First-principles and experimental investigation of the morphology of layer-structured LiNiO₂ and LiCoO₂†

Yongseon Kim,ab Hyundeok Leebc and Shinhoo Kang*a

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LiNiO₂ (LNO)-based layered materials for use as cathodes in lithium ion batteries generally take the form of agglomerates composed of small particles. Such morphologies produce low electrode densities compared with LiCoO₂ (LCO). In this study, the surface energies of various LNO and LCO crystal facets were calculated, and the morphological characteristics of the materials were interpreted based on these results. Crystal models were constructed and the energy of each facet was calculated using density functional theory methods. The chemical mechanisms underlying the atomic structure at each type of facet surface were analyzed using molecular orbital methods. All facet planes yielded surface energies for LNO that were lower than those for LCO. Atoms in the LNO crystal were found to be less ionized than in LCO, which provided weaker ionic bonding and a lower surface energy. The surface energy was proposed to be the main driving force underlying the morphological differences between LNO and LCO. LNO was expected to favor a high fraction of Li atoms at the facet planes. The interpretations based on the theoretical calculations were supported by the experimental results and showed excellent agreement.

1. Introduction

Layer-structured transition metal oxides have been used as cathode materials in lithium ion batteries. LiCoO₂ (LCO) is widely used due to its good electrochemical performance and reasonable stability. Nevertheless, the replacement of LCO with, for example, Ni-based oxides may be beneficial:1–5 LiNiO₂ (LNO) and LCO are isostructural and consist of layers of transition metal cations separated from Li layers by oxygen. The crystal structures belong to the $R\bar{3}m$ space group.6–10 LNO has advantages over conventional LCO in that it has a higher specific energy and a lower toxicity; however, several drawbacks such as the safety, cyclability, and thermal stability aspects must be addressed before LNO may become competitive.11–15

From a practical perspective, the low electrode density of LNO is the main drawback to its wide spread application in real devices. The volumetric energy density, along with the gravimetric capacity, is an important performance criterion for lithium ion batteries. Therefore, increase of the electrode density is required, which can be achieved not only by powder packing technology but also by increase of the material density itself. The crystal density, however, cannot be varied because it is determined by the composition, which is optimized for optimal electrochemical performances. Thus, increasing the bulk density of particles by reducing the pores and particle boundaries may be an effective means for enhancing the electrode density.

The particle morphologies of commercial LCO and LNO-based layered oxides (LiNi₀.₈₂Co₀.₁₅Al₀.₀₃O₂, NCA) are presented in Fig. 1. The LNO-based material is composed of small

Fig. 1 SEM images of commercial cathode materials of the layered structure: (a and c) LiCoO₂, and (b and d) LiNi₀.₈₂Co₀.₁₅Al₀.₀₃O₂.
~1 μm sized primary particles separated by distinct particle boundaries, whereas primary particles of LCO are 5–20 μm in size with few particle boundaries. The particle morphology in Fig. 1(b) is generally observed in Ni-based cathode materials and is a main factor underlying the poor electrode density compared with LCO; the theoretical crystal density of LNO is ~4.8 g cm⁻³, ~5% smaller than LCO whose crystal density is ~5.05 g cm⁻³, whereas the electrode density of commercial NCA and LCO is 3.3–3.5 g cm⁻³ and 3.8–3.9 g cm⁻³, respectively (measured after roll-pressing of the electrodes), showing a larger difference of over 10% even when their particle size distribution is similar. Thus, the low bulk density of LNO-based materials due to their morphology is one of the main factors for the low electrode density. Despite its practical importance, the morphological characteristics of electrode materials have been overlooked. Only a few researchers have investigated the morphology of LCO, 16–19 and no studies of LNO have been reported, to the best of our knowledge. An investigation of the morphological differences between two materials with the same crystal structure may suggest methods for improving the electrode density of LNO and could facilitate application of the material toward practical uses.

In this study, we examined the morphological characteristics of the materials in relation to the surface energy. First-principles calculations were performed to estimate the surface energies. To provide experimental support for the theoretical calculations, LNO, LCO, and LNO with dopants were synthesized using identical processing conditions, and the results were compared with the calculation results.

2. Methods

2.1. First-principles calculations

The surface energies of specific planes in the LNO and LCO crystals (facet planes) were calculated using first-principles density functional theory (DFT) methods. The relevant crystallographic facets were selected by simulating various possible layered structure growth morphologies (Fig. 2) using the Morphology tool embedded in the Material Studio simulation package (Accelrys Software Inc.). It was reported that the LCO crystal facets mainly include (0 0 3), (1 0 4), (0 1 2) planes and their crystallographic equivalent facets under a 3m point symmetry, 19 which is shown in Fig. 2(c). Our experiments revealed a bipyramidal shape for the LNO particles. Facet planes could be observed more clearly with higher synthesis temperature or use of fluxes 20 which may be interpreted as shown in Fig. 2(a) according to the same way as reported for LCO. However, a combination of (0 0 3), (1 1 1), and (0 1 2) facets was also possible from the simulation (Fig. 2(b) and (d)); thus, the energies of the (0 0 3), (1 1 1), (1 0 4), and (0 1 2) facets all were included in the calculation of this study.

Before selecting crystal models for the calculation of surface energies, the LNO and LCO bulk structures were firstly optimized by the Vienna Ab-initio Simulation Package (VASP) allowing full relaxation of the atoms. The crystals were then cleaved parallel to each plane, as shown in Fig. 3. A vacuum slab with a thickness of 15 Å was inserted inside the crystal to create a surface because DFT calculations can be performed only for periodic crystal models. In this study, we defined the surface formation energy (or referred as surface energy in brief) as follows:

$$\Delta E_{\text{surf}} = \Delta E_{\text{cleave}} + \Delta E_{\text{relax}}$$

$$= \frac{1}{2}(E_{\text{cleaved}} - E_{\text{bulk}}) + (E_{\text{relaxed}} - E_{\text{cleaved}}),$$

where $\Delta E_{\text{cleave}}$ is the cleaving energy which arises due to bond breaking between atoms to create two new surfaces on either side of the vacuum slab. $\Delta E_{\text{cleave}}$ was calculated by subtracting the energy of the original bulk crystal ($E_{\text{bulk}}$) from that of the as-cleaved crystal ($E_{\text{cleaved}}$, without relaxation of the surface atoms). This energy was then halved (1/2) because two surfaces were created. $\Delta E_{\text{relax}}$ indicated the energy change due to atomic relaxation into stable positions in the vicinity of one of the newly

![Fig. 2 Simulated morphologies of the layered structure.](image)

![Fig. 3 Cleavage of the LiTMO₃ crystal for facet formation: (a) (0 0 3), (b) (1 1 1), (c) (1 0 4), and (d) (0 1 2).](image)
formed surfaces. $\Delta E_{\text{relax}}$ could be obtained by subtracting the energy of the as-cleaved crystal ($E_{\text{cleaved}}$) from that of the surface-relaxed crystal ($E_{\text{relaxed}}$).

We considered two main aspects in this study which affects reliability of the calculation model. The first aspect was related to the determination of the number of surface atoms whose positions were to be relaxed. Generally, all atoms are set free to move when a bulk crystal structure is optimized in DFT calculations; however, this condition was not applicable here. The size of a crystal model in DFT calculations is always limited by the computational capabilities. If the number of atoms at a surface were large compared to the total number of atoms considered, almost all atoms in the model would be affected by the surfaces. This condition is true only for very small systems: a few nanometers across or smaller. Thus, the relaxation of all atomic positions is not generally applicable. To avoid this situation, we divided the model into two regions: the bulk region, in which the atomic positions are fixed, and the surface region, in which the atoms can move and relax. We defined the surface region consisting of one metal layer and one oxygen layer.

Determination of an appropriate crystal model size for the calculation was another factor to be considered because the ratio between the number of atoms at the surface and in the bulk region depends on the size of the crystal model. Fig. 4 shows the calculated formation energies of a (0 0 3) facet as a function of the number of stoichiometric formula units included in the crystal model. As the size of the model decreased, the surface energy increased most likely due to an increase in the atomic ratio between atoms at the surface and in the bulk regions. Systems with smaller fixed bulk regions may become unstable. Thus, it is obvious that the energies must be compared only when the number of atoms in the calculation models is identical. In this study, all crystal models were designed to include 12 formula units (48 atoms) to provide an exact assessment of the surface energies.

The energies were calculated using first-principles DFT methods. The generalized gradient approximation including corrections for the self-interactions of d electrons (the GGA + U method) and the projector augmented wave (PAW) pseudopotentials was implemented in the VASP program, with an energy cutoff of 500 eV and a self-consistent field (SCF) convergence of $10^{-5}$ eV. The U parameters were set to 6.0, 5.5, and 4.2 eV for Ni, Co, and Mn, respectively, in the GGA + U calculations, as reported previously. The bulk crystal structure and energy calculations ($E_{\text{bulk}}$) were performed allowing full relaxation of the atomic positions and lattice vectors. The optimized crystal was cleaved, a 15 Å thick vacuum slab was inserted, and the surface energies of the crystal were calculated with and without relaxation of the atoms in the surface region, $E_{\text{cleaved}}$ and $E_{\text{relaxed}}$, respectively. The surface energy for each facet plane was obtained from these values using the equation above.

The properties and strengths of the chemical bonds were analyzed by the first-principles discrete variational Xz (DV-Xz) molecular orbital method. This method approximates the exchange–correlation interaction with the Xz potential proposed by Slater and numerically solves the Schrödinger equation using the Hartree–Fock–Slater method. No restriction is imposed on the form of the base functions because the calculation is conducted numerically; consequently, linear combinations of atomic orbitals (LCAO) can be used without any modification. In addition, this method does not use the pseudopotential approximation; all the atomic orbitals are included in the calculation. This permits reliable information regarding the molecular orbitals and the electron distributions. The [Li$_6$Ni$_7$O$_{14}$] and [Li$_6$Co$_7$O$_{14}$] cluster models were used in this study. The transition metals of interest were located at the center of the clusters to improve the accuracy. The clusters were located at the center of the Madelung field that was generated by translating nine unit cells in each direction.

### 2.2. Experimental

LNO and LCO powders were synthesized via high-temperature solid-state reactions and the surface morphologies were observed. LiOH·H$_2$O (SAMCHUN Chemicals, >98%) and TM(OH)$_2$ (TM = Co, Ni, or Mn, Aldrich, >95%) were used as starting materials. The transition metal hydroxide powders were pulverized to yield submicron particles by ball milling using ZrO$_2$ beads. The powders were then mixed with LiOH·H$_2$O and fired at 800°C and 900°C for 15 hours under the flow of dry air at a rate of 40 L min$^{-1}$ to supply oxygen. We used hydroxide precursors instead of oxides and crushed them into small particles to remove the possibility that the size and morphology of the final products would be affected by the properties of the raw materials. It was confirmed that layer-structured LNO and LCO crystals are synthesized from XRD analysis (Rigaku D-max...
3. Results and discussion

3.1. Calculation

The (0 0 3) facet plane consisted of only one atomic species because the LTMO assumes a layered structure in which O, Li, and transition metal (TM) layers are alternately stacked along the c-axis. Consequently, cleaving the crystal normal to the [0 0 3] direction produced polar surfaces in that two different types of surfaces were formed on either side of the vacuum slab. Two types of polar cleavage methods could be considered: cleaving between the Li and O layers by breaking the Li–O bonds or between the TM and O layers by breaking TM–O bonds, as shown in Fig. 5. The calculated surface energies are shown in Table 1. For LNO, the Li-terminated surface yielded the lowest energy facet planes formed by polar cleavage. In contrast, the energy of the O-terminated surface was slightly lower than that of the Li-terminated surface for LCO. TM(O) and O(Li)-terminated surfaces, in which the atom in parentheses indicates the composition of the second layer located just beneath the outer-most surface layer, showed far larger energies compared with the surface energies of Li(O) and O(TM) because of the large cleaving energy ($\Delta E_{\text{cleave}}$) between the TM and O layers. This indicated that TM–O bonds are stronger than Li–O bonds, requiring more energy to break the bonds and cleave the crystal.

Nonpolar cleavage was also considered, in which atoms in a given layer were divided over the two surfaces on opposite sides of the vacuum slab. For example, if some Li atoms on a Li-terminated surface were moved to the opposite O-terminated surface, Li$_{x}$(O) and Li$_{1-x}$(O) surfaces were obtained. For $x = 0.5$, cleaving was perfectly nonpolar and two identical surfaces were generated. The surface formation energies calculated with respect to the Li-coverage (the $x$ value) of the (0 0 3) surface are shown in Fig. 6(a). The energies of the nonpolar cleaved surfaces were lower than those of the polar Li(O) ($x = 1$) and O(TM) ($x = 0$) surfaces. The energy reached a minimum for 50% Li coverage (Li$_{0.5}$(O) surface) for LCO. A high Li coverage was preferred for LNO, and Li$_{0.75}$(O) provided the most stable surface; however, the Li$_{0.50}$(O) and Li$_{1.00}$(O) surfaces also displayed low energies. In general, the pH of the slurry used to coat LNO layers during the preparation of lithium ion battery cathodes is higher than the pH of a LCO slurry, which causes rapid polymerization of the binding materials and results in instabilities of the slurry. A high LNO pH is maintained, even after washing away surface impurities. It seems the fact that Li-rich termination is energetically favorable for the (0 0 3) facets of LNO than LCO may be a reason for the high pH of the LNO-slurry.

The (1 1 0) facets also consisted of only one type of atom after cleavage between layers (Fig. 7). As in the case of the (0 0 3) facets, polar cleavage between the Li and O layers or between the Ni and O layers could be considered. The surface energies of the (1 1 0) facets were higher than those of the (0 0 3) facets; however, a comparison of the surface energies of the (1 1 0) facets produced by various terminations revealed a trend similar to the case of the (0 0 3) surfaces; the energy corresponding to cleavage between the TM and O layers was larger than that produced for Li–O. The only exception occurred for LCO, in which the energy of the Li(O) facet was lower than that of the O(Co) facet for (1 1 0). This was opposite to the case of the (0 0 3) surface. Both LNO and LCO displayed the lowest surface energies for the (1 1 0) surface with perfect nonpolar cleaving (the Li$_{0.5}$(O) surfaces). The calculated results for the (1 1 0) surfaces are shown in Fig. 6(b).

The results of the (0 0 3) and (1 1 0) facets revealed that facet formation, including TM–O cleavage, required a large amount of energy. Li and TM coexisted on the same planes in the (1 0 4) and (0 1 2) facet planes. Therefore, non-polar cleavage of stable surfaces can be obtained by dividing O atoms onto both surfaces, i.e., O$_{0.5}$(Li, TM) surface, as shown in Fig. 8. The surface energies calculated for the (1 0 4) facets of LNO and LCO were 3.019 and 7.008 eV nm$^{-2}$, respectively, and 7.554 and 13.169 eV nm$^{-2}$ for the (0 1 2) facets of LNO and LCO, respectively. The energies of the surfaces generated by polar cleavage fell in the range of 14–15 eV nm$^{-2}$ and 38–42 eV nm$^{-2}$ for LNO and LCO, respectively, much higher than the surface energies for the nonpolar cleavage cases because the metal layers were exposed on the surfaces for polar cleavage.

The minimum surface energies for various LNO and LCO facet planes are presented in Fig. 9. The energy was smallest for the (0 0 3) facets, and it increased in the order of the (1 0 4), (1 1 0) and (0 1 2) facets. This indicated that the surface energy for the crystal morphology of Fig. 1(b), the surface of which consisted mainly of (0 0 3) and (1 1 0) facets and their equivalent planes under a 3$\eta$ point symmetry, was lower than that shown in Fig. 1(a), which consisted mainly of (0 0 3), (0 1 2) facets and their equivalent planes. Considering that surface energy is a major determining factor for the crystal morphology, bi-pyramidal LNO particles were expected to have the morphologies shown in Fig. 1(b).

The energies of the LNO facets were plotted as a function of the number of broken Ni–O bonds per unit area (Fig. 10). The results show that they are proportional to each other, regardless of index planes or types of atoms, consistent with previous
Only the energy of the (1 0 4) surface was exceptionally low. The nonpolar (1 0 4) plane revealed a high atomic density compared with other planes, and O atoms were present between the TM and Li atoms on the surface, as shown in Fig. 8(a). The configurational characteristics of the (1 0 4) surface may have reduced electrostatic repulsion among atoms on the surface, resulting in a relatively low energy. We found that the shift of atomic positions on the (1 0 4) surface was far less than on other surfaces from the comparison of the atomic positions between the as-cleaved and relaxed crystal models. This supports that electrostatic forces are well balanced on the as-cleaved (0 1 4) surface. Thus, the surface formation energy depended to some extent on the surface geometry and was mainly determined by the number of TM–O broken bonds.

Table 1  Calculated cleaving energy ($\Delta E_{\text{cleave}}$), relaxation energy ($\Delta E_{\text{relax}}$), and surface energy ($\Delta E_{\text{surf}}$) of the (0 0 3) facet plane. $\Delta E_{\text{cleave}}$ is defined as the energy required to break bonds between layers and create a facet; $\Delta E_{\text{relax}}$ is the energy change upon relaxation of the atomic positions in the vicinity of a surface region; and $\Delta E_{\text{surf}}$ is the surface energy and is the sum of $\Delta E_{\text{cleave}}$ and $\Delta E_{\text{relax}}$

<table>
<thead>
<tr>
<th>Facet Plane</th>
<th>Terminated Surface</th>
<th>$\Delta E_{\text{cleave}}$ (eV nm$^{-2}$)</th>
<th>$\Delta E_{\text{relax}}$ (eV nm$^{-2}$)</th>
<th>$\Delta E_{\text{surf}}$ (eV nm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNO (Li–O cleaving)</td>
<td>Li(O)-terminated</td>
<td>3.428</td>
<td>-2.090</td>
<td>1.338</td>
</tr>
<tr>
<td></td>
<td>O(Ni)-terminated</td>
<td>2.090</td>
<td>-0.578</td>
<td>2.668</td>
</tr>
<tr>
<td>LNO (Ni–O cleaving)</td>
<td>Ni(O)-terminated</td>
<td>8.176</td>
<td>-0.761</td>
<td>7.415</td>
</tr>
<tr>
<td></td>
<td>O(Li)-terminated</td>
<td>5.761</td>
<td>-0.548</td>
<td>6.283</td>
</tr>
<tr>
<td>LCO (Li–O cleaving)</td>
<td>Li(O)-terminated</td>
<td>5.241</td>
<td>-0.396</td>
<td>4.845</td>
</tr>
<tr>
<td></td>
<td>O(Co)-terminated</td>
<td>5.048</td>
<td>-0.606</td>
<td>4.635</td>
</tr>
<tr>
<td>LCO (Co–O cleaving)</td>
<td>Co(O)-terminated</td>
<td>12.386</td>
<td>-0.121</td>
<td>12.265</td>
</tr>
<tr>
<td></td>
<td>O(Li)-terminated</td>
<td>12.057</td>
<td>-0.088</td>
<td>12.069</td>
</tr>
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</table>

Fig. 6  Surface energies calculated for the (0 0 3) (a) and (1 1 1) (b) facet planes with respect to the fraction of Li atoms at the surfaces.

Fig. 7  Crystal model for calculating the surface energy of the (1 1 1) facet planes: (a) Li-terminated and (b) O-terminated.

Fig. 8  Crystal model for calculating the surface energy of the nonpolar (a) (1 0 4) and (b) (0 1 2) facet planes.

Although overall behavior of energy changes with respect to various facets and to the number of broken bonds is similar for LNO and LCO, the absolute values differed. The energies of LNO were smaller than those of LCO for all facets calculated. This difference originated mainly from the different cleaving energies ($E_{\text{cleave}}$), indicating that Li–O and TM–O bonding in LNO was weaker than in LCO. This interpretation was supported by the bonding nature revealed using the DV-Xα molecular orbital method. Table 2 shows the calculated effective charges of each atom in the LNO and LCO crystals. The atoms in
LNO were less ionized than those in LCO, indicating that both Li–O and TM–O bonds were weaker in terms of the ionic bond strength in LNO.

Covalent bonding was also examined based on the overlap population (OP) in the TM–O bonding. The OP diagrams calculated using the DV-Xα method are presented in Fig. 11. The covalent nature of the Li–O bond was not significant because the Li–O bond was mainly ionic in character and the OP was very small compared with the OP for TM–O bonding. A comparison of the OP diagrams for Ni–O and Co–O bonding showed that the antibonding molecular orbitals in Ni–O were located in a lower energy region than those of Co–O. This indicates the bond overlap population (BOP), which is defined as the difference between electron population of bonding orbitals and that of anti-bonding orbitals, is larger for Co–O bond. The Ni–O covalent bond strength was, therefore, weaker. However, the shapes of OP diagrams were similar for Ni–O and Co–O bonds. Consequently, the main difference in bond strengths for LNO and LCO appeared to be due to their ionic bonding character.

Fig. 12 shows the position shifts of surface atoms at the (0 0 3) and (1 1 1) planes upon relaxation. Li atoms on the facet moved closer to the O atoms in the second layer in both cases. Li atoms at the (0 0 3) facet, which were equidistant from the O atoms (see Fig. 12(c)), only moved vertically, whereas Li atoms at the (1 1 1) facet moved both vertically and horizontally. These movement trends resulted from the asymmetric arrangement of O atoms around the Li atom (see Fig. 12(d)). The O atoms in the second layer shifted slightly toward the surface due to the absence of electrostatic repulsion with the O layers that existed on top of the Li layer before cleaving. These results indicated that relaxation in the atomic positions at the surface was mainly controlled by coulombic forces among atoms; the cleaving and relaxation energies were mainly affected by the ionic bonding character of the crystal. In summary, Li–O and TM–O bonds were weaker in LNO than in LCO due to differences in the ionic bond strength; thus, the cleaving energy was smaller for LNO, resulting in a lower surface energy.

Table 2 Effective charge of the ions in LNO and LCO crystals calculated using the DV-Xα molecular orbital method

<table>
<thead>
<tr>
<th></th>
<th>LNO</th>
<th>LCO</th>
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<tbody>
<tr>
<td>Li</td>
<td>+0.872</td>
<td>+0.917</td>
</tr>
<tr>
<td>O</td>
<td>-0.929</td>
<td>-1.118</td>
</tr>
<tr>
<td>Ni</td>
<td>+1.155</td>
<td>—</td>
</tr>
<tr>
<td>Co</td>
<td>—</td>
<td>+1.372</td>
</tr>
</tbody>
</table>
3.2. Experimental

It is previously mentioned that the LNO-based layered material particles are composed of agglomerated small primary particles and the bulk density is lower than that of the LCO-based layered material, which did not include small particles. The morphological differences could have arisen from differences in the synthesis method or the firing temperatures. To eliminate this possibility, we synthesized LNO and LCO at equal temperatures, 800°C and 900°C. XRD analysis confirmed that perfect LCO and LNO phases were obtained at these temperatures. The SEM images of the powders are shown in Fig. 13. Firing at 800°C yielded powders composed of agglomerated small particles for both materials, but the LCO particle size was larger. Increasing the temperature to 900°C increased the LCO particle size greatly, and each particle developed as a single grain (Fig. 13(d)). In contrast, LNO grew slightly in size and was composed of agglomerates (Fig. 13(b)).

Considering that the optimum firing temperature for commercial LCO is higher than that of LNO, this result indicated that the LNO morphology shown in Fig. 1 was not due to different firing temperatures, but to the material nature itself. The first principle calculations described in the previous sections demonstrated that the LNO surface energy is smaller than that of LCO for all facet planes considered. Because the surface energy is a major driving force for particle growth and coalescence, we concluded that the morphological characteristics of LNO and LCO originated from differences in the surface energy. LNO particles would remain as small particles with many particle boundaries due to low surface energy. In contrast, the LCO particles, with a high surface energy, tend to grow to reduce the surface energy.

The kinetics of particle growth (mobility of atoms) could potentially affect the ultimate particle morphology; however, longer firing times did not produce different morphologies, indicating that the synthetic conditions of our experiments provided enough time for the development of the particle morphology. The energy barrier for the migration of Ni is lower than that of Co in a layered structure, that is, Ni has a higher mobility and can diffuse faster during particle growth. Thus, LNO has more favorable kinetic conditions for grain growth, but it is opposite to the experimental results. Consequently, the morphological characteristics of LNO and LCO were determined by thermodynamic factors, i.e., surface energy, rather than by kinetic factors.

The SEM images of LNO doped with other transition metals: (a) Co, and (b) Mn. The amount of dopants was fixed at 10 atomic% and the firing temperature was 800°C.

![Fig. 12](image12.png) Changes in the atomic positions upon relaxation at the LNO surfaces: (a and c) the Li-terminated (0 0 3) facet plane and (b and d) the Li-terminated (1 1 1) facet plane. The original positions prior to formation of new surfaces are indicated by empty circles (dashed lines).

![Fig. 13](image13.png) SEM images of the LNO and LCO particles prepared under identical synthetic conditions: (a) LNO sintered at 800°C, (b) LNO at 900°C, (c) LCO at 800°C, and (d) LCO at 900°C.

![Fig. 14](image14.png) SEM images of LNO doped with other transition metals: (a) Co, and (b) Mn. The amount of dopants was fixed at 10 atomic% and the firing temperature was 800°C.

![Fig. 15](image15.png) Surface energies of the (0 0 3) facet planes for the Co- or Mn-doped LNO crystals.
Co or Mn was added to LNO to confirm the relationship between the morphology and surface energy discussed above. Two new compositions, LiNi_{0.9}Co_{0.1}O_2 (LNCO) and LiNi_{0.9}Mn_{0.1}O_2 (LNMO), were synthesized at 800 °C. The SEM images shown in Fig. 14 revealed that the introduction of Co increased the particle size, whereas Mn did not affect the particle size. The surface energies of the LNCO and LNMO (0 0 3) facets were calculated and are presented in Fig. 15 along with those of LNO and LCO. The energy of the LNCO surface exceeded that of LNO, but LNMO showed a surface energy similar to that of LNO. The result supported the conclusion that the grain size is closely related to the surface energy. The addition of Co to LNO is expected to increase the volumetric capacity of lithium ion batteries by promoting the growth of particles, in addition to the known effect of improvement in LNO structural stability conveyed by Co.

4. Conclusions

The surface energies of LNO and LCO crystals were calculated by first-principles methods, and the crystal morphologies were interpreted based on the calculated results. Simulations showed that LNO crystal facets preferentially presented (0 0 3), (1 1 1), (1 0 4) planes and their crystallographic equivalents. The surface energies were found to be proportional to the number of broken TM–O bonds at the surface because TM–O bonds are stronger than Li–O bonds. In both materials, Li or O-exposed facets formed by nonpolar cleavage showed higher stabilities. LNO preferred a higher Li coverage than LCO. The overall energy of the LNO surface was lower than the energy of the LCO surface, suggesting a small driving force for LNO particle growth during firing. We propose this as the main factor that determines the morphology of LNO.

References