First-principles investigation of the effect of Co in stabilizing the structures of layer-structured cathodes in delithiated state

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Abstract

The structural and chemical features of delithiated layer-structured cathodes (Li_{0.333}TM_{O2}, TM = Ni and Co) are investigated. Energetically stable structures are evaluated by combing particle swarm optimization algorithm and density functional theory calculations. The concentration of defects is calculated assuming that the entire crystal is the statistical combination of the lowest-energy structures. TM antisites that occupy Li sites and interstitial Li ions at tetrahedral sites are the major defect types in Li_{0.333}TM_{O2}; their prevalence decreases with increase in Co content. The oxidation state of Ni ions increases in the presence of Co, because the Co ions sustain low oxidation numbers, which results in decrease in the possibility of Ni^{2+} formation. In addition, the covalent bond of Co−O appears to be stronger than that of Ni−O. Therefore, the suppression of Ni^{2+} formation and the strong covalent bonding are proposed as the mechanisms underlying the stabilizing effect of Co.

1. Introduction

Li-ion battery (LIB) industry is rapidly growing with a broadening application in electric vehicles (EVs) [1−3]. However, the performance of LIBs still falls short of consumer expectations. In particular, advanced positive electrode materials to achieve high-capacity and low-cost LIBs are urgently required [4−7]. Several alternative materials such as LiFePO4, LiMn2O4, and LiNi0.333Mn1.667O2 have been developed to replace the conventional LiCoO2 (LCO) cathode, but their low theoretical capacities have limited their application in high-capacity LIBs [7−11]. Therefore, the most realistic short- or mid-term solution for LIB cathodes seems to be Ni-based layer-structured materials.

By increasing the Ni content in layer-structured cathode materials by replacing Co, the available capacity at commercial charging voltage of 4.2−4.3 V is increased, while the cost of raw material is decreased [12−14]. Therefore, higher energy storage density and lower battery cost, both among the most critical issues in the current LIB industry, can be achieved by developing Ni-based layer-structured cathodes. However, the problems of inferior durability, thermal safety, high-defect concentration, and low structural stability become significant with increasing substitution of Ni for Co [14−17]; therefore, research efforts are focused on increasing the stability of Ni-based cathodes.

Many studies have attempted to improve the structural stability of Ni-based cathode materials, generally by optimizing the chemical compositions and/or the processing conditions for the syntheses, yielding cathode materials such as LiNi0.3Co0.7Mn0.2 (LNCM) and LiNi0.5Co0.5Al0.5O2 (LNCA) with a gradual increase in the proportion of Ni [18−23]. Recently, research and development efforts are underway to increase the Ni content to 80%−90%. To this end, a fundamental consideration of the structural stability of Ni-rich cathode materials is necessary. Because the crystal structures of cathodes generally degrades when the battery is in the charged state, an understanding of the structural features and the types and formation mechanisms of defects in delithiated cathode crystals is required.

Therefore, in this study, the crystal structure of the layer-structured LiTMO2 (LTMO, TM = Ni and Co) cathode is investigated, with special attention to the changes in the structure at the delithiated state as the ratio of Ni and Co in TM is changed. The defect types that are formed in the delithiated crystal are examined, and a
calculation model for the quantitative analysis of the defect concentration is proposed. In addition, the mechanisms of defect formation in Ni-based cathodes is investigated by analyzing the chemical bonding characteristics and the oxidation numbers of the transition metals in the material. It is expected that this investigation may provide a theoretical foundation for developing layer-structured cathode materials with high Ni content and improved structural stability.

2. Methods

Structural searching for low-energy layer-structured cathode materials at 66.7% delithiated state (Li_{0.333}TMO_2, TM = Ni, Co) was performed by an unbiased searching method via particle swarm optimization (PSO) algorithm using the Crystal structure AnaLysis by Particle Swarm Optimization (CALYPSO) code [24] (figure 1). Frame cells with the composition of Li_3TM_7O_24 were prepared by removing nine Li and five TM atoms from the Li_12TM_12O_24 supercells. One Li and five TM atoms were then added to the frame cell at random places with no limitations except for the minimum distance between ions in the crystal, which was set to be 1.0 Å. Applying only this minimum necessary condition enabled the examination of both the insertion of atoms at vacant lattice sites and possible interstitial site occupation. The delithiation level of 66.7% is higher than general state of charge (SOC) of commercial LiCoO_2 while it is lower than those of Ni-rich cathodes. Considering that a comparative study with change of TM composition is performed in this study, along with the convenience of making the delithiated crystal models, the 66.7% delithiation level is commonly applied to all the crystal models of delithiated cathodes.

The structures generated by the PSO algorithm were optimized by a density functional theory (DFT) calculation using the Vienna Ab initio Simulation Package (VASP) [25, 26], and the crystal energy obtained from the calculation was fed back to the PSO algorithm. This routine was repeated for 15 generations, with 50 pop-up structures per generation; thus, the most stable structures for Li_4TM_12O_24 were derived. The DFT calculations were performed using VASP code with a 3 × 3 × 1 k-point grid based on the Perdew–Burke–Ernzerhof generalized-gradient approximation and projector-augmented plane-wave pseudopotentials [27, 28], with an energy cutoff of 500 eV. Both the atomic positions and lattice vectors were allowed to relax during the optimization of each structure, and the energy was obtained with the convergence threshold of 10^{-5}.

The energies of the five lowest-energy structures identified by the PSO-DFT method were calculated again more precisely using the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional [29]. Using the charge distribution data obtained from the calculation, the chemical features of the ions in the crystal are analyzed: the bond order, net atomic charge, and spin moment are analyzed by the atomic population analysis performed by the density-derived electrostatic and chemical method using the Chargemol program [30–33].

3. Results and discussion

3.1. Crystal structure in delithiated state
The energies of the Li_4TM_12O_24 supercells obtained from the structure searching are presented in figure 2. Two main structures, named as N- and D-structures in this study, have lower energy than the others, commonly for the supercell compositions of Li_4Ni_12O_24, Li_4Ni_11CoO_24, and Li_4Co_12O_24. The features of the N- and
D-structures are presented in figure 3. The N-structure has no defects other than the Li vacancies resulting from the delithiation. Meanwhile, the D-structure has both antisite- and interstitial-type defects: two out of 12 TM atoms are positioned at vacant Li sites, and three out of four Li atoms are moved from their original octahedral lattice sites to adjacent tetrahedral interstitial sites. Therefore, the D-structure contains 16.7% TM antisite defects ($TMLi$) and TM vacancies ($VTM$), as well as 75% interstitial defects ($Litet$).

The stabilities of the two structures differ depending on the Ni–Co ratio comprising the TM. The energy of the D-structure is lower than that of the N-structure for the composition of Li$_4$Ni$_{12}$O$_{24}$, while the N-structure has a lower energy than the D-structure for Li$_4$Co$_{12}$O$_{24}$. In Li$_4$Ni$_{11}$CoO$_{24}$, the D-structure energy is lower, but the difference between the energies of the D- and N-structures is smaller than that in Li$_4$Ni$_{12}$O$_{24}$. This result suggests that the energy of the N-structure becomes lower compared to that of the D-structure, that is, the N-structure becomes more stable over the D-structure as the Co content is increased. For a more precise examination of this expectation, the energy of the N- and D-structured Li$_4$TM$_{12}$O$_{24}$ supercell is calculated and plotted as a function of the Co content in figure 4, which clearly shows that the N-structure is more stable than the D-structure as the Co content increases to exceed 25%.

The structure of the entire delithiated crystal may be considered a combination of the identified lowest-energy cells. That is, the entire crystal may be considered an ensemble of the unit-supercells, in which the sub-systems (unit-supercells) are statistically combined according to their Boltzmann factors. Because structures
other than the two main structures have relatively higher energies, they have near-negligible Boltzmann factors. Therefore, the macro-crystal of delithiated LTMO may be constructed by combining the N- and D-structures, which are the two main structures in the delithiated state of the crystal. Based on this assumption, the equations for calculating the proportion of N- and D-structures in the overall macro-crystal are proposed as follows:

\[
P_N = \left[ e^{\frac{E_{N}}{kT}} \sum_{s} e^{\frac{-E_{s}}{kT}} \right] \approx \left[ e^{\frac{E_{N}}{kT}} \sum_{s=N,D} e^{\frac{-E_{s}}{kT}} \right] \tag{1-1}
\]

\[
P_D = \left[ e^{\frac{E_{D}}{kT}} \sum_{s} e^{\frac{-E_{s}}{kT}} \right] \approx \left[ e^{\frac{E_{D}}{kT}} \sum_{s=N,D} e^{\frac{-E_{s}}{kT}} \right] \tag{1-2}
\]

In equation (1), \( e^{\frac{E_{N}}{kT}} \) and \( e^{\frac{E_{D}}{kT}} \) are the Boltzmann factors of the N- and D-structures, respectively. The partition function \( \sum_{s} e^{\frac{-E_{s}}{kT}} \) is theoretically the summation of all the super-unit’s Boltzmann factors, but the Boltzmann factors of the other structures are negligible compared to those of the N- and D-structures, as discussed above. Therefore, the partition function can be approximated as the sum of only the N- and D-structures’ Boltzmann factor. The calculation result for the proportion of the D-structure \( (P_D) \) is presented in figure 4 as a function of the Co content, where the decrease of \( P_D \) is verified with the increase in Co content. From the calculation of equation (1), the overall concentration of defects can also be obtained by multiplying \( P_D \) by the concentration of each defect contained in the D-structure, as expressed in equation (2).

\[
C_{\text{defect}} = P_D \times c_{d \text{ in } D} \approx \left[ e^{\frac{E_{D}}{kT}} \sum_{s=N,D} e^{\frac{-E_{s}}{kT}} \right] \times c_{d \text{ in } D} \tag{2}
\]

In equation (2), \( C_{\text{defect}} \) denotes the concentration of a certain point defect in the entire crystal, which is obtained from the multiplication of \( P_D \) and \( c_{d \text{ in } D} \), the concentration of the defect in the D-structure. The calculation results for the concentrations of TM_{Li} and Li_{tet} are presented in figure 5. In Li_{0.333}NiO_{2}, the concentration of Ni_{Li} is 16.7%, while it is only \( 1.43 \times 10^{-7} \% \) in LCO. The antisite defect is known to obstruct the migration of Li, which induces degradation of the cathode performance. The result of figure 5 shows the antisite defect increases with increasing Ni content in the layer-structured cathode materials, indicating that Ni-rich cathodes may be vulnerable to the degradation caused by antisite defects generated in the charged states of the LIBs.

### 3.2. Chemical examination of Co doping effect

The chemical features of the N- and D-structures, the two most stable supercell structures identified by the PSO-DFT method, are investigated by analyzing the bonding characteristics, net charge, and oxidation states of the ions. In particular, the properties are compared between the Li_{4}Ni_{12}O_{24} and Li_{4}Ni_{9}Co_{3}O_{24} supercells to examine the effect of Co. The covalent bonding characteristics can be examined by analyzing the bond-order. The average bond-order of Ni ions appears similar irrespective of the composition and defects. Although the bond-order of Li shows a slight increase in the D-structure, it does not seem to have a significant effect, considering that Li–O
bonds are mainly ionic in nature (Table 1(a)). Therefore, the covalent bonding characteristics do not seem relevant to the energies of the supercells. The ionic charges of Li and Ni show no significant differences among the supercells either, being commonly in the range of 0.856–0.875 and 1.208–1.232, respectively (Table 1(b)).

To examine the oxidation states, the atomic spin moments of the TM ions are analyzed, with the results summarized in Table 2. The spin moments of Ni and Co are within 0–2 and 0–1, respectively, which correspond to high-spin Ni$^{3+}$, low-spin Ni$^{3+}$ and Ni$^{4+}$, and low-spin Co$^{3+}$ and Co$^{4+}$. High-spin Ni$^{3+}$ and Ni$^{4+}$ ions are not considered because their theoretical spin moments are 3 and 4 respectively, far exceeding the values observed from the calculation. As the spin moments obtained are not exact integers, a proper criterion is necessary to determine the oxidation numbers from the non-integer spin moments. In this study, the TM ions whose spin moments are in the ranges 0–0.5, 0.5–1.5, and >1.5 are classified as Ni$^{3+}$ (Co$^{3+}$), Ni$^{3+}$ (Co$^{3+}$), and Ni$^{4+}$, respectively. The average oxidation state of the TM ions calculated from this classification is in the range 3.58–3.67, which shows good agreement with the theoretical value of 3.667 in Li$_4$TM$_{12}$O$_{24}$. Therefore, the determination of the oxidation number may be accepted as reasonable.

The oxidation numbers of the TM ions determined from the above method are presented in Figure 5, which indicates that all the Ni ions in N-structured Li$_4$Ni$_{12}$O$_{24}$ are Ni$^{3+}$ or Ni$^{4+}$. A smaller number of Ni$^{3+}$ is present in

**Table 1.** Bond-order (a) and net atomic charge (b) of the ions in the N- or D-structured Li$_4$Ni$_{12}$O$_{24}$ and Li$_4$Ni$_9$Co$_3$O$_{24}$ supercells.

|                | Li$_{Li}$ | Li$_{tot}$ | Ni$_{Ni}$ | Ni$_{tot}$ | Co$_{Ni}$ |
|----------------|-----------|------------|-----------|------------|-----------|
| Li$_4$Ni$_{12}$O$_{24}$ N | 0.394     | —          | 2.948     | —          | —         |
| D              | 0.407     | 0.440      | 2.941     | 2.750      | 2.909     |
| Li$_4$Ni$_9$Co$_3$O$_{24}$ N | 0.387     | 0.387      | 2.972     | —          | 3.178     |
| D              | 0.448     | 0.428      | 2.920     | 2.768      | 2.886     |

|                | Li$_{Li}$ | Li$_{tot}$ | Ni$_{Ni}$ | Ni$_{tot}$ | Co$_{Ni}$ |
|----------------|-----------|------------|-----------|------------|-----------|
| Li$_4$Ni$_{12}$O$_{24}$ N | 0.872     | —          | 1.208     | —          | —         |
| D              | 0.869     | 0.851      | 1.224     | 1.194      | 1.219     |
| Li$_4$Ni$_9$Co$_3$O$_{24}$ N | 0.872     | —          | 1.208     | —          | 1.169     |
| D              | 0.852     | 0.858      | 1.232     | 1.232      | 1.222     |

**Table 2.** Average oxidation states of TM ions at different occupation sites in the N- or D-structured Li$_4$Ni$_{12}$O$_{24}$ and Li$_4$Ni$_9$Co$_3$O$_{24}$ supercells.

|                | Ni$_{Ni}$ | Ni$_{tot}$ | Ni$_{tot}$ | Co$_{Ni}$ | TM$_{tot}$ |
|----------------|-----------|------------|------------|-----------|------------|
| Li$_4$Ni$_{12}$O$_{24}$ N | +3.58     | —          | +3.58      | —         | +3.58      |
| D              | +3.80     | +2.50      | +3.58      | —         | +3.58      |
| Li$_4$Ni$_9$Co$_3$O$_{24}$ N | +3.89     | —          | +3.89      | +3.00     | +3.67      |
| D              | +3.86     | +3.50      | +3.78      | +3.33     | +3.67      |
the D-structured Li$_4$Ni$_{12}$O$_{24}$, while the amounts of Ni$^{4+}$ and Ni$^{2+}$ are increased, and some of the Ni$^{2+}$ is located in the Li layer. This is a typical example of charge disproportionation, with the transition of $2\text{Ni}^{3+} \rightarrow \text{Ni}^{2+} + \text{Ni}^{4+}$. The ionic radius of Ni$^{2+}$ (0.69 Å) is larger than those of Ni$^{3+}$ (0.56 Å) and Ni$^{4+}$ (0.48 Å), and close to that of Li$^+$ (0.76 Å); therefore, the Ni$^{2+}$ ion is likely easily accommodated by the vacant Li site, thus reinforcing the Li slab where the Li ions supporting the structure are deficient due to the delithiation. This reinforcement by Ni$^{2+}$ may contribute to stabilizing the crystal structure and lowering the energy. This is proposed as the mechanism explaining the lower energy (i.e., higher stability) of the D-structure than that of the N-structure in the Li$_4$Ni$_{12}$O$_{24}$ composition.

Meanwhile, charge disproportionation does not appear in the D-structured Li$_4$Ni$_9$Co$_3$O$_{24}$: all the Ni ions are at $+3$ and $+4$ oxidation states without the formation of Ni$^{2+}$, indicating that the introduction of Co suppresses the generation of Ni$^{2+}$, as discussed above. The Ni ions at Li sites show oxidation states of $+3$ or $+4$ in the D-structure of this composition. Considering that the ionic radii of Ni$^{3+}$ and Ni$^{4+}$ are significantly different from that of Li$^+$ compared to the difference between Ni$^{2+}$ and Li$^+$, the D-structure of Li$_4$Ni$_9$Co$_3$O$_{24}$ would be relatively unstable compared to the D-structure of Li$_4$Ni$_{12}$O$_{24}$ in which Ni$^{2+}$ occupies Li sites. Thus, it seems that the stability of the N-structure is better than that of the D-structure because the introduction of Co prevents Ni$^{2+}$ formation.

The oxidation numbers of the ions in each composition and structure are summarized in table 2. For Li$_4$Ni$_{12}$O$_{24}$, the average oxidation number of Ni ions at the normal lattice site (Ni$_{Ni}$) is higher in the D-structure than in the N-structure (+3.80 in the D-structure and +3.58 in the Ni-structure), whereas that of Ni ions at Li sites is lower in the D-structure (+2.50 in the D-structure and +3.50 in the N-structure). This is because the Ni$^{2+}$ ions are generated by the charge disproportionation of Ni$^{3+}$ and occupy the vacant Li sites, as discussed above. On the contrary, in Li$_4$Ni$_9$Co$_3$O$_{24}$, the average Co oxidation numbers are +3.00 in the N-structure and +3.33 in the D-structure, which are lower than the oxidation number of Ni. That is, the Ni ions are highly oxidized in the presence of Co, because Ni$^{3+}$ oxidizes to Ni$^{4+}$ prior to the oxidation of Co$^{3+}$ as the crystal is delithiated; therefore, the concentration of Ni$^{3+}$ is lower in the Co-containing composition and the formation probability of Ni$^{2+}$ is lowered, which suppresses Ni$_{Li}$ defects.

Thus, the introduction of Co prevents the formation of Ni$_{Li}$-type antisite defects by suppressing the formation of Ni$^{2+}$ ions, which otherwise easily occupy the Li sites. In addition to this, Co has a higher covalent bonding nature than Ni, as can be noticed from the bond-order data of table 1(a). Although the introduction of Co does not cause any significant change in the bond-order of Ni, the bond-order of Co is higher than that of Ni by $\sim 10\%$, which indicates that Co forms stronger covalent bonds with O than Ni does. The strong Co–O bonding is expected to sustain the crystal structure in the delithiated state.

4. Conclusions

The structures of Li$_4$TM$_{12}$O$_{24}$ (TM = Ni and Co) supercells are investigated by a combined method of the PSO algorithm and DFT calculations to evaluate the crystal structures of LiTMO$_2$ cathodes for LIBs in their
delithiated state. Two structures, one with no defects other than Li vacancies (N-structure) and the other with defects, such as Li sites occupied by TM (TM$_{Li}$), TM vacancies (V$_{TM}$), and Li at tetrahedral sites (Li$_{tet}$) as well as Li vacancies (D-structure), are established as the main structures with the lowest supercell energies. The overall crystal structure of the delithiated cathode is assumed to be a statistical combination of these two main supercells as building units, with the proportion of each structure determined according to its Boltzmann factor. The defect concentration in the entire crystal is also obtained based on the calculated result. The D-structure is more stable than the N-structure for the composition of Li$_x$Ni$_{12}$O$_{24}$, but the N-structure becomes more stable as the Co content increases, indicating that introducing Co suppresses defect formation and stabilizes the delithiated crystal of layer-structured cathode materials.

The Ni$_{Li}$-type antisite defect is generated by the occupation of Li sites by Ni$^{2+}$ ions, which are formed by the charge disproportionation of Ni$^{3+}$ to Ni$^{2+}$ and Ni$^{4+}$ in Li$_{0.333}$NiO$_2$. When Co is introduced in the crystal, the oxidation number of the Co ions remains lower than that of the Ni ions, which increases the average oxidation state of Ni. This reduces the number of Ni$^{3+}$ ions, resulting in the suppression of Ni$^{2+}$ formation; this species otherwise easily occupies Li sites, generating Ni$_{Li}$-type defects. In addition, Co shows a higher bond-order than Ni, which indicates that a stronger covalent bonding of Co–O compared to that of Ni–O stabilizes the crystal structure. Thus, Co introduced into Ni-rich cathode materials stabilizes the structures via two mechanisms: suppressing the Ni$^{2+}$ generation and forming strong covalent Co–O bonds. These effects of Co suppress the formation of Ni$_{Li}$-type antisite defect and strengthens the crystal structure, which result in better durability and safety of the layer-structured cathodes of Li-ion batteries.

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