

## Local Structure of Spinel Oxides for the Cathode of Lithium Ion Battery

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The partial substitution of  $\text{LiMn}_2\text{O}_4$  has been improved the electrochemical property especially for cycle performance. In order to elucidate the performance, we estimate the local crystal structure of spinel type solid solution,  $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$  ( $M=\text{Al,Co,Cr}$ ) using Molecular Dynamics (MD) simulation and extended X-ray absorption fine structure (EXAFS), respectively.

The stoichiometric compounds  $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$  ( $M=\text{Al,Co,Cr}$ ) were synthesized by solid-state reaction. Rietveld analysis was carried out for the prepared samples at room temperature using the RIETAN profile refinement program[1]. X-ray absorption measurements were carried out at the Mn K-edge. The data were recorded in transmission mode at the BL-9A beam line synchrotron facility, Japan, using Si[111] double monochromators and Rh-coated mirror for harmonic rejection. The parameters for MD calculation were evaluated by try and error method using the experimental data of lattice parameter in each temperature. The MD simulation was performed using MXDORTO code developed by Kawamura[2]. The cell for the simulation was composed of 7000 particles (5 x 5 x 5 unit cells) for 15,000 steps with a time step of 2 fs.

The MD simulation was carried out using a partially ionic model. The compositional dependence of the lattice parameters and the thermal expansion coefficients of  $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$  ( $M=\text{Al,Co,Cr}$ ) obtained by the MD simulation show good agreement with the experimental values. The peak top of each p.c.f. curve refers to the bond length of M-O. In the bond length of M-O, there are following relation;  $\text{Mn}^{3+}\text{-O} > \text{Cr}^{3+}\text{-O} > \text{Al}^{3+}\text{-O} > \text{Co}^{3+}\text{-O} > \text{Mn}^{4+}\text{-O}$ . This behavior can be understood from the ionic radii[3]. The peak width of the pair correlation function (p.c.f.) curve for  $\text{Mn}^{4+}\text{-O}$  decreases with  $y$  in  $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$  ( $M=\text{Al,Co,Cr}$ ). The decreasing of the standard deviation means the depressing of geometrical distortion in the lattice, and more concretely it means that replacement of  $\text{Mn}^{3+}$  by  $\text{Al}^{3+}$ ,  $\text{Co}^{3+}$  or  $\text{Cr}^{3+}$  leads to the suppression of the distortion of  $\text{MO}_6$  octahedron.

To evaluate the octahedral distortion experimentally, XAS (X-ray absorption spectroscopy) measurements were carried out. Fourier-transformed (FT) EXAFS oscillations for Mn K-edge for  $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$  ( $M=\text{Al,Co,Cr}$ ) are shown in Fig. 1. The first two intense peaks around 1.5 Å and 2.5 Å result from simple backscattering of the photoelectron from the first coordination shell of six oxygen atoms and the second coordination shell of cations occupying the six neighboring 16d octahedral sites. The changes of peak intensity mainly depend on the distortion of  $\text{MO}_6$  ( $M=\text{Al,Co,Cr}$  and Mn) octahedron. With increasing of the M ( $M=\text{Al,Co,Cr}$ ) content, the intensity of the FT spectra of Mn K-edge increased. Therefore the local distortions around Mn ions were depressed by introducing the M ( $M=\text{Al,Co,Cr}$ ) ions.

We also investigated the bond strength by

analyzing the lattice energy change with displacement of  $\text{M}^{3+}$  ion by MD simulation in  $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ . The potential curve was fitted with the following equation[4] and the force constant of the bond,  $k$  was evaluated.

$$U(x) = \frac{1}{2}kx^2 - gx^3 - fx^4$$

The  $k$  values for each direction in  $\text{LiCrMnO}_4$  are larger than those in  $\text{LiMn}_2\text{O}_4$ . Therefore it is concluded that the  $\text{M}^{3+}\text{-O}$  bond in  $\text{LiCrMnO}_4$  is stronger than that in  $\text{LiMn}_2\text{O}_4$ .

The increasing of the bond strength and decreasing of local distortion may be the reason of the improvement of cycle ability in substituted spinels.

### References

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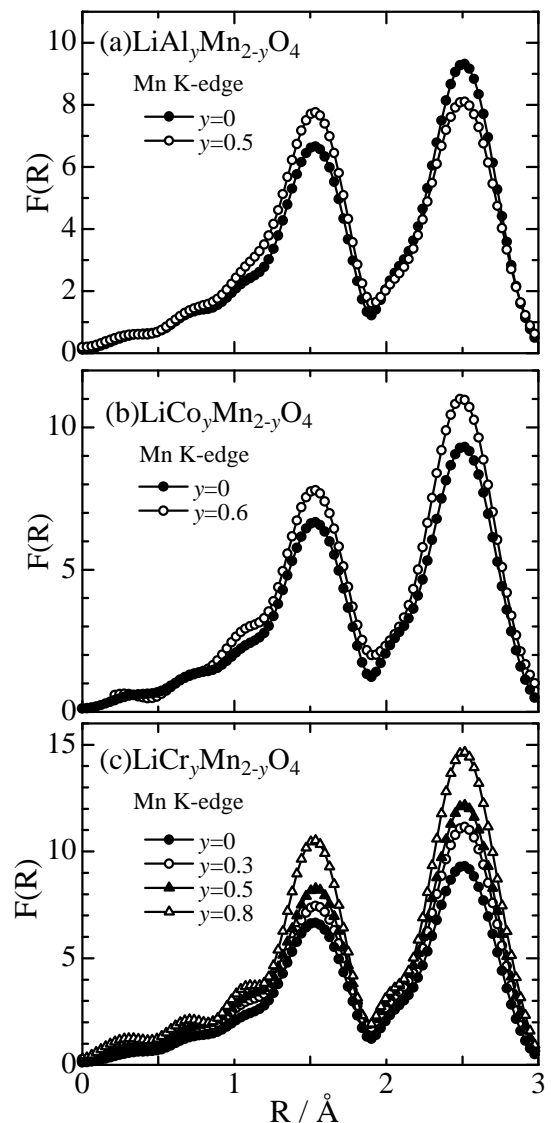


Fig. 1 EXAFS spectra for Mn K-edge of  $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$  ( $M=(a)\text{Al}$ , (b)Co and (c)Cr)