First-principles investigation of the structural characteristics of LiMO₂ cathode materials for lithium secondary batteries

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ARTICLE INFO

Article history:
Received 21 May 2015
Received in revised form
17 June 2015
Accepted 18 June 2015
Available online 20 June 2015

Keywords:
Lithium ion battery
Cathode
LiMO₂
Defects
First-principle method

ABSTRACT

The structural features related to the defects of LiMO₂ (M = Ni, Co, Mn) cathode materials for lithium secondary batteries were investigated by a simulation of phase diagrams based on first-principle calculations. Crystal models with various types of point defects were designed and dealt with as independent phases, which enabled an examination of the thermodynamic stability of the defects. A perfect phase without defects appeared to be the most stable for LiCoO₂, whereas the formation of Li vacancies, O vacancies, and antisites between Li and Ni was thermodynamically unavoidable for LiNiO₂. The introduction of both Co and Mn in LiNiO₂ was effective in reducing the formation of point defects, but increasing the relative amount of Mn was undesirable because the antisite defect remained stable with Mn doping. The simulation showed good agreement with the experimental data and previous reports. Therefore, the method and the results of this study are expected to be useful for examining the synthesis, structure and related properties of layer-structured cathode materials.

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1. Introduction

Lithium ion batteries (LIBs) are used widely as power sources for mobile electronic gadgets owing to their high energy storage density [1,2]. The applications have recently been diversified to electric vehicles, power tools, energy storage systems, etc.; thus, the demand for LIBs has increasing sharply. On the other hand, despite the industrial scale-up, the improvements in performance do not appear to have kept pace with demand. In particular, advanced technology of positive electrode materials for high-capacity LIBs is urgently required. Structural and thermal safety, and the suppression of side reactions with an electrolyte liquid is also an important property to be secured with the increasing demand for large scale pouch type LIBs [3–6].

Layer-structured materials, whose composition is LiMO₂ (M = Ni, Co, Mn), are used widely as a cathode material for LIBs. LiCoO₂ is representative among them owing to its balanced properties of reasonable capacity, rate performance and safety [1,2,7]. This material has high volumetric capacity and is considered suitable for small size devices. With increasing Ni content in this structure, the available capacity with the commercial charging voltage (generally 4.2–4.3 V) increases and the material cost can be reduced, but it has been reported that LiMO₂ with a high Ni content is difficult to synthesize in precise compositions; Li-deficient Li₁₋ₓNiₓO₂ generally being obtained for LiNiO₂ [8–10]. In addition, the thermal and chemical stability of high-Ni LiMO₂ is still inferior to Co-based LiCoO₂ [6,11–14].

Therefore, it is important to understand the structural features and formation of internal defects arising during the synthesis of LiNiO₂. In this study, point defects in the LiMO₂ composition of materials, which are used widely as cathode materials for lithium ion batteries, were investigated via a thermodynamic approach through simulations of the phase diagrams based on the first-principle method. The structural characteristics of LiNiO₂ were examined in comparison with those of LiCoO₂ and the doping effects of Co or Mn in LiNiO₂ were also investigated. These results can be used as an effective research tool for the design of improved properties of layer-structured cathode materials.

2. Method

Phase diagrams of the Li–M–O system were simulated under typical synthesis conditions and the thermodynamic stability of the defects were analyzed. The generally known phases of the Li–M–O system and the newly designed crystal models of LiMO₂ with various types of point defects were included as independent phases in the simulation. This method enabled comparative analysis of the
thermodynamic stability among the defects. A total 15 types of defect phases were designed by combining point defects, such as O or Li vacancies, antisites between Li and M, and M at the tetrahedral sites instead the normal octahedral site. Table 1 lists the Kröger-Vink notation of the 13 types of defect phase.

To construct the ternary phase diagram of the Li–M–O system, the normalized Gibbs free energy of each phase included in the system should be calculated as follows and compared with one another [15,16]:

\[
\mathcal{G}(Li_{1}\text{M}_2\text{O}_3) = \frac{G(T, P, Li_{1}\text{M}_2\text{O}_3)}{a + b + c}
\]

(1)

For each phase, the position on the Li–M–O ternary diagram (x and y) and the normalized Gibbs free energy obtained from Eq. (1) can make a unique coordination in 3-D space. The ternary phase diagrams could be constructed by taking the vertices and edges that form a convex hull [17] to the -z direction and projecting them on a 2-D plane.

The changes in the Gibbs free energy with temperature or pressure need to be reflected in the simulation as a function of the synthetic conditions, but it was reported that the PV and entropy have only a negligible effect on the Gibbs free energy of solids [15,16]. In addition, the difference in heat capacity (Cp) and thermal expansion coefficient (α) was not expected to be significant among the same LiMO2 phases with different types of defects, of which stability is the major focus of this study:

\[
\mathcal{G}(Li_{1}\text{M}_2\text{O}_3) = \frac{G(T, P, Li_{1}\text{M}_2\text{O}_3)}{a + b + c} - \frac{E^0(0 K, Li_{1}\text{M}_2\text{O}_3)}{a + b + c}
\]

(2)

\[
G = E + PV - TS = E^0(0 K) + PV(0 K) + \int_0^T C_P dT + \int_0^p \{V(1 - zT)\} dp - TS = E^0(0 K)
\]

Therefore, the Gibbs free energy was approximated with the internal energy at 0 K for solid phases, which is provided by density functional theory (DFT) calculations with full relaxation of the atomic positions and lattice vectors of the bulk crystal models. As mentioned above, the error related to this approximation was reported to be insignificant for solid phases [10,19,20].

On the other hand, the Gibbs free energy of the gas phase is difficult to calculate using the DFT method, which is based on a periodic boundary condition, and the effects of temperature and partial pressure cannot be neglected. Therefore, the energy of oxygen was determined from a combination of DFT calculations and the experimentally available data of the standard formation energy of Ni-, Co-, and Mn- oxides:

\[
xM + \frac{1}{2}O_2 \rightarrow MxO
\]

(3)

\[
\Delta G_{\text{form,DFT}}(MxO) = \Delta G_{\text{form,EXP}}(MxO) - \frac{1}{2} \Delta G_{\text{DFT}}(O_2)
\]

(4)

\[\rightarrow\text{determination of } \Delta G_{\text{DFT}}(O_2) \text{ so that } \Delta G_{\text{form,DFT}}(MxO) = \Delta G_{\text{form,EXP}}(MxO)
\]

For a general chemical reaction that includes a metal (M = Ni, Co, Mn) and oxygen (Eq. (3)), the standard formation Gibbs free energy of the product \( \Delta G_{\text{form,DFT}}(MxO) \) may be calculated by DFT, as shown in Eq. (4), and the standard Gibbs free energy of the gas \( \Delta G_{\text{DFT}}(O_2) \) was determined so that \( \Delta G_{\text{form,DFT}}(MxO) \) may be equal to \( \Delta G_{\text{form,EXP}}(MxO) \), which is the actual standard formation Gibbs free energy of \( MxO \) [10,18,19]. Therefore, the room-temperature standard Gibbs free energy of \( O_2 \) was determined to be \(-8.95 \text{ eV per formula unit, and the value was used with a modification of the enthalpy and entropy change with temperature and pressure based on the JANAF thermochromical table} [21].

The energy of all the compounds of the Li–M–O system registered in the international crystal structure database [22] and the defect phases of LiMO2 designed by the introduction of various types of point defects in the Li12M12O24 supercells were calculated by DFT based on the generalized gradient + U (GGA + U) approximation of Perdew–Burke–Ernzerhof and the projector-augmented plane wave (PAW) pseudopotentials implemented in the Vienna ab initio simulation package [23–27] with an energy cutoff of 500 eV. All calculations were performed with the elimination of symmetry (i.e., with P1 space group) and spin-polarized state of the transition metals. The U values for the GGA + U method for Co, Ni and Mn was 5.5, 6.0 and 4.2 eV, respectively, referring to reports [15,16] that were confirmed to be reasonable from our previous research [10].

Several compositions of LiNi1-x-yCo1-xMn1-xO2 powder samples were prepared and the pH of a dispersion of them in water was measured: LiOH–H2O and Ni1-x-yCo1-xMn1-x(OH)2 were mixed at a molar ratio of 1:03:1 and heated to 1000–1300 K for 10 h in air. The Ni1-x-yCo1-xMn1-x(OH)2 precursors were prepared by a coprecipitation method, in which the chelate compound of the transition metal and ammonia were reacted with NaOH in a aqueous solution (all the starting materials from DUKSAN Pure Chem. Co., Korea). After heating, the powder samples were sieved through a #300 mesh, and 1 g of the powder was dispersed in 50 g of distilled water. After stirring for 5 min, the pH of the dispersion solution was measured. The pH of the commercial LiNi0,82Co0,15Al0,03O2 (Ecopro Co., Korea), LiNi0,82Co0,15Mn0,03O2 and LiNi0,82Co0,15Mn0,03O2 (SAMSUNG SDI Co., Korea) powders was measured in the same manner for comparison.

### 3. Results and discussion

As mentioned in the methodology section, the formation energy of each phase in the system was calculated using the DFT method,
and the thermodynamic relative stability among them was compared from a simulation of the phase diagrams. Regarding the layer-structured cathode materials, which are the focus of this study, crystal models containing various types of point defects were designed and each were included in the simulation as independent phases. This requires the most stable (i.e., the lowest energy) arrangement of the defects to be determined in advance. That is, the most stable and probable configuration of each defect phase should be determined so they can be used as a representative of the phase for the cases in which the defect phase contains a combination of different types of defects.

The most stable configuration of the point defects was searched by changing the relative positions of the defects and comparing the energy obtained by DFT calculations. An examination of the number of defect phases revealed the decisive factor of the relative position of point defects in the LiMO2 phase to be the electrostatic interaction among the point defects. The 15 representative configurations of the defect phases determined in this way were included in the phase diagram simulation. The locations of Co and Mn in LiNiO2 were determined in the same manner: After calculating the energy of various arrangements of Co or Mn in the LiNiO2 crystal, the configuration presented in Fig. 1(a) was found to be the most stable. Regarding the co-doping case of Co and Mn, the arrangement of Co and Mn of Fig. 1(b) was the lowest energy configuration of the Li12Ni8Co2Mn2O24 super cell.

Fig. 2 presents the phase diagrams of the Li—Co—O and Li—Ni—O systems simulated assuming the synthesis temperature of 1300 K and 1000 K, respectively, in air (i.e., pH2 = 0.02 MPa). As shown in Fig. 2(a), phase ①, a perfect crystal without point defects appeared on the phase diagram for LiCoO2. This suggests that a defect free perfect crystal of LiCoO2 is more stable than the other defect phases and can be synthesized easily from the viewpoint of thermodynamics. In contrast, the defect phases of ②, ③, ④, and ⑥ were stable and a perfect phase did not appear on the phase diagram for LiNiO2. Because the composition of perfect LiNiO2 is located on the tie-line connecting phase ① and O, phase ④, which contains Vo, NiLi, and LiNi point defects, is expected to be synthesized, even though the starting materials are mixed at the stoichiometric composition. This expectation, however, would be valid only when thermodynamic equilibrium is satisfied over the experimental sample. In actual synthesis, LiNiO2, which is a mix of ⑤, ⑥, ⑦, and ⑧ phases, would be synthesized due to the partial inhomogeneity of the composition, remaining Vo, VLi, NiLi, and Ni–Li exchange point defects in the crystal. This result is in accordance with previous reports by H. Chen et al. [28] and Y. Bi et al. [29], who reported that the Vo, extra Ni, and Li—Ni antisites are the main form of defects in LiNiO2 and caused structural instability. In this study, the formation of the point defects was found to be inevitable thermodynamic features for the synthesis of LiNiO2.

In this discussion, the stability of the phases was determined from the phase diagrams that had been simulated based solely on the formation energy. That is, the configuration entropy was not considered. Therefore, it may be necessary to determine if the effect of entropy is really insignificant, particularly for defect phases containing multi types of point defects. For example, the crystal model of this defect phase has the same chemical composition as the perfect phase but contains a pair of CoLi and LiCo. This phase appeared to be unstable from the simulation of phase diagram, and the formation energy can be obtained from the DFT calculations of the reaction equation below:

\[
\text{Li}_{12}\text{Co}_{12}\text{O}_{24} \rightarrow \text{Li}_{12}\text{Co}_{12}\text{O}_{24}
\]

\[\Delta E = \text{E} - kT\ln \Omega \text{ for the reaction was calculated to be } 1.6023 \text{ eV. The energy related to the entropy of the CoLi and LiCo configuration is expressed as } -kT\ln\Omega, \text{ where } k \text{ is the Boltzmann constant and } \Omega \text{ is the number of arrangements. If it is assumed that the position of CoLi and LiCo in the Li}_{12}\text{Co}_{12}\text{O}_{24} \text{ crystal model is random, there would be 144 configurations and the calculated } -kT\ln\Omega \text{ would be } -0.5 \text{ eV, which may not appear to be negligible compared to the } \Delta E \text{ of } 1.6023 \text{ eV. However, } \Omega \text{ would be smaller because some arrangements are identical due to the periodic boundary condition of the crystal model for DFT calculations. In addition, the arrangement is actually not fully random because the energy calculated by DFT was...}

![Fig. 1. Optimal crystal structure of LiNi2/3Co1/3O2 (a) and LiNi2/3Co1/6 Mn1/6O2 (b) with the transition metal arrangement of the lowest energy.](image-url)
The simulation temperature was determined considering the experimentally reported system simulated at 1300 K in air, and (b) Li\textsuperscript{+} different among the configurations. Therefore, the position of the point defects would have a preference to a certain type of arrangement, resulting in a much smaller –K\textsubscript{ThTb}.

This preference for certain types of configurations may be disturbed by thermal agitation at high temperatures, but the preferred configuration of the lowest energy would still have higher probability than others. Therefore, the error related to a determination of the phase stability based on the energy (i.e., energy of the most probable configuration) of each phase without considering the configuration entropy does not appear to be significant. Table 2 lists the formation reaction and the energy for other types of multi-defected LiCoO\textsubscript{2} phase, which shows that the absolute value of the formation energy is expected to be sufficiently large compared to the configuration entropy effect.

For LiNiO\textsubscript{2}, phases with defects, such as \(\oplus\), \(\ominus\), \(\odot\), and \(\odot\), appeared to be more stable than the perfect crystal (phase \(\odot\)). As the composition of phase \(\oplus\) lies on the \(\odot\)--O tie-line at 1000 K in air, the formation energy \(\Delta E\) can be obtained from DFT calculations of the following reaction equation:

\[
\text{Li}_{12}\text{Ni}_{12}\text{O}_{23}(\oplus) + 1/2\text{O}_2 \rightarrow \text{Li}_{12}\text{Ni}_{12}\text{O}_{24}(\odot)
\]  

(6)

\(\Delta E\) for the reaction was calculated to be 1.3213 eV. Considering that the configuration entropy effect, if any, induces the formation of point defects, the relative stability of the defected phases \(\oplus\), \(\ominus\), \(\odot\), and \(\odot\) over the phase \(\odot\) is still expected to be valid or even strengthened with consideration of the configuration entropy.

Parts of Ni in LiNiO\textsubscript{2} were substituted with Co, Mn or Co + Mn, and the phase diagrams were simulated at the expected synthesis temperature (1000–1100 K) in air. The results are presented in Fig. 3(b–d) along with that of the Li–Ni–O system without substitution (Fig. 3(a)) for comparison. In the Li–Ni\textsubscript{2/3},Co\textsubscript{1/3}–O system (Fig. 3(b)), phases \(\odot\) and \(\ominus\) of LiNi\textsubscript{2/3}Co\textsubscript{1/3}O\textsubscript{2} appeared to be stable. These phases contain no point defects (phase \(\odot\)) or only V\textsubscript{O} (phase \(\ominus\)). Therefore, LiNi\textsubscript{2/3}Co\textsubscript{1/3}O\textsubscript{2} is expected to be synthesized with an almost perfect crystal structure with few point defects other than some oxygen vacancies. With Mn doping (Fig. 3(c)), the \(\odot\), \(\ominus\), \(\odot\), and \(\odot\) phases were found to be stable, suggesting that the synthesis possibility of phases without significant defects, such as \(\odot\) and \(\odot\) phases, increases with the introduction of Mn in LiNiO\textsubscript{2} but the defects of the transition metal occupying the Li site (M\textsubscript{Li}) are still stable for LiNi\textsubscript{2/3}Mn\textsubscript{1/3}O\textsubscript{2}.

For Li–Ni\textsubscript{2/3},Co\textsubscript{1/6},Mn\textsubscript{1/6}–O, the co-doped system of Co and Mn, LiNi\textsubscript{2/3}Co\textsubscript{1/6}Mn\textsubscript{1/6}O\textsubscript{2} of phases \(\odot\), \(\odot\), and \(\oplus\) was stable on the phase diagram. This might be an intermediate state between the Co-only doped and the Mn-only doped systems, in which phases \(\odot\) and \(\ominus\), and phases \(\odot\), \(\odot\), \(\ominus\), \(\odot\) were stable respectively. Hence, the co-doping of Co and Mn in LiNiO\textsubscript{2} does not appear to have a synergistic effect and increasing the amount of Co instead of Mn appears to be desirable in terms of reducing the formation of defects during synthesis. However, some positive effect of Mn doping on the electrochemical cycling performance was reported \cite{30}. Therefore, co-doping may be considered to improve the performance as a cathode material, such as charge/discharge capacity, rate performance, durability, and thermal safety, not in terms of the better

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**Table 2**

<table>
<thead>
<tr>
<th>Equation of formation reaction</th>
<th>(\Delta E) (eV)</th>
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<tr>
<td>(\odot) LiCo\textsubscript{2},Co\textsubscript{2}LiCo</td>
<td>(\text{Li}_2\text{Co}_2\text{O}_2(\odot) \rightarrow \text{Li}_2\text{Co}_2\text{O}_2(\odot))</td>
</tr>
<tr>
<td>(\odot) LiCo\textsubscript{2},Co\textsubscript{2}CoCo</td>
<td>(\text{Li}_2\text{Co}_2\text{O}_2(\odot) \rightarrow \text{Li}_2\text{Co}_2\text{O}_2(\odot))</td>
</tr>
<tr>
<td>(\odot) LiCo\textsubscript{2},Co\textsubscript{2}CoCo</td>
<td>(11/12\text{Li}_2\text{Co}_2\text{O}_2(\odot) + \text{CoO} + 1/2\text{O}_2 \rightarrow 11/12\text{Li}_2\text{Co}_2\text{O}_2(\odot))</td>
</tr>
<tr>
<td>(\odot) LiCo\textsubscript{2},Co\textsubscript{2}LiCo</td>
<td>(11/12\text{Li}_2\text{Co}_2\text{O}_2(\odot) + \text{CoO} \rightarrow 11/12\text{Li}_2\text{Co}_2\text{O}_2(\odot))</td>
</tr>
<tr>
<td>(\odot) LiCo\textsubscript{2},Co\textsubscript{2}CoCo</td>
<td>(17/18\text{Li}_2\text{Co}_2\text{O}_2(\odot) + 1/2\text{Li}_2\text{O} + 2/3\text{CoO} \rightarrow \text{Li}_2\text{Co}_2\text{O}_2(\odot))</td>
</tr>
<tr>
<td>(\odot) LiCo\textsubscript{2},Co\textsubscript{2}CoCo</td>
<td>(11/12\text{Li}_2\text{Co}_2\text{O}_2(\odot) + \text{CoO} \rightarrow 11/12\text{Li}_2\text{Co}_2\text{O}_2(\odot))</td>
</tr>
<tr>
<td>(\odot) LiCo\textsubscript{2},Co\textsubscript{2}CoCo</td>
<td>(11/12\text{Li}_2\text{Co}_2\text{O}_2(\odot) + \text{CoO} \rightarrow 11/12\text{Li}_2\text{Co}_2\text{O}_2(\odot))</td>
</tr>
<tr>
<td>(\odot) LiCo\textsubscript{2},Co\textsubscript{2}CoCo</td>
<td>(11/12\text{Li}_2\text{Co}_2\text{O}_2(\odot) + 2\text{COO} \rightarrow 11/12\text{Li}_2\text{Co}_2\text{O}_2(\odot))</td>
</tr>
<tr>
<td>(\odot) LiCo\textsubscript{2},Co\textsubscript{2}CoCo</td>
<td>(11/12\text{Li}_2\text{Co}_2\text{O}_2(\odot) + 1/2\text{O}_2 \rightarrow 11/12\text{Li}_2\text{Co}_2\text{O}_2(\odot))</td>
</tr>
<tr>
<td>(\odot) LiCo\textsubscript{2},Co\textsubscript{2}CoCo</td>
<td>(5/6\text{Li}_2\text{Co}_2\text{O}_2(\odot) + 3\text{CoO} + 1/2\text{O}_2 \rightarrow 11/12\text{Li}_2\text{Co}_2\text{O}_2(\odot))</td>
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crystal perfection during synthesis.

Fig. 4 summarizes the characteristics of defect formation in the synthesis of LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$, as a function of the transition metal composition. The defect phases of ⑧, ⑩, ⑫, and ⑭ are expected to become stable with increasing Ni-content, resulting in the formation of V$_0$, V$_{Li}$, M$_{Li}$ and M$_{Mn}$ point defects. Therefore, Li- and O-deficiencies and cation mixing between the Li and transition metal is predicted to be significant in LiNi$_{1-x-y}$CoxMn$_y$O$_2$ with a high Ni-content. This simulation result may allow a proper explanation of previous studies, which reported that a Li$_{1-x}$Ni$_{1+y}$O$_2$ composition is generally obtained in the synthesis of LiNiO$_2$ [8–10,28]. The substitution of both Co and Mn appears to improve the perfection of the crystal structure, but an increase in the relative portion of Mn stabilizes phases ⑧ and ⑩, which contain M$_{Li}$. Therefore, increasing the relative Co content may be desirable at a given Ni content because the cation-mixing type defects can be reduced.

From Figs. 3 and 4, it is predicted that a Li deficiency in the Li$_{1-y}$Ni$_{1+y}$O$_2$ crystal forms the secondary phase, Li$_2$O, which would react with CO$_2$ or H$_2$O in air after synthesis resulting in residual Li-compounds of Li$_2$CO$_3$ or LiOH on the Li$_{1-x}$Ni$_{1+y}$O$_2$ surface. These residual Li-compounds were reported to cause some significant problems: LiOH affects the polymerization tendency of polyvinylidenefluoride (PVDF), which is generally used as a binder material for the positive electrode. Rapid clotting of the electrode coating slurry, in which PVDF is used, is observed frequently for high Ni-content materials, such as LiNi$_{1-x-y}$Co$_x$Al$_y$O$_2$ (generally known as NCA, in which the Ni content is normally more than 80%), and this is a major problem limiting the applications of the material.

Gas evolution from the side reaction between the residual Li compounds and electrolyte solution is another significant problem. Li$_2$CO$_3$ and LiOH react with the carbonate solvents at the charged state of a battery cell and generate a large amount of gas, which causes distortion or swelling of the battery [6,11,31]. This problem becomes more significant with increasing Ni content. Thus, these experimental features appear to show good agreement with the simulation of this study, which predicts more Li-deficiency; hence, more free Li-compounds with a higher Ni content of LiMO$_2$, supporting the reliability of the simulation.

The pH of a dispersion of the cathode material in water is known to be proportional to the amount of free residual Li-compounds; thus, it has been used as a measure of the free Li-compounds in industry [6,10]. Several compositions of LiNi$_{1-x}$-
\( \gamma \text{Co}_{x} \text{Mn}_{y} \text{O}_{2} \) samples were prepared and the pH of the dispersion in water was measured. As shown in Table 3, the pH increased with increasing Ni content. This also supports the prediction of the simulation (Fig. 4) in that \( \text{V}_{1} \) in \( \text{LiNi}_{1-x} \gamma \text{Co}_{x} \text{Mn}_{y} \text{O}_{2} \) increases with increasing Ni fraction, resulting in a larger amount of free \( \text{Li}_{2} \text{CO}_{3} \) or \( \text{LiOH} \) residues.

Therefore, the simulation of phase diagrams for \( \text{Li}--\text{M}--\text{O} \) systems in this study appears to properly explain the synthetic features of the \( \text{LiMO}_{2} \) cathode materials and is expected to be used as an effective guide for the experiments. On the other hand, some changes in structure can occur during the cooling process after synthesis: If the samples are cooled rapidly to room temperature by quenching, the equilibrium state of defect formation at the synthesis temperature can be fixed, whereas if cooling proceeds very slowly, equilibrium at the lower temperature may be reflected in the defect structure. Therefore, in order for the simulation method to be used as an effective preliminary research tool, further study will be necessary on the kinetic aspects during the cooling process, such as the diffusion motion of atoms, activation energy of thermal diffusion and the freezing temperature of diffusion.

### 4. Conclusions

The crystal structural features of \( \text{LiNiO}_{2} \) synthesis were compared with those of \( \text{LiCoO}_{2} \) through a simulation of the phase diagram of the \( \text{Li}--\text{M}--\text{O} \) systems. Crystal models containing various types of point defects were designed and included in the simulation as if each of them was an independent phase. This method enabled an assessment of their thermodynamic stability. The results showed that a defect free state is the most stable for \( \text{LiCoO}_{2} \), whereas \( \text{LiNiO}_{2} \) appeared to be stable when it contains defects, such as Li vacancies, O vacancies, and cation mixing between Li and Ni. This explains why \( \text{LiNiO}_{2} \) is difficult to synthesize at the precise stoichiometric composition. A simulation of the introduction of Co or Mn in \( \text{LiNiO}_{2} \) showed that doping with Co is effective in preventing the formation of defects. Doping of Mn also appears to be effective but the effect is limited because O vacancies and cation mixing still remain stable, and an increase in the relative content of Mn at a given Ni-content induces cation mixing. The synergy of Co and Mn co-doping was not observed for the reduction of the defects. The simulation results showed good agreement with the experiments and previous reports. Thus, the simulation method and the results are expected to provide a useful guide for studies into the synthesis and defect formation in Ni-based layer-structured cathode materials.

### Acknowledgement

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2014R1A1A1007800). This work was also supported by Inha University Research Grant (INHA-50263).

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