Corresponding author: idemoto@rs.noda.tus.ac.jp

The stability of the crystal structure was investigated based on the replaced portion of the Co atoms with Mn. Charge-discharge testing using MgCo2−xMnxO4/AZ31 cells with Ag reference electrodes demonstrated a discharge capacity of 80 mAhg−1 and a high coulombic efficiency below 60°C, with cut-off voltages in the range of 0.345 to −1.155 V vs. Ag/Ag+ (3.5 to 2.0 V vs. Mg/Mg2+). The improved cycling performance of this material is ascribed to the replacement of a portion of the Co atoms with Mn.

Keywords : Magnesium Secondary Battery, Cathode, Crystal Structure, Quantum Beam

1. Introduction

Secondary batteries are a potential solution to current challenges associated with carbon emissions and climate change, partly due to their high energy density. Magnesium (Mg) secondary batteries, which offer both superior energy density and divalent ion are potential candidates for the next generation of these devices. The standard electrode potential of Mg (−2.356 V vs. standard hydrogen electrode (SHE)) is 0.699 V higher than that of Li (−3.045 V vs. SHE), and so Mg should have applications as a practical high-voltage anode material. The theoretical capacity of Mg metal is also high (approximately 2200 mAh/g) and, combined with the superior stability of Mg, suggests that this metal could be used in secondary battery anodes. Furthermore, the theoretical capacity per unit volume of Mg (3832 mAh/cm3) is larger than that of Li (2064 mAh/cm3), meaning that Mg secondary batteries should exhibit higher capacities.1,2

Recently, Mg secondary batteries incorporating Chevrel compounds,3 such as V2O5,4 MnO2,5 MoO3,6 poly-anion systems,7 and spinel systems,8 have been investigated. MgCoO2 is expected to generate the highest voltage among the spinel system cathode materials because Co atoms serve as the redox species in this system.8 The fabrication of MgCoO2 via inverse co-precipitation has been examined, together with its properties as a component of battery units. The associated reaction has been reported to be MgCoO2 + Mg2+ + 2e− ↔ Mg2CoO4, with a theoretical capacity of 260 mAh/g. Unfortunately, the performance of such batteries has been inferior because the low firing temperature applied during the synthesis process results in the mixing of Mg and Co cations and minimal crystallinity.9 This might be avoided by the substitution of a portion of the Co atoms serving as redox species by another transition metal having 3d electrons in the spinel MgCoO2 system, but such substitutions have not yet been reported.

In this study, we synthesized a new Mg-based cathode material, MgCo2−xMnxO4 (x = 0.1, 0.2, 0.4), that withstands repeated charging and discharging and has a host structure into which Mg2+ ions can be inserted and extracted. This compound, with a spinel structure, is expected to have applications as a cathode material in Mg batteries. Both spinel MgCo2O4 and MgCo2−xMnxO4 were synthesized and investigated using an estimation method. This new material was expected to provide the redox pair Mn3+/Mn4+ rather than the Co3+/Co4+ pair, and thus to exhibit higher performance. The redox of Mn3+/4+ must promote the Mg deintercalation from MgCo2−xMnxO4 and suppress the phase transition to rock-salt phase. This hypothesis was based on previous reports of research in which Mn atoms were partly substituted for Co atoms. Furthermore, since Mn is a low-cost element and the spinel type material LiMn2O4 exhibits reversible redox of the Mn3+/4+ ion pair in Li ion batteries, the substitution of Mn for Co is expected to provide a new cathode material for future Mg secondary batteries. This work explored the synthesis method and the resulting crystal structure, and performed charge and discharge tests using the spinel materials MgCo2O4 and MgCo2−xMnxO4.
2.2 Sample characterization and local structural analysis

The composition of the sample was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Shimadzu Corporation, ICPE-9000). In addition, powder X-ray diffraction (XRD, PANalytical, X’PertPro, CuKα radiation, 1°/min, 45 kV, 40 mA, 2θ = 10–70°) analyses were performed to identify the phases. Lattice constants were obtained from least-squares fits using the XRD data.

Powder neutron diffraction data were acquired using the IMATERIA instrument at the Japan Proton Accelerator Research Complex (J-PARC) and a Rietveld analysis was performed by employing the Z-Code software program. Synchrotron XRD analyses were conducted on the BL19B2 beamline of the SPring-8 facility and the associated Rietveld analysis was performed using the RIETAN-FP software package. X-ray absorption fine structure (XAFS) data were obtained on the BL14B2 beamline at SPring-8 and analyzed using the Athena (Ver. 0.8.056) code to identify local and electronic structures.

2.3 Electrochemical measurements

Electrochemical measurements were performed with a two-electrode flat cell (HS cell, Hosen Ltd.). The experimental cathodes were fabricated by mixing synthesized samples with acetylene black (AB, Denka Co., Ltd.) as an electrical conductor and polytetrafluoroethylene (PTFE, FluonCD145, Asahi Glass Co., Ltd.) as an adhesive in a 5:1:1 mass ratio at 60°C and 90°C, respectively. An Al mesh (Nilaco Co., Ltd.) was used as the current collector and was vacuum-degassed overnight at 120°C in air and then pressure-bonded at approximately 20 MPa. The active material loading in the cathode was about 4.5 mg cm⁻². The anode was composed of Mg metal (AZ31, Mg:Al:Zn = 96:3:1 mass ratio, 60 μm thickness, Fujisyo Co., Ltd.) and Li, 1.0 mol/L Mg[Li(SO2CF3)2]2/triglyme (Kishida Chemical Co., Ltd.) was employed as the electrolyte together with a glass fiber separator (GA100, Whatman).

The final charge and discharge voltages in the three-electrode cell (Toyo System Co. Ltd.) were 0.345 and -1.155 V vs. Ag/Ag⁺ (3.5 to 2.0 V vs. Mg/Mg²⁺), respectively. Charging and discharging were performed at an electron density of 5 mA g⁻¹ (0.02 C), with a rest time of 5 min between each charge/discharge cycle. A 1 C rate was defined as the theoretical capacity over a time span of one hour. Each cell was assembled under Ar inside a glove box (Mipa Mfg. Co., Ltd.) with a dew point lower than -60°C. Charging and discharging experiments were conducted using a specialized measurement apparatus (HJR-110m SM8, Hokuto Denko Corporation).

2.4 First principles calculations

First principles calculations involving the spinel compound MgCo₂₋ₓMnₓO₄ (x = 0.25) were performed using the Vienna Ab initio Simulation Package (VASP, ver. 5.3.3). Two models comprising (2 × 2 × 1) super cells were constructed and employed to determine stable structures for relaxation calculations. The generalized gradient approximation-Perdew Burke Ernzerhof (GGA-PBE) exchange-correlation potential was used in conjunction with a plane-wave cutoff energy of 500 eV. A 2(1 × 1 × 2) k-point mesh was sampled, corresponding to the inverse values of the lattice constants. The convergence criterion for structural optimization was an energy difference between subsequent iterations of ≤0.02 eV/Å.

3. Results and Discussion

3.1 Sample characterization

Several MgCo₂₋ₓMnₓO₄ samples were synthesized using an inverse co-precipitation method, with different Mn concentrations, such that the x values were 0, 0.1, 0.2 and 0.4. These materials are referred to herein as MCMO01, MCMO02 and MCMO04, respectively. Figure 1(a) presents the powder XRD pattern obtained for MgCo₂₋ₓMnₓO₄ (x = 0, referred to as MCO). The primary peak is attributed to the spinel material having the Fd3m space group (ICSD #290602). The peaks in the XRD patterns are broad with low intensities due to the presence of small particles with minimal crystallinity as a result of the calcination temperature of 500°C. Figure 1(b) shows the SEM image of secondary particle agglomerated by the finer particles. The particle size of the primary particle was determined to be approximately 100 nm using Scherrer’s formula and, based on the peak intensity ratio, Mg/Co/Mn cation mixing was apparent. Synchrotron XRD analyses were performed to assess the presence of MCO, MCMO01, MCMO02 and MCMO04 subphases because it was difficult to evaluate the low-intensity peaks associated with these subphases in the standard XRD patterns. Table 1 summarizes the lattice parameters obtained by synchrotron XRD as well as the compositions of the samples as determined by ICP-AES. It is evident that the lattice parameters increased with increasing Mn substitution, and this effect is discussed in detail in Section 3.2.

3.2 Electronic structure analysis by XAFS measurements

3.2.1 XANES

The XAFS spectra of powdered MCO and the MCMO samples were acquired in order to determine the valence states of the transition metals. Figure 2 presents Co and Mn K-edge X-ray absorption near edge structure (XANES) spectra for the samples. This figure also includes the spectra of CoO (a typical divalent Co atom compound), Co₂O₃ (2.7 valence Co), LiCoO₂ (trivalent Co), MnO (divalent Mn), Mn₂O₃ (trivalent Mn) and MnO₂ (tetravalent Mn). It is evident from these spectra that the Mn atoms were tetravalent in all samples while the valence state of the Co atoms became lower than trivalent with increasing Mn substitution because of charge compensation. Therefore, the substitution mechanism is believed to involve the reaction 2Co³⁺ ↔ Co²⁺ + Mn⁴⁺. In this manner, a portion of the Co³⁺ is transitioned to Co²⁺ and Mn⁴⁺ is introduced. This leads to an increase in the lattice parameters.
Debye-Waller factors. In this analysis, the Tables 2(a) and 2(b) summarize the Co atoms at 16 sites with increasing Mn substitution, likely because the tetravalent Mn did not change for any of the samples. The valence state and degree of substitution at these sites were because the majority of these atoms remained in the tetravalent state, and so the EXAFS spectra were able to provide information about the local structure near the Mn atoms. It was found that the local structure of the powdered samples was estimated based on their EXAFS spectra. Figure 3(a) provides the Co K-edge EXAFS spectra of both materials while the Mn K-edge spectra are provided in Fig. 3(b). It is apparent that the distortion of the first neighboring M–O bond increased with increasing Mn substitution, because of the difference between the ionic radii of Co and Mn. The octahedral Co–O6 geometry was also distorted due to increasing Mn substitution. In addition, the distortion of Mn–O6 was not change in all samples at varying amount of Mn substitution. It is believed that the ionic radii of Mn4+ and Co2+ differ significantly, which means that the distortion of the Mn–O6 geometry was also affected by increasing Mn substitution. The structural model applied was spinel with the Fd3m space group. The Mn atoms primarily occupied the 16d site and the occupancy of these Mn atoms decreased because a portion of these Mn atoms were replaced by Mn. It is likely that a greater number of Co atoms at these sites decreased because a portion of these Co atoms were replaced by Mn. The sum of the occupancies at 8a and 16d sites were 1, respectively and replicated the metal composition obtained from the ICP data.

EXAFS fitting of data for the samples was performed to further investigate variations in local structure with increasing Mn substitution. Figures 3(c) and 3(d) show EXAFS fits for octahedral Co–O groups in MCO and MCMO01, respectively, while Tables 2(a) and 2(b) summarize the Co–O bond lengths and Debye-Waller factors. In this analysis, the fitting range was from 1 to 2 Å based on the first-neighbor bond in the Co K-edge data for the averaged structure obtained from the Rietveld analysis in Section 3.4. The MCO sample was determined to have an average M(16d)–O bond length of 0.1925 nm, while the value for the MCMO01 sample was 0.1899 nm after EXAFS fitting. It was determined that the average M(16d)–O bond length increased with increasing Mn substitution, likely because the tetravalent Mn atoms at 16d sites would strongly attract the O atoms.

3.3 Crystal structure analysis by neutron powder diffraction
A Rietveld analysis of the diffraction pattern for MCMO02 synthesized by inverse co-precipitation was performed to assess the crystal structure and electronic configuration of this material. Figure 4(a) shows the resulting patterns, and Table 3(a) summarizes the final results of Rietveld refinements for MCMO02 based on neutron powder diffraction. The structural model applied was spinel with the Fd3m space group. The Rietveld analysis was performed for Mg, Co and Mn atoms occupying both 8a and 16d sites and for O atoms occupying 32e sites. The sum of the occupancies at each 8a and 16d site were 1, respectively and replicated the metal composition obtained from the ICP data.

It was found that the Mg, Co and Mn atoms were located at 16d sites and that cation mixing occurred (see Fig. 4(a) and Table 3(b)). The Mn atoms primarily occupied the 16d sites and the occupancy of Co atoms at these sites decreased because a portion of these Co atoms were replaced by Mn. It is likely that a greater number of Co atoms were present in the Mg ion diffusion pathways at 8a sites because the ratio of Co and Mg to these sites was 1:1.

3.4 Crystal structure analysis by synchrotron X-ray diffraction
Rietveld analysis of the MCMO synthesized by inverse co-precipitation was performed based on the diffraction patterns so as to examine the crystal structure and electronic configuration in detail. Figure 4(b) presents the MCMO01 pattern used for Rietveld refinement while Table 3 provides the final results of Rietveld refinements for (b) MCMO01, (c) MCMO02 and (d) MCMO04 based on synchrotron X-ray diffraction. A spinel structural model was applied in conjunction with the Fd3m space group. A Rietveld analysis was performed for Mg, Co and Mn atoms occupying both 8a and 16d sites and O atoms occupying 32e sites. The sum of the occupancies at the 8a and 16d sites was 1, respectively and replicated
the metal composition obtained from the ICP analysis. The isotropic displacement parameters, $B_a$, at all sites were first refined and then diverged, so they were fixed at their pre-divergent values.

The data show that Mg, Co and Mn atoms were located at $16d$ sites, and that cation mixing occurred (see Fig. 4(b) and Tables 3(b), 3(c) and 3(d)). However, more Mn atoms occupied $16d$ sites and the occupancy of Co atom at $16d$ sites was decreased (as indicated by the neutron powder diffraction data) because a portion of the Co atoms at $16d$ sites was substituted by Mn atoms. Then, Mn and Co could be distinguished from Rietveld analysis in synchrotron X-ray diffraction. Table 4 shows the site occupancies for the samples. It is apparent that the occupancy of Mg atoms at $8a$ sites in MCMO01, MCMO02 and MCMO04 increased to a greater extent than that in MCO. This would be expected to improve the charge and discharge

| Table 2. | Co–O$_n$ bond lengths refined by EXAFS fitting. |
|----------|-----------------------------------------------|
|          | Co–O(Å)                                       |
| MCO      | 1.925                                         |
| MCMO01   | 1.899                                         |

(b) Debye-Waller factors for Co–O$_n$ refined by EXAFS fitting.

|          | Co–O(Å$^2$) |
|----------|-------------|
| MCO      | 0.006(5)    |
| MCMO01   | 0.001(2)    |

The data show that Mg, Co and Mn atoms were located at $16d$ sites, and that cation mixing occurred (see Fig. 4(b) and Tables 3(b), 3(c) and 3(d)). However, more Mn atoms occupied $16d$ sites and the occupancy of Co atom at $16d$ sites was decreased (as indicated by the neutron powder diffraction data) because a portion of the Co atoms at $16d$ sites was substituted by Mn atoms. Then, Mn and Co could be distinguished from Rietveld analysis in synchrotron X-ray diffraction. Table 4 shows the site occupancies for the samples. It is apparent that the occupancy of Mg atoms at $8a$ sites in MCMO01, MCMO02 and MCMO04 increased to a greater extent than that in MCO. This would be expected to improve the charge and discharge

Figure 4. Rietveld refinement patterns for (a) MgCo$_{1.8}$Mn$_{0.2}$O$_4$ (based on neutron powder diffraction; iMATERIA) and (b) MgCo$_{1.9}$–Mn$_{0.1}$O$_4$ (based on X-ray diffraction; SPring-8). The cross symbols in (a) and (b) indicate experimentally acquired patterns while the solid lines represent calculated intensities. The vertical marks indicate the positions of allowed Bragg reflections. The curves at the bottom of the spectra show the difference between the observed and calculated intensities on the same scale.
Table 3. Results of Rietveld refinements for (a) MgCo$_{1.9}$Mn$_{0.1}$O$_4$ (based on neutron powder diffraction), and for (b) MgCo$_{1.8}$Mn$_{0.2}$O$_4$, (c) MgCo$_{1.8}$Mn$_{0.2}$O$_4$ and (d) MgCo$_{1.6}$Mn$_{0.4}$O$_4$ (based on synchrotron X-ray diffraction).

(a) $R$-factor: $R_{wp} = 4.27\%$, $R_p = 3.42\%$, $R_e = 1.34\%$

| Atom | Site | $x$  | $y$  | $z$  | $10^2 \times B$/nm$^2$ | Site occupancy |
|------|------|------|------|------|----------------|----------------|
| Mg1  | 8$a$ | 0    | 0    | 0    | 2.10(3)  | 0.475(2)       |
| Co1  | 8$a$ | =Mg1(x) | =Mg1(y) | =Mg1(z) | =Mg1(B) | 0.520(1) |
| Mn1  | 8$a$ | =Mg1(x) | =Mg1(y) | =Mg1(z) | =Mg1(B) | 0.005(1) |
| Co2  | 16$d$ | 5/8  | 5/8  | 5/8  | 0.0265   | 0.6709(8)      |
| Mn2  | 16$d$ | =Co2(x) | =Co2(y) | =Co2(z) | =Co2(B) | 0.1040(2)    |
| Mg2  | 16$d$ | =Co2(x) | =Co2(y) | =Co2(z) | =Co2(B) | 0.225(1)    |
| O    | 32$e$ | 0.3865(1) | =O(x)  | =O(x)  | 0.278(7) | 1             |

(b) $R$-factor: $R_{wp} = 3.96\%$, $R_p = 2.76\%$, $R_e = 2.34\%$, $S = 1.69$

| Atom | Site | $x$  | $y$  | $z$  | $10^2 \times B$/nm$^2$ | Site occupancy |
|------|------|------|------|------|----------------|----------------|
| Mg1  | 8$a$ | 0    | 0    | 0    | 0.57(3)  | 0.530          |
| Co1  | 8$a$ | =Mg1(x) | =Mg1(y) | =Mg1(z) | =Mg1(B) | 0.468         |
| Mn1  | 8$a$ | =Mg1(x) | =Mg1(y) | =Mg1(z) | =Mg1(B) | 0.002(2)      |
| Co2  | 16$d$ | 5/8  | 5/8  | 5/8  | 0.026    | 0.748         |
| Mn2  | 16$d$ | =Co2(x) | =Co2(y) | =Co2(z) | =Co2(B) | 0.053         |
| Mg2  | 16$d$ | =Co2(x) | =Co2(y) | =Co2(z) | =Co2(B) | 0.199         |
| O    | 32$e$ | 0.3850(1) | =O(x)  | =O(x)  | 0.40(3)  | 1             |

(c) $R$-factor: $R_{wp} = 2.98\%$, $R_p = 2.24\%$, $R_e = 3.57\%$, $S = 0.83$

| Atom | Site | $x$  | $y$  | $z$  | $10^2 \times B$/nm$^2$ | Site occupancy |
|------|------|------|------|------|----------------|----------------|
| Mg1  | 8$a$ | 0    | 0    | 0    | 0.48(2)  | 0.550          |
| Co1  | 8$a$ | =Mg1(x) | =Mg1(y) | =Mg1(z) | =Mg1(B) | 0.447         |
| Mn1  | 8$a$ | =Mg1(x) | =Mg1(y) | =Mg1(z) | =Mg1(B) | 0.003(1)      |
| Co2  | 16$d$ | 5/8  | 5/8  | 5/8  | 0.026    | 0.708         |
| Mn2  | 16$d$ | =Co2(x) | =Co2(y) | =Co2(z) | =Co2(B) | 0.105         |
| Mg2  | 16$d$ | =Co2(x) | =Co2(y) | =Co2(z) | =Co2(B) | 0.187         |
| O    | 32$e$ | 0.3856(1) | =O(x)  | =O(x)  | 0.30(2)  | 1             |

(d) $R$-factor: $R_{wp} = 2.36\%$, $R_p = 1.79\%$, $R_e = 2.46\%$, $S = 0.96$

| Atom | Site | $x$  | $y$  | $z$  | $10^2 \times B$/nm$^2$ | Site occupancy |
|------|------|------|------|------|----------------|----------------|
| Mg1  | 8$a$ | 0    | 0    | 0    | 0.39(1)  | 0.545          |
| Co1  | 8$a$ | =Mg1(x) | =Mg1(y) | =Mg1(z) | =Mg1(B) | 0.454         |
| Mn1  | 8$a$ | =Mg1(x) | =Mg1(y) | =Mg1(z) | =Mg1(B) | 0.001(1)      |
| Co2  | 16$d$ | 5/8  | 5/8  | 5/8  | 0.08     | 0.584         |
| Mn2  | 16$d$ | =Co2(x) | =Co2(y) | =Co2(z) | =Co2(B) | 0.208         |
| Mg2  | 16$d$ | =Co2(x) | =Co2(y) | =Co2(z) | =Co2(B) | 0.208         |
| O    | 32$e$ | 0.3858(8) | =O(x)  | =O(x)  | 0.36(1)  | 1             |
properties by increasing the number of Mg atoms in diffusion pathways.

Table 5 summarizes the bond valence sum (BVS) values and distortion parameters, \( \lambda \) and \( \sigma^2 \), for the M(16d)-O6 octahedra in MgCo2-xMnxO4 ( \( x = 0, 0.1, 0.2, 0.4 \)).

| Sample     | BVS   | \( \lambda \) | \( \sigma^2 \) (deg^2) |
|------------|-------|---------------|------------------------|
| MCO        | 2.60  | 1.006         | 21.98                  |
| MCMO01     | 2.69  | 1.007         | 26.02                  |
| MCMO02     | 2.73  | 1.008         | 29.08                  |
| MCMO04     | 2.82  | 1.008         | 30.55                  |

Figure 5. Line profiles of electron densities between (a) 8a-32e, and (b) 16d-32e in MgCo2-xMnxO4 ( \( x = 0, 0.1, 0.2, 0.4 \)). \( \text{RA} \) (\%): MgCo3O4 = 2.81, MgCo0.9Mn0.1O4 = 3.22, MgCo1.8Mn0.2O4 = 4.89 and MgCo1.8Mn0.4O4 = 3.09.

3.5 Electrode properties

3.5.1 Charge and discharge properties using a three-electrode cell

The charge and discharge cycling test were performed in a three-electrode cell with AZ31 (Mg:Al:Zn = 96:3:1, by volume) as the anode, 1.0 mol/L Mg[N(SO2CF3)2]2/triglyme as the electrolytic fluid, and a glass fiber separator. The final charging voltage was 0.345 V vs. Ag/Ag\(^+\) and the final discharging voltage was -1.155 V vs. Ag/Ag\(^+\) (3.5 to 2.0 V vs. Mg/Mg\(^{2+}\)). The charge and discharge profiles for MCO and MCMO04 are presented in Figs. 6(a) and 6(b), respectively. Although the 1st discharge capacity was 54 mAh/g in the case of MCMO04, the degradation of the discharge capacity during the 2nd cycle for MCMO04 was smaller than that for MCO. In addition, the discharge capacity for MCMO04 became greater than that for MCO with increasing cycles. The discharge capacity was drastically reduced after the second cycle, although reversibility was observed for all systems. It is probable that Mg atoms inserted at 16c sites underwent strong covalent bonding with O atoms and thus were trapped during discharging. Therefore, it is important to perform a detailed crystal structure analysis after charging and discharging.

3.5.2 Cycling performance

Figure 6(c) shows the cycling performance for the samples. The discharge capacities for MCO, MCMO01 and MCMO02 were clearly reduced after the second cycle. However, the discharge capacity for MCMO04 became larger after the second cycle because the redox species were transformed and Mn atoms contributed to the redox process. Thus, it is important to investigate the local structure and the valence states of the Co and Mn atoms. Based on the EXAFS spectra in Fig. 3, it appears that the stability of the host structure and the cycling performance were both improved in association with the substitution of Mn atoms, because the M(16d)-O bond length became shorter and the strength of the covalent bond was enhanced. The redox reaction of the Mn atoms and the changes in the local structure near the transition metal atoms during discharge could be confirmed based on XANES and EXAFS spectra and from XAFS analysis of the electrode after charging and discharging.
lower because the Mg ion diffusion pathways became more established as a result of the cycling process. However, the first discharge voltage for MCMO04 was higher than those for MCMO01 and MCMO02. The action potential would be expected to change based on the degree of substitution by Mn atoms, and a more detailed discussion of the local structure will be provided in a future paper.

3.5.3 Dependence of charge and discharge properties on temperature

Applying the same conditions as described in Section 3.5.1, charge and discharge tests were performed at 90°C. Figure 6 shows the charge and discharge properties for (d) MCO and (e) MCMO04 during the 1st cycle at 90 and 60°C, respectively. The charge and discharge capacity became larger and the over-voltage became lower at 90°C, and it is possible that the Mg ions more readily diffused due to the higher temperature. From Figs. 6(e) and 6(d), we can determine that the first discharge capacity of MCO was about 110 mAh/g while that of MCMO04 was about 140 mAh/g at 90°C. The discharge capacity evidently increased because of the increased Mg ion diffusion pathway resulting from Mn substitution.

3.6 Discussion of local structure based on first principles calculations

The effect of Mn substitution on the local structure was examined by performing first principles calculations, while the electronic configuration of powdered MCMO was assessed using the VASP code. Two initial models were employed in these calculations, based on the Fd3m space group. The insertion and extraction of Mg atoms and the structural stability of the cathode were investigated using a (2©1) super cell for both models. These models comprised a total of 224 atoms, including 32 Mg atoms, 56 Co atoms, 8 Mn atoms and 128 O atoms. Figure 8 shows the local structural models developed for MgCo2O4. Figure 8(a) presents a model in which 32 Mg atoms are located at 8a sites and 56 Co atoms and 8 Mn atoms are situated at 16d sites. In Fig. 8(b), the model has 24 and 8 Mg atoms located at 8a and 16d sites, respectively, along with 56 Co atoms at 16d sites and 8 Mn atoms at 8a sites.

After structural relaxation calculations, the total energy values for the models in (a) and (b) were determined to be −1498.2 and −1491.9 eV, respectively. In model (b), the Mn atoms are at 16d sites and form a host structure based on Mn-O6 octahedra. Model (a), which has Mn atoms at 16d sites, was more stable than model (b), in which the Mn atoms are at 8a sites.

This is in agreement with the results of the Rietveld analysis of the synchrotron X-ray diffraction and neutron diffraction data, as shown in Table 3. In future work, it should be possible to develop a Mg/Co cation mixing model using structural relaxation calculations.
4. Conclusions

MgCo$_{2-x}$Mn$_x$O$_4$ was successfully synthesized as a new cathode material for use in magnesium secondary batteries, using the inverse co-precipitation method. Synchrotron X-ray diffraction and neutron diffraction showed that the presence of Co atom in the Mg diffusion pathways in the MgCo$_{2-x}$Mn$_x$O$_4$ ($x = 0.1$ to $0.4$) samples was reduced compared to that in MgCo$_2$O$_4$. This occurred because the proportion of Mg atoms in these same pathways was increased as a result of the substitution of Mn atoms. The results of a MEM analysis demonstrated that the covalent nature of the M(8$a$)–O bond decreased with increasing Mn substitution, such that a greater number of Mg atoms would be expected to be eliminated during the charging process. The cycling performance of the MCMO$04$ sample was improved after the second cycle during charge and discharge tests in a three-electrode cell. The valence state of the Co atoms in these materials became lower with increasing substitution of tetravalent Mn atoms based on XANES and XAFS data. It was also confirmed that Co atoms were replaced by Mn atoms, which contributed to the redox process during charging and discharging of MCMO. The results of first principles calculations confirmed that the structural stability and electronic properties of these compounds should be improved by Mn substitution. A more detailed analysis of the Mn substitution process and the associated changes in crystal structure and stability will be required in future work.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.19-00007.

Acknowledgments

This research was financially supported by the ALCA-SPRING project, JST. The authors are also deeply grateful to Dr. Keiichi Osaka of JASRI for the synchrotron X-ray diffraction experiments (SPring-8, BL19B2 beamline, proposal nos. 2016A1509 and 2016A1859), Dr. Tetsuo Honma and Dr. Hironori Ofuchi of JASRI for XAFS analyses (SPring-8, BL14B2 beamline, proposal nos. 2016A1510 and 2016B1852), and Prof. Tohru Ishigaki and Dr. Akinori Hoshikawa of Ibaraki University for the powder neutron diffraction experiments (J-PARC, iMATERIA).
References

1. H. D. Yoo, I. Stherenberg, Y. Gofer, G. Gershinsky, N. Pour, and D. Aurbach, *Energy Environ. Sci.*, 6, 2265 (2013).
2. Y. Zheng, Y. Nuli, Q. Chen, Y. Wang, J. Yang, and J. Wang, *Electrochim. Acta*, 66, 75 (2012).
3. E. Levi, A. Mitelman, D. Aurbach, and M. Brunelli, *Chem. Mater.*, 19, 5131 (2007).
4. G. Gershinsky, H. D. Yoo, Y. Gofer, and D. Aurbach, *Langmuir*, 29, 10964 (2013).
5. C. Yuan, Y. Zhang, Y. Pan, X. Liu, G. Wang, and D. Cao, *Electrochim. Acta*, 116, 404 (2014).
6. Y. Orikasa, T. Masese, Y. Koyama, T. Mori, M. Hattori, K. Yamamoto, T. Okado, Z. Huang, T. Minato, C. Tassel, J. Kim, Y. Kobayashi, T. Abe, H. Kageyama, and Y. Uchimoto, *Sci. Rep.*, 4, 5622 (2014).
7. S. Yagi, Y. Ichikawa, I. Yamada, T. Doi, T. Ichitsubo, and E. Matsubara, *Jpn. J. Appl. Phys.*, 52, 025501 (2013).
8. N. Kamioka, T. Ichitubo, T. Uda, S. Imashuku, Y. Taninuchi, and E. Matsubara, *Mater. Trans.*, 49, 824 (2008).
9. T. Ichitsubo, T. Adachi, S. Yagi, and T. Doi, *J. Mater. Chem.*, 21, 11764 (2011).
10. R. Oishi, M. Yonemura, Y. Nishimaki, S. Torii, A. Hoshikawa, T. Ishigaki, T. Morishima, K. Mori, and T. Kamiyama, *Nucl. Instrum. Methods Phys. Res. A*, 600, 94 (2009).
11. F. Irumi and K. Momma, *Solid State Phenom.*, 130, 15 (2007).