Self-assembly of core–shell structures driven by low doping limit of Ti in LiCoO$_2$: first-principles thermodynamic and experimental investigation

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Introducing additives is a general method of performance improvement in materials engineering, but details regarding whether the additive is doped in the host crystal or present as a secondary phase are usually examined from experimental experience, with a systematic theoretical prediction lacking, which sometimes causes controversy on the role of additives. In this study, the dopability of Ti in crystalline LiCoO$_2$ (LCO) is investigated by a first-principles simulation method, and the doping limit is quantitatively calculated. The probability of Ti substitution for Co is examined and related to point-defect formation in LCO as a function of the general experimental variables of temperature and gas-phase partial pressures, enabling practical use of the theoretical model for real experiments. It was found that Ti substitution for Co, accompanied by the formation of a Li vacancy, is the most probable Ti doping form in LCO, but the doping limit is very low and most Ti would segregate into secondary phases. The theoretical prediction showed good agreement with the experimental results. Based on theoretical predictions, particles having LCO cores and Ti-rich shells are obtained from a simple sol–gel route followed by one-step firing without additional surface treatment. The high-voltage cyclability of LCO is greatly improved. The method demonstrated in this study may be a useful tool for screening suitable coating or doping elements for various material systems and provide a guide for designing simple spontaneous coating processes, as in this study.

1. Introduction

Li-ion batteries (LIBs) are widely used to supply electric power for mobile electric devices because they show high energy-storage densities. Application of LIBs is expected to broaden to include large systems, such as electric vehicles (EVs) and energy storage systems.1–3 Unfortunately, the performance of LIBs remains below consumer expectations. Improved energy capacity and user safety are particularly desired, for these properties are closely related to the mileage of EVs per charge and to the prevention of fatal explosions of large-scale batteries.3 The positive and negative electrodes, electrolyte, and separator are the four main parts of LIBs; the materials for positive electrodes are subject to particularly active research because they are crucial in determining the capacity and safety of LIBs.1,4–8

Positive electrode materials with mechanisms based on the insertion and desorption of Li ions are classified into layered, spinel, and olivine materials, according to the crystal structure.2,3,9 Among these, layer-structured materials including LiCoO$_2$ (LCO), LiNi$_{1−x}$Mn$_x$O$_2$ (LNCM), and LiNi$_{1−x}$Co$_x$Al$_2$O$_4$ (LNCA) are commonly used. LCO is the most widely used material in the current LIB industry because it shows good properties in every aspect required for LIBs, such as capacity, operation voltage, efficiency, rate performance, durability, and safety.2,4 The high volumetric capacity, particularly necessary for mobile devices, may also contribute to the general use of LCO in small-sized LIBs, which comprise much of the LIB market. As a measure to increase the energy capacity of LIBs using the excellent properties of LCO, the high-voltage operation of LCO is actively researched.

Many efforts have attempted to address the structural and thermal instability of LCO appearing during high-voltage charging of LIBs by doping impurity elements in the LCO crystal or coating the surfaces of LCO particles.10–14 Doping and coating are general materials engineering methods, with applications beyond the case of LCO. However, trials of these methods often yield unexpected results; coating layers can disappear during post-processing, or elements introduced for doping might not reside in the host crystal, and instead, segregate on the surface or grain boundary. Thus, it is possible to achieve unintended results with the doping or coating treatment of materials. The controversy regarding the mechanism of F treatment of positive electrode materials, that
is, whether the effect arises from F substituting for O or the formation of fluoride shells on crystal surfaces, is one example of the uncertainties of doping and coating methods.\textsuperscript{15-17}

To determine whether an added element is doped in host-material crystals or is part of a coating or segregation layer, empirical knowledge is commonly collected from experimental trials and analyses of the resultant output. Approximate predictions may be possible for simple material systems with available phase diagrams, but in many cases, especially for systems with a complicated chemistry, it is difficult to find the appropriate phase information for the combination of the host material and added impurity elements. Thus, theoretical predictions of the results of the intended coating or doping treatment are difficult. In this study, we attempt to provide a systematic prediction model for this topic, focusing on the system of Ti-added LCO: the probability of the impurity becoming doped in the host crystal is discerned by a simulation of phase diagrams based on first-principles calculations, and the doping limit is quantitatively estimated through a thermodynamic approach. The reliability of the theoretical prediction was examined by experiments.

The doping limits of several elements in Co- or Ni-based layer-structured cathode materials were previously investigated by Koyama \textit{et al.} and Chen \textit{et al.}\textsuperscript{18,19} They examined the dopability of impurities in terms of their oxidation numbers and chemical potentials. Despite these excellent recent studies, we believe that advanced investigations on the topic are still required, for it is necessary to examine the type and formation possibility of defects that could be induced with the introduction of dopants in the host crystal. In previous first-principles studies, dopability was generally examined based on chemical potential differences ($\Delta \mu$) before and after the doping reaction. However, this method focuses only on the stability of the dopant in the host material, without considering the possibility that the dopant becomes stable with the formation of additional point defects. In an ionic crystal of $\text{M}^{2+}\text{O}_2^-$, as a simple example, even if a substitution of $\text{M}^{2+}$ by a dopant $\text{D}^{\text{3+}}(\text{D}_\text{M}^{\text{3+}}\text{D}_\text{M}^{\text{3+}})$ is unstable, it may be possible for a combination of the dopant and a defect, such as $\text{D}_\text{M}^{\text{3+}}+1/2\text{V}_\text{O}^\text{2-}$, to become stable. In this example, the sign of the Gibbs free energy change ($\Delta G$) of each doping reaction may be as follows:

$$\text{MO} + x\text{D} \rightarrow \text{M}_{1-x}\text{D}_x\text{O} + x\text{M} \quad \Delta G > 0 \quad (1)$$

$$\text{MO} + x\text{D} \rightarrow \text{M}_{1-x}\text{D}_x\text{O}_1-(1/2)x + x\text{M} + (1/4)x\text{O}_2 \quad \Delta G < 0 \quad (2)$$

As seen from the example, the possibility of an impurity element being doped in the host crystal in combination with point defects should not be excluded. Therefore, the thermodynamic study of doping should be systematically connected with defect chemistry. Another point to consider is the types of reactants and products involved in the doping reaction: in the above example, the dopant and the host element substituted by the dopant (D and M) are assumed to be purely metallic in state, but metallic elements commonly form oxides, hydroxides, or carbonates upon reactions with air. Thus, reactions of D or M with gas phases in air, such as $\text{O}_2$, $\text{H}_2\text{O}$, and $\text{CO}_2$, or with the gas of a reaction product like $(1/4)x\text{O}_2$ in eqn (2), should be examined for effects on the overall doping reaction: changes in $\Delta G$ of the doping reaction when metallic compounds are involved in the reaction, instead of the pure metals, must be investigated. In addition, thermodynamic conditions such as ambient temperature and gas pressure should be considered in calculating $\Delta G$. This feature is reflected in the changing input values of elemental chemical potentials in the works of Hoang \textit{et al.} and Koyama \textit{et al.}\textsuperscript{18,20-22} However, the chemical potential values ($\mu_\text{D}$, $\mu_\text{M}$, and $\mu_\text{O}$ in the example above) cannot be directly measured or controlled under general experimental environments; therefore, a new simulation technique designed as a function of the typical thermodynamic variables of composition, temperature, and (partial) pressure is necessary.

In this study, in view of the aforementioned discussion, the dopability was examined in relation with defect chemistry, considering not only pure metal states but also oxide, hydroxide, and carbonate states of metallic elements. A simulative investigation based on first-principles calculations was performed for the Ti-added LCO system as a function of composition and temperature, including considerations of the partial pressure of gas phases; thus, the doping ability of Ti in crystalline LCO, the doping limit, and the probable types of dopant-defect combinations were investigated using a thermodynamic examination of the combination of the Ti dopant species of $\text{Ti}_{\text{Co}}\text{Ti}_{\text{Li}}$, and Ti and point defects, such as vacancies and antisites, in the host LCO crystal. The simulation results were presented on Li-M-O ternary phase diagrams as functions of temperature and partial pressures ($\mu_\text{O}_2$, $\mu_\text{CO}_2$, $\mu_\text{H}_2\text{O}$), other than of elemental chemical potentials. This may enable the practical use of the simulation in general laboratory environments.

The results of the theoretical investigation and the reliability of the simulation model were confirmed experimentally. Ti-added LCO samples were synthesized and the physical and electrochemical properties were analyzed to examine the performance of the systems as cathode materials for LIBs. The simulation predicted that Ti added to LCO tends to segregate on the surface rather than becoming doped in the LCO crystal, which was supported by the experimental results. We found that a Ti-based coating layer might spontaneously develop during the calcination process for the synthesis of LCO; thus, surface-coated LCO could be synthesized by a simple sol–gel route with only one firing process and no additional treatment. Our simulation method may provide predictions of dopability of certain elements in host crystals. This information may be useful in classifying impurity elements as suitable for doping versus coating, depending on the host materials, and may provide help in designing simple spontaneous coating methods. The approach of this study should be applicable to many impurity-added material systems, providing useful information on the phenomena related to the addition of impurities.

\section{2. Method}

\subsection{2.1. First-principles simulation}

Various types of associated Ti and point defects were designed by changing the Ti doping site and combining point defects in the LCO crystal: Co or Li replacement and embedment at tetrahedral sites were considered as Ti doping sites, denoted
by Ti$_{Co}$, Ti$_{Li}$, and Ti$_{tet}$, respectively; vacancies (V$_{Li}$, V$_{O}$, and V$_{Co}$) and cation antisites (Co$_{Li}$ and Li$_{Co}$) were considered as point defects. Point defects other than these were excluded by pre-screening because they had high formation energies. Thus, 22 types of Ti-doping and defect combinations were considered, as presented in Table 1. Model crystals for density functional theory (DFT) calculations were obtained by introducing each of the combinations in a Li$_{12}$Co$_{1/12}$Ti$_{12}$ frame crystal. The Ti/(Co + Ti) ratio was fixed at 1/12; differently sized frame crystals were used as necessary for cases including Ti$_{tet}$ or Ti$_{Li}$. For each case, the most stable arrangement of Ti and the associated defects was determined by changing their positions in the crystal model and comparing the energies calculated by DFT.

In addition to these Ti-doped models, the cases in which Ti is not in the crystal but instead a separate secondary phase were also considered. The formation of Li$_{5}$Ti$_{4}$O$_{12}$, TiO$_{2}$, Li$_{5}$Ti$_{4}$O$_{12}$, LiTiO$_{2}$, LiTi$_{2}$O$_{4}$, and Li$_{5}$Ti$_{2}$O$_{16}$ phases was considered, and the point defects presented in Table 1 were also introduced to the point defects presented in Table 1 were also introduced in the LCO crystal. Thus, 66 total cases of [LTCO + defect(s)] or [LCO + defect(s) + Ti-secondary phase] were produced. The [LTCO + defect(s)] phases, in which Ti is doped in the LCO crystal, are expressed as numbers in solid circles, such as 1, 2, 3, ..., whereas [LCO + defect(s) + Ti-secondary phase] phases, in which Ti is not doped in LCO but forms secondary phases, are indicated as open-circle numbers (1, 2, 3, ...). These were included in the simulation of phase diagrams, as if each were an independent phase. The energy of the 66 models, as well as that of the regular phases of the Li–(11/12Co, 1/12Ti)–O system as reported in the Inorganic Crystal Structure Database, was calculated by DFT, and the normalized Gibbs free energy was obtained from eqn (3):

$$
\frac{G}{G_{0}} = \frac{G}{G_{0}}^{\text{Li}_5\text{M}_7\text{O}_{16}([\text{CO}_2\text{O}_4\text{H}_2\text{O}])_a} - a\frac{G_{\text{CO}_2}}{G_{\text{H}_2\text{O}}} - c
$$

The equation was designed to reflect the energy changes related to the addition or removal of CO$_2$ and H$_2$O, which enabled the examination of hydroxide or carbonate phases such as Li$_3$Co$_{10}$, LiOH, and LiOH·H$_2$O. Taking x- and y-coordinates from the position of a phase on the Li–(11/12Co, 1/12Ti)–O ternary composition system, and the z-coordinate from G of eqn (3), an (x, y, z) coordinate can be allotted for each phase. By projecting the coordinate points and binary joins, forming a convex hull to the –z direction at a given thermodynamic condition of temperature and partial pressure of gas phases, ternary phase diagrams of Li–(11/12Co, 1/12Ti)–O were simulated. Because the [LTCO + defect(s)] or [LCO + defect(s) + Ti-secondary phase] states were included in the simulation, the phase diagrams provided information regarding the stability of Ti doping, secondary phases, and point defects under certain conditions. When unstable phases are of interest, the composition triangle in which the phase is located can be identified from the phase diagram. Based on this information, the reaction equation for phase formation can be determined. (This type of reaction equation is necessary to calculate the doping limit of Ti in LCO, as discussed in detail in the Results and discussion section.)

The energy of each solid phase was calculated using DFT, based on the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation with Kresse-Joubert projector augmented-wave (KPJAW)-type PBEsol pseudopotentials. QUANTUM-ESPRESSO code was used with a kinetic energy cutoff of 50 Ry for wavefunctions and a convergence threshold of 10$^{-3}$ Ry Bohr$^{-1}$ on forces for electronic minimization. The k-point spacing was 0.5 Å$^{-1}$ for each lattice vector, and full relaxation of atomic positions and lattice vectors was allowed during the DFT calculation. The isobaric heat capacity was obtained by a quasi-harmonic approximation (QHA) calculation provided in the Thermo-PW package; using this, the Gibbs free energy of each solid phase was calculated as a function of temperature (i.e., G(T)). The standard state chemical potentials of the gas phases were determined semi-empirically to minimize the discrepancy between experimentally reported formation energies of oxide, hydroxide, or carbonate materials and those obtained from DFT calculations (see ref. 24 and 32 for details on the gas-phase chemical potential). The effects of temperature and pressure on the gas-phase chemical potential were accommodated by referring to the JANAF Thermochemical Table.

### Table 1 Phases of LiMO$_2$, where M = Co$_{11/12}$Ti$_{1/12}$, containing combinations of Ti-doping and point defects, included in the simulation of phase diagrams

<table>
<thead>
<tr>
<th>Description</th>
<th>Ti-doping + defects</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti$_{Co}$</td>
<td>LiMO$_2$</td>
</tr>
<tr>
<td>2</td>
<td>Ti$<em>{Co}$ + Co$</em>{Li}$Li$_{Co}$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ti$<em>{Li}$ + Li$</em>{Co}$</td>
<td>LiMO$_2$</td>
</tr>
<tr>
<td>4</td>
<td>Ti$<em>{tet}$ + V$</em>{Co}$</td>
<td>Li$_{11/12}$MO$_3$</td>
</tr>
<tr>
<td>5</td>
<td>Ti$<em>{Co}$ + V$</em>{Li}$</td>
<td>Li$_{11/12}$MO$_3$</td>
</tr>
<tr>
<td>6</td>
<td>Ti$<em>{Co}$ + Co$</em>{Li}$V$_{Co}$</td>
<td>Li$_{11/12}$MO$_3$</td>
</tr>
<tr>
<td>7</td>
<td>Ti$<em>{Co}$ + V$</em>{O}$</td>
<td>LiMO$_{23/12}$</td>
</tr>
<tr>
<td>8</td>
<td>Ti$<em>{Co}$ + V$</em>{Co}$Co$<em>{Li}$Li$</em>{Co}$</td>
<td>Li$<em>{11/12}$MO$</em>{23/12}$</td>
</tr>
<tr>
<td>9</td>
<td>Ti$<em>{Co}$ + V$</em>{Co}$V$_{Li}$</td>
<td>Li$<em>{11/12}$MO$</em>{23/12}$</td>
</tr>
<tr>
<td>10</td>
<td>Ti$<em>{Co}$ + V$</em>{Co}$Co$<em>{Li}$V$</em>{Co}$</td>
<td>Li$<em>{11/2}$M$</em>{13/2}$O$_2$</td>
</tr>
<tr>
<td>11</td>
<td>Ti$<em>{Co}$ + Co$</em>{Li}$</td>
<td>Li$<em>{11/2}$M$</em>{13/2}$O$_2$</td>
</tr>
<tr>
<td>12</td>
<td>Ti$<em>{Li}$ + V$</em>{Li}$</td>
<td>Li$<em>{11/2}$M$</em>{13/2}$O$_2$</td>
</tr>
<tr>
<td>13</td>
<td>Ti$<em>{tet}$ + V$</em>{Li}$</td>
<td>Li$<em>{11/2}$M$</em>{13/2}$O$_2$</td>
</tr>
<tr>
<td>14</td>
<td>Ti$<em>{Co}$ + Co$</em>{Li}$Li$_{Co}$</td>
<td>Li$<em>{11/2}$M$</em>{13/2}$O$_2$</td>
</tr>
<tr>
<td>15</td>
<td>Ti$<em>{tet}$ + V$</em>{Li}$</td>
<td>Li$<em>{11/2}$M$</em>{13/2}$O$_2$</td>
</tr>
</tbody>
</table>

### 2.2. Experiments

Ti-added LCO was synthesized by a sol–gel process. Ti/(Co + Ti) was set to 0, 0.025, 0.05, and 0.1 (i.e., x = 0, 0.025, 0.05, and 0.1 for the expression of Ti-added LCO as Li$_{1/12}$(1 − x)CoO$_{1/12}$xTiO$_{4}$). LiNO$_3$ (98%, Junsei Chem., Japan), Co(NO$_3$)$_2$·6H$_2$O
(97%, Samchun Chem., Korea), C_{12}H_{28}O_{4}Ti (98%, Daejung Chem., Korea), and citric acid (99.5%, Duksan Chem., Korea) were dissolved in distilled water. The molar ratio of Li to citric acid was 1:2. After 4 h stirring, the solution was stored at 80 °C for 24 h and then dried at 120 °C. The obtained purple-colored gel was ground and fired at 900 °C for 10 h under flowing O₂. The powder samples obtained after firing were analyzed by X-ray powder diffraction (XRD, Rigaku Dmax 2500), scanning electron microscopy (FE-SEM, JEOL JEM-2100F), and X-ray photoelectron spectroscopy (XPS, Thermo Scientific, K-Alpha). The XRD patterns were analyzed by the Rietveld method using FullProf Suite software. The electrochemical properties were measured using CR2032-type coin cells. The powder samples were mixed with 5 wt% of each of carbon black and polyvinylidene fluoride binder in N-methylpyrrolidone solvent, and the resulting slurry was coated on Al foil. The loading level of the sample was fixed at ~8.5 mg cm⁻². The electrode was roll-pressed and then vacuum-dried at 110 °C, and the coin cells were assembled in an Ar-filled glove box. Li metal foil was used as the counter electrode, and 1.3 M LiPF₆ solution in a mixed solvent of ethylene carbonate/ethyl methyl carbonate/diethyl carbonate (3/4/3 volume proportion) was used as the electrolyte. The charge/discharge profile was obtained by charging the cells to 4.3 V vs. Li⁺/Li in constant current–constant voltage mode and then discharging to 3.0 V (WonA tech. WBCS3000). The high-voltage cyclic performance was monitored by repeated charging/discharging (4.6–3.0 V) at a rate of 1C (160 mA h g⁻¹). The electrochemical impedance spectroscopy (EIS, WonA tech, ZIVE SP1) profile was obtained at the charged state of 4.6 V in the frequency range of 1 MHz to 5 mHz under 5 mV of AC voltage. The investigational process is presented schematically in Fig. 1.

3. Results and discussion

3.1. First-principles simulation

3.1.1. Stability of Ti doping and defects. The simulation results of the Li–(11/12Co, 1/12Ti)–O phase diagrams are presented in Fig. 2. The phase diagrams were simulated as a function of temperature, with the partial pressures of O₂, CO₂, and H₂O set as 0.02, 3.0 × 10⁻⁵, and 1.5 × 10⁻³ MPa, respectively, assuming a general ambient atmosphere. Because Ti replaces 1/12 of Co in the Li–Co–O system, phases containing Ti and Co among the possible cases should be investigated for stability, i.e., the stability of cases among those in which Ti substitutes Co, Ti does not replace Co but makes a secondary phase, and mixed states of both cases. For the metallic phases, complete solid solutions of Ti and Co are stable. On the compositional line of the (11/12Co, 1/12Ti)–O system, CoO and Co₃O₄ appear as stable phases, and the CoTi₂O₅ secondary phase coexisting with CoO or Co₃O₄ is more stable than phases of Ti-doped cobalt oxides.

On the Li–O line, Li₂CO₃ is the stable phase at low temperatures, but LiO is more stable than Li₂O, LiOH, or LiOH·H₂O at temperatures over 800 K. Assuming a simple Boltzmann distribution, determined from the normalized Gibbs free energy, the proportions of Li existing as oxides, carbonates, and hydroxides were estimated as shown in Fig. 3: it is thermodynamically predicted that Li₂CO₃ is converted to Li₂O at ~800 K. This conversion is known to occur at higher temperatures in actual experiments due to the slow reaction kinetics. Considering that the firing temperatures for layer-structured cathode materials are generally above 1000 K, residual Li from the imperfect reaction of raw materials mainly exists as Li₂O at the synthesis temperature. This Li₂O is converted into Li₂CO₃ or LiOH during the cooling process, mainly present as Li₂CO₃ under normal air conditions as seen in Fig. 3. However, the

![Fig. 1](https://example.com/fig1.png)  
**Fig. 1** Schematic representation of the theoretical and experimental processes of this study.
ratio of oxide, carbonate, and hydroxide may also be affected by the cooling profile and the atmospheric composition.

As for ternary compounds of Li–TM–O, where TM = Co, Ti, layer-structured LiTMO$_2$ and LiTM$_2$O$_4$ spinel appear as stable phases in the phase diagram. The spinel phase is stable only at low temperatures of $300–600$ K. From the simulation including all [LTCO + defect(s)] and [LCO + defect(s) + Ti-secondary phase], the formation of secondary phases such as TiO$_2$, Li$_2$TiO$_3$, and Li$_4$TiO$_4$ is thermodynamically favored over the substitution of Ti for Co in LCO. For the LCO crystal itself, phase $\alpha$ with no defects is the most stable. In summary, [LCO + Ti-secondary phase] combinations (as presented by expressions of $\alpha$ + TiO$_2$, $\beta$ + Li$_2$TiO$_3$, and $\gamma$ + Li$_4$TiO$_4$ in Fig. 2) are thermodynamically stable, and the stability of the secondary phase varies with temperature and design composition.

From the simulation results, it is predicted that the synthesis of Ti-added LiCoO$_2$ would cause the formation of Ti-containing secondary phases, rather than the incorporation of Ti in the LCO crystal. Li$_4$TiO$_4$, Li$_2$TiO$_3$, or TiO$_2$ are the secondary phases most likely to form at the LCO synthesis temperature, generally $1200–1300$ K, but the types and proportions of the secondary phases in the final product may differ depending on the overall composition and the cooling profile of the firing process. For example, for a composition of Li/(Co + Ti) = 1, aimed at the synthesis of stoichiometric Li(Co$_{11/12}$Ti$_{1/12}$)O$_2$, the phase diagram of Fig. 2 predicts that not the Li(Co$_{11/12}$Ti$_{1/12}$)O$_2$ phase but that of [Li$_4$TiO$_4$ + 1/2Li$_2$TiO$_3$ + 1/2TiO$_2$] would be obtained with sufficient O. This is expressed as the reaction in eqn (4), assuming that Li$_4$CoO$_3$, Co$_3$O$_4$, and TiO$_2$ are used as starting materials and that Ti/(Co + Ti) = $x$.

\[
\frac{1}{2}2\text{Li}_2\text{CO}_3 + (1 - x)/3\text{Co}_3\text{O}_4 + x\text{TiO}_2 + (1 - x)/12\text{O}_2 \\
\rightarrow (1 - x)\text{LiCoO}_2 + x/2\text{Li}_2\text{TiO}_3 + x/2\text{TiO}_2 + 1/2\text{CO}_2
\]  

3.1.2. Calculation of doping limit. As discussed, Ti doping of the LCO crystal seems to be thermodynamically unfavorable. This is drawn from the comparison of relative stability among the cases of [LTCO + defect(s)] and [LCO + defect(s) + Ti-secondary phase]. For a quantitative examination of the doping limit of Ti, the driving force for doping by the effect of the entropy of mixing must be considered; the equation reflecting this point may be developed as follows:36

\[
\delta G = \delta G_{\text{fem,CM}_0} + \delta G_{\text{mix}} \approx G_{\text{CM}_0} N_{\text{CM}_0} + \left(H_{\text{mix}} - TS_{\text{mix}}\right)N_{\text{CM}_0}
\]

\[
\delta_{\text{CM}_0} = \frac{\delta G_{\text{fem,CM}_0}}{N_{\text{CM}_0}}, \quad S_{\text{mix}} = \frac{\delta S_{\text{mix}}}{N_{\text{CM}_0}} \approx -k \ln N_{\text{CM}_0}
\]

The equation expresses the change in Gibbs free energy when a crystal model in Table 1 is mixed with the host crystal. That is, it expresses the change in Gibbs free energy ($\delta G$) that arises when a small amount of a crystal containing certain defect types (crystal model of phase $\ominus$) is mixed in a given crystal phase model. $\delta G$ is the sum of the Gibbs free energy of forming the type-\(\ominus\) crystal model ($\delta G_{\text{fem,CM}_0}$) and the mixing energy of the type-\(\ominus\) crystal in the matrix crystal ($\delta G_{\text{mix}}$). With the assumptions of a very low concentration of the type-\(\ominus\) defect phase and negligible strain energies due to lattice-parameter mismatches between type-\(\ominus\) and the host crystal models, the mixing may be treated as ideal, and the equation for calculating the concentration of the type-\(\ominus\) crystal model in the matrix crystal can be derived from the point that $\delta G/N_{\text{CM}_0} = 0$ at the equilibrium concentration:

\[
\delta G \equiv G_{\text{CM}_0} \delta N_{\text{CM}_0} + kT \ln N_{\text{CM}_0} \delta N_{\text{CM}_0} \rightarrow N_{\text{CM}_0}^{\text{eq}} = \exp\left(-\frac{G_{\text{CM}_0}}{kT}\right)
\]

where $G_{\text{CM}_0}$ denotes the formation Gibbs free energy of one unit of the type-\(\ominus\) crystal model, obtained as a function of temperature from DFT and QHA calculations, and $N_{\text{CM}_0}^{\text{eq}}$ is the equilibrium
The concentration of an individual defect may be obtained by summing the concentration of all defect-combinations containing that defect. For example, to calculate \( c_{V_{\text{Li}}} \), the concentrations of the defect-combinations type-\( \Theta \), \( \Theta_{\text{Li}} \), \( \Theta_{\text{Co}} \), \( \Theta_{\text{Ti}} \), \( \Theta_{\text{Li}_{2} \text{TiO}_3} \), and \( \Theta_{\text{Co}_{11/12} \text{Ti}_{1/12}} \) that contain \( V_{\text{Li}} \) species are summed. This may be expressed in the general form of the following equation for calculating the equilibrium concentration of a specific point defect (type-\( \Theta \)), where \( Z_{D_{\Theta}} \) indicates the number of point defects included in the defect combination:

\[
N^m_{D_{\Theta}} = \exp \left( - \frac{G_{\text{CM}_{\Theta}}}{kT} \right) \times n_{D_{\Theta}} \times Z_{D_{\Theta}}
\]

The overall concentration of Ti in the LCO crystal can be obtained by summing the concentrations of all cases listed in Table 1. To calculate \( c_{\text{Ti}_{\text{Co}}} \), the concentrations of cases in which Ti occupies Li or interstitial sites are subtracted from the summation.

\[
G_{\text{CM}_{\Theta}} \text{, the Gibbs free energy of formation for the type-\( \Theta \) crystal model, is necessary for the calculation of eqn (5). Because } G_{\text{CM}_{\Theta}} \text{ can be considered as the change of Gibbs free energy when a unit of the type-\( \Theta \) crystal model is formed from the most stable phases under given thermodynamic conditions of temperature and pressure, and information on the thermodynamically stable phases at this condition is required for the calculation. This information can be obtained from the phase diagrams; therefore, simulating the phase diagrams (Fig. 2) is a prerequisite to obtaining \( G_{\text{CM}_{\Theta}} \). For the crystal model type-\( \Theta \), which contains \( \Theta_{\text{Co}_{11/12} \text{Ti}_{1/12}} \), for example, the formation reaction is composed as follows at 1300 K in air, because the type-\( \Theta \) phase is located in the composition triangle of \([\text{LiCoO}_2 + 1/11\text{Li}_2\text{TiO}_3] - [\text{Co}_{11/12} \text{Ti}_{1/12}] - [\text{CoO} + 1/21\text{CoTi}_2\text{O}_5] \) in the phase diagram of Fig. 2(d) for the overall composition of an Li/TM ratio of 1 and Ti/(Co + Ti) of 1/12:

\[
\begin{align*}
11/13[\text{LiCoO}_2 + 1/11\text{Li}_2\text{TiO}_3] + 1/169[\text{Co}_{11/12} \text{Ti}_{1/12}] & - [\text{CoO} + 1/21\text{CoTi}_2\text{O}_5] \\
+ 21/338[\text{CoO} + 1/21\text{CoTi}_2\text{O}_5] & \rightarrow \text{LiCo}_{11/12} \text{Ti}_{1/12} \text{O}_2 
\end{align*}
\]

(9a)

Conventionally, the reaction equation and the Gibbs free energy change for the formation of a defect were approached in terms of individual atoms and their chemical potentials. In this conventional approach, the formation reaction of the type-\( \Theta \) crystal model might be suggested as:

\[
\text{Li} + 11/12\text{Co} + 1/12\text{Ti} + \text{O}_2 \rightarrow \text{LiCo}_{11/12} \text{Ti}_{1/12} \text{O}_2
\]

(9b)

As seen from Fig. 4, the three-dimensional presentation of the phase diagram Fig. 2(d), the Gibbs free energy of forming the type-\( \Theta \) phase is negative with the reaction of in eqn (9b); therefore, Ti doping is predicted to be thermodynamically favorable because the position of the type-\( \Theta \) phase is located under the Li–M–O triangle. However, this conventional method that considers only elemental states as the baseline does not provide a thorough examination: although the type-\( \Theta \) phase is located under the triangle of Li–M–O, it is located over the \([\text{LiCoO}_2 + 1/11\text{Li}_2\text{TiO}_3] - [\text{Co}_{11/12} \text{Ti}_{1/12}] - [\text{CoO} + 1/21\text{CoTi}_2\text{O}_5] \) triangle; therefore, the type-\( \Theta \) phase is unstable relative to the \([\text{LiCoO}_2 + 1/11\text{Li}_2\text{TiO}_3] - [\text{Co}_{11/12} \text{Ti}_{1/12}] \) and \([\text{CoO} + 1/21\text{CoTi}_2\text{O}_5] \) phases. That is, \( \Delta G \) calculated from eqn (9a) is positive, while that from eqn (9b) is negative. From the examination of this example case, it is clear that a thermodynamic investigation of a point defect requires the identification of the exact compositional triangle comprising the most stable phases at the selected condition. Thus, we claim that thermodynamic defect chemistry must be based on proper phase diagrams; therefore, the simulation of phase diagrams is an essential foundation for the study of point defects or dopants, as in the proposed methodology of this work.

By substituting the \( \Delta G \) value calculated from eqn (9a) for \( G_{\text{CM}_{\Theta}} \) of eqn (7), the concentration of the type-\( \Theta \) defect combination \( \Theta_{\text{Co}_{11/12} \text{Ti}_{1/12}} \) was calculated. In the same manner, other concentrations of defect combinations can be obtained. In Table 2, the calculated concentrations of major defect combinations including \( \Theta_{\text{Co}_{11/12} \text{Ti}_{1/12}} \) are presented, and the doping limit of Ti is estimated by summing them up. Ti doping at Li or interstitial sites appeared far less stable than Ti doping at Co sites; thus, the concentration of defect combinations containing \( \Theta_{\text{Li}_{2} \text{TiO}_3} \) or \( \Theta_{\text{Co}_{11/12} \text{Ti}_{1/12}} \) is almost negligible.

The probability of Ti doping is the highest in combination with \( V_{\text{Li}} \), so the overall doping concentration of Ti is mainly determined by this type of combination (i.e., type-\( \Theta \) \( (\Theta_{\text{Co}_{11/12} \text{Ti}_{1/12}} + V_{\text{Li}}) \)), which is calculated to be \( \sim 0.15\% \) at 1300 K (synthesis temperature) and \( \sim 10^{-6}\% \) at 298 K (room temperature). The actual doping amount of Ti may be between these two doping limits, depending on the cooling condition after calcination. Thus, the doping limit of Ti in LCO crystal is expected to be very small, maximized at 0.15%. The oxidation state of Ti, analyzed from the magnetic moment calculated by DFT, was +4 for all the models. The highest concentration of Ti occurring in combination with \( V_{\text{Li}} \) may be because the change in charge arising
when Ti$^{4+}$ replaces Co$^{3+}$ could be effectively compensated by the removal of a Li$^{+}$ ion:

$$\text{Ti}_{\text{Co}}^* + \text{V}_{\text{Li}} \rightarrow \text{null charge}$$ (10)

### 3.2. Experiments

#### 3.2.1. Structure and morphology

It was expected from the simulation in the previous sections that the doping limit of Ti in LCO would be very small, and that the formation of secondary phases such as Li$_2$TiO$_3$ or TiO$_2$ would be thermodynamically favored over doping. To support this experimentally, LiO$_{1/2}$/C$_{1-x}$CoO$_{3/2}$TiO$_y$ (Ti-added LCO is expressed as this chemical formula, considering the uncertain location of Ti) was synthesized by a sol–gel process for $x = 0, 0.025, 0.05$, and $0.1$ followed by a heating process. Considering that metallic elements can be mixed on the atomic scale through the sol–gel route, the possibility that Ti could not be doped because of the low diffusion rate into the LCO crystal was thus excluded. Therefore, we expect the method to be advantageous in examining the thermodynamic aspects of the mixture with minimal kinetic effects. The XRD patterns and lattice parameters, as refined by the Rietveld method, are presented in Fig. 5 and 6, respectively. For $x = 0.05$ and $0.1$, trace impurity peaks are observed at $2\theta = 36.5$ and $43^\circ$, corresponding to the main peak positions of the Li$_2$TiO$_3$ phase. Except for the impurity peaks, the XRD patterns of the four samples are nearly identical, without changes as $x$ increases.

Along with the lattice parameters refined from the XRD patterns, those obtained from the DFT-optimized structure are presented in Fig. 6. The calculation predicts both the $a$ and $c$ lattice parameters to increase with increased Ti doping (Fig. 6, right). However, the lattice parameters of the experimental samples are almost unchanged, showing only slight increases in the low-Ti region (Fig. 6, left). This comparison may support the simulation results of the previous sections, which predicted that the Ti-content doped in the LCO crystal would be very small.

Yu et al. reported that Ti added to LCO was mainly detected near the surface, even after 10 h heat treatment at the seemingly high temperature of $920^\circ$C.$^{37,38}$ This result may also be regarded to be in agreement with the simulation in this study, but the kinetic explanation of the system not reaching equilibrium because of the slow diffusion rate of Ti in LCO may not be excluded, because they added Ti to already-synthesized LCO using post-treatment. In our study, Ti was homogeneously mixed with Co at the atomic level by a sol–gel route to provide a kinetically favorable condition for Ti doping, but it still appears that doping of Ti in the LCO crystal is difficult. Therefore, we propose that the segregation of Ti at the surface is a thermodynamically driven phenomenon, as our first-principles study predicted that Ti doping in the LCO crystal is thermodynamically unfavorable.

The SEM images of the samples are shown in Fig. 7. The particle morphology of the Ti-added samples differs from that of pure LCO: the primary particle sizes of the Ti-added samples are much smaller than that of pure LCO, and the particles are severely agglomerated as secondary particles of $\sim 10-20$ $\mu$m in size. Thus, the morphology dramatically changes depending on the addition of Ti, but no difference in morphology is observed among the Ti-added samples. These morphological characteristics

### Table 2  Major types of [Ti-doping + point defect(s)] combinations and their equilibrium concentrations calculated at room temperature (298 K) and synthesis temperature (1300 K) using eqn (5)

<table>
<thead>
<tr>
<th></th>
<th>4 (Ti$<em>{\text{Co}}$ + V$</em>{\text{Li}}$)</th>
<th>1 (Ti$_{\text{Co}}$)</th>
<th>2 (Ti$<em>{\text{Co}}$ + Co$</em>{\text{Li}}$, Li$_{\text{Co}}$)</th>
<th>3 (Ti$<em>{\text{Co}}$ + Co$</em>{\text{Li}}$, V$_{\text{Co}}$)</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>298 K</td>
<td>$8.18 \times 10^{-9}$</td>
<td>$3.25 \times 10^{-34}$</td>
<td>$4.01 \times 10^{-37}$</td>
<td>$4.51 \times 10^{-36}$</td>
<td>8.18 $\times 10^{-9}$</td>
</tr>
<tr>
<td>1300 K</td>
<td>$1.48 \times 10^{-3}$</td>
<td>$6.80 \times 10^{-6}$</td>
<td>$1.37 \times 10^{-8}$</td>
<td>$1.03 \times 10^{-9}$</td>
<td>1.48 $\times 10^{-3}$</td>
</tr>
</tbody>
</table>
seem to be caused by Ti-related secondary phases formed on the LCO surfaces, which suppress particle growth and induce aggregation. Because the particle morphology of the three Ti-added samples is similar regardless of the Ti amount, it seems that sufficient volumes of secondary phases are available to cause these morphologies at the low level of 2.5% Ti. This supports the prediction that most Ti resides on the LCO surface, with only a small amount becoming doped in the LCO crystal.

Fig. 8(a) shows the TEM image of the 5% Ti-added LCO sample and Fig. 8(b) shows the EDS mapping of the Co distribution on the same area. Comparing the figures, some parts of the surface (between the yellow lines of Fig. 8(a and b)) are verified to contain no Co. Because Ti is detected in this area, it may be concluded that a Ti-rich surface layer, free of Co, is formed by the segregation of Ti from the LCO crystal. This layer seems to be an additional layer generated on the LCO surface, not a Ti rich region inside the LCO, considering that Co was not detected in this area and that the doping limit of Ti in the LCO crystal is simulated to be very low. The Ti/(Co + Ti) compositions of the Ti-added LCO samples, obtained from XPS analyses, are shown in Fig. 8(c). If Ti were homogeneously doped in the LCO crystal, the measured composition would be equal to the overall mixing composition of Ti/(Co + Ti) and fall on the dashed line in Fig. 8(c); instead, the measured Ti composition is much higher. Considering that XPS provides information for the near-surface area of materials, Ti is again confirmed to be distributed mainly on the surface. This argument is supported by the composition depth profile presented in Fig. 8(d): the initial Ti content is high (~20%) and decreases with etching time. (Although the Ti composition shows a rapid drop with sample etching, it does not converge to 0 after long etching times, which may be because of the small particle size of the powder sample: both the cross-sections of the bulk crystal and those of the grain boundaries are included in the probed location.) Thus, all analytical results consistently support the theoretical prediction that Ti becomes segregated on the surface, rather than doped in the LCO crystal.

3.2.2. Electrochemical characterization. The electrochemical properties of the samples are presented in Fig. 9. Ti addition causes no noticeable changes in the shape of the charge/discharge profile, except for a capacity decrease proportional to the amount of Ti added (Fig. 9(a)). From eqn (4), the weight proportion of LCO in a solid mixture comprising LCO and secondary phases can be calculated as 100, 97.6, 95.2, and 90.3 wt% for Ti/(Co + Ti) = 0, 0.025, 0.05, and 0.1, respectively. The measured discharge capacity of the samples is 100, 96.7, 91.4, and 83.4%, the changing trend of which is proportional to the LCO weights calculated from eqn (4), although the absolute values are somewhat different. This difference may originate from the increased surface resistance from the formation of secondary phases, but this interpretation may be flawed because all samples show similarly good rate performances (1C/0.2C capacity ratios of 99.0, 99.0, 98.9, and 98.8%, respectively), and Ti-added samples show smaller charge-transfer resistances, as seen in Fig. 9(b). Therefore, it is speculated that other secondary phases, such as Li4TiO4, were formed in the actual experiment, causing a smaller proportion of LCO than that expected from eqn (4), which is based entirely on thermodynamic features. Further systematic experiments are necessary to determine the correct interpretation.

Fig. 9(c) presents the change of discharge capacity with high-voltage cycling (4.6 V vs. Li+/Li). Ti addition greatly improves capacity retention, although the capacity of the samples deteriorates rapidly because of the high charging voltage of 4.6 V. Improvement of capacity retention by addition of a foreign element is generally explained in terms of structural stabilization by the doping or in terms of reduced side reactions between the cathode and electrolyte by a blocking effect of the surface coating layer. The effect of Ti-addition to LCO in this study seems to originate from the coating effect rather than the doping effect, considering the very low expected solubility of Ti in the LCO.
crystal. A remarkable change in the charge-transfer resistance upon addition of Ti, as shown in Fig. 9(b) may support this interpretation. While the rate of capacity degradation largely depends on the addition of Ti, the amount of Ti has no effect on the cyclability. This behavior is similar to that of the particle morphology (Fig. 7) and the impedance spectra (Fig. 9(b)), which may be explained by 2.5% of Ti addition providing enough secondary-phase volume to cover the LCO surface and thereby changing the morphology, impedance, and cycle performance.

It was previously reported that the electrochemical performance of LCO could be improved by the formation of a Ti-rich shell near the surface of LCO or by coating LCO particles with TiO₂ or Li₂TiO₃,13,37,39–41 but these methods require additional surface treatment after synthesizing the active material. However, our study shows the achievement of surface-treatment effects using a one-step heating process, based on the first-principles thermodynamic simulation that predicts the formation of secondary phases to be more thermodynamically favorable than doping for the Ti-added LCO system. We propose that a Ti-containing shell or coating layer is self-assembled simultaneously during the calcination process of LCO synthesis, which may greatly reduce processing costs for electrode materials.

4. Conclusions

In the context of a Ti-added LiCoO₂ system, we investigated whether Ti impurities could be doped in the LCO host crystal based on phase diagrams simulated using first-principles calculations. The doping limit of Ti in the LCO crystal was quantitatively estimated through a thermodynamic approach. The dopability was systematically examined in relation with defect chemistry, taking temperature and gas phase partial pressure as variables. The results indicated that the substitution of Ti for Co in crystalline LCO is thermodynamically unfavorable under typical LCO synthetic conditions. The simulation predicted that Ti would form secondary phases such as Li₂TiO₄ or Li₂TiO₃, rather than becoming incorporated in the LCO crystal. The combination of TiCo and V Li (TiCo + V Li) defects was expected to be the most probable form of doping, but the doping limit of Ti in LCO was estimated to be ~0.15% at the most. Thus, the simulation result predicted that added Ti would become segregated on the surface or grain boundaries, spontaneously forming coating-like layers on LCO particles.

Ti-added LCO samples with Ti/(Co + Ti) = 0, 0.025, 0.05 and 0.1 were synthesized by a sol−gel route followed by calcination. The lattice parameters of the samples, determined by Rietveld refinement, showed no significant changes with respect to the Ti content. Particles of the Ti-added samples became severely aggregated, and the primary particle size was much decreased relative to that for pure LiCoO₂. However, the particle morphology remained similar among the Ti-added samples, showing no significant changes with increased Ti content. Nanoscale Ti-rich areas were observed by TEM, and XPS analysis also showed that the Ti concentration was much higher at the surface than in the bulk material. All analytical results supported the theoretical simulation, which predicted that Ti added to LCO would tend to form oxide coating layers and that the doping of Ti in the LCO host would be thermodynamically unfavorable.

Thus, a powder of particles with LCO cores and Ti-rich shells was obtained by a simple sol−gel route and one-step calcination, without additional surface treatment. The LIB cells using the samples showed smaller impedance and enhanced high-voltage cyclability relative to those using pure LCO. It is expected that the simulation method of this study may be expanded to many impurity-added material systems, providing useful information on doping limits and the possibility of the self-assembly of coating layers. This may be a good guide for the screening of additive elements for doping or coating treatments of inorganic compounds.

Author contributions

The manuscript was written through contributions of all authors.

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