Electronic States of $\text{Li}_y\text{Mn}_{2-x}\text{M}_x\text{O}_4$ ($\text{M} = \text{Mn, Mg, Ni, Co}$) as a Cathode Active Material for Li Secondary Battery by First-Principles Calculation using DV- $X\alpha$ Method

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We investigated the electronic states of $\text{Li}_y\text{Mn}_{2-x}\text{M}_x\text{O}_4$ ($\text{M} = \text{Mn, Mg, Ni, Co}$) as cathode active materials for the 4 V class lithium secondary battery. We calculated the electronic states of $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ ($\text{M} = \text{Mn}$; $y = 0$, Mg, Ni ; $y = 0.5$, Co ; $y = 0.25$) using first-principles calculations by the DV- $X\alpha$ method. The net charge of each atom, and the bond overlap populations of Mn-O and M-O were calculated. The strong covalency between Mn and O existed in the Li defect model and $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ ($\text{M} = \text{Mg, Ni, Co}$). The bonding change in Mn-O is small and maintained the spinel structure during the charge-discharge process by substitution of Mn with M ($= \text{Mg, Ni, Co}$).

Key Words : DV- $X\alpha$ Method, Li Secondary Battery, Cathode Active Material, Lithium Manganese Oxide

1 Introduction

LiCoO_2 as a cathode active material for lithium secondary batteries is expensive and cobalt is toxicity. LiMn_2O_4 has attracted attention as a promising cathode active material because of its advantage of low cost and low toxicity. A problem in the practical use of LiMn_2O_4 is that capacity fading occurs with charge-discharge cycles in the 4 V region particularly at high temperature. One of the main factors of these problems is the dissolution of manganese into the electrolyte solution with the insertion and removal of Li from the structure due to the weak Mn-O bond.¹⁾ Another factors in LiMn_2O_4 , where the average valence of Mn is 3.5, a tetragonal unit cell distortion has been found since, Mn^{3+} is a Jahn-Teller ion.²⁾ In order to improve the cycle performance, recent work is to substitute another metal for part of the Mn with M ($\text{M} = \text{Ti, Ge, Fe, Co, Zn, Ni, Ga, Cu, Mg, Cr, Li, Al}$).³⁻⁸⁾ We recently investigated the relation between the properties, thermodynamics stability and electrode performances of $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ ($\text{M} = \text{Mn, Li, Mg, Zn}$).⁹⁻¹²⁾ It is reported that the capacity fading decreased and good cycle performance is obtained from the Mn substituted with M at 25°C and 50°C. This means that the cycle performance at 25°C and 50°C is controlled by the same factor. Furthermore, it is mentioned that the capacity fading decreased and was thermodynamically stabilized with the increasing M content. An improvement in the cycle performance was the observed with an increase in the M content. We also investigated the relation between the crystal structures determined by neutron diffraction, the strength of the covalent bonding of Mn-O, M-O by the DV- $X\alpha$ method,^{13,14)} and electrode performances of $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ ($\text{M} = \text{Mn, Mg, Al, Co, Ni, Zn}$) at room temperature and high temperature.^{11,15)}

In this study, we investigated the electronic states of $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ ($\text{M} = \text{Mn, Mg, Co, Ni}$) during the charg-

ing process. We estimated the ionicity, the bond overlap population (BOP), density of states, and electron density distribution of these materials using the first-principles calculation by the DV- $X\alpha$ method.

2 Experimental

Electronic states calculations have been carried out by the DV- $X\alpha$ method on model clusters. The cluster model is a spinel cubic representation of $\text{LiMn}_{1.75}\text{M}_{0.25}\text{O}_4$ ($\text{M} = \text{Mn, Mg, Co, Ni}$) and its space group is $Fd3m$. The M ion is located at the center of the model and consists of 83 atoms within the circumference of a 0.6 nm diameter. Next, $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ ($\text{M} = \text{Mn, Mg, Co, Ni}$), which is the after-charging model, used the same location, but some Li was removed. The Li determined content will be mentioned later. The average valence of Mn for $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ is 4 when the limit of Li removal uses as 4 V class Li secondary battery. Accordingly, M put the Madelung potential on the surroundings of the model, which are Mn_2O_4 consists of 69 atoms and lattice parameter, a is 0.804 nm, $\text{Li}_{0.5}\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ ($\text{M} = \text{Mg, Ni}$) consists of 73 atoms and a are 0.812 nm ($\text{M} = \text{Mg}$), and 0.813 nm ($\text{M} = \text{Ni}$), and $\text{Li}_{0.25}\text{Mn}_{1.75}\text{Co}_{0.25}\text{O}_4$ consists of 77 atoms and a is 0.808 nm. From the results of the calculation by Mülliken population analysis, the net charge of Mn, M, and O, BOP of Mn-O and M-O, the density states of each atomic orbital and the electronic density of the (100) plane were also examined.

3 Results and Discussion

The net charge of Mn, M and O in $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ are shown in Table 1. The results using the two kinds of model clusters shows (a) $y = 1$ [before charge],¹⁵⁾ and (b) Mn_2O_4 , $\text{Li}_{0.5}\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ ($\text{M} = \text{Mg, Ni}$), and $\text{Li}_{0.25}\text{Mn}_{1.75}\text{Co}_{0.25}\text{O}_4$ [Li defect models] in Table 1. The Mn ionicity is a little low when part of the Mn is substituted

Table 1 Results of net charge of atom for (a) $\text{LiMn}_{1.75}\text{M}_{0.25}\text{O}_4^{12)}$ and (b) $\text{Li}_2\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$

(a)			
M	Mn	M	O
Mn	2.128	—	-0.835
Mg	2.116	1.673	-0.842
Co	2.103	2.029	-0.841
Ni	2.084	1.874	-0.849
(b)			
M	Mn	M	O
Mn	1.780	—	-0.351
Mg	1.708	1.577	-0.311
Co	1.718	1.774	-0.491
Ni	1.773	1.781	-0.440

with M (=Mg, Co, Ni) in (b), and the same tendency was obtained in (a). Particularly, the Mn ionicity is low for Mn substituted with Co and Mg in (b). The ionicity of Mn, M and oxygen in (b) are lower than those in (a). Figure 1 shows the overlap population of Mn-O for $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$. The energy level defined the Highest Occupied Molecular Orbital (HOMO) as 0 eV. From the comparison of the overlap population of Mn-O for $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ and $\text{LiMn}_{1.75}\text{M}_{0.25}\text{O}_4$,¹⁵⁾ the energy level of Mn-O in the Li defect model $\text{Li}_{0.25}\text{Mn}_{1.75}\text{Co}_{0.25}\text{O}_4$ shifts from $-1.0\text{ eV} \sim -7.5\text{ eV}$ ¹⁵⁾ to $-1.0\text{ eV} \sim -10.0\text{ eV}$. The area of bonding of Mn_2O_4 is greater than that of LiMn_2O_4 . On the other hand, $\text{Li}_{0.5}\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ (M=Mg, Ni) is not observed for a large change in the Li content. Next, Table 2 shows the BOP of Mn-O and M-O of $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ for (a) $y=1$ [before charge],¹⁵⁾ and (b) $y=0$ (M=Mn), $y=0.5$ (M=Mg, Ni), $y=0.25$ (M=Co)

Table 2 Results of bond overlap population of each atom for (a) $\text{LiMn}_{1.75}\text{M}_{0.25}\text{O}_4^{12)}$ and (b) $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$

(a)		
M	M-O	Mn-O
Mn	—	0.203
Mg	—	0.269
Co	0.230	0.253
Ni	0.219	0.253
(b)		
M	M-O	Mn-O
Mn	—	0.256
Mg	—	0.285
Co	0.254	0.270
Ni	0.235	0.256

[Li defect models]. The BOP of Mn-O of M=Mg, Co, Ni is slightly different from M=Mn in (b). The BOP of Mn-O of all in (b) is larger than those in (a). From the results, the covalency of Mn-O in the Li defect models is stronger than that of $\text{LiMn}_{1.75}\text{M}_{0.25}\text{O}_4$. The density states (DOS) of $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ (M=Co, Ni) are shown in Fig. 2. These orbitals show the covalency of the overlap population in Fig. 1. The DOS of Mn_{3d} and O_{2p} are broadened for $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ ($y<1$), and particularly, it is a remarkable tendency of M=Co. The overlap of Mn_{3d} and O_{2p} for $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ ($y<1$) is greater than that of $\text{LiMn}_{1.75}\text{M}_{0.25}\text{O}_4$. The O_{2p} orbital and M_{3d} orbital give the overlap, and the BOP of M-O for $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ ($y<1$) is larger than that of $\text{LiMn}_{1.75}\text{M}_{0.25}\text{O}_4$.

The electron density distributions of $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ ($y<1$) are shown in Fig. 3. From these results, the electrons concentrate between Mn and O. Moreover, the electrons also concentrate between each metal, M, and O of M=Ni, Co.

These results show that the covalency of Mn-O of $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ ($y<1$) is stronger than that of

Fig. 1 Overlap population of Mn-O for $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$. (a) M=Mn; $y=0$, (b) M=Mg; $y=0.5$, (c) M=Co; $y=0.25$, (d) M=Ni; $y=0.5$. ■: Bonding, □: Anti-bonding. **Fig. 2** Density of States of $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$. (a) M=Co; $y=1$, (b) M=Ni; $y=1$, (c) M=Co; $y=0.25$, (d) M=Ni; $y=0.5$. O_{2p} : — Mn_{3d} : - - - M_{3d} : ····

Fig. 3 Electron density map of $\text{LiMn}_{1.75}\text{M}_{0.25}\text{O}_4(100)$ plane calculated by DV- $X\alpha$ method. Contours are drawn from 0 to 640 e/nm^3 with the interval of $2^n \times 10 \text{ e/nm}^3$ (n : 0 to 6). (a) $\text{M} = \text{Mn}$; $y = 0$, (b) $\text{M} = \text{Mg}$; $y = 0.5$, (c) $\text{M} = \text{Co}$; $y = 0.25$, (d) $\text{M} = \text{Ni}$; $y = 0.5$.

$\text{LiMn}_{1.75}\text{M}_{0.25}\text{O}_4$. Moreover, the BOP of Mn-O keeps both $y = 1$ and $y < 1$ of substituted $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$ ($\text{M} = \text{Mg}$, Co , Ni) high, and the host structure is stable for both $y = 1$ and $y < 1$. On the other hand, the BOP of Mn-O is different between $y = 1$ and $y = 0$ in the nonsubstituted $\text{Li}_y\text{Mn}_2\text{O}_4$. Accordingly, the bonding change is small and maintains the spinel structure during the charge-discharge process for substituted $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$, and it should provide an effective cycle performance.

4 Conclusion

- (1) The host structure of the Li defect models is stable based on the results of the ionicity and BOP.
- (2) The covalency of Mn and O of the Li defect models

is stronger than that of $\text{LiMn}_{1.75}\text{M}_{0.25}\text{O}_4$.

- (3) The energy level of the overlap of Mn_{3d} and O_{2p} for the Li defect model is wider compared to that of $\text{Li}_y\text{Mn}_{1.75}\text{M}_{0.25}\text{O}_4$.
- (4) The bonding change is small and maintains the spinel structure during the charge-discharge process by substitution of Mn with M ($= \text{Mg}$, Ni , Co), and it provides an effective cycle performance.

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