Lithium Ion Conduction in $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$

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$LiMn_2O_4$ based spinel type oxides are one of the most promising cathode materials used in lithium ion batteries because their high rate property, low cost and low toxicity. To improve their cycle performance, the charge-discharge property of manganese substituted spinels of $LiM_yMn_{2-y}O_4$ (M=Cr, Co, Ni etc). These spinels show a slight decreased capacity on the 4.1 V plateau compared with parent $LiMn_2O_4$, however, improved cycle life was obtained for Cr, Ni and Co doped spinels[1].

Furthermore, many researchers have pointed out that Co, Ni, Cr and Cu doped spinels show reversible redox process at potentials above 4.5 V. $LiNi_{0.5}Mn_{1.5}O_4$ is interesting cathode active material because the valence of Mn should be +4, and accordingly, direct oxidation of Ni^{2+} to Ni^{4+} occurs depending upon lithium deintercalation near at 4.7 V plateau.

In the present study, stoichiomertic $LiNi_{0.5}Mn_{1.5}O_4$ ordered-type spinel structure ($P4_332$) and non-stoichiometric $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ with disoredered-type spinel structure (Fd-3m) by controlling oxygen partial pressure were prepared at high temperature. The remarkable high rate property was observed in the ordered-type structure. The results agree well with that of Kim et al[2].The effect of the difference of diffusion path of lithium ion for discharge-charge rate property will be discussed by considering Coulomb potential estimation for both ordered-type and disordered-type structures using MD calculation.

Stoichiometric $LiNi_{0.5}Mn_{1.5}O_4$ was prepared by solid-solid reaction using Li_2CO_3, Mn_3O_4 and $NiC_2O_4\ 2H_2O$ at 820 °C and then annealed at 700 °C under oxygen atmosphere for 2 days. $LiNi_{0.5}Mn_{1.5}O_{4-\delta}$ were synthesized at 820 °C under controlled P_{o2} . After equilibrium, each sample was quenched. The defect amount was estimated from the weight difference before and after oxidation at 700 °C under the oxygen atmosphere. The samples were characterized by powder XRD and ND (KENS;Vega) techniques. Electrochemical lithium deintercalation was done by galvanostatic technique with various current densities. The XAFS measurements for the Ni and Mn K-edge spectra were carried out by transmission mode at BL-7C, Photon Factory, KEK, Japan. MD simulation was done using partially ionic model by following equation:

$$U_{ij} = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6} + D_{ij}\left\{\exp\left[-2\beta_{ij}(r_{ij} - r_{ij}^*)\right] - 2\exp\left[-\beta_{ij}(r_{ij} - r_{ij}^*)\right]\right\} \quad \textbf{(1)}$$

Parameters in eq(1) are summarized in Table 1. The valence of Mn^{4+} and Ni^{2+} was set as +2.20 and +1.10, respectively.

The nonstoichiometric samples showed higher rate property than the stoichiometric sample. Fig. 1 shows diffusion pass of Li both disordered (a) and ordered (b) structures. Disordered structure has the diffusion path in tetrahedral site and following octahedral site like, 8a-16c-8a-16c, while in ordered structure, 8c-4a and 8c-12d are distributed alternately.

Fig. 2 shows the results of Coulomb potential calculation for ordered and disordered diffusion paths of Li. Coulomb potential shows a maximum at octahedral vacant site. From the data, the order of easier diffusion can be estimated as follows: 8c-4a>8a-16c>8c-12d. The diffusion of Li in the ordered state seems to be more difficult than the ordered state. The MD simulation supports our experimental results.

References

[1] G. Li, H. Ikuta, T. Uchida and M. Wakihara, J. Electrochem. Soc., 1996, 143, 178.
[2] J. H. Kim, S. T. Myung, C. S. Yoon, S. G. Kang and Y. K. Sun, Chem. Mater., 2004, 16, 906.

	z	*a*	*b*	*c*		*D*	b	g*
O^{2-}	-1.2125	1.9265	0.180	40.91				
Mn^{4+}	2.2000	0.9501	0.100	0.00	Mn^{4+}-O	15.04	2.0	1.91
Ni^{2+}	1.1000	0.7346	0.100	0.00	Ni^{2+}-O	11.20	2.0	2,07
Li^+	1.0000	1.0010	0.080	1.64				

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Table 1 Parameters for partial ionic model.

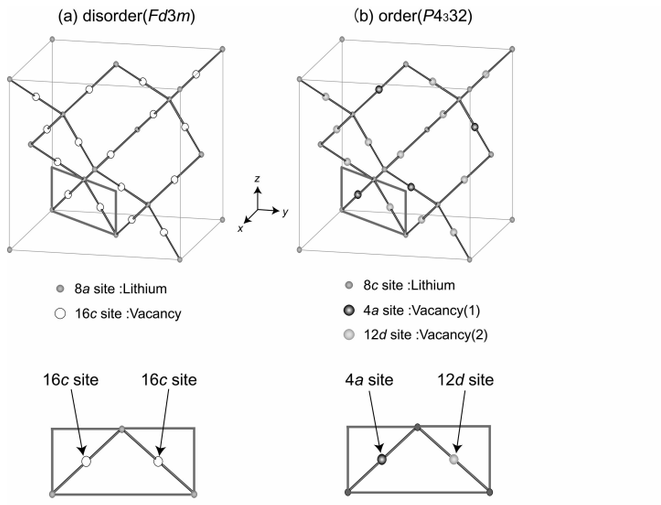

Fig.1 Diffusion path for (a) disorderd (b) ordered $LiMn_{1.5}Ni_{0.5}O_4$.

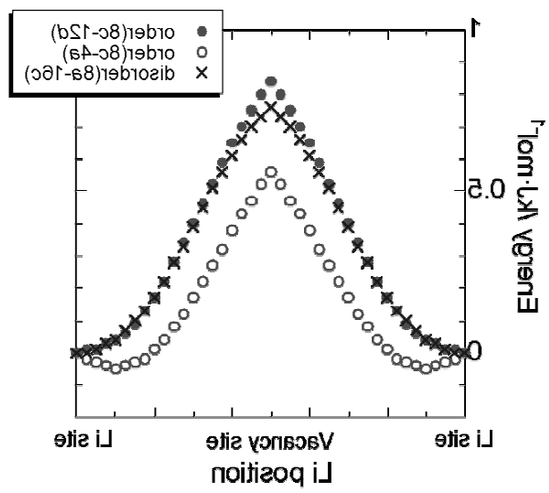

Fig. 2 Coulomb potential of diffusion path for Li-ion in ordered and disordered spinel structure.