Theoretical Study Using First-Principles Calculations of the Electronic Structures of Magnesium Secondary Battery Cathode Materials MgCo_{2-x}Mn_xO_4 (x = 0, 0.5) in the Pristine and Discharged States

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ABSTRACT

In this study, the projected density of states (PDOS) of the stable normal-spinel structure and stable Mg/Co mixed-cation spinel structure of Mg^{1+}_{1+y}Co_{2-x}Mn_xO_4 (x = 0, 0.5; y = 0, 0.5, 1) in the pristine and discharged states are obtained using first-principles calculations. The spin state and the valence state of the transition metals are investigated. The overlaps of the d orbitals of the transition metals and the p orbitals of oxygen are large, and the covalency between the transition metal and oxygen is strong in the pristine MgCo_2O_4 and MgCo_{1.5}Mn_{0.5}O_4. The M–O_6 (M = Co, Mn) octahedra become stable as a host structure. From the PDOS spectra, Co atoms are in the trivalent low-spin state in pristine MgCo_2O_4 and MgCo_{1.5}Mn_{0.5}O_4 and Mn atoms are nearly tetravalent in pristine MgCo_{1.5}Mn_{0.5}O_4. In the discharge process, the overlap of the d orbitals of the transition metals and the p orbitals of oxygen becomes narrow and the valence of the transition metals decreases with increasing Mg insertion. The results of the first-principles calculations are consistent with those of X-ray absorption near edge structure spectra.

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1. Introduction

Since the twentieth century, global warming has been occurring because of the emission of greenhouse gases; research into clean energy materials has therefore become necessary. Secondary batteries are attractive as clean energy-storage materials that do not exhaust greenhouse gases. Lithium-ion secondary batteries, which can be repeatedly charged and discharged, are already used in laptops and smartphones. In the future, the application range of secondary batteries will include large equipment such as electric vehicles, which will greatly reduce the environmental load generated by the transportation sector.

However, Li metal is scarce because of its small reserves. Recently, Mg metal, which is earth-abundant, has been attracting attention as a next-generation secondary battery material. Mg secondary batteries are expected to exhibit a greater energy density than Li^+ ion batteries. V_2O_5, MnO_2, MoO_3, polyanionic compounds (olivine-type Mg_xMSiO_4 (M = Fe, Mn, Co), MgFePO_4F, NASICON-type Mg_xV_2(PO_4)_3 (0 ≤ x ≤ 1.5), and spinel-structured
MgMnO₄ doped with Sr²⁺ has been reported to function as host structures for Mg secondary battery cathode materials.

Research related to Mg secondary battery cathode materials using first-principles calculations has been active.²⁰⁻²¹ Co-authors synthesized and conducted charge/discharge tests of rocksalt-structured MgNiₓCo₂₋ₓO₄ (x = y = z ≤ 2.0),¹² hexagonal crystal system Mg₂MoO₆,²¹ and spinel-structured Mg(MgₓNi₁₋ₓ)O₄ (x = 0, 0.1, 0.2, 0.3) and MgVₓNi₁₋ₓO₁₂ (x = 0, 0.3, 0.6, 1.0) and achieved an initial discharge capacity greater than 100 mAh/g. We reported that these materials can function as Mg secondary battery cathodes. Single-phase spinel-structured MgCo₂O₄ can be synthesized via an inverse coprecipitation method at low temperatures.¹⁶⁻¹⁸ Spinel-structured MgCo₂O₄ can also be synthesized via a one-pot supercritical fluid (SCF) method.¹⁹ Because the Co⁴⁺ ions in spinel-structured MgCo₂O₄ can be reduced to Co²⁺ ions, the redox reaction during the discharge process is Mg²⁺ + MgCo₂O₄ + 2e⁻ → Mg₂CoO₄ and the theoretical capacity is 260 mAh/g. Ceder et al. The Co atoms in MgCo₂O₄ reported to be a high spin states from *ab initio* calculation.¹⁸ We have calculated the average potential and the minimum-energy pathway of the intercalation of Mg²⁺ into a vacant tetrahedral site in the spinel structure.²⁰⁻²¹ Reverse Monte Carlo modeling using X-ray and neutron total scattering data has been performed for spinel-structured MgCo₂O₄, clarifying that Mg²⁺ atoms at tetrahedral sites can easily migrate into vacancies.²²

We reported the synthesis, charge/discharge testing, and X-ray- and neutron-diffraction-based crystal-structure analysis of spinel-structured MgCo₂−ₓMnₓO₄ (0 ≤ x ≤ 0.6) in previous studies.²³⁻²⁴ We found from charge/discharge tests that the first discharge capacity of MgCo₂−ₓMnₓO₄ (0.4 ≤ x ≤ 0.6) was greater than 200 mAh/g, whereas that of MgCo₂O₄ was 120 mAh/g. We also reported that, according to synchrotron X-ray diffraction measurements, Mg/Co cation mixing in spinel-structured MgCo₂MnₓO₄ was slightly decreased than that in MgCo₂O₄.²³ Other authors have reported investigations based on first-principles calculations of the stable structures of MgCo₂O₄ and MgCo₂MnₓO₄ in their pristine and discharged states.²³⁻²⁴ In these computational studies, Mg²⁺ ions occupying tetrahedral (8a) sites were reported to migrate to vacant (16c) sites when Mg²⁺ ions were inserted into the vacant 16c sites in spinel-structured MgCo₂−ₓMnₓO₄, which led to a structural change from the spinel to the rocksalt structure during discharge.²³ Although the mechanism of the structural change of MgCo₂−ₓMnₓO₄ (x = 0, 0.5) during the discharge process has been elucidated, the changes in electronic properties, such as the spin state and the valence state, during the discharge process remain unclear.

In the present study, the stable structures and the projected density of states (PDOS) of pristine and discharged MgCo₂−ₓMnₓO₄ (x = 0, 0.5) are investigated by first-principles calculations; the spin state and valence state during the discharge process are investigated.

2. Methods

2.1 Calculation method

The stable structures of pristine and discharged Mg₁₋ₓCoₓMnₓO₄ (x = 0, 0.5; y = 0, 0.5, 0.75) are referenced from previous studies.²⁵⁻²⁶ The stable structure of the fully discharged models of MgCo₂−ₓMnₓO₄ (x = 0, 0.5) are newly investigated in the present work. The PDOS of two stable models are calculated: the normal spinel model, which is most stable in its pristine state, and the Mg/Co mixed-cation model, which is more stable during discharge than the normal spinel. The program package used for the first-principles calculations was the Vienna *Ab-initio* Simulation Package (VASP), version 5.4.1.²⁷ The model cell size was 1 × 1 × 1 with 56+⁴⁺ atoms (Mg₁₋ₓCoₓMnₓO₄ (x = 0, 0.5; y = 0, 0.5, 0.75, 1); Mg₈⁺y⁺ (y = 0, 4, 6, 8); Co₁₆₋ₓ⁺ (x = 0 in x = 0; 4 in x = 0.5), Mn₄⁺, O₃₂); the space group was Fd-3m. The exchange-correlation potential of the Perdew–Burke–Emzerhof generalized gradient approximation (GGA-PBE)²⁸ with Hubbard model correction was applied with a self-consistent calculation U parameter of 5.0 eV for Mn atoms and 6.0 eV for Co atoms. A J parameter of 0.88 eV was selected for Co and Mn atoms in this model.²⁹ A plane-wave cutoff energy of 550 eV was selected, and a k-point mesh of 1 × 1 × 1 or 7 × 7 × 7 was used for the structural calculation and the PDOS calculation, respectively. The convergence criterion for the structural optimization was that the energy difference per iteration be less than or equal to 0.02 eV/A. The crystal structures were drawn using VESTA (version 3.4.0).²⁹

2.2 Experimental method

The pristine spinel MgCo₂−ₓMnₓO₄ (x = 0, 0.5) was synthesized by an inverse coprecipitation method. The single-phase spinel-structured MgCo₂O₄ was sintered at 300 °C, and MgCo₁.5Mn₀.5O₄ was sintered at 500 °C. In this paper, the valence of Co and Mn in the Mg₁.₇₅Co₁.₅Mn₀.₅O₄, which was similar to the model in the first discharge process, from PDOS spectra were compared with those obtained from X-ray absorption near edge structure (XANES) spectra.

Electrochemical measurements were conducted with a three-electrode flat cell (Hokohs Corporation). The charging/discharging experiments were conducted using a charge–discharge measurement instrument (Hokuto Denko Corporation, HJR-110m SM8). Details of the electrochemical measurement method have been reported elsewhere.²⁴ X-ray absorption fine structure (XAFS) data were obtained on the BL14B2 beamline at SPring-8 and were analyzed using the Athena (version 0.8.056) code to identify local and electronic structures.

3. Results and Discussion

3.1 Electronic structure of the normal-spinel-based model of Mg₁₊₂Co₂O₄ (y = 0, 0.5, 1)

In previous studies, it was reported from X-ray diffraction crystal-structure analysis that the tetrahedral (8a) sites site is shared half by Mg and Co atoms, respectively.²³⁻²⁴ Although the Mg/Co mixed-cation spinel model of MgCo₂−ₓMnₓO₄ (x = 0, 0.5) was not found to be more stable than the model of the normal spinel structure, the mixed-cation spinel-based model eventually became more stable than the normal spinel model with increasing Mg²⁺ ion insertion during discharge.²³⁻²⁴ We therefore investigated the electronic structures of the Mg/Co mixed-cation spinel and the normal spinel models in the present study.

Figure 1 shows the stable structures of the normal-spinel-based model of Mg₁₊₂Co₂O₄ with (a) y = 0, (b) y = 0.5, and (c) y = 1. The models shown in Figs. 1(b) and 1(c) are the stable structures in the reaction MgCo₂O₄ + yMg²⁺ + 2ye⁻ → Mg₁₊₂Co₂O₄. The pristine MgCo₂O₄ shown in Fig. 1(a) has eight Mg atoms on the 8a sites and 16 Co atoms on the 16d sites. In the discharged structures shown in Figs. 1(b) and 1(c), Mg atoms have been inserted into the vacant 16c sites of the spinel structure. Some of the Mg atoms remain on the 8a sites; however, many Mg atoms on the 8a sites migrate to the vacant 16c sites in the stable structure with y = 0.5 (Fig. 1(b)). In the stable structure with y = 1 (Fig. 1(c)), all of the Mg atoms on the 8a sites have completely migrated to the vacant 16c sites and the structure has completely transformed from spinel to rocksalt. The numbers N of MO₆ (M = Mg, Co) octahedra, the average M–O bond length, the distortion parameters²⁰ A and r², and the bond valence sum (BVS) of Mg₁₊₂Co₂O₄ (y = 0, 0.5, 1) are listed in Table 1. Because all of the 16c sites are vacant in the structure in Fig. 1(a), N is equal to 0. From Table 1, the Co–O bond length associated with the 16d sites increases with increasing y. The BVS of the Co–O₆ octahedra of Co atoms at the 16d sites decreases with increasing y; the BVS of the y = 1 compound is approximately 2. Other authors have speculated that the valence of Co atoms
changes from trivalent to divalent with increasing \( y \) because the ionic radius of Co\(^{3+} \) at sixfold coordination is 0.0545 nm for low-spin (LS) Co\(^{3+} \) and 0.061 nm for high-spin (HS) Co\(^{3+} \), whereas that of Co\(^{2+} \) is 0.065 nm for LS Co\(^{2+} \) and 0.0745 nm for HS Co\(^{2+} \), respectively.\[^{31}\] Although the bond-angle variance \( \sigma^2 \) of Co-O\(_6 \) octahedra of Co atoms on the 16\( d \) sites becomes small with increasing \( y \), quadratic elongation \( \lambda \) in the \( y = 1 \) compound is much larger than those in the \( y = 0 \) and 0.5 compounds. The distribution of the Co-O bond lengths and the corresponding numbers in Mg\(_2\)Co\(_2\)O\(_4\) are shown in Fig. S-1. These results suggest that short (LS) Co\(^{3+} \) and 0.20 nm) and long (0.24 \( \pm \) 0.0745 nm for HS Co\(^{2+} \) of the Co\(^{2+} \) orbitals in the conduction band shift to the lower-energy region with increasing \( y \) as shown in Figs. 2(b-2) and 2(b-3). Co is found to be reduced during the discharge process. The quadratic elongation \( \lambda \), which depends on the bond length in the Co-O\(_6 \) octahedra in Mg\(_2\)Co\(_2\)O\(_4\), becomes large because of Jahn–Teller distortion resulting from the Co\(^{2+} \) LS state (Table 1 and Fig. S-1).

3.2 Electronic structure of the normal-spinel-based model of Mg\(_{1+x}\)Co\(_2\)Mn\(_{1-x}\)O\(_4\) (\( y = 0, 0.5, 1 \))

The PDOS spectra for the \( d \) orbitals of Co, and the \( p \) orbitals of O of the normal-spinel-based model of Mg\(_{1+x}\)Co\(_2\)O\(_4\) with (a-1) \( y = 0 \), (a-2) \( y = 0.5 \), and (a-3) \( y = 1 \) are shown in Figs. 2(a-1) to 2(a-3). In all of the PDOS spectra, the Fermi level is at 0 eV. In the \( y = 0 \) case shown in Fig. 2(a-1), the down-spin \( d \) orbitals of Co and the \( p \) orbitals of O overlap near the Fermi level. The spin-up \( d \) orbitals of Co and the \( p \) orbitals of O overlap in the valence band. Therefore, there is covalency between the Co and O atoms in the \( y = 0 \) compound. However, covalency does not exist between the Mg and O because Mg lacks an orbital component. The overlap of the \( d \) orbitals of Co and the \( p \) orbitals of O in the valence band of the \( y = 0.5 \) compound (Fig. 2(a-2)) is smaller than that in the valence band of the \( y = 0 \) compound. The peaks derived from the \( d \) orbitals of Co shift to the lower-energy region, and the bandgap becomes narrow (Fig. 2(a-2)). The conductivity increases upon insertion of Mg. The \( p \) orbitals of O reside in the low-energy region, and the \( d \) orbitals of Co are near the Fermi level in the \( y = 1 \) compound (Fig. 2(a-3)). The covalency between Co and O in the \( y = 1 \) case becomes weaker than that in the \( y = 0 \) and 0.5 cases. This result is also consistent with the geometrical features shown in Table 1. The peaks derived from the \( d \) orbitals of Co in Fig. 2(a-3) shift to the lower-energy region, and the bandgap becomes narrow in Figs. 2(a-1) and 2(a-2).

The PDOS spectra for the \( e_p \) and \( t_{2g} \) orbitals of Co in the (b-1) \( y = 0 \), (b-2) \( y = 0.5 \), and (b-3) \( y = 1 \) cases are shown in Figs. 2(b-1) to 2(b-3). In the \( y = 0 \) case (Fig. 2(b-1)), the spin-up and spin-down \( d \)-orbitals in the Co valence band are clearly derived from \( t_{2g} \) orbitals and those in the Co conduction band are clearly derived from \( e_g \) orbitals. The Co in the \( y = 0 \) case is trivalent and in the LS state. Our result of the spin state of Co atoms in MgCo\(_2\)O\(_4\) is different from that of Ref. 18. Using the electron density obtained by self-consistent calculations with the stable structure after structural relaxation, the PDOS calculations show that Co in MgCo\(_2\)O\(_4\) is characterized by a low spin state and otherwise a high spin state. During discharge, because the electrons of LS Co\(^{3+} \) occupy the empty \( e_g \) orbitals according to the Pauli exclusion principle, the \( e_g \) orbitals in the conduction band shift to the lower-energy region with increasing \( y \) as shown in Figs. 2(b) and 2(b-3). Co is found to be reduced during the discharge process. The quadratic elongation \( \lambda \), which depends on the bond length in the Co-O\(_6 \) octahedra in Mg\(_2\)Co\(_2\)O\(_4\), becomes large because of Jahn–Teller distortion resulting from the Co\(^{3+} \) LS state (Table 1 and Fig. S-1).

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Stable structures of the normal-spinel-based model of Mg\(_{1+x}\)Co\(_2\)O\(_4\) in the (a) \( y = 0 \) pristine state and the (b) \( y = 0.5 \) and (c) \( y = 1 \) discharged states.

### Table 1. Number \( N \) of \( M\text{-O}_6 \) (\( M = \text{Co, Mg} \)) octahedra, average \( M\text{-O} \) bond lengths, distortion parameters \( \lambda \) and \( \sigma^2 \), and bond valence sum (BVS) for Mg\(_{1+x}\)Co\(_2\)O\(_4\) (\( y = 0, 0.5, 1 \)) based on the normal spinel-based model.

| Site | Octahedra | \( y \) | \( N \) | Average bond length/nm | \( \lambda \) | \( \sigma^2/\text{deg}^2 \) | BVS |
|------|-----------|------|----|----------------|------|------------------|-----|
| 16d  | Co\(_6\)   | 0    | 16 | 0.194(0)      | 1.014 | 51.71            | 2.656 |
|      |           | 0.5  | 16 | 0.201(6)      | 1.010 | 30.52            | 2.374 |
|      |           | 1    | 16 | 0.216(28)     | 1.039 | 26.24            | 2.054 |
| 16c  | Mg\(_6\)   | 0    | 0  | 0              |      |                   |      |
|      |           | 0.5  | 9  | 0.212(9)      | 1.014 | 42.44            | 1.924 |
|      |           | 1    | 16 | 0.210(1)      | 1.005 | 17.36            | 2.015 |

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The number \( N \) of \( M\text{–O}_6 \) (\( M = \text{Co, Mn, Mg} \)) octahedra, the average \( M\text{–O} \) bond length, the distortion parameters\(^{30} \) \( \lambda \) and \( \sigma^2 \), and the BVS of \( \text{Mg}_{1+y}\text{Co}_{1.5}\text{Mn}_{0.5}\text{O}_4 \) (\( y = 0, 0.5, 1 \)) of \( M\text{–O}_6 \) octahedra are listed in Table 2. The average bond length \( M\text{–O} \) and the BVS of the \( M\text{–O}_6 \) octahedra on the 16\( d \) sites become longer and smaller with increasing \( y \) as same as \( \text{Mg}_{1+y}\text{Co}_2\text{O}_4 \), respectively. Because the ionic radius of \( \text{Co}^{2+} \) in sixfold coordination and in the LS and HS states is larger than that of \( \text{Co}^{3+} \), and because Co atoms are reduced during discharge, the BVS of \( M\text{–O}_6 \) octahedra on the 16\( d \) sites in \( \text{Mg}_{1+y}\text{Co}_{1.5}\text{Mn}_{0.5}\text{O}_4 \) becomes smaller with increasing \( y \).\(^{31} \) Although the \( \sigma^2 \) of the \( \text{Co–O}_6 \) octahedra of Co atoms on the 16\( d \) sites becomes small with increasing \( y \), \( \lambda \) in the \( y = 1 \) case is larger than \( \lambda \) in the \( y = 0 \) and 0.5 cases. Conceivably, Jahn–Teller strain is present and \( \text{Co–O} \) bonds extend in the \( c \)-axis direction because Co becomes divalent, as in \( \text{Mg}_{1+y}\text{Co}_2\text{O}_4 \). However, the \( \lambda \) for \( M\text{–O}_6 \) octahedra with \( M \) atoms on the 16\( d \) sites in \( \text{Mg}_{1+y}\text{Co}_{1.5}\text{Mn}_{0.5}\text{O}_4 \) is smaller than that in \( \text{Mg}_2\text{Co}_2\text{O}_4 \) (Tables 1 and 2). The distribution of the \( Co\text{–O} \) bond length and its numbers in \( \text{Mg}_2\text{Co}_{1.5}\text{Mn}_{0.5}\text{O}_4 \) are shown in Fig. S-2. Because short (0.19–0.20 nm) and long (0.22–0.25 nm) \( Co\text{–O} \) bonds are present in the normal-spinel-based model of \( \text{Mg}_2\text{Co}_{1.5}\text{Mn}_{0.5}\text{O}_4 \), the distribution of the \( Co\text{–O} \) bond lengths is not extreme compared with the distribution of \( Co\text{–O} \) bond lengths in \( \text{Mg}_2\text{Co}_2\text{O}_4 \). The formation energy of \( \text{Mg}_2\text{Co}_2\text{O}_4 \) is calculated to be \(-9.46 \) eV, and that of \( \text{Mg}_2\text{Co}_{1.5}\text{Mn}_{0.5}\text{O}_4 \) is calculated to be \(-9.93 \) eV, respectively. Because the strain of \( \text{Co–O}_6 \) is small, and because the entire crystal structure is not distorted in \( \text{Mg}_2\text{Co}_{1.5}\text{Mn}_{0.5}\text{O}_4 \), we considered that \( \text{Mg}_2\text{Co}_{1.5}\text{Mn}_{0.5}\text{O}_4 \) exhibits a lower formation energy and is more stable than \( \text{Mg}_2\text{Co}_2\text{O}_4 \). The average \( Mn\text{–O} \) bond length for Mn occupying the 16\( d \) sites (Table 2) increases with increasing \( y \) because the ionic radius of six-coordinate \( \text{Mn}^{2+} \) is 0.053 nm, whereas the ionic radii of \( \text{Mn}^{3+} \) in the LS and HS states are 0.058 nm and 0.0645 nm, respectively, and those of \( \text{Mn}^{4+} \) in the LS and HS states are 0.067 nm and 0.083 nm, respectively.\(^{31} \) The BVS of the \( Mn\text{–O}_6 \) octahedra of Mn atoms occupying the 16\( d \) sites is 3–3.5 in the \( y = 0 \) case and 2–3 in the \( y = 0.5 \) and 1 cases. The distortion parameters \( \lambda \) and \( \sigma^2 \) of \( Mn\text{–O}_6 \) octahedra of Mn atoms

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Figure 2. Projected density of states (PDOS) for the \( d \) orbitals of Co and the \( p \) orbitals of O of the normal-spinel-based model of \( \text{Mg}_{1+y}\text{Co}_2\text{O}_4 \) in the (a-1) \( y = 0 \) pristine state and (a-2) \( y = 0.5 \) and (a-3) \( y = 1 \) discharged states, and the \( eg \) and \( t_{2g} \) orbitals of Co in the (b-1) \( y = 0 \), (b-2) \( y = 0.5 \), and (b-3) \( y = 1 \) compounds.

Figure 3. Stable structures of the normal-spinel-based model of \( \text{Mg}_{1+y}\text{Co}_{1.5}\text{Mn}_{0.5}\text{O}_4 \) in the (a) \( y = 0 \) pristine state and the (b) \( y = 0.5 \) and (c) \( y = 1 \) discharged states.
occupying the 16d sites in the y = 1 case become smaller than those in the y = 0 and 0.5 cases because of the complete structural change to the rocksalt structure in the y = 1 case. The average Mg–O bond length is constant and the BVS of Mg–O6 octahedra on the 16c sites is divalent irrespective of y.

The PDOS spectra for the d orbitals of Co and Mn, and the p orbitals of O in the normal-spinel-based model of Mg1.5Co1.5Mn0.5O4 with (a–1) y = 0, (a–2) y = 0.5, and (a–3) y = 1 are shown in Figs. 4(a–1) to 4(a–3). The PDOS spectrum in Fig. 4(a–1) shows d orbitals of Mn and p orbitals of O with up and down spins near the Fermi level of pristine MgCo1.5Mn0.5O4. The spin-up peaks in the range from −4 to −2 eV and the spin-down peaks in the range from −2 to −1 eV are derived from the d orbitals of Co and the p orbitals of O, respectively. The overlap between the d orbitals of the transition metal and p orbitals of O is broad, and covalency exists between the transition metal and O in MgCo1.5Mn0.5O4. Both the Co and Mn atoms might be reduced during discharge because the peaks derived from the d orbitals of Co and Mn are near the Fermi level. Because there is no band component of Mg in the energy range beyond −20 eV, Mg does not directly contribute to the physical properties as an electronic state. The results in Figs. 4(a–1) to 4(a–3) suggest that the overlap between the d orbitals of the transition metals and the p orbitals of O become narrower and that the covalency between the transition metal and O becomes weaker with increasing y. However, the overlap between the d orbitals of Co and the p orbitals of O in Mg1.5Co1.5Mn0.5O4 (Fig. 4(a–2)) is broader than that in Mg1.5Co1.5O4 (Fig. 2(a–2)). The covalency between the Co and O in Mg1.5Co1.5Mn0.5O4 is stronger than that in Mg1.5Co1.5O4.

The average Co–O bond length for Co on the 16d sites in Mg1.5Co1.5Mn0.5O4 is stronger than that in Mg1.5Co1.5O4 (Tables 1 and 2). The PDOS spectra for the eg and t2g orbitals of Co and Mn in the y = 0, 0.5, and 1 are shown in Figs. 4(b–1) to 4(b–3) and 4(c–1) to 4(c–2), respectively. As in the case of MgCo1.5Mn0.5O4 (Fig. 4(b–1)), the peaks associated with spin-up and spin-down orbitals in the valence band are derived from t2g orbitals, and the peaks associated with spin-up and spin-down orbitals in the conduction band are derived from eg orbitals in Fig. 4(b–1). Co atoms in pristine MgCo1.5Mn0.5O4 are LS Co3+. The spin-up eg orbitals in the conduction band of Co gradually shift to the lower-energy region with increasing y (Figs. 4(b–2) and 4(b–3)). In Fig. 4(b–3), because some of the eg orbitals shift to the valence band, the Co atoms are reduced from the trivalent LS to the divalent LS state. Therefore, the Co–O bond length on the 16d sites in Mg2Co1.5Mn0.5O4 increases because Jahn–Teller distortion occurs as a result of the Co3+ LS state (Table 2 and Fig. S-2). In Fig. 4(c–1), the peaks in the valence band contain the t2g orbitals of spin-up and slight spin-down Mn atoms, and the peaks in the conduction band include the spin-down t2g orbitals and spin-up and spin-down eg orbitals of Mn atoms. The Mn atoms are found to be trivalent and in the LS state in pristine MgCo1.5Mn0.5O4. Although the peaks associated with the spin-up and spin-down eg orbitals in the conduction band are constant during discharge, the components of the spin-down t2g orbitals in the valence band increase, whereas those in the conduction band decrease. During discharge, the Mn atoms in this normal-spinel-based model of Mg1.5Co1.5Mn0.5O4 are expected to be reduced and in the LS state because electrons occupy the vacant spin-down t2g orbitals of the Mn atoms.

3.3 Electronic structure of the Mg/Co mixed-cation spinel-based model of Mg1.5+Co1.5O4 (y = 0, 0.5, 1)

The stable structures of the Mg/Co mixed-cation spinel-based model of Mg1.5+Co1.5O4 with (a) y = 0, (b) y = 0.5, and (c) y = 1 are shown in Figs. 5(a)–5(c). In Fig. 5(a), the same numbers of Mg and Co atoms are arranged at the 8a sites. In our previous study, Mg/Co cation mixing was observed in pristine MgCo2O4 by Rietveld analysis of synchrotron X-ray and the neutron diffraction data.23,24 This stable structure of the Mg/Co mixed-cation spinel-based model shown in Fig. 5(a) is similar to the local structure obtained from the Rietveld analysis. In the stable structure of Mg1.5Co1.5O4 shown in Fig. 5(b), although all of the Mg atoms on the 8a sites migrate to vacant 16c sites, some of the Co atoms remain on the 8a sites. In previous study,26 because the electron density and bond strength of Co–O bond is higher and stronger than that of Mg–O bond, it was reported that the Mg on the 8a site tends to move to the 16c site more than Co atom during discharge. Therefore, a part of Co atom remains on the 8a site though all Mg atom on the 8a site move to the 16c site.26 In the stable structure of MgCo2O4 shown in Fig. 5(c), all the sites on the 8a sites migrate to vacant 16c sites and complete transformation to the rocksalt structure occurs. These discharged stable models shown in Figs. 5(b) and 5(c) are 1.8 eV and 1.5 eV more stable than the discharged normal-spinel-based models shown in Figs. 1(b) and 1(c). The number N of M–O6 (M = Co, Mg) octahedra, the average M–O bond length, the distortion parameters26 λ and σ2, and the BVS of the Mg1.5Co1.5O4 (y = 0, 0.5, 1) M–O6 octahedra are listed in Table 3. During discharge, because the Co was reduced to Co2+, whose ionic radius is greater than that of Co3+, the average Co–O bond length and the BVS in the Co–O6 octahedra of Co atoms on the 16d sites increased and decreased with increasing y, respectively. The λ of the Co–O6 octahedra on the 16d sites in y = 1 (Table 3) are smaller than that of the normal-spinel-based model shown in Table 1. The distribution of the Co–O bond lengths and the number of Co–O bonds in MgCo2O4 are shown in Fig. S-3. Jahn–Teller distortion may occur in the Mg/Co mixed-cation spinel-based model of MgCo2O4 because the Co–O bonds in the c-axis direction tend to be long and the lattice constant corresponding to the c-axis increases (lattice parameters a = 0.8271 nm, b = 0.8291 nm, and c = 0.8561 nm). However, we found that the distribution of Co–O bond lengths in the Mg/Co mixed-cation spinel-based model of MgCo2O4 is narrower than that in the normal-spinel-based model because the distribution of Co–O bond lengths in Fig. S-3 is 0.20–0.22 nm and that in Fig. S-1 is 0.19–0.20 nm and 0.24–0.27 nm. We considered that this model is more stable than the normal-spinel-based model because the distortion of the crystal structure is smaller. The average Mg–O bond length in the Mg–O6 octahedra of Mg atoms on the 16d and 16c sites is constant irrespective of y. The distortion parameters λ and σ2(deg2) of the Mg–O6 octahedra on the 16d and 16c sites in the y = 1 compound are smaller than those in the y = 0 and 0.5 compounds because the rocksalt structure completely formed at y = 1. The BVS of the Co–O6 octahedra of Co atoms on the 16c sites is smaller than that of the Co–O6 octahedra of Co atoms on the 16d sites in y = 0.5.
Because Co atoms at the 16c sites were originally coordinated to the 8a sites, and because the BVS indicated divalent Co in the pristine compound, the BVS of the Co–O$_6$ octahedra with Co at the 16c sites is considered to be smaller than that of the Co–O$_6$ octahedra with Co at the 16d sites.

The PDOS spectra for the $d$ orbitals of Co, and the $p$ orbitals of O of the Mg/Co mixed-cation spinel-based model of Mg$_{1+y}$Co$_{1.5}$Mn$_{0.5}$O$_4$ with (a-1) $y = 0$, (a-2) $y = 0.5$, and (a-3) $y = 1$ compounds, and the $e_g$ and $t_{2g}$ orbitals of Mn in the (c-1) $y = 0$, (c-2) $y = 0.5$, and (c-3) $y = 1$ compounds.

Figure 4. Projected density of states (PDOS) for the $d$ orbitals of Co and Mn and $p$ orbitals of O in the normal-spinel-based model of Mg$_{1+y}$Co$_{1.5}$Mn$_{0.5}$O$_4$ in the (a-1) $y = 0$ pristine state and the (a-2) $y = 0.5$ and (a-3) $y = 1$ discharged states, the $e_g$ and $t_{2g}$ orbitals of Co in the (b-1) $y = 0$, (b-2) $y = 0.5$, and (b-3) $y = 1$ compounds, and the $e_g$ and $t_{2g}$ orbitals of Mn in the (c-1) $y = 0$, (c-2) $y = 0.5$, and (c-3) $y = 1$ compounds.

Because Co atoms at the 16c sites were originally coordinated to the 8a sites, and because the BVS indicated divalent Co in the pristine compound, the BVS of the Co–O$_6$ octahedra with Co at the 16c sites is considered to be smaller than that of the Co–O$_6$ octahedra with Co at the 16d sites.
respectively, with increasing the covalency between Co and O become narrow and weak, from the spin-up and spin-down cases, (Figs. 6(a-2) and 6(a-3), respectively), the peak arising shown in Fig. 6(b-1), the peaks in the valence band are constituted by the orbitals of Co and the normal-spinel-based model (Fig. 2(a-1)). The overlap between the orbitals of Co and the orbitals of O near the Fermi level disappears. In the spectrum of the 0 case. Peaks arising from spin-up d orbitals of Co atoms exist near the Fermi level in the conduction band. These results reveal that Co on the 8a sites was four-coordinated HS Co⁴⁺−Co²⁺⁺ because the electrons occupied the spin-up and spin-down e_g orbitals, the spin-up t_2g orbitals. In Fig. S-4(b), the spin-up and spin-down t_2g orbitals are present in the valence band, and the spin-up and spin-down e_g orbitals are present in the conduction band of Co on the 16d sites. Co occupying the 16d sites is trivalent and LS, like the Co in the normal-spinel-based model in Fig. 2(b-1). Since the valence of Co atoms on the 8a site in Mg/Co cation mixing spinel of MgCoO₄ are between divalent and trivalent, the charge balance of whole system is not balanced. In previous study, when the sample of MgCoO₄ which was Mg/Co cation mixing spinel was synthesized, the Mg and Co content of the specimen were reported as 0.933(4) and 2.067(4) using inductively coupled plasma-atomic emission spectroscopy (ICP), respectively. It was thought that the charge balance is kept by including more Co atom of which valence is higher than Mg atom. In theoretical calculation, the pristine of the normal spinel of MgCoO₄, of which charge balance is maintained, is more stable than that of Mg/Co cation mixing spinel. In Figs. 6(b-2) and 6(b-3), the peaks constituted by the spin-up e_g orbitals are gradually shifted to the lower-energy region with increasing y. In Fig. 6(b-2), although almost all of the e_g orbitals are in the conduction band, the tail of the peaks of the e_g orbitals is near the Fermi level. In addition, there are two peaks associated with the e_g orbitals in the y = 1 compound (Fig. 6(b-3)); one is in the conduction band, and the other is in the valence band. Co atoms are reduced from trivalent to divalent upon the insertion of Mg. In Figs. 6(b-2) and 6(b-3), because the Co atoms on the 8a sites migrate to the 16c sites, the spin-up t_2g orbitals near the Fermi level in the y = 0 case (Fig. 6(b-1)) disappear in the y = 0.5 and 1 cases (Figs. 6(b-2) and 6(b-3), respectively).

Table 3. Number N of M–O₆ (M = Co, Mg) octahedra, average M–O bond lengths, distortion parameters λ and σ², and bond valence sum (BVS) for Mg₁ₓCo₂O₄ (y = 0, 0.5, 1) based on the Mg/Co mixed-cation spinel-based model.

| Site Octahedra | y N | Average bond length/Å | λ | σ²/deg² | BVS |
|----------------|-----|------------------------|---|---------|-----|
| 16d Mg–O₆      | 0   | 0.207(5)   | 0.020 | 73.59    | 2.202 |
|                | 0.5 | 0.211(5)   | 0.018 | 63.52    | 1.974 |
|                | 1   | 0.211(4)   | 0.002 | 4.03     | 1.953 |
|                | 0   | 0.194(3)   | 0.006 | 22.56    | 2.681 |
|                | 0.5 | 0.198(6)   | 0.007 | 22.13    | 2.572 |
|                | 1   | 0.209(8)   | 0.003 | 2.97     | 2.044 |
| 16c Mg–O₆      | 0   | —          | —    | —       | —    |
|                | 0.5 | 0.212(9)   | 0.011 | 36.17    | 1.922 |
|                | 1   | 0.211(4)   | 0.001 | 3.12     | 1.961 |
|                | 0   | —          | —    | —       | —    |
|                | 0.5 | 0.205(4)   | 0.007 | 24.81    | 2.124 |
|                | 1   | 0.204(3)   | 0.001 | 3.69     | 2.292 |

3.4 Stable and electronic structure of the Mg/Co mixed-cation spinel-based model of Mg₁₆ₓCo₁₂ₓMn₀.75O₄ (y = 0, 0.5, 1)

The stable structures of the Mg/Co mixed-cation spinel-based model of Mg₁₆₊ₓCo₁₂₋ₓMn₀.75O₄ with (a) y = 0, (b) y = 0.5, and (c) y = 1 are shown in Figs. 7(a)–7(c). The same numbers of Mg and Co atoms on the 8a sites in y = 0 are shown in Fig. 7(a). In previous studies, this Mg/Co mixed-cation spinel-based model existed in a quantum beam because the Mg/Co cation mixing was observed by Rietveld analysis of the synchrotron X-ray diffraction data and the neutron diffraction data. It was reported that Mg/Co cation mixing in MgCoO₄ is reduced than that in MgCoO₄ because the occupancy of the Co atoms on the 8a site in MgCoO₄ is slightly lower than that in MgCoO₄ from Rietveld analysis of synchrotron X-ray diffraction data. Therefore, MgCoO₄ is expected to have a slightly higher proportion of normal spinel in the system than MgCoO₄ due to the slightly higher occupancy of Mg on the 8a site and Co on the 16d site. Although all of the Mg atoms on the 8a sites in the...
y = 0.5 structure migrate to vacant 16c sites, a portion of the Co atoms do not (Fig. 7(b)). All of the Mg and Co atoms on the 8a sites migrate to the 16c sites and the rocksalt structure is completely formed in the y = 1 case (Fig. 7(c)). The number \( N \) of \( M-O_6 \) (\( M = \text{Co}, \text{Mn}, \text{Mg} \)) octahedra, the average \( M-O \) bond length, the distortion parameters \( \alpha \) and \( \sigma^2 \), and the BVS of the \( M-O_6 \) (\( M = \text{Co}, \text{Mn}, \text{Mg} \)) octahedra of \( \text{Mg}_{1+y}\text{Co}_{2}\text{Mn}_{0.5}\text{O}_4 \) (y = 0, 0.5, 1) are listed in Table 4. The average Co–O bond length and the BVS of the Co–O6 octahedra for Co atoms on the 16d sites both increased with increasing y (Table 4). The distortion parameter \( \sigma^2 \) decreased with increasing \( y \) because the structure transformed to the rocksalt structure, like that of \( \text{Mg}_{1+y}\text{Co}_{2}\text{O}_4 \) shown in Table 3. The distribution of the bond length and the number of Co–O in the \( y = 1 \) case are shown in Fig. S-5. The results show that the Co–O bond length is localized at 0.20–0.21 nm, similar to that in \( \text{Mg}_2\text{Co}_2\text{O}_4 \) (Fig. S-3). The distortion parameter \( \lambda \) of this model is smaller than that of the normal-spinel-based model shown in Fig. S-2. The formation energy of the model of the \( y = 1 \) compound shown in Fig. 7(c) is \(-10.32 \text{ eV}\), which is lower than that of the normal-spinel-based model of the \( y = 1 \) compound (\(-9.93 \text{ eV}\)) shown in Fig. 3(c). The average Mn–O bond length and the BVS of Mn–O6 octahedra with Mn atoms on the 16d sites become longer and smaller, respectively, with increasing \( y \) (Table 4). Therefore, not only Co but also Mn may be reduced during discharge in the Mg/Co mixed-cation spinel-based model. The average Mg–O bond length and the BVSs of the Mg–O6 octahedra on the 16c and 16d sites is constant irrespective of \( y \). The distortion parameters \( \lambda \) and \( \sigma^2 \) of \( y = 1 \) become smaller than those associated with other \( y \) values because the rocksalt structure is completely formed.

The PDOS spectra for all of the orbitals of all atoms, the \( d \) orbitals of Co and Mn, and the \( p \) orbitals of O of the Mg/Co mixed-cation spinel-based model of \( \text{Mg}_{1+y}\text{Co}_{1.5}\text{Mn}_{0.5}\text{O}_4 \) with (a-1) \( y = 0 \), (a-2) \( y = 0.5 \) and (a-3) \( y = 1 \) discharged states.

Figure 6. Projected density of states (PDOS) for the \( d \) orbitals of Co and \( p \) orbitals of O of the Mg/Co mixed-cation spinel-based model of \( \text{Mg}_{1+y}\text{Co}_{2}\text{O}_4 \) in the (a-1) \( y = 0 \) pristine state and (a-2) \( y = 0.5 \) and (a-3) \( y = 1 \) discharged states, and for the \( e_g \) and \( t_{2g} \) orbitals of Co in the (b-1) \( y = 0 \), (b-2) \( y = 0.5 \), and (b-3) \( y = 1 \) compounds.

Figure 7. Stable structures of the Mg/Co mixed-cation spinel-based model of \( \text{Mg}_{1+y}\text{Co}_{1.5}\text{Mn}_{0.5}\text{O}_4 \) in the (a) \( y = 0 \) pristine state and (b) \( y = 0.5 \) and (c) \( y = 1 \) discharged states.
(a-2) $\gamma = 0.5$, and (a-3) $\gamma = 1$ are shown in Figs. 8(a-1) to 8(a-3). The peaks in the range from $-8$ to $-3$ eV formed by the spin-up $d$ orbitals of Co and the $p$ orbitals of O, and the peaks in the range from $-2$ to 0 eV formed by the spin-up $d$ orbitals of Mn and Co and the spin-down $p$ orbitals of O are shown in Fig. 4(a-1), along with the PDOS spectrum of the normal-spinel-based model. In Fig. 8(a-1), the overlap near the Fermi level between the $d$ orbitals of the transition metal and the $p$ orbitals of O is broad and the covalency between the transition metal and O is strong. Because the $d$ orbitals of Co and Mn are near the Fermi level, both Co and Mn can be reduced during the discharge process. The overlap in the valence band and the spin-up and spin-down $t_{2g}$ orbitals in the conduction band. The Mn atoms in the $y = 0$ compound are Mn$^{2+}$. The spin-down $t_{2g}$ orbitals in the pristine material (Fig. 8(c-1)) gradually shift to the lower-energy region with increasing $y$ during discharge (Figs. 8(c-2) and 8(c-3)). Because electrons occupy the vacant $t_{2g}$ orbitals of Mn$^{2+}$ during discharge, Mn is reduced to a LS state when the material is discharged. We considered that Mg$_{2}$Co$_{2}$Mn$_{2}$O$_{10}$ has a greater discharge capacity than Mg$_{2}$Co$_{2}$O$_{10}$ because not only Co but also Mn participates in the redox reactions.

Next we compare our calculation results with our experimental results. The charge/discharge characteristics of Mg$_{2}$Co$_{2}$Mn$_{2}$O$_{10}$ in a three-electrode cell, as reported in a previous study, are shown in Figs. S-6(a). The value of insertion of Mg ($\gamma$) in the first discharge process is considered to be 0.81 because the initial discharge capacity is $\sim 210$ mAh/g. The reduction of Co and Mn to the constant-potential region near 2.1 V vs. Mg/Mg$^{2+}$ in Fig. S-6(a). XANES spectra of the Co $K$-edge and the Mn $K$-edge for the pristine Mg$_{2}$Co$_{2}$Mn$_{2}$O$_{10}$ and the specimen after the first discharge are shown in Figs. S-6(b) and S-6(c), respectively. In Fig. S-6(b), we observe that the valence of Co atoms in the pristine material are almost 2.667, whereas the Co atoms after the first discharge are divalent. In Fig. S-6(c), Mn atoms in the pristine state are almost tetravalent; however, the valence of Mn atoms after the first discharge decreases to between the trivalent and divalent states.

The stable Mg/Co mixed-cation spinel-based model of Mg$_{2}$Co$_{2}$Mn$_{2}$O$_{10}$, which is similar to the component after the first discharge, was obtained, and its PDOS spectra were calculated. The stable structure of this model is shown in Fig. 9(a). The Co and Mg atoms on the 8a sites completely migrate to 16c sites, and the rocksalt structure completely forms in this stable structure (Fig. 9(a)). The Co and Mg atoms also put on the 16d sites. PDOS spectra for the $d$ orbitals of Co and Mn and the $p$ orbitals of O of the Mg$_{2}$Co$_{2}$Mn$_{2}$O$_{10}$ are shown in Fig. 9(b). In Fig. 9(b), many of the $p$ orbitals of O are in the low-energy region and many of the $d$ orbitals of the transition metal are in the high-energy region of the valence band. The covalency of the transition metal and O has become lower because this model has assumed the stable rocksalt structure. The PDOS spectra for the $e_g$ and $t_{2g}$ orbitals of Co and Mn in the $\gamma = 0$, 0.5, and 1 are shown in Figs. 8(b-1) to 8(b-3) and 8(c-1) to 8(c-2), respectively. In Fig. 8(b-1), the peaks in the valence band include spin-up and spin-down $t_{2g}$ orbitals of Co atoms and the peaks in the conduction band include spin-up and spin-down $e_g$ orbitals as same as Mg$_2$Co$_2$O$_{10}$ shown in Fig. 6(b-1). Like the Mg/Co mixed-cation model of Mg$_{2}$Co$_{2}$O$_{10}$ shown in Fig. 6(b-1), the spin-up $t_{2g}$ orbitals near the Fermi level and the spin-down $t_{2g}$ orbitals in the conduction band are derived from the Co on the 8a site in Fig. 8(b-1). The Co atoms on the 8a sites are four-coordinated HS Co$^{3+}$ ions. In previous study, it was reported that the BVS of Co on the 8a site in pristine Mg$_{2}$Co$_{2}$O$_{10}$ and Mg$_{2}$Co$_{2}$Mn$_{2}$O$_{10}$ are smaller than that on the 16d site, respectively. It is also suggested that the valence of Co atoms on the 8a site in both Mg/Co cation mixing spinel of Mg$_{2}$Co$_{2}$O$_{10}$ and Mg$_{2}$Co$_{2}$Mn$_{2}$O$_{10}$ is smaller than trivalent from BVS value and PDOS calculation. For the Co atoms on the 16d sites, the spin-up and spin-down $t_{2g}$ orbitals are in the valence band and the spin-up and spin-down $e_g$ orbitals are in the conduction band. The Co atoms on the 16d sites are six-coordinated LS Co$^{3+}$. The spin-up $e_g$ orbitals in the conduction band in the pristine material gradually shift to the lower-energy region with increasing $y$ during discharge. In Fig. 8(b-3), because the spin-up $e_g$ orbitals are included in both the valence and the conduction bands, the Co atoms are LS Co$^{3+}$. In Fig. 8(c-1), because the spin-up $e_g$ orbitals of Mn are in the valence band and the spin-down $t_{2g}$ orbitals and spin-up and spin-down $e_g$ orbitals are in the conduction band, the Mn atoms in the $y = 0$ compound are Mn$^{2+}$. The spin-down $t_{2g}$ orbitals in the pristine material (Fig. 8(c-1)) gradually shift to the lower-energy region with increasing $y$ during discharge (Figs. 8(c-2) and 8(c-3)). Because electrons occupy the vacant $t_{2g}$ orbitals of Mn$^{2+}$ during discharge, Mn is reduced to a LS state when the material is discharged. We considered that Mg$_{2}$Co$_{2}$Mn$_{2}$O$_{10}$ has a greater discharge capacity than Mg$_{2}$Co$_{2}$O$_{10}$ because not only Co but also Mn participates in the redox reactions.

4. Conclusion

In this study, the stable structures and the PDOS spectra of pristine and discharged Mg$_{1+y}$Co$_{2}$O$_{4}$ and Mg$_{1+y}$Co$_{2}$Mn$_{2}$O$_{4}$ ($\gamma = 0, 0.5, 1$) were obtained using first-principles calculations. The normal-spinel-based model, which was stable in the pristine state, and the Mg/Co mixed-cation spinel-based model, which became stable during the discharge process, were considered as models of stable structures in these calculations. PDOS calculations were performed for the normal-spinel-based models of Mg$_{1+y}$Co$_{2}$O$_{4}$
and Mg$_{1+y}$Co$_{1.5}$Mn$_{0.5}$O$_4$ using the first-principles calculations for the GGA+U method with a 7 × 7 × 7 k-point mesh. The results showed that Co atoms were trivalent and in the LS state in the pristine material, and that the valence of the Co atoms gradually decreased to the divalent LS state with the insertion of Mg during discharge. Mn atoms in the Mg$_{1+y}$Co$_{1.5}$Mn$_{0.5}$O$_4$ are tetravalent in the pristine material, and the valence of the Mn atoms gradually decreases to between trivalent and divalent LS states during discharge. In the Mg$_{1+y}$Co$_{1.5}$Mn$_{0.5}$O$_4$ mixed-cation spinel-based models of MgCo$_{1.5}$Mn$_{0.5}$O$_4$ and MgCo$_2$O$_4$, the Co atoms on the 8$a$ sites are typical four-coordinated HS cations and those on the 16$d$ sites are trivalent LS cations.

Figure 8. Projected density of states (PDOS) for the $d$ orbitals of Co and Mn and $p$ orbitals of O of the Mg/Co mixed-cation spinel-based model of Mg$_{1+y}$Co$_{1.5}$Mn$_{0.5}$O$_4$ in the (a-1) $y = 0$ pristine state and (a-2) $y = 0.5$ and (a-3) $y = 1$ discharged states, for the $e_g$ and $t_{2g}$ orbitals of Co in the (b-1) $y = 0$, (b-2) $y = 0.5$, and (b-3) $y = 1$ compounds, and for the $e_g$ and $t_{2g}$ orbitals of Mn in the (c-1) $y = 0$, (c-2) $y = 0.5$, and (c-3) $y = 1$ compounds.
Therefore, we considered that the Co atoms on the 8a sites do not participate in the redox reaction during discharge, even from the viewpoint of their electronic states. Because the valences of Co and Mn obtained from XANES spectra are in good agreement with the valences obtained from PDOS calculations, our theoretical calculation is consistent with the experimental results.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.21-00024.

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Figure 9. (a) Stable structure of Mg1.75Co1.5Mn0.5O4 (Mg/Co mixed-cation-based model) at discharge. (b) Projected density of states (PDOS) for the d orbitals of Co and Mn and the p orbitals of O, the (c) eg and t2g orbitals of Co, and (d) the eg and t2g orbitals of Mn.