

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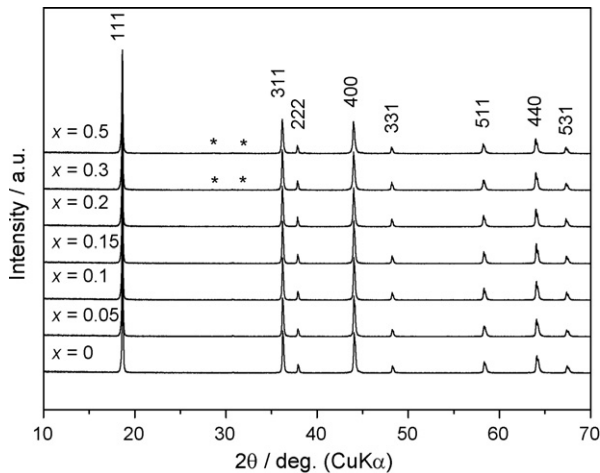


Fig. 1. XRD patterns of $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-x}\text{F}_x$ ($x=0, 0.05, 0.1, 0.15, 0.2, 0.3, 0.5$). The reflections marked with * refer to impurity phase.

For partial fluoridations, the obtained materials and NH_4HF_2 were mixed, and then heat-treated at 450°C for 5 h in air.

Powder X-ray diffraction technique (RINT-2200 V, Cu $K\alpha$) was used to examine the crystal structure of resulting materials. XAS experiments at Mn K-edge were performed to investigate local and electronic structures of resulting materials on BL-7C at Photon Factory, High Energy Accelerator Research Organization Tsukuba, Japan.

Charge–discharge measurements (1/24C) were carried out between 3.5 and 4.3 V vs. Li/Li^+ at room temperature using a three-electrode cell. Li foil was used as a counter and reference electrodes, and 1 mol m^{-3} LiClO_4/PC was used as an electrolyte solution. A working electrode was a mixture of 75 wt.% active material, 20 wt.% acetylene black, and 5 wt.% PVdF onto an aluminum current collector.

3. Results and discussion

XRD patterns of $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-x}\text{F}_x$ ($x=0.0, 0.05, 0.1, 0.15, 0.2, 0.3, 0.5$) are shown in Fig. 1. Under our experimental condition, only spinel phase was observed in the composition range from $x=0$ to $x=0.2$. More than $x=0.2$, impurity peak at around $2\theta=30^\circ$ was observed. Fig. 2 shows the variation of lattice parameter vs. F^-

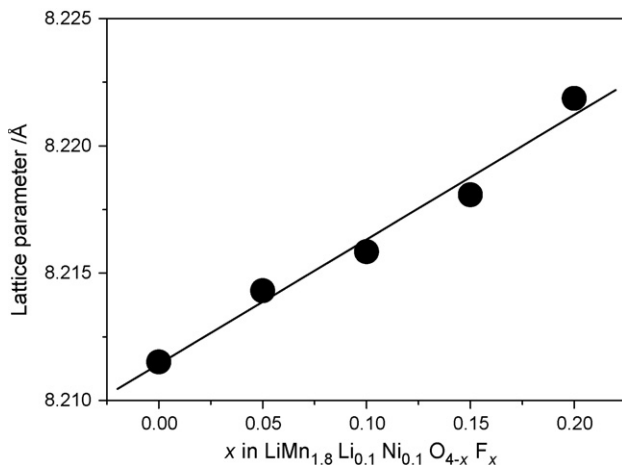


Fig. 2. Plots of lattice parameter against x in $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-x}\text{F}_x$ ($x=0, 0.05, 0.1, 0.15, 0.2$).

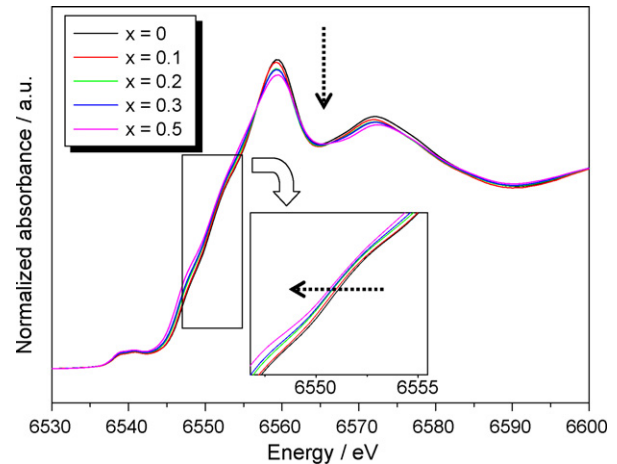


Fig. 3. XANES spectra of Mn K-edge in $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-x}\text{F}_x$.

content. As shown in this figure, lattice parameter increased monotonically with increasing F^- content range from $x=0$ to $x=0.2$. Based on the Shannon's ionic radius, this result indicates that Mn^{4+} (0.670 \AA [10]) was reduced to Mn^{3+} (0.785 \AA [10]) by the partial substitution of F^- for O^{2-} .

It is known that the XANES provides useful information about electronic configurations and oxidation states of certain atoms. Fig. 3 shows the Mn K-edge XANES spectra of $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-x}\text{F}_x$ ($x=0, 0.1, 0.2, 0.3, 0.5$). In the Mn K-edge XANES spectra, the main peak appears about 6550 eV. This peak represents the electron transition from 1s to 4p [11]. The shape of Mn K-edge spectra did not depend on the composition x , hence Mn ions is considered to exist in the octahedral 16d site [11]. The absorption edges were shifted to lower energy with increasing F^- content. This result indicates that the partial substitution of F^- for O^{2-} reduced the Mn average oxidation state, which is corresponding with the result of the variation of lattice parameter. The small pre-edge peak around 6540 eV represents the transitions of the 1s electron to an unoccupied 3d orbital of Mn ions. Although it is an electronic dipole-forbidden transition in an ideal octahedral symmetry, the appearance of the weak absorption peak is because of pure electronic quadruple coupling and the noncentrosymmetric environment of the slightly distorted MnO_6 octahedral site.

Fig. 4 shows the first discharge curves of LiMn_2O_4 and $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-x}\text{F}_x$ ($x=0, 0.1, 0.2$). Discharge capacities of

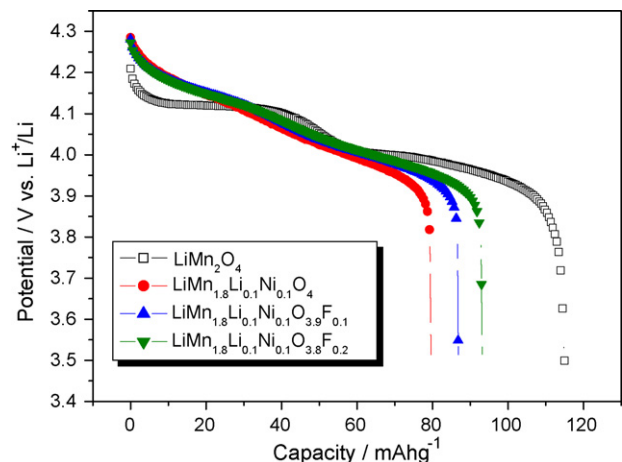


Fig. 4. First discharge curves of LiMn_2O_4 and $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-x}\text{F}_x$ ($x=0, 0.1, 0.2$).

$\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-x}\text{F}_x$ were smaller than that of LiMn_2O_4 as expected. As shown in this figure, discharge capacity of $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-x}\text{F}_x$ increased monotonically with increasing F^- content. This result shows that the increase of discharge capacity is because of the decrease of the Mn average oxidation state, which is corresponding with the result of XRD results and XANES spectra.

4. Conclusion

Spinel phase $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-x}\text{F}_x$ were obtained by solid-state reaction. The absorption edges of XANES were shifted to lower energy with increasing F^- content. This result revealed that the partial substitution of F^- for O^{2-} decreased Mn average oxidation state. It is considered that partial substitution of F^- for O^{2-} is effective to enhance the discharge capacity of nickel-substituted lithium

manganese spinel oxide ($\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_4$). Cycleability and local structure of $\text{LiMn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}\text{O}_{4-x}\text{F}_x$ will be reported in the future.

References

- [1] J. Gummow, A. deKock, M.M. Thackeray, *Solid State Ionics* 69 (1994) 59.
- [2] Y. Xia, Y. Zhou, M. Yoshio, *J. Electrochem. Soc.* 144 (1997) 2593.
- [3] M. Kaneko, S. Matsuno, T. Miki, M. Nakayama, H. Ikuta, Y. Uchimoto, M. Wakihara, K. Kawamura, *J. Phys. Chem. B* 107 (2003) 1727.
- [4] L. Guohua, H. Ikuta, T. Uchida, M. Wakihara, *J. Electrochem. Soc.* 143 (1996) 178.
- [5] F.L. Cras, D. Bloch, M. Anne, P. Strobel, *Solid State Ionics* 89 (1996) 203.
- [6] A.D. Robertson, S.H. Lu, W.F. Averill, W.F. Howard Jr., *J. Electrochem. Soc.* 144 (1997) 3500.
- [7] N. Hayashi, H. Ikuta, M. Wakihara, *J. Electrochem. Soc.* 146 (1999) 1351.
- [8] W. Choi, A. Manthiram, *Electrochem. Solid-State Lett.* 5 (2006) A245.
- [9] W. Choi, A. Manthiram, *J. Electrochem. Soc.* 154 (2007) A614.
- [10] R.D. Shannon, *Acta Crystallogr.* A32 (1976) 751.
- [11] H.S. Park, S.J. Hwang, J.H. Choy, *J. Phys. Chem. B* 105 (2001) 4860.