Effects and distribution of Zr introduced in Ni-based cathode material for Li-ion batteries†

Yongseon Kim

The spatial and site distribution of Zr introduced to the LiNiO₂ (LNO) host material and the related mechanism of performance improvement as a Li-ion battery electrode are theoretically investigated. It is found that the equilibrium doping limit of Zr is higher near the (012) surface than that near (003) among the main surface planes of LNO, and that the diffusion energy barrier in the [012] direction is lower than that in [003]. The thermodynamic and kinetic aspects indicate the main Zr diffusion pathway into crystalline LNO via the (012) surface in the perpendicular direction and its crystallographic equivalents. Regarding the site-distribution in the bulk crystal, Zr preferentially substitutes Ni, but becomes located at Li sites as the composition of the LNO host becomes Li-deficient. It is observed that Zr doping suppresses O release from the LNO surface, thus suppressing side reactions at the cathode–electrolyte interface. This is attributed to the mechanism of increased covalent and electrostatic interactions with the O ions by the introduction of Zr. The pillar effect of Zr is achievable with a suitable Li-deficient composition during heating, which induces Zr localization at Li sites. The distribution of Zr is found to be determined by the physical and chemical factors of the doping site size and the chemical bonding characteristics of Zr with neighboring O ions.

1. Introduction

Li-ion batteries (LIBs) are widely used as power supplies for mobile electronic devices, and their application is broadening to include large systems such as electric vehicles and power storage stations.¹,² As the LIB industry grows, consumer demand is increasing for improvements in energy density, safety, power, and so on, to yield better battery performance. The cathode material is a critical factor governing LIB performance, so high-performance cathode materials are under active investigation. Layer-structured LiCoO₂ (LCO) is the most widely used cathode material because it satisfies various LIB cathode property requirements relatively well; however, the use of Ni, which is advantageous in battery capacity, cost, and supply stability of the raw material, has recently increased.³

Despite the advantages attainable with the increase of Ni content in layer-structured cathode materials, drawbacks such as low structural stability, increase of unwanted reactions at the cathode–electrolyte interface, and battery swelling by gas evolution limit the application of Ni-based cathode materials.⁴ The spatial distribution of O as well as the diffusion energy barriers and other related aspects are investigated in this study. The most widely investigated measures for addressing these problems are the passivation of the cathode surface to suppress side reactions and the doping of foreign elements to stabilize the crystal structure.⁵ Zr is considered an effective doping and/or coating material by many researchers to improve the drawbacks of Ni-rich cathode materials.⁶–⁸ Both coating and doping strategies have been widely attempted as universal methods to control material properties in various fields, not limited to LIB cathodes. Although numerous success cases have been reported, the methods have been approached mainly empirically with insufficient investigations of the theoretical aspects of the mechanisms.

In particular, examination of the location of foreign elements, introduced to improve the property of host materials, is lacking. Elements in a coating layer may diffuse into the crystal structure of the host material during an annealing process; heating often follows coating processes for various purposes such as oxidation of the coating material, strengthening the adhesion, and crystallizing the coating layer. In an opposing example, an element intended for doping may become segregated on the host material surface, forming a coating-like layer, for an extremely low doping limit. In addition, the effects and mechanisms of foreign elements in improving the host material properties should differ depending on the location of the elements. Therefore, it is important to examine the actual distribution of foreign elements introduced with the intent of coating or doping, as well as the changes in the distribution with processing conditions. Thus, the selection of the proper elements for coating or doping, the processing design, and the exact mechanism causing property changes must be investigated with the distribution of foreign elements in the host material.

A hybrid treatment including both surface coating and doping was also attempted by controlling the annealing temperature after
coating cathode materials with ZrO$_2$. Huang et al.\textsuperscript{9} reported the heating of a ZrO$_2$-coated Li[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]O$_2$ cathode, which enabled partial Zr doping of the cathode crystal structure by thermal diffusion. They demonstrated improved cyclic performance and rate capability of the cathode using the treatment. Shipper et al.\textsuperscript{10} investigated the optimal heat-treatment conditions for ZrO$_2$-coated LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ to obtain the dual effects of ZrO$_2$ coating and Zr doping. He et al.\textsuperscript{11} reported that the doping effect of Zr could be maximized with a gradient distribution of Zr in the Ni-rich cathode. Thus, research interest seems to be shifting from simple coating or doping to the control of the distribution of foreign elements to optimize the effects of introducing foreign elements.\textsuperscript{12–17}

Following this research trend, theoretical investigation is required to interpret the mechanisms underlying these experimental achievements; such investigation is the purpose of this study. In this study, it is assumed that the distribution and the effect of Zr introduced to LiNiO$_2$ (LNO) could be examined in the three characteristic regions of the surface coating layer, the surface-to-bulk transitional area, and the inner bulk crystal (Fig. 1). Regarding the effects of coatings on cathode materials, the underlying mechanism seems to be well interpreted as the coating layer controlling the side reactions between the cathode and the electrolyte by limiting their direct contact.\textsuperscript{4,9,10} Therefore, this study mainly focuses on the other two regions. The spatial distribution of Zr near the surface, doping sites in the bulk crystal, and the effects of Zr on the performance of the LNO host as a cathode are investigated theoretically. While some studies have investigated the role of Zr introduced to cathode materials on an atomic level by first-principles methods,\textsuperscript{18–23} a systematic examination including both the distribution and the acting mechanism of Zr has not yet been reported, to our knowledge; thus, this study may provide useful insights on this topic.

2. Methods

The spatial distribution of Zr in an LNO crystal and the doping effects are investigated from computational calculations of the thermodynamic and kinetic aspects based on the density functional theory (DFT) method. The Vienna ab initio simulation package (VASP)\textsuperscript{24,25} program was mainly used for the structural optimization and energy calculation of the model crystals, with the QUANTUM ESPRESSO\textsuperscript{26,27} code used in the cases that optimization of a part of the lattice parameters was needed. The DFT calculations for structural optimization were performed with the $k$-point spacing of 0.3 Å$^{-1}$ based on the Perdew–Burke–Ernzerhof\textsuperscript{28} generalized gradient approximation and projector-augmented plane-wave pseudopotentials,\textsuperscript{29} while the energy and electronic properties were calculated using the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional.\textsuperscript{30} The Li$_{12}$Ni$_{12}$O$_{44}$ supercell was used as a frame bulk crystal model, and the structure of each model, with or without Zr introduction, was optimized by allowing full relaxation of the atomic position and lattice parameters. A 15 Å-thick vacuum slab was inserted in the structure-optimized frame bulk crystal model, and the structure of each model, with or without Zr introduction, was optimized by allowing full relaxation of the atomic position and lattice parameters. The number of atoms included in the surface crystal models was modified as necessary. Relaxation of the atomic positions was allowed, but the lattice parameters and the position of a single atom were fixed during the structure optimization of the surface models.

Zr-Doped bulk crystal structures of high formation probability were explored by an unbiased structure searching technique based on the particle swarm optimization (PSO) algorithm using the CALYPSO code;\textsuperscript{31,32} the structures were searched for 15 generations, with 50 pop-up structures per generation. The covalent and ionic bonding properties between metal and O ions were analyzed by examining the crystal orbital Hamilton population (COHP) and the partial charge of ions.\textsuperscript{33} The LOBSTER code\textsuperscript{34,35} was used for the calculation of COHP, and the partial charge was obtained from the Bader analysis.\textsuperscript{36,37} The activation barrier for Zr diffusion was calculated by the nudged elastic band (NEB) method to examine the kinetic aspect of Zr doping in the LNO crystal. All these analyses were performed with the codes connected with the VASP program.

The proper energy of O$_2$ was necessary to calculate the reaction energies. The standard state chemical potential of O$_2$ gas ($\mu_{O_2}$) was determined by a semi-empirical method,
in which $\mu_{O_2}$ was determined to dissipate the discrepancy of thermodynamic data between experimental database and DFT calculation in this study (see ref. 39–41 and ESI† S1 for details). The change of the gas-phase chemical potential with temperature and pressure was accommodated by referring to the JANAF Thermochemical Tables. In addition to general information on the computational methods of this section, details of the methodology regarding the formation of crystal models, calculations, analytical procedures, and so on are explained in each relevant Results section.

3. Results

3.1. Spatial distribution of Zr

In this section, the spatial distribution of Zr is quantitatively analyzed, from the surface to the inner bulk region of the LNO crystal. The crystal models for the calculation with (012) and (003) surfaces, respectively, are prepared, and the energy change with the substitution of Zr for Ni in the models is examined. The equilibrium concentration of Zr is calculated as functions of the depth (distance from the outermost surface) and the temperature for each crystal model. The (012) and (003) surfaces are selected according to Kramer et al., who reported that these surface planes and their symmetrical equivalents mainly comprise the surface morphology of layer-structured cathode materials.

Schipper et al. reported that the most stable doping site for Zr in Ni-rich cathodes was the Ni site, and suggested that Ni was expelled from the host by Zr doping and thus incorporated in ZrO$_2$ as (Zr$_{1-x}$Ni$_x$)$_2$O$_2$, when Zr thermally diffused into an Ni-rich cathode from a ZrO$_2$ coating layer. However, other candidates for the doping reaction by the thermal diffusion of Zr from a ZrO$_2$ coating layer can be suggested as the following; therefore, the exact reaction should be determined first to calculate the energy change related to the doping of Zr in the LNO crystals.

$$\text{LiNiO}_2 + x\text{ZrO}_2 \rightarrow \text{LiNi}_{1-x}\text{Zr}_x\text{O}_2 + x\text{NiO} + x/2\text{O}_2 \quad (1)$$

$$\text{LiNiO}_2 + y\text{ZrO}_2 \rightarrow \text{LiNi}_{1-x}\text{Zr}_x\text{O}_2 + (\text{Zr}_{y-x}\text{Ni}_x)\text{O}_2y \quad (2)$$

$$\text{LiNiO}_2 + 4x\text{ZrO}_2 \rightarrow \text{LiNi}_{1-x}\text{Zr}_x\text{O}_2 + x\text{Zr}_3\text{NiO} + 7x/2\text{O}_2 \quad (3)$$

$$\text{LiNiO}_2 + 3x\text{ZrO}_2 \rightarrow \text{LiNi}_{1-x}\text{Zr}_x\text{O}_2 + x/2\text{Zr}_4\text{Ni}_2\text{O} + 11x/2\text{O}_2 \quad (4)$$

To determine which is correct, phase diagrams of Zr–Ni–O system are simulated from the grand potential values obtained by the following equation:

$$\phi(Zr_{x1}\text{Ni}_{x2}\text{O}_2) = \frac{G(Zr_{x1}\text{Ni}_{x2}\text{O}_2) - c/2\mu_{O_2}}{a + b} \quad (5)$$

In eqn (5), the Gibbs free energy $G$ is approximated by the energy values obtained by DFT calculations; the error of this approximation is insignificant for solid phases. In addition, consideration of the ground potentials is not included in eqn (5), which may not cause a significant error considering that they are not significantly different among solids of similar atomic compositions, and that we need not absolute energy values but the relative values to determine thermodynamic stability of phases for the simulation of phase diagrams. The chemical potential of O$_2$ gas $\mu_{O_2}$ is modified with temperature and atmosphere, details of which are discussed in the Methods and ESI† S1 sections.

Fig. 2(a) shows the phase diagram (composition–energy) simulated under the conditions of room temperature and ambient air. All the ternary phases of Zr–Ni–O are located above the tie line connecting NiO and ZrO$_2$ in the diagram, indicating that they are thermodynamically unstable. Thus, Ni and Zr are not miscible in a single oxide phase. This feature is maintained at far higher temperatures in ambient atmospheric conditions.
Therefore, it is concluded that reaction (1) is the most probable, because reactions (2)–(4) include unstable phases such as (Zr₁₋ₓNiₓ)O and ZrₓNi₂₋ₓO in the reaction products. Fig. 2(b) is the phase diagram simulated assuming a carbothermal reduction over 1500 °C, which indicates that ZrₓNiO and ZrₓNi₂₋ₓO can be synthesized only under such a strongly reducing atmosphere. This expectation agrees with the experimental report, supporting the reliability of the simulation. Thus, reaction (1) is selected as the proper reaction mechanism for Zr doping through the thermal diffusion of Zr from a ZrO₂ coating layer into LNO; the energy involved in doping of Zr is thus calculated based on reaction (1) in this study.

When a Zr atom is introduced to an LNO crystal model including surface planes, a polarity arises in the direction perpendicular to the surface plane because the dopant breaks the crystal symmetry. As mentioned, non-polar cleaving yields the most stable surface crystal models; therefore, the creation of this polarity produces additional unwanted energy. This causes difficulties in calculating the pure Zr-doping energy (i.e., the reaction energy for (1)), because the calculation includes error from the creation of polarity. Two methods are available to address this polarity problem: the first locates the Zr dopant at the middle point between two surfaces, and the second introduces two Zr atoms to the crystal for polarity compensation. In the former case, the size of the crystal model should be changed to accommodate the placement of Zr away from the surface, as shown in Fig. 3(a–c), which may introduce error because of an insufficient number of atoms in some cases (Fig. 3(a)). The latter method avoids this problem, but in this case the energy of the crystal model is affected by the relative positions of the two Zr atoms. In this study, the former method is used, because the surface energy values with different numbers of atoms showed no significant error (ESI† S2), which supported the reliability of the method. The calculation result for Fig. 3(a), the case with the smallest model size, was double-checked using the latter method (Fig. 3(d)), which showed similar results, confirming that the selected method is reliable even for the small-sized model case.

All the reaction energy values calculated based on reaction (1) and on the doped surface crystal models of Fig. 3 were positive at room temperature, indicating that the Zr doping reaction is energetically unfavorable. However, doping is driven by configurational entropy; the macroscale structure of the entire surface may be considered as a combination of doped and undoped surface crystal models with the related mixing entropy providing some driving force toward the doped state (that is, the mixed state of doped and undoped surface models). Following this consideration, the equation for the thermodynamic equilibrium proportion

\[ P_{\text{doped}} = e^{-\frac{\Delta G}{kT}} \]

is derived as eqn (6) (ESI† S3):

\[ P_{\text{doped}} = \frac{e^{-\frac{E_{\text{reactants of (1)}}}{kT}}}{e^{-\frac{E_{\text{products of (1)}}}{kT}}} \]

\[ = \frac{e^{-\frac{E_{\text{reactants of (1)}}}{kT}}}{e^{-\frac{E_{\text{products of (1)}}}{kT}}} \approx \frac{e^{-\frac{E_{\text{reactants of (1)}}}{kT}}}{1 + e^{-\frac{E_{\text{products of (1)}}}{kT}} } \]

where, \( e^{-\frac{E_{\text{reactants of (1)}}}{kT}} \gg e^{-\frac{E_{\text{products of (1)}}}{kT}} \) is assumed with low doping concentration.

Eqn (6) shows that the proportion of Zr-doped surface crystal model units in the mixture is expressed as an exponential function including the doping energy calculated for reaction (1) and the temperature. The equation may be viewed as the ratio of the Boltzmann factor of the doped state (product side of reaction (1)) to the summation of the doped and undoped states' Boltzmann factors, as expressed in the additional development of eqn (6), which is in line with the general method of probability calculation from the Boltzmann factor of a specific state and the partition function in an ensemble system. As \( P_{\text{doped}} \) in the equation is the equilibrium proportion of the

![Fig. 3](image-url)
doped crystal model in the whole combined surface system, the Zr concentration in a unit of the doped crystal model should be multiplied by $P_{\text{doped}}$ to calculate the final equilibrium Zr concentration $N_{\text{Zr}}$:

$$N_{\text{Zr}} = N_{\text{Zr, model}} \cdot P_{\text{doped}} = N_{\text{Zr, model}} \cdot e^{\frac{\Delta F}{kT}} \quad (7)$$

In eqn (7), $N_{\text{Zr, model}}$ denotes the Zr concentration in a unit of the doped crystal model. The equilibrium Zr concentration can be obtained by multiplying $N_{\text{Zr, model}}$ by $P_{\text{doped}}$, as expressed above. From eqn (7), the concentration is calculated for different doping depths, and then the equilibrium distribution of Zr near the (012) and (003) surfaces are calculated, as presented in Fig. 4 as functions of the depth from each surface and of the temperature. The depth profile of the equilibrium Zr concentration shows a rapid decrease as the depth from the (012) surface increases, while a relatively small change of concentration is observed for the (003) case. However, increases in temperature increase the Zr concentrations in both the (012) and (003) cases, which corresponds to the exponential term of eqn (7).

Thus, the equilibrium concentration of Zr near the LNO crystal surface is successfully calculated as functions of the crystal plane, depth from the surface, and temperature. It should be noted that the calculation is mainly based on thermodynamic aspects; therefore, the validity should be examined considering the doping kinetics. Fig. 5(a and d) shows the diffusion paths of Zr from the (012) and (003) surfaces to inner region of LNO crystal.

In summary, the thermal diffusion of Zr from a ZrO$_2$ coating layer into crystalline LNO can be described as follows: first, Zr mainly migrates in the direction perpendicular to the (012) surface and in the symmetrically equivalent routes. Second, the equilibrium concentration of Zr in the LNO crystal is increased with increasing heating temperature. As the thermal diffusion proceeds, the initial state of ZrO$_2$@LNO (i.e., LNO with a ZrO$_2$ coating layer) changes to (ZrO$_2$ + NiO)@LNO:Zr$_{\text{shell}}$ + LNO$_{\text{core}}$ and finally to NiO@LNO:Zr (or (ZrO$_2$ + NiO)@LNO:Zr for a sufficiently thick ZrO$_2$ coating). The final state may be changed by controlling the heating time and temperature. A selectively face-coated state may be achieved in which ZrO$_2$ on the (012) and symmetrically equivalent surfaces is diffused into LNO, thus exposing the relevant surface planes, while the (003) surface remains coated with ZrO$_2$ because of the relatively low doping tendency of Zr near this surface. The equilibrium Zr concentration is generally very low in LNO except near the surface. This feature seems to have allowed the achievement of a coating–doping hybrid state from a ZrO$_2$-coated Ni-rich cathode system by controlling the after-heating temperature.

### 3.2. Doping effect of Zr near the surface

Side reactions at the cathode–electrolyte interfaces of LIBs are complicated processes including various chemical routes and...
reaction products. However, they can be simplified by focusing on the cathode side. The release of $O_2$ and the resulting change of the surface structure are the major phenomena experienced by the cathode during the initial stage of the side reactions. From a computational perspective, these phenomena may be modeled by calculating the energies related to the loss of $O$ near the surface plane and to the surface structure relaxation.

For a surface crystal model with the composition of $Li_{12}Ni_{12}O_{24}$, calculations for the following reaction steps are required for the computational examination of the side reactions:

\[
[Li_{12}Ni_{12}O_{24}]_{\text{surface model}} \rightarrow [Li_{12}Ni_{12}O_{23}]_{\text{surface model}} + \frac{1}{2}O_2
\]  \hspace{1cm} (8.1)

\[
[Li_{12}Ni_{12}O_{23}]_{\text{surface model}} \rightarrow [Li_{12}Ni_{12}O_{23}]_{\text{surface model, structure change}}
\]  \hspace{1cm} (8.2)

\[
\frac{1}{2}O_2 + \text{electrolyte} \rightarrow \text{SEI product}
\]  \hspace{1cm} (8.3)

where, (8.1) is the reaction for $O_2$ release from the LNO surface region, (8.2) is that for the structural change near the surface after $O$ loss, and (8.3) is that for the reaction between the $O_2$ released from the cathode and the electrolyte. The total Gibbs free energy of the surface reaction ($G_{\text{surface reaction}}$) is obtained by summing the Gibbs free energies for reactions (8.1)-(8.3). By comparing $G_{\text{surface reaction}}$ with and without Zr, the effect of Zr doping on the side reaction can be examined. Assuming that reaction (8.3) is the same regardless of $O_2$ release from the cathode and the electrolyte, the side reactions. In this study, $\Delta G_{\text{surface reaction}}$ is approximated by $\Delta E_{\text{surface reaction}}$, calculated using the DFT method, and examined as a measure for the stabilizing effect of Zr near the surface.

\[
\Delta G_{\text{surface reaction}} = [G_{8.1} + G_{8.2}]_{\text{Zr-doped}} - [G_{8.1} + G_{8.2}]_{\text{undoped}}
\]  \hspace{1cm} (10)

$O$ must be removed from the surface crystal models to calculate the energy related to $O_2$ release, but this again entails the problem of polarity induced by broken crystal symmetry. To address this problem, two $O$ vacancies ($V_O$) are placed symmetrically on both sides of the vacuum slab in this study. However, this approach has disadvantages such that the energy of $O$ release for individual $O$ locations cannot be obtained and/or the calculation may be affected by the relative position of the two $V_O$s. Therefore, considering these methodological limitations, the $\Delta G_{\text{surface reaction}}$ values are randomly collected to yield only an approximate view of statistical trends.

The $\Delta G_{\text{surface reaction}}$ values obtained for several lithiated and delithiated states are shown in Fig. 6(a–d), and the position of $V_O$ is shown in (e) and (f). Only half of the crystal model is shown in Fig. 6(e and f), showing only one $V_O$; the second $V_O$ at the symmetrical location is omitted for simplicity. Fig. 6(a–d) show that all the $\Delta G_{\text{surface reaction}}$ values are positive, except those for two cases out of the total 12 examined cases, and the negative values of these two are not significantly large. This indicates that the introduction of Zr near the LNO surface region suppresses O release, which may stabilize the electrode–electrolyte interface of LIBs by preventing the side reactions triggered by electrolyte oxidation. Fig. 6(a–d) also show that this effect tends to decrease as the Zr–O distance is increased, indicating that the suppression of $V_O$ formation by Zr doping is the most effective near Zr. Therefore, if it is focused on the prevention of the side reactions, the doping concentration of Zr...
should be increased near the surface region. This expectation agrees with the report of He et al., who improved the thermal stability of a Ni-rich cathode material without loss of specific capacity by inducing a gradient distribution of Zr doping, in which Zr was heavily concentrated near the surface.

In summary, the investigation of the Zr-doping effect near the LNO surface indicates the following. First, Zr introduction suppresses O$_2$ release from the LNO surface region, which is expected to prevent electrode–electrolyte side reactions. Second, this effect is particularly strong near Zr; therefore, heavy Zr doping is favored to stabilize the electrode–electrolyte interface. However, excessive Zr doping may decrease the capacity of the LNO active material, thus high Zr doping is recommended only near the LNO surface, while the Zr concentration in the bulk region should be controlled at an optimum dilute level to achieve simultaneous surface stability and good bulk electrochemical performance.

3.3. Zr doping sites in bulk crystal and the pillar effect

In the previous section, the O-release-limiting role of Zr in LNO near the surface was discussed; this is expected to decrease side reactions between the cathode and electrolyte. This effect may also be expected to work in the bulk crystal. However, O release from the bulk does not seem to significantly affect the performance of the LNO cathode, considering the length of the journey of O from deep inside to the crystal surface. Therefore, a different effect should be considered by Zr doping in the bulk LNO crystal; this effect has been well established by previous studies as the so-called “pillar effect.” The introduction of Zr has been reported to improve the rate properties of layer-structured cathode materials. He et al. attributed the improvement to the increase of the Li diffusion coefficient, that is, the improved mobility of Li in the bulk crystal of the cathode. This is from the pillar effect, which occurs by the occupation of some Li sites by other metal ions with higher oxidation numbers. The metal ions fixed in the Li layer buffer the repulsion between O$^-$ layers at delithiated states, thus improving the structural stability and Li ion mobility.

Because the pillar effect has been investigated by many researchers, this study focuses on the crystal structure of Zr-doped LNO, including a consideration of the defects, and on the distribution of Zr among the lattice sites, rather than on the mechanisms underlying property changes by the pillar effect of Zr. The Zr doping effect in the bulk crystal may be properly interpreted only after the proportion of Zr contributing to the pillar effect by occupying Li sites is determined and after control of the site distribution of Zr is achieved. Therefore, in this section, the structure of the Zr-doped LNO bulk crystal is investigated. In particular, an unbiased structure searching method is used to exclude preconceptions regarding the structure and defects. Searching is performed for crystals in the stoichiometric, Li-deficient, and delithiated states.

A frame crystal model with the composition of Li$_x$Ni$_{12}$O$_{24}$ was prepared by removing five Li and five Ni atoms from the Li$_{12}$Ni$_{12}$O$_{24}$ supercell. For the structure searching of the stoichiometric composition, five Li and five Ni (five Li, four Ni, and one Zr for Zr-doped cases) atoms were added to the frame crystal using the cell function of CALYPSO code. For the Li-deficient composition, one fewer Li, i.e., four Li and five Ni (four Li, four Ni, and one Zr for Zr-doped cases) atoms were added to the same frame. For the searching of 67% delithiated structures, one Li and five Ni (or one Li, four Ni, and one Zr) atoms were added to a Li$_{7}$Ni$_{7}$O$_{24}$ frame. The trial insertion positions of the atoms were randomly determined, limiting only the minimum distance among the atoms as 1.5 Å between positive–positive or negative–negative ions and 1.0 Å between positive–negative ions. With this random insertion method, the occupation of all types of interstitial site, as well as those of the lattice points, can be examined, and anti-site type defects can be considered. The CALYPSO code performs structural optimization and energy calculation by linking the randomly generated structures to VASP code and derives the next generation of structures by the PSO algorithm. The most stable (i.e., the most probable) structures are explored throughout the generations.

The five most stable structures for the stoichiometric composition (i.e., Li$_{12}$Ni$_{12}$O$_{24}$ or Li$_{12}$Ni$_{12}$ZrO$_{24}$) determined by the method are presented in Fig. 7. All the metal atoms are located at the lattice points with no occupation of tetrahedral sites, although some anti-site defects such as Ni$_{Li}$ (Ni at Li site) and Li$_{Ni}$ (Li at Ni site) are
observed. Zr occupies Ni sites in all the Li12Ni11ZrO24 structures and is not observed at Li sites. On the contrary, Zr preferentially occupies Li sites in the delithiated structure of Li4Ni11ZrO24, except for the fifth structure (Fig. 8, upper). In the Li-deficient Li11Ni11ZrO24, Zr is located at Li sites in two of the five most stable structures (Fig. 8, lower). These features indicate a clear tendency for Zr to occupy Li sites as Li deficiency in the LNO bulk crystal increases.

The location of Zr in layer-structured cathode materials is still subject to debate by researchers; however, a careful literature review shows that Zr is found at both transition metal and Li sites in high-Ni-content materials, while Zr is observed mainly at transition metal sites in mild Ni-content systems such as LiNi0.6Co0.2Mn0.2O2 or lower Ni cases.11,24,49 Li-deficient phases, whose compositions are expressed as Li1-xTmonyO2, are generally synthesized for layer-structured cathodes with high Ni contents.52–54 According to our computational study discussed above, Zr preferentially occupies Ni sites, but tends to occupy Li sites as Li becomes deficient in the crystal, which indicates that the occupation of Li sites by Zr increases in a high-Ni system that is apt to become Li-deficient. Thus, the computational expectation shows good agreement with conventional experimental observations.

The equation for the proportion of Zr at Li sites among the total Zr can be expressed as follows:

$$P_{Zr \text{ at } Li \text{ site}} = \frac{\sum_i e^{-E_{\text{th system } Zr_{Li} \text{ at } Li \text{ site}}/kT}}{Q}$$

$$Q = \sum_i e^{-E_{\text{th system } Zr_{Li} \text{ at } Li \text{ site}}/kT} + \sum_j e^{-E_{\text{th system } Zr_{Ni} \text{ at } Ni \text{ site}}/kT}$$

where \(E_{\text{th system } Zr_{Li} \text{ at } Li \text{ site}}\) and \(E_{\text{th system } Zr_{Ni} \text{ at } Ni \text{ site}}\) denote the energies of the model crystals in which Zr occupies Li sites and Ni sites, respectively, when the real macroscale crystal is considered as a combination of the probable model crystals presented in Fig. 7 and 8. Q is the partition function, that is, the total sum of the Boltzmann factor of each model crystal. For the ensemble system of the stoichiometric composition of crystal models presented in Fig. 7 (lower), \(P_{Zr \text{ at } Li \text{ site}}\) is calculated from eqn (11) to be only ~45 ppm at \(T = 800 \degree C\). Whereas, \(P_{Zr \text{ at } Li \text{ site}}\) for the ensemble of Li11Ni11ZrO24 models (Fig. 8, lower) is calculated to be much higher, ~4.5%; for the ensemble for the delithiated state (Fig. 8, upper) it approaches 99% (detailed calculation procedure is shown in ESI,† S5). The quantitative analysis of the Zr distribution among the sites clearly shows that Zr occupies not only transition metal sites but also Li sites as Li becomes deficient in the crystal.

In the discussion above, the results are based mainly on thermodynamic considerations: the kinetics aspect, that is, the relative ease of Zr motion from a Ni site to a Li site, should also be considered. The energy barrier calculated by the NEB method for the transition of Zr from a Ni site to the adjacent tetrahedral space is shown in Fig. 5(e and f). It was reported that passing through the tetrahedral site is the main route for the migration of metal atoms between transition metal and Li sites in layer-structured cathode materials.55 The jump frequency of Zr to a tetrahedral site can be estimated from the energy barrier values and eqn (12) (where \(\nu\) and \(E_b\) denote the lattice vibration frequency and the migration energy barrier, respectively), which indicate that the migration of Zr by this route is almost negligible with the very small jump frequency of
This journal is © the Owner Societies 2019 Phys. Chem. Chem. Phys., 2019, 21, 12505--12517 | 12513

This journal is © the Owner Societies 2019 Phys. Chem. Chem. Phys., 2019, 21, 12505--12517 | 12513

B\textsubscript{10}/C\textsubscript{0}14 s/C\textsubscript{0}1 at room temperature, even in the delithiated state. Therefore, the distribution of Zr in the bulk LNO crystal is mainly determined during the heating process, with negligible changes during the electrochemical operation of the electrode.

\omega = \nu e^{\frac{E_0}{kT}} \quad (12)

The pillar effect should be obtained by placing the minimum necessary number of pillar ions to prevent their obstruction of Li ion migration. Therefore, pillar atoms with high oxidation numbers and large ionic radii are desirable to obtain the pillar effect with fewer numbers of atoms. Considering this requirement, Zr is an appropriate pillar atom because of its high oxidation number, generally fixed at +4, and the ionic size (effective ionic radius of 0.72 Å with a coordination number of six) similar to that of Li (0.76 Å).\textsuperscript{56} A high Zr doping content is disadvantageous for the capacity of LNO as an LIB cathode because Zr is electrochemically inactive with current operation voltage of LIB; therefore, minimizing Zr doping as much as possible and maximizing the utilization of Zr as pillar ions is suggested. The site distribution of Zr should be controlled for this purpose. The computational investigation in this chapter suggests that the proportion of pillar Zr (i.e., Zr substituted at Li sites to the total Zr) is closely related to Li deficiency, and that inter-site movement of Zr occurs only at high temperatures, which indicates that the improved structural stability and cathodic rate performance by the Zr pillar effect may be controlled by the careful design of Li content and heat profiles during heat processing.

In summary, the investigation of the Zr doping sites and effects in the bulk LNO crystal shows the following. First, Zr preferentially occupies Ni sites over Li sites at the stoichiometric composition of LNO, but occupies Li sites as Li becomes increasingly deficient in the crystal. Second, the migration of Zr from a Ni to a Li site is nearly negligible at room temperature; therefore, the Zr site distribution in crystalline LNO is mainly determined during high-temperature heating. From this point, the pillar effect by Zr\textsubscript{Li} and the resultant improvement of structural stability and rate performance in the layer-structured cathode materials can be controlled by the careful design of the composition and heating conditions during synthesis.

4. Discussion

The distribution of Zr is predicted and the effect of Zr doping near the surface and in the bulk crystal is investigated assuming that Zr is introduced to LNO by thermal diffusion from a ZrO\textsubscript{2} coating layer. Regarding the distribution, the (012) surface region accommodates more Zr than the (003) surface does in a characteristic phenomenon; in addition, Zr preferentially occupies Ni sites at the stoichiometric LNO composition but tends to occupy Li sites as Li becomes deficient in the crystal. The distribution may be determined by the relative stability of Zr among the doping locations; the stability may be analytically considered regarding the physical and chemical aspects of the locations. We performed a relevant analysis focusing on the size of each site and the bonding character of Zr with adjacent O atoms in this section to investigate the underlying mechanisms for the results reported in previous sections.

As discussed in Section 3.1, Zr doping becomes easier as the doping position approaches the (012) surface, but the same
does not occur near the (003) surface. We examined the covalent and ionic bonding characteristics from the calculation of COHP and partial charge, but they showed no meaningful correlation with the positional variation of doping ability near the surface planes. On the other hands, the size of the Zr-doped site, analyzed according to the average Zr–O bonding distance in the optimized structures, is found to be closely associated with doping ability. This is shown by the comparison of Fig. 9, the diagram of Zr–O bond length with depth from the surface, with Fig. 4, the diagram of Zr distribution with depth: the two graphs show very similar behaviors with increasing depth from the surface. This indicates that the amount of space provided by a doping site is a determining factor for the near-surface Zr doping ability. An analysis of the strain-energy relation for the [012] and [003] directions showed that the LNO crystal has better elongation in the [012] direction than in [003] (ESI,† S6); thus, the region near the (012) surface provides better accommodation for Zr dopants than that near (003) does, yielding a higher Zr concentration limit near the (012) surface.

However, the above result may seem to contradict the other observation that Zr preferentially occupies Ni sites in the bulk LNO crystal: the height of the Ni slab of the structure-optimized LNO crystal is 2.0847 Å, which is smaller than that of the Li slab (2.5440 Å), thus the Ni site provides less space than the Li site does, yet Zr preferentially occupies Ni sites. Therefore, the site space is not the only determining factor for Zr doping ability, indicating that the chemical bonding nature must be investigated in addition to the physical factor of site space to obtain a full interpretation of the site stability of Zr. Table 1 presents the –COHP of Zr–O bonds when Zr is located at Li and Ni sites. At the stoichiometric composition of the crystal, the average –COHP value of ZrNi–O is higher than that of ZrLi–O (4.2922 and 3.0252, respectively), indicating that the Ni site provides more stable covalent bonding for Zr–O than the Li site does. Although the slab height is larger when Zr occupies the Li layer than when it occupies the Ni layer (2.5478 versus 2.3511 Å), the difference is not significantly large (~7%) in the structure-optimized crystal. Thus, in the bulk crystal of stoichiometric composition, it seems the stable doping site of Zr is mainly determined by covalent bonding stability, while the effect of site space is relatively small, if extant, because of the small difference in size of the different sites.

In the delithiated state, the –COHP value of Zr–O bonds remains larger at Ni sites than at Li sites, and the difference is similar to that of the stoichiometric composition case. This indicates that the chemical feature of the Zr–O bond does not significantly change with battery charging. A significant change is observed in the height difference of the metal layer slabs: the difference was ~7% between the Ni and Li slabs with Zr dopants at the stoichiometric composition, but the difference approaches ~19% in the delithiated crystal, probably due to the expansion of Li slab caused by the increase of O2−–O2− repulsion as Li ions are removed from the crystal. In this situation, Zr at Li sites is more stabilized by the increased site space; this effect is expected to outweigh the unfavorable condition of the lower covalent bonding stability (i.e., smaller –COHP value) at the Li site compared to that of the Ni site. This yields the increase in Li site occupation by Zr dopants in the delithiated crystal, as examined from Fig. 8 and the related discussion.

The effect of Zr doping in inhibiting O2 release near the surface, as discussed in Section 3.2, can be interpreted based on the bonding chemistry. Fig. 10(a) shows the difference of –COHP between ZrNi–O and NiNi–O (denoted as Δ(–COHP) in the figure) as a function of the distance between the Zr (originally Ni) ion and adjacent O ions when Ni is replaced by Zr in the (012) surface model crystal. The overall positive value of the Δ(–COHP) indicates the strengthening of the covalent interaction acting on O ions near the doping site with the substitution of Ni by Zr. This effect is greater for O ions near the doping site, and lessens as the distance between the O ion and doping site is increased. The electrostatic interaction that is assessed by the product of ionic partial charges shows the same tendency (Fig. 10(c and d)): the Coulombic attraction is increased with the substitution of Zr for Ni, and the effect is stronger with smaller distance between the doping site and O ions. Thus, it is concluded that the Zr dopant holds O ions more firmly near the surface because of the increases in both covalent and ionic interactions, which is expected to contribute to the prevention of electrode–electrolyte side reactions in batteries. We also examined the change in the density of states (DOS) considering that the relative position of the d-orbital energy level of metal and the p-orbital energy level of O may affect the O release from the crystal,57 but the DOS showed no significant change with Zr doping (ESI,† S7). Therefore, the doping effect of Zr in stabilizing the cathode–electrolyte

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Properties of Zr at Ni and Li sites in the stoichiometric and delithiated LNO crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Zr–O)</td>
</tr>
<tr>
<td>Stoichiometric</td>
<td>Zr at Ni site</td>
</tr>
<tr>
<td></td>
<td>Zr at Li site</td>
</tr>
<tr>
<td>Delithiated</td>
<td>Zr at Ni site</td>
</tr>
<tr>
<td></td>
<td>Zr at Li site</td>
</tr>
</tbody>
</table>

Fig. 9 Average bond length between Zr and O presented as a function of the location depth of Zr from the (012) and (003) surfaces.
interface is reasonably explained by the covalent and ionic interactions among the ions.

5. Conclusions

It is found that the equilibrium doping limit of Zr is relatively high near the (012) surface, with a decrease as the distance from the surface is increased, while only slight variation of the doping limit with depth is observed near the (003) surface. The activation barrier for Zr diffusion is lower in the direction of [012] compared to that of [003]. From these thermodynamic and kinetic aspects, it is concluded that the main route of Zr diffusion into the LNO crystal is from the (012) surface in the perpendicular direction and the crystallographically equivalent routes. The doping limit is expected to increase with increasing temperature. Zr preferentially substitutes at Ni sites in the stoichiometric LNO bulk crystal, but the tendency of Zr doping at Li sites increases as Li becomes deficient in LNO. As the migration of Zr is difficult at room temperature, the distribution of Zr among the lattice sites is expected to be determined during the heating process and to be strongly affected by the Li composition of the LNO host. The site preference of Zr is analyzed to depend on physical and chemical factors of the size of the doping sites and the bonding characteristics of Zr with neighboring O ions.

Zr doping suppresses O release from the LNO surface region, which reduces the side reactions at the cathode–electrolyte interface, thereby improving cycle performance. Increases in covalent and electrostatic interactions acting on O ions caused by the introduction of Zr is the underlying mechanism of improvement. As for the “pillar effect” of Zr, known to improve the cyclic and rate performance of the cathode, it is found that the effect is achievable especially in Ni-rich cathodes because their compositions are generally easy to be Li-deficient, which promotes the function of Zr as a pillar atom at Li sites. Based on these findings, it is proposed that the design of processing conditions in which the intentional change of Li content is considered, as well as the proper heating profile, may enable control of the site distribution of Zr and the resultant pillar effect.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Education (NRF-2016R1D1A1B03933704).

References


6 S. Gao, X. W. Zhan and Y. T. Cheng, Structural, electrochemical and Li-ion transport properties of Zr-modified \( \text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2 \) positive electrode materials for Li-ion batteries, *J. Power Sources*, 2019, 410, 45–52.


8 Z. J. He, Z. X. Wang, H. Chen, Z. M. Huang, X. H. Li, H. J. Guo and R. H. Wang, Electrochemical performance of zirconium doped lithium rich layered \( \text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2 \) oxide with porous hollow structure, *J. Power Sources*, 2015, 299, 334–341.


12 S. Xia, F. Li, F. Cheng, X. Li, C. Sun, J. J. Liu and G. Hong, Synthesis of Spherical Fluorine Modified Gradient Li-Ion Battery Cathode Material \( \text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2 \) by Simple Solid Phase Method, *J. Electrochem. Soc.*, 2018, 165, A1019–A1026.


16 J. Duan, G. Hu, Y. Cao, C. Tan, C. Wu, K. Du and Z. Peng, Enhanced electrochemical performance and storage property of \( \text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2 \) via Al gradient doping, *J. Power Sources*, 2016, 326, 322–330.


18 S. Liu, Z. Dang, D. Liu, C. Zhang, T. Huang and A. Yu, Comparative studies of zirconium doping and coating on \( \text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2 \) cathode material at elevated temperatures, *J. Power Sources*, 2018, 369, 288–296.


20 K. Park, J. H. Park, S. G. Hong, B. Choi, S. W. Seo, J. H. Park and K. Min, Enhancement in the electrochemical performance of zirconium/phosphate bi-functional coatings on \( \text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2 \) by the removal of Li residuals, *Phys. Chem. Chem. Phys.*, 2016, 18, 29076–29085.

21 F. Schipper, M. Dixin, D. Kovacheva, M. Talianker, O. Haik, J. Grinblat, E. M. Erickson, C. Ghany, D. T. Major, B. Markovskly and D. Aurbach, Stabilizing nickel-rich layered cathode materials by a high-charge cation doping strategy: zirconium-doped \( \text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2 \), *J. Mater. Chem. A*, 2016, 4, 16073–16084.


42 M. Chase, JANAF Thermochemical Tables, American Chemical Society, New York, 1986.
45 C. A. J. Fisher and M. S. Islam, Surface structures and crystal morphologies of LiFePO4: relevance to electrochemical behavior, J. Mater. Chem., 2008, 18, 1209–1215.
49 Q. X. Du, Z. F. Tang, X. H. Ma, Y. Zang, X. Sun, Y. Shao, Z. Y. Wen and C. H. Chen, Improving the electrochemical properties of high-energy cathode material LiNi0.5Co0.2Mn0.3O2 by Zr doping and sintering in oxygen, Solid State Ionics, 2015, 279, 11–17.
51 S. Sivaprakash and S. B. Majumder, Understanding the role of Zr4+ cation in improving the cyclability of LiNi0.8Co0.15Zr0.05O2 cathodes for Li ion rechargeable batteries, J. Alloys Compd., 2009, 479, 561–568.