Investigation on the Dissolution of Mn Ions from LiMn$_2$O$_4$ Cathode in the Application of Lithium ion Batteries: First Principle Molecular Orbital Method

Yongseon Kim, Jaehyuk Lim, and Shinhoo Kang

The dissolution phenomenon of Mn ions in LiMn$_2$O$_4$ (LMO) cathode material for lithium ion batteries (LIBs) was investigated by a first principle calculation using the discrete variational X$_a$ molecular orbital method. It was found that the oxidation number of Mn ions easily increases at high temperatures due to the empty levels of Mn 3d orbitals located in the vicinity of the Fermi energy level of LMO crystal. The changes of density of states (DOS) and Mn-O bonding properties with doping were examined. Analysis of DOS showed that the substitution of elements with a smaller oxidation number than Mn was found effective in keeping Mn ions at higher oxidation states. From the calculation of bonding properties, the dissolution of Mn was found to be strongly correlated with the covalent nature of Mn-O bond. Based on the results, we concluded that increasing the covalent character of Mn-O bond is effective to minimize the dissolution of Mn ions, along with suppressing the formation of Jahn-Teller-active Mn$^{3+}$ by inducing Mn ions at high oxidation state with proper selection of doping elements.

Introduction

Spinel LiMn$_2$O$_4$ (LMO) is drawing much attention as an alternative cathode material for lithium ion batteries (LIBs) because of its low material cost, environmental advantages, and safety compared with the LiCoO$_2$, which is widely used in current LIBs.$^{[11-25]}$ However, LMO shows fast capacity fading during cycling at high temperature, which has been an obstacle to its practical application. The problem has been ascribed to several possible factors such as dissolution of Mn$^{2+}$, Jahn-Teller distortion, and decomposition of electrolyte solution on the electrode.$^{[6-11]}$ Although the exact mechanism remains a matter of discussion, many research groups concur that dissolution of manganese into the electrolyte is the main factor.$^{[6,7,12-14]}$ Therefore, significant efforts have been made to reduce dissolution of Mn ions.

Doping is known to be an effective route. It is reported that substitution of Mn ions with other metals such as Li, Mg, Al, Cr, Co, Ni, Zn, Ga slows dissolution of Mn from the cathode into the electrolyte.$^{[15-27]}$ Many researchers have reported that the introduction of cations with a low oxidation number increases the oxidation state of Mn ions. This seems to prevent the generation of acids in the electrolyte solution or relieve Jahn-Teller distortion, resulting in the reduction of Mn dissolution.$^{[26,27,30]}$ Based on this interpretation, the investigations of doping effects have mostly been concentrated on the addition of the metal ions whose oxidation number is smaller than +3.5. However, several metal ions such as Y$^{3+}$ or In$^{3+}$ showed different behavior.$^{[31-33]}$ Doping these ions is reported to rather increase the dissolution of Mn ions although their oxidation number is under +3.5, while Al, which has the same oxidation number, is known to reduce the dissolution.$^{[19,20]}$ Moreover, In has a higher electronegativity than Al, which means that indium doping is expected to be more effective in inducing Mn ions be at higher oxidation states. Thus, the conventional interpretation seems to be insufficient explaining the exact mechanism of doping effect.

In this study, we investigated the dissolution of Mn ions from LMO using a first principle calculation. We discussed the dissolution of Mn ions and poor cyclic performance at high temperatures, in the light of the characteristics of density of states (DOS) of Mn 3d orbitals. Change of the bonding nature between Mn and O with doping of various cations was also checked. The calculation results were analyzed in relation to the experimental results reported by other research groups. The effects of dopants, and how to select a proper one, were discussed based on the first principle calculation results.

Methodology

Electronic properties were calculated by first principle calculation using discrete variational X$_a$ (DV-X$_a$) molecular orbital method.$^{[34]}$ This method approximates the exchange-correlation interaction with the X$_a$ potential that was proposed by Slater,$^{[35]}$ and solves the Schrödinger equation numerically through the Hartree–Fock–Slater method. There is no

[a] Y. Kim
Department of Materials Science and Engineering, Inha University, Incheon 402-751, Korea

[b] J. Lim, S. Kang
Department of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea
E-mail: shinkang@snu.ac.kr

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The electronic states of Mn ions, the cluster was arranged in the center of the cluster. Therefore, it is advantageous to locate the atoms of interest at generally low for the atoms located near the edge of clusters, width half maximum (FWHM) is 0.1 eV.

The cluster models used for the calculation are shown in Figure 1. In a cluster method, accuracy of the calculation is generally low for the atoms located near the edge of clusters, therefore it is advantageous to locate the atoms of interest at the center of the cluster. Thus, to get a higher accuracy for the electronic states of Mn ions, the cluster was arranged in sequence that a Mn ion (Mn1 in Table 1) is at the center with surrounding six O atoms (O1), then outer Mn atoms (Mn2), and Li atoms (Li1) followed by the surrounding O atoms (O2 – O5) in the cluster (Table 1). This $[\text{Li}_6\text{Mn}_7\text{O}_{38}]$ cluster was calculated assuming that all the Mn ions are at a high spin state. Although the model cluster deviates from stoichiometric composition of LMO, this does not seem to depreciate reliability of the method because outer atoms were excluded in the calculation. The outer atoms were just included in the cluster so that the inner atoms which were calculated may not have any broken bonds. Opposite magnetic moments were applied to Mn1 and Mn2, respectively, considering that LMO is an antiferromagnetic material. One of the Mn2 ions was substituted with other metal ions to study the doping effect. Electronic states and bonding characteristics of doped and undoped LMO cluster were calculated by the SCAT program of the DV-Xα software package. In case that high accuracy for Li ion is needed, Li-centered $[\text{Li}_5\text{Mn}_{12}\text{O}_{44}]$ cluster (Fig. 1b and Table 1) was used.

The DV-Xα method does not use periodic boundary conditions; instead, it analyzes the finite size of cluster models, which should be located inside a uniform Madelung potential field for the case of ionic bonding to reflect the electrostatic interaction with surrounding atoms. Madelung field can be constructed by positioning point charges equivalent to the effective charge of ions at their crystallographic sites. First, effective charge of each ion was assumed to be the same as its oxidation number, which is +3.5, −2.0, and +1.0 for Mn, O, and Li ions, respectively. Effective charges calculated with this first input were used making the Madelung potential field for the second run. This procedure was repeated until we can get a self-consistency: the input values of point charges for the Madelung potential field become identical to the calculated effective charges. The final values of effective charge were +1.4661 (Mn1), −0.9505 (O1), and −0.7440 (Li1). Thus, the Madelung potential field was composed with positioning these values of point charges at the atomic sites, and translating three unit cells for each direction.

### Results and Discussion

The DOS of LMO and MO (V$_0^1$Mn$_2$O$_4$) are calculated and part of them are presented in Figure 2. The band gap energies calculated were −0.1 and −2.3 eV, and the magnetic moments of Mn were 2.7 and 3.0 μ$_B$ for LMO and MO, respectively. Figure 2 shows the DOS of Mn$_1$ calculated using the Mn-centered cluster of Figure 1a. The DOS appears to be quasicontinuous near the Fermi level because it was assumed that each energy state shows Gaussian distribution with 0.1 eV of FWHM. In each figures, the energy level of highest occupied molecular orbital (HOMO) is positioned at 0 eV. Besides distinct t$_{2g}$ and e$_g$ levels of both up- and down-spin directions, there appear small energy states in the range of −8 to −4 eV in DOS of undoped LMO (Fig. 2a). Considering that their position

![Figure 1](image-url)
coincides with some of Mn 4s and Mn 4p projected DOS (Fig. 2c), they seem to be generated by ternary hybridization of Mn 3d, Mn 4s, and Mn 4p orbitals.

From Figure 2a which shows DOS of 3d orbitals in Mn, it can be noticed that the \( t_{2g} \) level of majority spin (down-spin side in the figure) is fully filled with electrons because it is located far below the HOMO level. However, only a small part of \( e_g \) of majority spin and \( t_{2g} \) of minority spin (up-spin side) are filled and \( e_g \) of minority spin is empty. In general, the electron configurations in an ideal high-spin Mn\(^{4+}\) ion is assumed that only the \( t_{2g} \) levels of one spin side are filled with three electrons, and there is one more electron in the \( e_g \) level of the same spin direction in high-spin Mn\(^{3+}\) or in the \( t_{2g} \) of opposite spin in low-spin Mn\(^{3+}\), respectively. Therefore, it seems that the electron configuration of Figure 1a is a mixed state of Mn\(^{3+}\) and Mn\(^{4+}\), showing that the Mn ion to be at a resonant state between \(+3\) and \(+4\). In addition, because \( t_{2g} \) of minority spin direction is partially filled, the Mn ion is not in a perfect high-spin state but a little low-spin character coexists.

This interpretation may be supported by the DOS of Figure 2b, which is the calculation result for \( V_x\text{LiMn}_2\text{O}_4 \) (MO) crystal. The cluster of MO was constructed by eliminating all Li atoms from the LMO crystal. This state is similar to that of the LMO cathode after full charge of the LIB cell. Figure 2b shows that only the \( t_{2g} \) of majority spin is filled while other energy levels are all empty because they lie far above the Fermi energy level. It indicates that the Mn ion in MO crystal is expected to be oxidation state of \(+4\) with a high-spin and this result is in accord with simple intuitive prediction for the oxidation number of Mn\(^{4+}\); it makes the total oxidation number of \( V_x\text{LiMn}_2\text{O}_4 \) zero.

It is expected that Mn ions in energetically activated LMO crystal are easily reduced to \(+3\) oxidation state. At higher temperatures, the number of electrons thermally activated over the Fermi energy (HOMO level of Figure 2a, the DOS diagram of ground state) would increase. It is likely that the activated electrons preferentially fill the empty 3d energy levels of Mn ions because the levels are located in the vicinity of the Fermi energy level. This process is schematically presented in Figure 2d. The formation of Mn\(^{3+}\) ions is known to be undesirable because it causes dissolution of Mn and Jahn-Teller distortion, which deteriorate cyclic performance of LIBs\(^{12-14}\). Therefore, the structure of DOS which is apt to generate \(+3\) oxidation state of Mn ions seem to be one of the main causes for poor high-temperature performance when LMO is used for cathode material of LIBs.

The changes in DOS of Mn 3d orbitals were calculated for the case that one of the Mn ions was substituted with other elements such as Mg, Co, Al, Ga, In, Y, or Sn and the results are shown in Figure 3. With doping of Mg \((+2)\), the relative position of Mn 3d levels is shifted to a high energy region. This makes only the \( t_{2g} \) levels of majority spin filled and other Mn

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Figure 2. DOS diagrams calculated by the DV-Xα molecular orbital method: a) Mn 3d projected DOS of LMO crystal, b) Mn 3d projected DOS of the crystal with all the Li extracted, c) Mn 4s and Mn 4p projected DOS, and d) schematic diagram showing change of the electron distribution in Mn 3d projected DOS with increase of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
Therefore, we also investigated if there are any changes in the bonding properties between Mn and O by calculating ionic and covalent character of the Mn-O bonding. The ionic character was estimated from electrostatic interaction between Mn and O, and the changes with doping are shown in Table 2. The electrostatic attraction was estimated using effective charge of each atom with and without doping obtained by the DV-Xα method (Supporting Information).

### Table 2. Changes of oxidation number of Mn, BOP, and electrostatic energy (ES) of Mn-O bond with doping.

<table>
<thead>
<tr>
<th>Doping effects</th>
<th>Change of Mn oxidation number</th>
<th>Change of BOP (Mn-O)</th>
<th>Change of ES (Mn-O)</th>
<th>Doping effects on Mn dissolution (reports)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMO</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>LMO: Mg</td>
<td>Increase</td>
<td>+15.1%</td>
<td>–9.60%</td>
<td>Effective [15,16]</td>
</tr>
<tr>
<td>LMO: Co</td>
<td>Increase</td>
<td>+1.77%</td>
<td>–2.42%</td>
<td>Effective [24,25]</td>
</tr>
<tr>
<td>LMO: Ni</td>
<td>Increase</td>
<td>+1.20%</td>
<td>–3.49%</td>
<td>Effective [27]</td>
</tr>
<tr>
<td>LMO: Al</td>
<td>Increase</td>
<td>+2.65%</td>
<td>–0.60%</td>
<td>Effective [19,20]</td>
</tr>
<tr>
<td>LMO: Ga</td>
<td>Increase</td>
<td>+3.68%</td>
<td>+3.24%</td>
<td>Effective [26]</td>
</tr>
<tr>
<td>LMO: In</td>
<td>Increase</td>
<td>–2.40%</td>
<td>+5.58%</td>
<td>Reversely effective [10]</td>
</tr>
<tr>
<td>LMO: Y</td>
<td>Increase</td>
<td>–0.69%</td>
<td>+3.70%</td>
<td>Reversely effective [37,33]</td>
</tr>
<tr>
<td>LMO: Sn</td>
<td>Decrease</td>
<td>–14.3%</td>
<td>+10.9%</td>
<td>Reversely effective [40]</td>
</tr>
<tr>
<td>LMO: Li,Mg</td>
<td>Increase</td>
<td>+6.79%</td>
<td>–1.12%</td>
<td>Effective [16]</td>
</tr>
</tbody>
</table>

Experimental results about doping effect of each element on Mn-dissolution reported by other research groups are added in the last column.

As for the covalent character, overlap population (OP) of DOS was used as a measure. Figure 4 shows OP diagrams of Mn-O, Mn-Mn, Mn-Li, and Li-O. The right and left part of each diagram shows the OP of the bonding and antibonding orbitals, respectively, and a minus sign is assigned to the antibonding side. The Fermi energy level is positioned at 0 eV in all the figures. From the summation of all the OP values under the Fermi energy, the bond overlap population (BOP) can be obtained, which is an indicator of covalent character of a chemical bonding. As expected, the calculation results show that there is a strong covalent bonding interaction between Mn and O, while Mn-Mn and Mn-Li has only weak interactions. BOP of Li-O (Fig. 4d) was found to be significantly small compared to that of Mn-O. This indicates that Li-O bonding is mainly ionic in the bonding nature.

The OP diagrams of several doped clusters with Mg, Al, or Sn substitution are presented as examples in Figure 5 with integrated BOP values in the diagrams. The changes in the BOP values with the introduction of dopants are summarized in Table 2. As mentioned above, the covalent interactions of Mn-Mn and Mn-Li are very small and the same is true for the doped cases. Therefore, only the change in BOP of Mn-O is presented in the table as an indicator of covalent character. Thus, in Table 2, the changes in the ionic and covalent characters of Mn-O bonding with doping are presented with references for comparison.

From Table 2, it is obvious that there exists a strong correlation between the covalency change and dissolution tendency of Mn ions reported: in all cases, it is found that the use of 3d levels empty. It implies that Mn ions would have a low possibility to be +3 with this configuration. On the other hand, the reverse is true for the substitution of Mn with Sn4+, therefore the average oxidation number of Mn would be smaller in this case. All these results agree well with existing interpretation that doping of elements with low oxidation number increases the oxidation number of Mn, suppressing the formation of Mn3+ ions. This may result in reduced dissolution of Mn ions and improved high-temperature cyclic performance.

However, the interpretation mentioned above could not explain the doping effects of elements whose oxidation number is +3. In Figure 3, it can be seen that positions of Mn 3d levels shifted to the same direction for Al3+, Ga3+, In3+, and Y3+ doping. But it is reported that doping of Al3+ and Ga3+ improves the dissolution problem and cyclic stability, whereas In3+ and Y3+ provides negative impact.[19,20,26,31,32] Moreover, if we consider the electronegativity of the elements used, doping of In (1.78 on the Pauling scale), whose electronegativity is larger than Al (1.61), would be more effective in increasing the oxidation number of Mn. In contrary, this expectation is contradicting to the results reported. Thus, the conventional interpretation in terms of the oxidation state does not provide a complete explanation for the doping effect and underlying mechanisms.
Figure 4. OP diagrams of LMO crystal: a) OP diagram of Mn1-O1 bonding, b) Mn1-Mn2, c) Mn1-Li1, and d) Li1-O1. a)–c) are calculated using Mn-centered cluster shown in Figure 1a, while d) calculated using Li-centered one of Figure 1b. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. OP diagrams of Mn1-O1 bonds: a) without doping, and b)–d) with doping of Mg$^{2+}$, Al$^{3+}$, and Sn$^{4+}$, respectively. Integrated OP values for bonding (right, plus sign) and antibonding (left, minus sign) under the Fermi energy are added in each diagram. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
dopants reduces the dissolution tendency of Mn as long as the covalency of the Mn-O bond is increased due to the presence of the dopant(s). This study shows that the BOP of Mn-O is increased when Li, Mg, Al, Ga, Co, or Ni is used. Codoping of Li and Mg also showed the same behavior. However, In, Y, and Sn, which are known to cause an enhanced Mn dissolution, exhibited a reduced covalent character of Mn-O bond.

In cases that doping increases the BOP, ionic character generally decreases. The only exception was doping of Ga, which increased both the covalent and the ionic character of Mn-O bond. Considering the experimental results that reported dissolution of Mn is reduced by doping Co or Ni, the Mn-dissolution is likely to depend on the nature of bonding properties rather than the overall bonding forces: the calculation results show that doping of Co or Ni does not seem to increase overall bonding strength because ionic attraction between Mn and O decreased although covalent interaction increased. This indicates that it may be desirable to improve the covalent nature in the Mn-O bond to minimize the Mn dissolution in the system.

The relation between the bonding nature and Mn-dissolution may be explained by general behavior of chemical bonds. It is known that solids with high ionic bonding character tend to be easily dissolved in solvents with high dielectric constants. Ions in an ionic crystal easily dissolve by Coulombic interaction with polar molecules in the solvents, and once they are separated from the crystal, it is difficult for them to recombine because the high dielectric constant of polar solvents attenuates the electrostatic energy which is the driving force for the formation of an ionic bonding. Thus, crystals with high ionic bonding nature tend to be easily dissolved into polar solvents remaining as separate ions in the solvents. Considering that the solvents used for electrolytes of LIBs such as ethylene carbonate or propylene carbonate have large polarity (~4.9 D of dipole moment while water is 1.85 D), it seems reasonable to conclude that covalent nature of bonding plays an important role and thus increase in covalency with doping may be a influential factor for reduction of Mn dissolution in LIBs.

We investigated the dissolution of Mn by considering the oxidation number, covalent character of the Mn-O bond, and the doping effects based on a DOS analysis. Other important factors were not considered, such as distortions in the crystal structure or formation of defects on doping. A precise structure refinement and simulation of the dissolution mechanisms in the presence of defects have yet to be done. However, the diffusion of Mn ions following dissociation of the Mn-O bonds is a fundamental process in dissolution regardless of the details of the reaction routes, and so it seems to be reasonable to investigate the local chemical properties of Mn ions and the bonds with nearest oxygen ions. This study was designed to provide insight into the problem of Mn dissolution in LMO cathodes in terms of the local bonding properties and to guide the selection of appropriate doping elements.

**Conclusions**

Dissolution of Mn ions, which is known to be a cause of poor high temperature cycle performance of LMO cathode material for LiBs, was investigated in terms of the bonding nature using a first principle DV-Xz molecular orbital method. Analysis of DOS of Mn 3d orbitals in a LMO crystal showed that Mn ions’ oxidation number lies between +3 and +4, and they are not at a perfect high-spin state but a little low-spin state is mixed. Because some empty levels of Mn 3d are located just around the Fermi energy level, it is expected that thermally activated electrons in the LMO crystal preferentially fill these levels. This would increase the probability of Mn ions having +3 oxidation state, resulting in degradation of cycle performance at high temperatures.

Changes of DOS and Mn-O bonding properties with doping were examined. Analysis of DOS showed that substitution of elements that have low oxidation number is effective in keeping Mn ions at higher oxidation states. But this mechanism could not explain different doping effects among the elements whose oxidation number is +3. From the calculation of bonding properties (ionic and covalent character of Mn-O bonding), it is found out that dissolution of Mn is strongly correlated with the covalent nature of Mn-O bond. Thus, it is suggested that not only formation of Jahn-Teller-active Mn$^{3+}$ should be suppressed, but also covalent character of Mn-O bond should be increased to reduce the dissolution of Mn ions at high temperatures.

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**Keywords:** LiMn$_2$O$_4$ · dissolution · energy storage material · electronic band structure · DV-Xz

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