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Atomic Structure of MgCo_2O_4 Nanoparticle for Positive Electrode of Mg Rechargeable BatteryNaoto Kitamura,^{*a} Yuhei Tanabe,^a Naoya Ishida,^a and Yasushi Idemoto^aReceived 00th January 20xx,
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The atomic structure of spinel-type MgCo_2O_4 nanoparticle was investigated by the reverse Monte Carlo modelling using X-ray and neutron total scattering data. It is found that Mg at an octahedral site induces significant structural distortion, while Mg at a tetrahedral site is considered to move easily to a vacant site. Based on the results, we propose a guideline for the development of a better positive electrode material for Mg rechargeable battery.

A magnesium rechargeable battery (MRB) can be regarded as one of the most promising candidates for a next generation battery with higher energetic density than commercially used lithium-ion batteries (LIB) because of the difference in the valences of the ionic charge carriers. However, MRB proposed in previous studies exhibited inferior battery characteristics compared to LIB at this moment. For improving the performance of MRB with a Mg negative electrode, it is mandatory to develop a novel positive electrode material as this determines the achievable energy density basically. Among the reported positive electrode materials,^{1–8} MgCo_2O_4 with a spinel structure has attracted much attention because of its high theoretical capacity (260 mAh g^{-1} for $\text{MgCo}_2\text{O}_4 + \text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}_2\text{Co}_2\text{O}_4$) and high redox potential of Co.^{5–8} In general, MgCo_2O_4 powder must be nano-sized for rechargeable behaviour since a long diffusion distance of Mg^{2+} within the crystal is not preferable due to the strong electrostatic interaction between Mg^{2+} and O^{2-} . In addition, the atomic structure of MgCo_2O_4 nanoparticle must be clarified in order to develop a novel material with superior positive electrode property, because the structure should have a significant influence on the Mg insertion/deinsertion into/from the electrode material during discharge/charge cycles. As is well known, however, nanoparticle does not exhibit prominent Bragg diffraction peaks, and thus the atomic structure of MgCo_2O_4 nanoparticle cannot be determined precisely by

structure analysis using the Bragg peaks, such as the Rietveld refinement.

In this study, we performed total scattering measurements on MgCo_2O_4 nanoparticle to visualize its disordered structure, since such a structure cannot be revealed by other experimental methods like nuclear magnetic resonance, extended X-ray absorption fine structure, and so on. Taking the advantage into account, we investigated the atomic structure of MgCo_2O_4 nanoparticle by analyzing total scattering data, and then tried to gain deeper understanding on the relationship between the atomic structure and the positive electrode property than was hitherto available in previous studies. We employed the Monte Carlo algorithm where experimental data (total scattering data) were used instead of energy calculation, i.e., the reverse Monte Carlo (RMC) modelling.^{9–11}

We synthesized the spinel-type MgCo_2O_4 nanoparticle according to a previous work.⁶ The metal composition of the sample was determined by inductively coupled plasma (ICP) spectroscopy (ICPE-9000, Shimadzu). We also confirmed that the MgCo_2O_4 could work as a positive electrode material by a charge/discharge cycle test (Fig. S1).

To reveal the atomic structure of the sample, synchrotron X-ray and neutron total scattering measurements were carried out. The Rietveld refinement (Z-Rietveld program¹²) was performed with the neutron Bragg profile recorded by a backward detector bank of iMATERIA at J-PARC, and then a $3 \times 3 \times 3$ simulation box for the RMC modelling was constructed from the refined unit cell, considering the lowest Q values of the X-ray and neutron total scattering data. An X-ray total scattering pattern was measured with a photon energy of 61.2 keV at the SPring-8 high-energy X-ray diffraction beamline BL04B2.¹³ The incident beam intensity was monitored with an ionization chamber filled with Ar gas, and the diffracted X-rays were collected by Ge and CdTe detectors. The obtained pattern was corrected by a standard program.¹³ In the case of neutron total scattering, the pattern recorded with a 45° bank of NOVA at J-PARC was normalized into a structure factor $S(Q)$ with

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background, V-rod, and empty-can data. These $S(Q)$ data were convolved by taking the size of the simulation box into account, and they are represented as $S_{\text{box}}(Q)$ in this paper. The RMC modelling was performed by using the RMCProfile program,¹⁰ and then the simulated snapshot of the atomic configuration was analyzed; that is, polyhedral volumes and distortions were investigated. Based on the obtained results, we discussed the relationship between the structural and electrochemical properties as a positive electrode material for MRB.

Fig. 1 shows the result of the Rietveld refinement using the neutron Bragg profile, and the refined structural parameters are summarized in Table 1. According to previous works,⁵⁻⁷ we assumed that MgCo_2O_4 had a spinel structure, and fixed the Mg:Co ratio taking a result of the ICP measurement into account. As can be seen in Fig. 1, the observed Bragg peaks are considerably broad, suggesting that the particle size of the synthesized MgCo_2O_4 is nano level. It is also found that all the Bragg peaks can be attributed to a spinel structure, and that Mg and Co respectively occupy the octahedral and tetrahedral sites partially. The results indicate that the sample has the “disordered” spinel structure. However, local environments around Mg and Co cannot be distinguished by crystallography, and thus we performed the RMC modelling using the simulation box (1512 atoms) constructed from the unit cell. In the RMC modelling, Mg and Co distributions were determined by

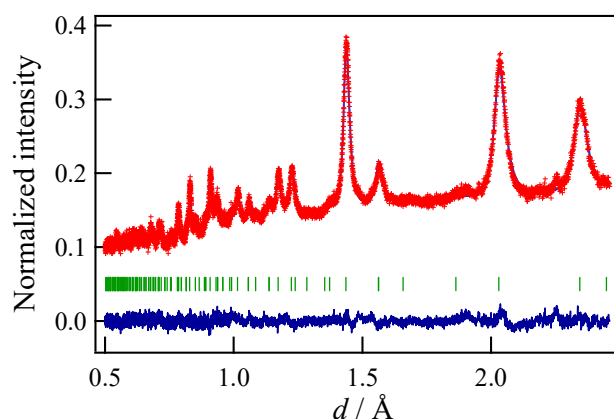


Fig. 1 Rietveld refinement pattern for MgCo_2O_4 nanoparticle (Neutron). The red marks and the solid line represent observed and calculated neutron diffraction intensities, respectively. The vertical marks below the patterns indicate positions of allowed Bragg reflections. The curve at the bottom is a difference between the observed and calculated intensities.

Table 1 Refined structural parameters of MgCo_2O_4 nanoparticle (Space group: $Fd-3m$). B and g means an atomic displacement parameter and a site occupancy, respectively.

Lattice parameter: $a=8.1213(2)$ Å.

R -factors: $R_{\text{wp}}=3.03$ %, $R_p=2.59$ %, $R_e=2.27$ % and $S=1.33$.

Atom	Site	x	y	z	$B / \text{\AA}^2$	g
Mg1	8a	0	0	0	4.5(1)	0.494(1)
Co1	8a	0	0	0	$=B(\text{Mg1})$	0.506(1)
Co2	16d	5/8	5/8	5/8	1.09(4)	0.7411(7)
Mg2	16d	5/8	5/8	5/8	$=B(\text{Co2})$	0.2589(7)
O	32e	0.38463(5)	$=x(\text{O})$	$=x(\text{O})$	1.35(3)	1

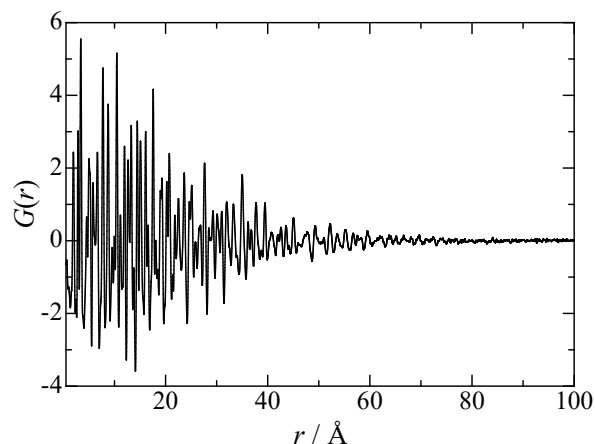


Fig. 2 Reduced pair distribution function of MgCo_2O_4 nanoparticle (X-ray).

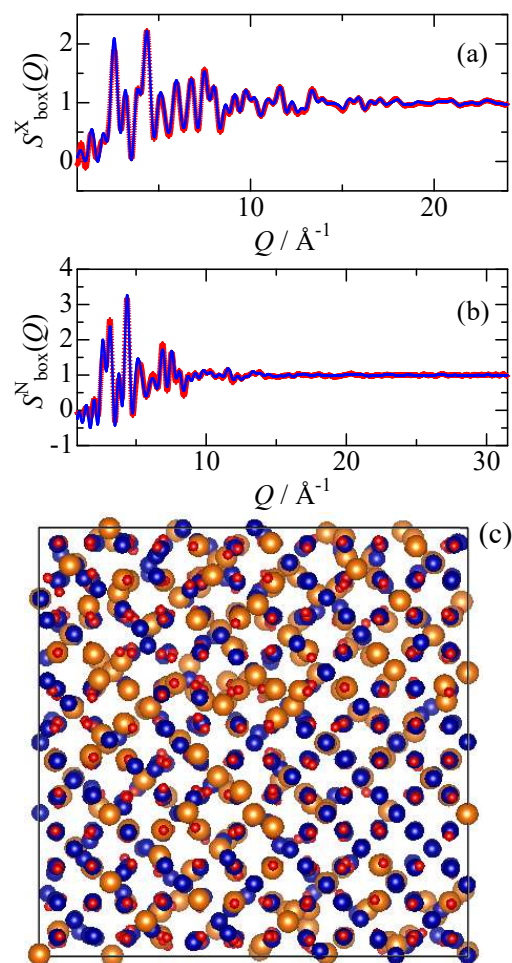


Fig. 3 (a) X-ray, and (b) neutron structure factors of MgCo_2O_4 nanoparticle. The red marks and the blue solid line represent the experimental data and RMC model, respectively. (c) Atomic-configuration snapshot of MgCo_2O_4 . The snapshot was visualized by a VESTA program.¹⁵ Color code: Mg, orange; Co, Blue; and O, red.

swapping Mg and Co in the simulation box, and X-ray and neutron structure factors were fitted simultaneously by optimizing the weighting factors. Fig. 2 shows the X-ray reduced pair distribution function $G(r)$ which was obtained from the structure factor $S(Q)$ by a Fourier transform.¹⁴ As can be seen, we can find correlation peaks for MgCo_2O_4 nanoparticle up to 80 Å. The results of the RMC modelling for MgCo_2O_4 nanoparticle is presented in Fig. 3. It can be seen in Figs. 3 (a) and 3 (b) that both the $S_{\text{box}}(Q)$ are well reproduced by the modelling.

It is well known that the spinel structure has a vacant octahedral site denoted as 16c site [Fig. 4 (a)], which is close to the tetrahedral site (8a site). After discharging of MRB using MgCo_2O_4 as a positive electrode material, Mg^{2+} is inserted into the vacant site of MgCo_2O_4 , and then cations at the tetrahedral site are simultaneously pushed out to the vacant site.⁷ As a result, the spinel structure is converted to the rock-salt structure, where the cations occupy both the 16c and 16d sites in the spinel structure [Fig. 4 (b)]. Figs. 4 (c) and (d) show a condensed view of MgCo_2O_4 which is a time-averaged structure (a crystal structure) constructed from the snapshot of the atomic configuration [Fig. 3 (c)]. As can be seen in the figures, cations at the tetrahedral sites spread slightly toward the vacant sites in the nanoparticle. This implies that the phase transition to the rock-salt structure can easily occur in the MgCo_2O_4 nanoparticle during a discharge process. Such structural information is considerably hard to be obtained by analysis using only Bragg peaks.

We paid attention on local environments around Mg and Co in the snapshot of the atomic configuration [Fig. 3 (c)],

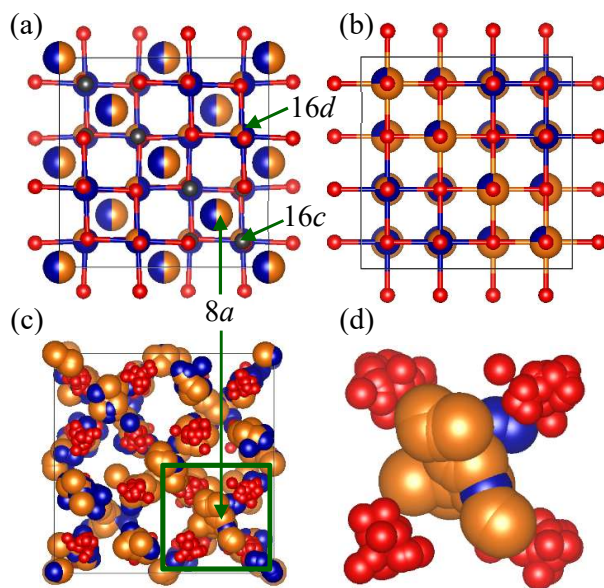


Fig. 4 (a) Refined unit cell of MgCo_2O_4 with the disordered spinel structure. Gray small spheres represent the vacant site (16c site). (b) Rock-salt structure after discharging. (c) Condensed view of MgCo_2O_4 constructed by RMC modelling and (d) the enlarged view within a green square of (c). Color code: Mg, orange; Co, blue; and O, red.

Table 2 Bond lengths of Mg-O and Co-O, and bond-angle variances σ^2 of polyhedra in MgCo_2O_4 nanoparticle.

Polyhedron	Bond length / Å	Bond angle variance / deg. ²
MgO_6	2.085	157.7
CoO_6	1.978	115.2
MgO_4	1.969	196.6
CoO_4	1.830	118.5

Table 3 Volume around the vacant site (16c site), MgO_6 and CoO_6 volumes in MgCo_2O_4 nanoparticle.

Octahedron	Volume / Å ³
Vacancy (16c)-O ₆	12.16
MgO_6	11.22
CoO_6	9.77

and investigated bond distances, polyhedral volumes and bond-angle variances (distortions)¹⁶. From the results given in Table 2, it is confirmed that bond length of Mg-O is longer than that of Co-O, as predicted by a difference in ionic radii between Mg^{2+} and Co^{3+} .¹⁷ Furthermore, it is found that the distortion around Mg at the octahedral site is larger than that around Co at the same crystallographic site. Since the cations at this site can be regarded as a pillar of the spinel structure, it is considered that the Mg amount of the octahedral site should be decreased for stable positive electrode property. In other words, a disorder in the spinel structure of MgCo_2O_4 should be suppressed.

Table 3 compares the volume around the vacant site (16c site) to MgO_6 and CoO_6 volumes in MgCo_2O_4 nanoparticle with the disordered spinel structure. An important finding noted in this table is the fact that the volume around the vacancy is almost equal to the MgO_6 volume. This result indicates that Mg^{2+} at the tetrahedral site (8a site) can move to the vacant site more easily than Co^{3+} at the tetrahedral site, due to the smaller volume mismatch. From this viewpoint, it is also considered that the disorder in the spinel structure must be suppressed, to facilitate the phase change from the spinel structure to the rock-salt structure during a discharging process.

Based on these analytical results, a partial substitution of Mn for Co can be regarded promising, since MgMn_2O_4 has an ordered spinel structure (a normal spinel structure).⁶ Indeed, the Mn-substituted sample showed higher discharge capacity in comparison to the pure MgCo_2O_4 , as reported elsewhere.¹⁸ It is also useful to choose another cation (M) which can be expected to form MO_6 with the same volume as the vacant site.

In this work, we focused on MgCo_2O_4 nanoparticle, which is one of the most promising candidates for positive electrode material of MRB. Structural investigation employing the reverse Monte Carlo modelling could reveal the cation distribution, polyhedral distortions, and local environment around the vacancy successfully. Based on these results, a guideline for development of a novel positive electrode material was proposed.

Conflicts of interest

There are no conflicts of interest to declare.

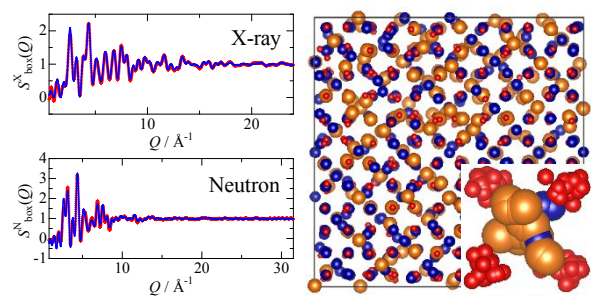
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