Thermochemical investigation of Zr doping in LiNi$_{8/12}$Co$_{2/12}$Mn$_{2/12}$O$_2$ based on phase equilibria simulation

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Abstract
The doping behavior of Zr in LiNi$_{8/12}$Co$_{2/12}$Mn$_{2/12}$O$_2$ (LNCM) is investigated by a simulation of the phase equilibria for the Li-(M*,Zr)-O system (M* = Ni, Co, Mn) based on first-principles calculations followed by a thermochemical post-analysis of the resultant phase diagrams. The results indicate that the stable state at the synthetically stoichiometric composition of LNCM with Zr is a mixture of undoped LNCM with a Li$_2$ZrO$_3$ secondary phase; doping of Zr in the LNCM crystal is not thermodynamically favored. The energies of various states comprising LNCM supercells with defects, secondary phases, and Zr doping are examined, and the equilibrium doping concentration of Zr is calculated by considering the entire LNCM:Zr crystal as a statistical combination of these states. The doping concentration of Zr in the LNCM crystal is calculated to be very low, which enables balanced control between doping and coating, as recently reported through experimentation. The dopability of Zr is expected to increase with the depletion of O$_2$ supply during the heating of a system with a precisely controlled Li to M* ratio, but this behavior is affected by the formation of defects, especially by M* substitution for Li.

KEYWORDS
cathode material, doping, lithium ion battery, phase diagram

1 | INTRODUCTION

Li-ion batteries are widely used as power sources for small mobile devices because they offer high energy storage densities; recently, their use has expanded to large applications such as electric cars and power storage stations.[1,2] Along with the growth of the market, consumer demand for battery performance is continuously increasing, particularly the need to improve the energy storage capacity, which determines the device use time per charge and the travel distance of electric vehicles. To this end, efforts to develop and apply Ni-based layer-structured cathode materials to replace conventional LiCoO$_2$ are underway.[3–5] By replacing Co with Ni in the layer-structured cathode material, a larger capacity can be achieved in the present voltage range of battery operation and raw material costs can be reduced. However, as the content of Ni increases, structural and thermal instabilities of the cathode material increase, which requires research attention.[6,5]

To compensate for these problems, methods such as the doping of foreign elements to improve the structural stability of crystals or coating surfaces with other materials to suppress side reactions at the cathode-electrolyte interface have been widely attempted.[4,5] Zr is considered an effective doping and/or coating material by many researchers.[6–11] Improvements in the cycle and rate properties of cathodes through Zr doping have been reported and attributed to the so-called pillar effect: Metals with higher oxidation numbers than Li are located in the Li layer by Zr doping, reducing the repulsive interactions between O$^{2-}$ ions around the Li layer. This helps to sustain the structural stability of the cathode crystal and achieve smooth Li migration during charge and discharge of the battery.[6–8] Because Zr forms highly chemically stable oxides, it has also been studied as a surface treatment material that has improved cyclic performance through the suppression of side reactions.[9–11]
Recently, locational control of the introduction of Zr has been attempted, developing from the traditional dichotomy of simple doping vs coating. Experimental results have been reported on inducing some Zr in the ZrO$_2$ coating layer to dope the crystal interior through thermal diffusion,[12–14] as well as simultaneously forming a coating layer of Zr oxide with the synthesis of Zr-doped cathode materials.[15] In this hybrid doping-coating technique, the doping limit of Zr in the host cathode crystal is likely to affect significantly; for systems in which a dopant can be readily incorporated in the host crystal, properly controlling the thermal diffusion speed of the dopant would be difficult, because generally the doping reaction is too fast to retain some of the surface coating on the host surface as a separate phase. Therefore, in order to study the mechanisms behind these techniques, design appropriate processes, or select appropriate elements for such treatments, quantitative predictive techniques for the doping limits are required. Information on the adjustment of process variables may also be necessary to effectively control doping limitations.

Therefore, in this study, a methodology to quantitatively predict the precise doping limit of a dopant and to interpret the effects of defects and processing conditions on the dopability is investigated through a theoretical approach. The doping limit of Zr in the LiNi$_{8/12}$Co$_{2/12}$Mn$_{2/12}$O$_2$ (LNCM) crystal, in which Zr replaces part of Ni, is analyzed by simulating the phase diagrams based on first-principles calculations. Simulation and post-analysis are performed considering point defects within the LNCM, formation of secondary phases, and combinations thereof. Through these techniques, the thermodynamic stabilities of Zr-doped LNCM states and the combined states of undoped LNCM and Zr-containing secondary phases, the equilibrium doping concentration of Zr in LNCM, and the defects generated natively or with the introduction of Zr were investigated in detail. In particular, a study of how these properties change in the synthetic atmosphere was conducted to provide information on process control variables during an actual synthesis. These analytical and predictive models are expected to provide good guidance for experimental attempts to improve the performance of LNCM cathodes through the introduction of Zr, and the methodology is expected to be universally applicable to other material systems as well.

2 | METHODS

The phase diagrams of the Li-$\cdot$M$^+$-O and Li-(M$^+$,Zr)-O systems were simulated by first-principles calculations, and analyses related to Zr doping in LNCM were performed based on these diagrams. M$^+$ denotes transition metals with the fixed composition of Ni:Co:Mn = 4:1:1, and the ratio of Zr to (M$^+$ + Zr) was fixed at 1:12 in the Li-(M$^+$,Zr)-O system. The normalized Gibbs free energy of all crystal phases of the systems, expressed as Equation (1), was obtained from density functional theory (DFT) calculations:

$$G[\text{aLi|bM|cZr|dO|eCO}_2|fH_2O] = \frac{G[\text{aLi|bM'|cZr|dO|eCO}_2|fH_2O] - eG_{\text{CO}_2} - fG_{\text{H}_2O}}{a+b+c+d}$$

In the equation, “aLi|bM|cZr|dO|eCO$_2$|fH$_2$O” denotes a phase that can contain Li, M$^+$, Zr, O, CO$_2$, and H$_2$O with compositional coefficients of $a-f$, respectively. If Zr is not introduced, the phases belong to the Li-M$^+$-O system; if Zr is introduced, the phases can be classified into two categories of Zr doped in the Li-M$^+$-O host crystal and Zr as part of a separate secondary phase. For the layer-structured cathode material, [LNCM:Zr], the Zr-doped state, and [LNCM + secondary phase] formed in the case of poor Zr dopability in the LNCM crystal structure, may be considered.

The energy of a “aLi|bM|cZr|dO|eCO$_2$|fH$_2$O” phase calculated by the DFT method was approximated for the Gibbs free energy of that phase. This approximation was previously reported to cause no significant error between solid phases, thus permitting reliable phase diagram simulation.[16–18] However, the gas phases are significantly affected by the temperature and pressure; therefore, the standard-state Gibbs free energies of O$_2$, CO$_2$, and H$_2$O were determined in a semi-empirical way to eliminate the discrepancy in the formation energy between the DFT calculations of this study and conventional experimental databases for compounds including gas phases in their standard formation reactions, and the effects of temperature and pressure were reflected by referring to the JANAF[19] thermochemical table (see References [18,20–22] for details). The composition of each phase was assigned to a coordinate point on the x-y plane, and the G value was taken as the z-coordinate, allowing the location of the composition and energy of each phase in a three-dimensional space. Ternary phase diagrams were finally obtained by projecting the convex hull to the –z direction, composed of the coordinate points and the lines connecting them.[17,18,23]

LNCM crystals containing point defects were included in the phase diagram simulation by treating them as independent phases, in order to examine the defect types that can exist in the native crystal because of its thermodynamic stability. In addition, the cases in which Zr was doped in the crystals and those in which Zr formed a separate secondary phase rather than doping were all included in the simulation. ZrO$_2$, Li$_2$ZrO$_3$, and Li$_2$Zr$_2$O$_6$ were examined as the main species of secondary phase. All the phases derived by reflecting point defects and secondary phases are summarized in Table 1, where the compounds with no Zr doped in the crystal are expressed by numbers in open circles (ie, ①, ②, ③, ...), while the Zr-doped ones (LNCM:Zr) are denoted by numbers in solid circles (①, ②, ③, ...). The symbols of phases containing cation antisite type defects (so-called cation mixing) are underlined, and those in which Li is deficient in the LNCM crystal because of the formation of secondary phases are marked by a sharp ( '). Although the transition metal site is considered as the default Zr doping site in the LNCM crystals, doping of Zr at the Li site is also considered, in which case the phase symbols are marked by a single quotation mark. Thus, by including all cases of defects and secondary phases in the phase diagram simulation, the possibility of Zr doping, defect stability, and secondary phase formation could be systematically examined.
The simulation result for the Li-M\textsuperscript{3+}-O system is presented in Figure 1, which shows that LNCMs of phases ①, ⑦, and ⑩ appear thermodynamically stable on the phase diagram at 1100 K, the temperature expected to approach the optimum synthetic temperature of LNCM cathode. These

### Table 1

The Zr-added LNCM phases generated by the combination of point defects and secondary phases, which are included in the simulation of Li-\(\text{M}^\text{3+}\)-Zr-O phase diagrams

<table>
<thead>
<tr>
<th>Symbol and description</th>
<th>Composition</th>
<th>Defects</th>
</tr>
</thead>
<tbody>
<tr>
<td>①/②</td>
<td>LiM\textsuperscript{3+}O\textsubscript{2} / LiM\textsuperscript{11/12}Zr\textsubscript{1/12}O\textsubscript{2}</td>
<td>M\textsuperscript{3+}\textsuperscript{m} + Li\textsuperscript{m}</td>
</tr>
<tr>
<td>③</td>
<td>Li\textsubscript{11/12}M\textsuperscript{3+}O\textsubscript{2} / Li\textsubscript{11/12}(M\textsuperscript{11/12}Zr\textsubscript{1/12})O\textsubscript{2}</td>
<td>V\textsubscript{1} + M\textsuperscript{3+}</td>
</tr>
<tr>
<td>④</td>
<td>Li\textsubscript{11/12}Zr\textsubscript{11/12}O\textsubscript{23/12} / Li\textsubscript{11/12}(M\textsuperscript{11/12}Zr\textsubscript{1/12})O\textsubscript{23/12}</td>
<td>V\textsubscript{1} + 2M\textsuperscript{3+}</td>
</tr>
<tr>
<td>⑤</td>
<td>Li\textsubscript{11/12}Zr\textsubscript{11/12}O\textsubscript{23/12} / Li\textsubscript{11/12}(M\textsuperscript{11/12}Zr\textsubscript{1/12})O\textsubscript{23/12}</td>
<td>V\textsubscript{1} + M\textsuperscript{3+} + M\textsuperscript{3+} + Li\textsuperscript{m}</td>
</tr>
<tr>
<td>⑥</td>
<td>Li\textsubscript{11/12}Zr\textsubscript{11/12}O\textsubscript{23/12} / Li\textsubscript{11/12}(M\textsuperscript{11/12}Zr\textsubscript{1/12})O\textsubscript{23/12}</td>
<td>V\textsubscript{1} + M\textsuperscript{3+} + M\textsuperscript{3+} + Li\textsuperscript{m}</td>
</tr>
<tr>
<td>⑦</td>
<td>Li\textsubscript{11/12}Zr\textsubscript{11/12}O\textsubscript{23/12} / Li\textsubscript{11/12}(M\textsuperscript{11/12}Zr\textsubscript{1/12})O\textsubscript{23/12}</td>
<td>V\textsubscript{1} + M\textsuperscript{3+} + M\textsuperscript{3+} + Li\textsuperscript{m}</td>
</tr>
<tr>
<td>⑧</td>
<td>Li\textsubscript{11/12}Zr\textsubscript{11/12}O\textsubscript{23/12} / Li\textsubscript{11/12}(M\textsuperscript{11/12}Zr\textsubscript{1/12})O\textsubscript{23/12}</td>
<td>V\textsubscript{1} + 2M\textsuperscript{3+} + 3M\textsuperscript{3+} + Li\textsuperscript{m}</td>
</tr>
<tr>
<td>⑨</td>
<td>Li\textsubscript{11/12}Zr\textsubscript{11/12}O\textsubscript{23/12} / Li\textsubscript{11/12}(M\textsuperscript{11/12}Zr\textsubscript{1/12})O\textsubscript{23/12}</td>
<td>V\textsubscript{1} + 2M\textsuperscript{3+} + 3M\textsuperscript{3+} + Li\textsuperscript{m}</td>
</tr>
<tr>
<td>⑩</td>
<td>Li\textsubscript{11/12}Zr\textsubscript{11/12}O\textsubscript{23/12} / Li\textsubscript{11/12}(M\textsuperscript{11/12}Zr\textsubscript{1/12})O\textsubscript{23/12}</td>
<td>V\textsubscript{1} + 2M\textsuperscript{3+} + 3M\textsuperscript{3+} + Li\textsuperscript{m}</td>
</tr>
</tbody>
</table>

Note: LNCM and M\textsuperscript{3+} denote LiNi\textsubscript{8/12}Co\textsubscript{2/12}Mn\textsubscript{2/12}O\textsubscript{2} and Ni\textsubscript{8/12} + Co\textsubscript{2/12} + Mn\textsubscript{2/12}, respectively; point defects are expressed by Kröger–Vink notation with the formal oxidation numbers of +1, +3, +4, and −2 for Li, M\textsuperscript{3+}, Zr, and O ions, respectively; M\textsubscript{tot} denotes an interstitial defect of M\textsuperscript{3+} at a tetrahedral site.

### Results

The simulation result for the Li-M\textsuperscript{3+}-O system is presented in Figure 1, which shows that LNCMs of phases ①, ⑦, and ⑩ appear thermodynamically stable on the phase diagram at 1100 K, the temperature expected to approach the optimum synthetic temperature of LNCM cathode. These
are the LNCM phases of a perfect crystal with no point defects (①), an O-deficient state (⑦), and a Li-deficient and M⁺-rich state via M⁺ substitution for Li (⑮). Because phase ① is stable at this condition, theoretically the perfect LNCM phase may be obtained if the composition is controlled at exact stoichiometry and O₂ is properly supplied until the synthesis reaches thermodynamic equilibrium. However, in actual experimental environments, the synthetic reaction may not reach the thermodynamic equilibrium state of phase ① because of partial compositional imbalances, incomplete chemical reactions for kinetic reasons, and local O₂ depletion, which are commonly occurring imperfections in real experiments. Therefore, a mixture of the phases of comparable stability, mainly comprising ①, ⑦, and ⑮, is expected to be obtained in the actual synthesis of LNCM, rather than obtaining the perfect phase ①, which is an ideal state accomplishable only in theoretical syntheses.

Because the ⑦ and ⑮ phases contain defects such as V_{Li}^* and M_{Li}^{*+}, the overall composition of synthesized LNCM would be Li-deficient compared to that of the mixing composition of the raw materials. This off-stoichiometric behavior was reported as a feature of Ni-based layer-structured cathode materials, and was also confirmed from our previous experimental and simulation investigation.\[^{21,23}\] The Li that is not incorporated in the LNCM is expected to form a secondary phase of LiO, which would be converted to Li₂CO₃ or LiOH by reaction with CO₂ and H₂O in air during and/or after the cooling, thus forming residual Li compounds on the surface of LNCM. In this study, cation antisite defects are expressed in Kröger-Vink notation as M_{Li}^{*+}, considering the formal charges of transition metals and Li in a stoichiometric composition of layer-structured cathode materials are analyzed to be +3 and +1 in previous studies.\[^{8,30,31}\] (Although it was reported the oxidation state of Mn is generally +4 in the layer-structured cathode materials, the overall average oxidation state of transition metals is known to be +3, therefore in this study the defects of transition metals' occupation of lithium sites are expressed as M_{Li}^{*+} on the basis.) The DFT analysis indicated that the antisite defect formed by the substitution of Li by Ni is more stable than those by Co or Mn, and that the actual oxidation state of Ni at the Li site is +2. Therefore, it seems that most of the M_{Li}^{*+} is Ni_{Li}; however, in this study, we used M_{Li}^{*+} as a representative expression for antisite defects, considering the possibility of Li-substitution by Co^{3+} or Mn^{4+}, although these substitutions are not as likely as that by Ni.

Figure 2 shows the phase diagrams with the introduction of Zr. The ①, ⑦, and ⑮ phases are stable at 1100 K, like the simulation results without Zr, but additionally phase ⑩ appears stable on the phase diagram. Secondary phases containing Zr, such as ZrO₂, Li₂ZrO₃, and Li₂ZrO₃, are found to be stable, while Zr doping in the LNCM crystal structure is not favored. Thus, the mixed state of undoped LNCM and secondary phases, which may be expressed as ① + ⑦ + ⑩ + ⑮, appears as stable states, while the doped states such as ① + ⑦ + ⑩ or ① + ⑦ + ⑮ are thermodynamically unstable. Phase ⑩, which appears with the introduction of Zr, contains V_{Li}^* and M_{Li}^{*+}. This phase may become stable with the introduction of Zr because the stabilization of Zr by forming a separate compound in the Li-Zr-O system is preferred to the substitution of Zr at the lattice points in the LNCM crystal. The formation of Li₂ZrO₃-type secondary phases requires some Li and O to be added to Zr, which may be extracted from the LNCM, leaving V_{Li}^* and M_{Li}^{*+} in the LNCM crystal, thus stabilizing ⑩.

Thus, the simulation results show that the doping of Zr in LNCM is not thermodynamically favored. However, this may not indicate that doping is completely impossible: Although doping is not energetically favored, a driving force exists for the doping to increase the configurational entropy by lattice-point substitution with Zr. In our previous reports, an entire crystal was considered as the combination of unit supercells containing each type of defect. The probability of each defect type, or the proportion of each supercell unit in the entire crystal, was calculated by considering the mixing entropy of the units, which demonstrated that the proportion of each unit was determined by the Boltzmann factor. Therefore, in this study, the macroscale LNCM crystal is considered as an ensemble system comprising a combination of supercell units that may
be Zr-doped or undoped, and the ratio between the doped and undoped units is determined by the Boltzmann factors. Therefore, the doping limit of Zr can be calculated quantitatively based on the Boltzmann factor of each phase, which is obtainable from DFT calculations.

Generally, the synthesis of phase ①, the stoichiometrically perfect crystal of Zr-doped LNCM, is the experimental goal, and the starting raw materials of Li and transition metals are mixed in the corresponding ratio (ie, 1:1, with some excess Li to compensate for its loss during synthesis). However, the targeted phase ① is not stable, as indicated from the simulated phase diagrams; therefore, the direct synthesis of this phase is not achievable. Instead, a mixture of ①, ⑪, and Li2ZrO3 is expected, because the design composition (ie, that equivalent to phase ①) is located on the composition line connecting the two stable compositional points of [① + Li2ZrO3] and [⑪ + Li2ZrO3] on the phase diagram, while phase ① itself is thermodynamically unstable (Figure 2). Therefore, when the synthesis is performed targeting phase ①, the mixed state of ①, ⑪, and Li2ZrO3 is expected to be mainly obtained. If some Zr-doped phase is synthesized, it may be mostly phase ②, not phase ①. The stoichiometric relation between the two states of stable [① + ⑪ + Li2ZrO3] and the Zr-doped phase ② is expressed as follows:

$$
\frac{3}{8}LiM^{*}O_{2}(①) + 1/2Li_{11/12}M^{*11/12}Zr_{1/2}O_{24} ⑪ + 1/12Li_{2}ZrO_{3} = LiM^{*}_{11/12}Zr_{1/12}O_{24} ② (M^{*} = Ni, Co, Mn)
$$

(2)

The ratio between ② and [① + ⑪ + Li2ZrO3] states can be determined from their Boltzmann factors, as discussed above; therefore, the proportion of the supercell unit of phase ② in the entire LNCM crystal can be quantitatively estimated as:

$$
p_{②\_right} = \frac{8}{7} \left[ e^{-\frac{E_{left}}{kB T}} / \left( e^{-\frac{E_{left}}{kB T}} + e^{-\frac{E_{right}}{kB T}} \right) \right] \approx \frac{8}{7} e^{-\frac{\Delta E}{kB T}}
$$

(3)

where $E_{left}$ and $E_{right}$ denote the energies of the left- and right-side states of Equation (2). Because the Li11/12M11/12Zr1/12O24 composition of the crystal model is used for the DFT calculation of phase ② in this study, the final equilibrium doping concentration of Zr is obtained by multiplying $p_{②\_right}$ by 1/12. The calculation result indicates that the equilibrium concentration of Zr substituting for the transition metals in the stoichiometric LNCM crystal is very low at approximately 0.003%.

Ni-based layer-structured cathode materials are generally synthesized using hydroxide or carbonate precursors ([Ni,Co,Mn](OH)2 or (Ni,Co,Mn)CO3) as the starting materials and reacting them with LiOH·H2O or Li2CO3. Because the overall oxidation number of the transition metals in the precursor is close to +2, O2 should be supplied during the synthetic reaction to obtain the cathode material in which the average oxidation state of the transition metals is +3. For this reason, it is common to provide air or O2 gas during the heating process. However, temporal and/or local shortages of the O2 supply in the sample may possibly occur during the synthesis. If O2 is insufficiently supplied, the compositional point shifts from the compositional line connecting [① + Li2ZrO3] and [⑪ + Li2ZrO3] to the compositional triangle of [① + Li2ZrO3]-[⑪ + Li2ZrO3]-[⑦ + Li2ZrO3], to the
To examine the behavior of equilibrium doping concentration of Zr with this change in composition caused by the insufficient O2 supply, the stoichiometric relation between the thermodynamically stable phases and the imaginary Zr-doped phase is summarized in Table 2 for the compositions ⓐ-ⓢ in Figure 3A (where the compositional point moves from ⓐ to ⓢ as O becomes deficient). In the same manner as the ratio between phase ❷ and ⓪+[Li2ZrO3] was determined from their Boltzmann factors, the equilibrium proportion of Zr-doped phases is calculated based on the chemical equations of Table 2 and using Equation (3) with modification of the numerical coefficients. Multiplying by 1/12, the Zr concentration in the model supercell units for DFT calculation, the equilibrium concentrations of Zr are finally obtained for the compositional states.

**TABLE 2** The changes occurring as O becomes deficient in the composition

<table>
<thead>
<tr>
<th>Composition point</th>
<th>Location on phase diagram</th>
<th>Chemical equation between unstable and stable states</th>
<th>Concentration of Zr in LNCM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ⓐ</td>
<td>⓪+[Li2ZrO3]-[.addAll]+Li2ZrO3</td>
<td>3/8LiM<em>O2 (①) + 1/2Li11/12M</em>13/12Zr1/12O2 (ⓩ)+1/12Li2ZrO3 = LiM*11/12Zr1/12O2 ⑩</td>
<td>0.0028</td>
</tr>
<tr>
<td>ⓑ</td>
<td>⓪+[Li2ZrO3]-[addAll]+Li2ZrO3</td>
<td>3/8LiM<em>O23/12 (⑦)+1/2Li11/12M</em>13/12O2 (ⓩ)+1/12Li2ZrO3 = LiM*11/12Zr1/12O23/12+1/8/12(5/8⑩)+3/8⑩</td>
<td>0.0071</td>
</tr>
<tr>
<td>ⓒ</td>
<td>⓪+[Li2ZrO3]-[addAll]+Li2ZrO3</td>
<td>3/8LiM<em>O23/12 (⑦)+1/2Li11/12M</em>13/12O23/12 (ⓩ)+1/12Li2ZrO3 = LiM*11/12Zr1/12O23/12+1/8/12(1/8⑩)+7/8⑩</td>
<td>0.11</td>
</tr>
<tr>
<td>ⓓ</td>
<td>⓪+[Li2ZrO3]-[addAll]+Li6Zr2O7-[addAll]+Li2ZrO3</td>
<td>5/22LiM<em>O23/12 (⑦)+7/11Li11/12M</em>13/12Zr1/12O23/12 (ⓩ)+1/88Li6Zr2O7+2/33Li2ZrO3 = LiM*11/12Zr1/12O23/12</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Note: Thermodynamically stable phases at each compositional point, the chemical equations between the unstable Zr-doped and the stable undoped states, and the calculation results of the equilibrium Zr concentrations at each compositional state are presented.

To examine the behavior of equilibrium doping concentration of Zr with this change in composition caused by the insufficient O2 supply, the stoichiometric relation between the thermodynamically stable phases and the imaginary Zr-doped phase is summarized in Table 2 for the compositions ⓐ-ⓢ in Figure 3A (where the compositional point moves from ⓐ to ⓢ as O becomes deficient). In the same manner as the ratio between phase ❷ and ⓪+[Li2ZrO3] was determined from their Boltzmann factors, the equilibrium proportion of Zr-doped phases is calculated based on the chemical equations of Table 2 and using Equation (3) with modification of the numerical coefficients. Multiplying by 1/12, the Zr concentration in the model supercell units for DFT calculation, the equilibrium concentrations of Zr are finally obtained for the compositional states.

**FIGURE 3** Characteristics of Zr-added LNCM, whose composition among the metal elements is at the stoichiometric composition for LNCM:Zr (ie, the ratio of Li to M*+Zr is unity), with increases in O deficiency. A, The shift of the compositional point of phase ❷ with increasing O deficiency (shown on a magnified phase diagram from Figure 2). B, The equilibrium doping concentrations of Zr and the compositions of secondary phases at each composition point.
The results in Figure 3 indicate that the equilibrium doping concentration of Zr increases as the O deficiency increases. This shows that the shortage of O is favorable for Zr-doped LNCM (LNCM:Zr) formation, rather than that of a mixed state of undoped LNCM and secondary phases. For example, when the composition moves from ④ to ⑤, the number of cases wherein the compositional change is accommodated by the system may be listed as the reaction equations of (4-1), (4-3), and (4-4). In reactions (4-1) and (4-3), O vacancies are formed in undoped LNCM or in the Li2ZrO3 secondary phase; therefore, the O deficiency is resolved in the left sides of the chemical equations given in Table 2. Whereas, in reaction (4-4), the O deficiency forms vacancies in LNCM:Zr. By reaction (4-1), phase ① gradually changes to ②, while by (4-4), phase ③ changes to ④. It seems the O vacancy is preferentially generated in LNCM:Zr rather than undoped LNCM, which may decrease the ΔE value of the reaction equation in Table 2 as the composition changes from ④ to ⑤, resulting in an increased proportion of the LNCM:Zr phase and an increase in the Zr equilibrium doping concentration, as presented in Figure 3.

\[ \text{LiM}^{+}\text{O}_{2} (\text{①}) \longrightarrow \text{LiM}^{+}\text{O}_{2-\delta} (\text{④}) \] (4-1)

\[ \text{Li}_{11/12}\text{M}^{+}_{13/12}\text{O}_{2} (\text{⑥}) \longrightarrow \text{Li}_{11/12}\text{M}^{+}_{13/12}\text{O}_{2-\delta} (\text{⑨}) \] (4-2)

\[ \text{Li}_{2}\text{ZrO}_{3} \longrightarrow \text{Li}_{2}\text{ZrO}_{3-\delta} \] (4-3)

\[ \text{LiM}^{+}_{11/12}\text{Zr}_{1/12}\text{O}_{2} (\text{⑧}) \longrightarrow \text{LiM}^{+}_{11/12}\text{Zr}_{1/12}\text{O}_{2-\delta} (\text{⑪}) \] (4-4)

\[ \text{Li}^{+}\text{O}_{23/12} (\text{⑦}) + 8\text{iLi}_{2}\text{ZrO}_{3} \longrightarrow \text{Li}_{1+}\text{i}\text{M}^{+}\text{Zr}_{4}\text{O}_{23/12} + 8\text{iLi}_{6}\text{Zr}_{2}\text{O}_{7} + 2\delta\text{Li}_{2}\text{ZrO}_{3} \] (4-5)

For a more detailed investigation of the above discussion, the changes expected to occur with a shortage of O, such as changes in the oxidation numbers of metals, formation of defects, and changes of secondary phases, are examined and summarized in Table 3. Comparing the cases of reactions (4-1) and (4-4), both cases involve the formation of V_{M}^{\ast}, similar decreases in the oxidation number of M\textsuperscript{+}, and no secondary phase changes. Therefore, these factors do not seem to cause any significant difference in the tendency of accommodating O deficiencies between (4-1) and (4-4). Another factor that can be considered to cause a difference in the receptivity to O deficiency is the strain energy. The strain energy may be generated with defect formation and the resulting distortion of the crystal structure. In Table 4, the changes in the lattice parameters of the Li_{12}M_{12}O_{24} supercell with the formation of O vacancies or Zr doping is presented, which indicates that O vacancies decrease the lattice parameters while Zr doping increases them.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Oxidation state</th>
<th>Change in defects</th>
<th>Secondary phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4-1)</td>
<td>M\textsuperscript{2+} \rightarrow M\textsuperscript{2.85\textsuperscript{+}}</td>
<td>2\delta[V_{M}^{\ast}]_{\text{LNCM}}</td>
<td>No change</td>
</tr>
<tr>
<td>(4-2)</td>
<td>M\textsuperscript{2.85\textsuperscript{+}} \rightarrow M\textsuperscript{2.85\textsuperscript{+}}</td>
<td>2\delta[V_{M}^{\ast}]_{\text{LNCM}}</td>
<td>No change</td>
</tr>
<tr>
<td>(4-3)</td>
<td>Li\textsuperscript{1\textsuperscript{+}} \rightarrow Li\textsuperscript{1\textsuperscript{+}}</td>
<td>No change</td>
<td></td>
</tr>
<tr>
<td>(4-4)</td>
<td>M\textsuperscript{2.91\textsuperscript{+}} \rightarrow M\textsuperscript{2.91\textsuperscript{+}}</td>
<td>No change</td>
<td></td>
</tr>
<tr>
<td>(4-5)</td>
<td>M\textsuperscript{2.83\textsuperscript{+}} \rightarrow M\textsuperscript{2.83\textsuperscript{+}}</td>
<td>No change</td>
<td></td>
</tr>
</tbody>
</table>

Note: \| and \} represent increases and decreases of the amounts, respectively.
As the shortage of O increases, the entire composition moves through point ⑥ to point ④, where there is no change in the type of stable LNCM phases, but the compositions of the secondary phases change ([①, ③], Li2ZrO3) → ([⑦, ④], Li2ZrO3, Li6Zr2O7). This type of change can be interpreted by reaction (4-5), which is characterized by the production of LNCM:Zr and Li6Zr2O7 phases while the original secondary phase of Li2ZrO3 decreases in amount. This may be attributed to the increased efficiency of O deficiency accommodation by the disassembly and reconstruction of phases in this severely O-deficient state, relative to the formation of O vacancies in a phase, as was the case for the mild O shortage section of ②-⑥. In other words, the mechanism for adapting to the O-deficient synthesis circumstance changes from the formation of O vacancies to the redistribution of the phases as the O shortage increases. Reaction (4-5) indicates that O deficiency induces the extraction of 4δ amount of Li-Zr-2O from Li2ZrO3 and the formation of a layered structure containing Zr, which increases the Li:Zr ratio in the Li2ZrO3 phase from 2:1 to (2-4δ):(1-4δ), thus inducing the formation of Li2Zr2O7 as a new secondary phase with a higher Li:Zr ratio. Thus, the equilibrium Zr concentration in LNCM decreases in the ⑥ to ④ section with the change in secondary phases.

### DISCUSSION

The simulation results may be summarized as: (a) The entire LNCM crystal, with the introduction of Zr, is considered as a combination of the states modeled as supercells with certain defects, with or without secondary phases, as listed in Table 1. The proportion of each state in the overall crystal is determined by the Boltzmann factor. (b) When the Li to M+ + Zr ratio is set at unity, aiming to obtain the stoichiometric composition of LNCM:Zr phase, the actual thermodynamically stable phase is simulated as a mixture of [①] (perfect LNCM supercell crystal), [⑦] (the LNCM supercell with a vacancy of O), and [④] (the LNCM supercell with an excess M+ substituting Li), with the secondary phase of Li2ZrO3. (c) At this Li to M+ + Zr ratio, the equilibrium doping concentration of Zr in LNCM is expected to be very low, and to increase when an insufficient O supply introduces O deficiencies during the synthesis. Recently, researchers have reported improved performances from LNCM cathodes by the addition of Zr. They have even controlled the distribution of Zr by optimizing the heating condition, or designed processes in which a coating layer of Zr is expected to diffuse into the host crystals if the doping limit of the coating element in the host is sufficiently high, but the experimental results show that Zr still exists as a coating material on the LNCM surface even after high-temperature heating processes. This indicates that the doping limit of Zr in LNCM is very low, and that Li2ZrO3 can stably coexist with LNCM as a coating layer, which show good agreement with our simulation results predicting the low equilibrium doping concentration of Zr in LNCM and the main secondary phase of Li2ZrO3.

Song et al.\(^{[33]}\) reported the improved performance of a Ni-rich layered oxide cathode by the inclusion of a Li2ZrO3 coating. In their experiment, the coating layer remained after high-temperature heating (even at 800°C, which is the typical synthetic temperature for Ni-rich cathodes). Zhan et al.\(^{[34]}\) also reported that a Li2ZrO3 coating layer remained on the surface of LiNi0.5Co0.2Mn0.3O2 and LiNi0.5Co0.2Mn0.3O2 after heat treatment. Coating materials are expected to diffuse into the host crystals if the doping limit of the coating element in the host is sufficiently high, but the experimental results show that Zr still exists as a coating material on the LNCM surface even after high-temperature heating processes. This indicates that the doping limit of Zr in LNCM is very low, and that Li2ZrO3 can stably coexist with LNCM as a coating layer, which show good agreement with our simulation results predicting the low equilibrium doping concentration of Zr in LNCM and the main secondary phase of Li2ZrO3. The reliability of the simulation is also supported by Du et al.\(^{[35]}\) who reported the detection of Li2ZrO3 as an impurity phase in their LiNi0.5Co0.2Mn0.3O2 sample upon adding Zr as an intended dopant.

Recently, a hybrid treatment method has been reported in which coating and doping effects are achieved simultaneously by controlling the annealing temperature of ZrO2-coated Ni-based cathode materials. This may be possible because of the low doping limit of Zr in the cathode. Yoon et al.\(^{[15]}\) reported that, by introducing Zr to the Ni(OH)2 precursor, they could induce partial Zr doping in the cathode material while the remaining Zr formed a surface coating layer; thus, they accomplished the synthesis of a Zr-doped and Zr-coated cathode by a single heating process. Huang et al.\(^{[12]}\) reported that they obtained both coating and doping effects by the annealing of ZrO2-coated Li(Ni1/3Co1/3Mn1/3)O2, and that the degrees of the two effects could be adjusted through temperature control. Such doping and coating hybrid treatment is possible owing to the slow kinetics of thermal diffusion of Zr into Ni-based cathode materials because of the low equilibrium doping concentration, which agrees well with the prediction of the simulation performed in this study.

**Table 4** Changes of the lattice parameters (a, c), cell volume (V), and average M+ oxidation number of the Li12M+12O24 and Li12M+13O24 supercell units with doping of Zr or formation of an O vacancy.

<table>
<thead>
<tr>
<th>Description</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>M+ oxidation no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li12M+12O24</td>
<td>5.741</td>
<td>13.879</td>
<td>396.21</td>
<td>+3.00</td>
</tr>
<tr>
<td>Li12M+12O23</td>
<td>5.731</td>
<td>13.861</td>
<td>394.34</td>
<td>+2.83</td>
</tr>
<tr>
<td>Li12M+11ZrO24</td>
<td>5.794</td>
<td>14.061</td>
<td>408.89</td>
<td>+2.91</td>
</tr>
<tr>
<td>Li12M+11ZrO23</td>
<td>5.789</td>
<td>14.037</td>
<td>407.39</td>
<td>+2.73</td>
</tr>
<tr>
<td>Li11M+12O24</td>
<td>5.743</td>
<td>13.947</td>
<td>398.37</td>
<td>+2.85</td>
</tr>
<tr>
<td>Li11M+12ZrO24</td>
<td>5.820</td>
<td>14.113</td>
<td>414.06</td>
<td>+2.54</td>
</tr>
<tr>
<td>Li11M+12ZrO23</td>
<td>5.792</td>
<td>14.077</td>
<td>409.00</td>
<td>+2.38</td>
</tr>
</tbody>
</table>
Our simulation also predicts a decrease in the Zr doping limit and change in the secondary phases for O deficiency during synthesis. Song et al.\textsuperscript{[33]} and Zhan et al.\textsuperscript{[34]} flowed O\textsubscript{2} during the annealing of their Li\textsubscript{2}ZrO\textsubscript{3}-coated cathode samples. From our simulation results, the O\textsubscript{2} atmosphere contributed to preventing the thermal diffusion of Zr into the cathode material, thus preserving the Li\textsubscript{2}ZrO\textsubscript{3} coating layer, by maintaining the low Zr doping limit of the cathode material. However, a disagreement between the experimental results and our predictions is observed from Zhan et al.'s comparative annealing test of atmosphere between O\textsubscript{2} and air flow\textsuperscript{[34]}: the amount of Zr doped in LiNi\textsubscript{0.6}Co\textsubscript{0.2}Mn\textsubscript{0.2}O\textsubscript{2} did not differ significantly, which is inconsistent with the simulation predicting an increase in Zr doping with O deficiency. Two explanations are likely to be available for this. First, it is assumed that the air atmosphere did not cause a lack of O, and thus did not differ substantially from the oxygen atmosphere. Second, it may be assumed that the doping concentration was affected by defects present within the LNCM.

For a more in-depth examination of the second assumption, the equilibrium Zr doping concentrations in phases \(\text{Li}_{\text{c}}\) with O deficiency are analyzed (Figure 4) in the same manner as that for phase \(\text{Li}_{\text{b}}\). These are Li-deficient or M\textsuperscript{+} excess phases, known to be observed in layer-structured cathode materials with high Ni contents.\textsuperscript{[4,5]} The result presented in Figure 4C shows that O insufficiency increases the doping limit in phase \(\text{Li}_{\text{b}}\), opposing the behavior observed in other cases (Figure 3 and Figure 4B). As shown in Table 4, the supercell of \(\text{Li}_{\text{b}}\) has a larger lattice volume than those of the stable majority phases such as \(\text{Li}_{\text{c}}\), \(\text{Li}_{\text{d}}\), and \(\text{Li}_{\text{e}}\). Therefore, the formation of O vacancy in phase \(\text{Li}_{\text{b}}\) would relieve the strain energy between this phase and the surrounding undoped phases, somewhat increasing the phase stability, which may increase the formation possibility of phase \(\text{Li}_{\text{b}}\), that is, increase the Zr doping concentration in this phase type. Thus, concerning the strain energy, O-deficient conditions are expected to increase the doping limit in phase \(\text{Li}_{\text{b}}\), as they do for phase \(\text{Li}_{\text{c}}\). However, this expectation does not agree with the analytical result in Figure 4; therefore, the behavior of the Zr doping limit in phase \(\text{Li}_{\text{b}}\) must be interpreted with a mechanism other than one based on the strain energy. It is suggested that the M\textsuperscript{+} oxidation state (Table 4) provides a proper explanation: in phase \(\text{Li}_{\text{b}}\), O vacancy formation in the supercell lowers the average formal oxidation number of M\textsuperscript{+} to +2.38, which is very low compared to +3 in the stoichiometric LiM\textsuperscript{+}O\textsubscript{2} and +2.73 of phase \(\text{Li}_{\text{c}}\) with an O vacancy. This excessively low oxidation number of M\textsuperscript{+} provides unfavorable conditions for the formation of O vacancies in phase \(\text{Li}_{\text{b}}\). This effect prevails over the stabilizing effect of the O vacancy caused by the alleviation of the strain energy, which decreases the possibility of the coexistence of Zr doping and O vacancies, thereby decreasing the Zr doping concentration in phase \(\text{Li}_{\text{b}}\), while the oxidation number changes within a tolerable range, therefore the behavior is mainly affected by the strain energy in phase \(\text{Li}_{\text{c}}\).

The Li to (M\textsuperscript{+} + Zr) ratio is 11:13 in phase \(\text{Li}_{\text{c}}\), which is somewhat deviated from that of 1:1 in the stoichiometric composition of the layer-structured cathode material. Therefore, the formation probability of this phase is assumed to be very low, only generated under local or temporary compositional inhomogeneity between Li and (M\textsuperscript{+} + Zr). Nevertheless, as presented in Figure 4, the equilibrium doping concentration of Zr in this phase is relatively high compared to those in other phases, and its behavior with insufficient O is opposite to those of others. Therefore, the characteristics of this phase cannot be neglected in some cases, depending on the experimental conditions. The inconsistency between the simulated expectation of Zr doping concentration shown in Figure 3 and the experiment of Zhan et al.\textsuperscript{[34]} is caused for this reason. This interpretation is supported by their detection of ZrO\textsubscript{2} from their annealing atmosphere-dependent test samples: ZrO\textsubscript{2} is predicted in our simulation to appear as a component of the secondary phases for the composition of phase \(\text{Li}_{\text{c}}\) (Figure 4C), while Li\textsubscript{2}ZrO\textsubscript{3} is the major secondary phase component for the composition of phase \(\text{Li}_{\text{d}}\) (Figure 3); therefore, the existence of ZrO\textsubscript{2} as an impurity may indicate that the samples of Zhan et al.\textsuperscript{[34]} were affected by the characteristics of phase \(\text{Li}_{\text{b}}\) shown in Figure 4C.

From all the above discussions, it may be confirmed that the simulation performed in this study provides proper interpretations for the mechanisms underlying recent experimental achievements in the improved performance of Ni-based cathodes by Zr addition. The equilibrium doping concentration of Zr in LNCM can be predicted from the simulation results. In addition, information on the doping behaviors and secondary phases with varied heating conditions can also be obtained. The methodology and the post-analysis procedure may be applied to other host crystal + additive
systems, which would provide useful guidance for the selection of proper doping or coating elements, prediction of doping limits, secondary phases, and defects in the host crystal, and suggestions on controlling the processing conditions to achieve certain desired properties.

5 | CONCLUSIONS

A thermochemical investigation was performed on the defects in LNCM crystals, equilibrium doping concentrations of Zr in LNCM, secondary phases, and the effects of insufficient O supply during the heating process, by the simulation of phase diagrams for the Zr-added Li-M*O system. By including considerations for various defect-containing LNCM phases and their combinations with secondary phases, the simulation enabled a systematic examination of Zr doping, LNCM crystal defects, secondary impurity phases, and the interrelationships among them. The simulation results indicated that O vacancies, substitution of Li by M*, and resulting Li deficiencies were the main defects, and that the introduction of Zr slightly expedited their formation. Zr was shown to preferentially form secondary phases rather than becoming doped in the LNCM crystal; therefore, the equilibrium doping concentration of Zr in the LNCM was calculated to be very low. The low doping limit of Zr enabled the maintenance of coating layers of Li-Zr-O compounds on LNCM surfaces even after high-temperature annealing, or the spontaneous formation of a coating layer during LNCM synthesis by the addition of excess Zr to the precursor. For an insufficient O2 supply during the synthesis of the stoichiometric designed composition of LNCM:Zr, the Zr doping amount was predicted to increase and the composition of secondary phases was predicted to change, indicating that the heating atmosphere could be an effective factor in controlling the dopability of Zr and the components of secondary phases in the coating layer. The change of equilibrium doping limit of Zr with O deficiency can be interpreted in terms of the strain energy induced or released by Zr doping and formation of O vacancy, and in terms of the extent of deviation of the transition metals’ oxidation state from their normal average value of +3. The simulation in this study permitted a systematic investigation including defects, secondary phases, and the effects of heating conditions for Zr-added LNCM, and provided a quantitative post-analysis method. The demonstrated methodology is expected to be applicable to many other doping and coating systems, providing useful guidance for experimental research.

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REFERENCES

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