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MgMn_2O_4 having a spinel structure is a very attractive material for the positive electrode in Mg-ion batteries, since its reversible Mg extraction/insertion reaction can lead to a large reversible capacity. While the Mg extraction from MgMn_2O_4 has been reported, the reaction mechanism remains unclear. In this paper, Mg ions were chemically extracted from MgMn_2O_4 by acid digestion at various concentrations to produce $\text{Mg}_x\text{Mn}_2\text{O}_4$ ($0 < x < 1$). The results showed that Mg extraction from MgMn_2O_4 is a two-step two-phase reaction, via the intermediate $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ to the fully oxidised Mn_2O_4 . The kinetics of Mg extraction was clarified using acid digestion experiments of different durations, and the direct reaction pathway of MgMn_2O_4 oxidation to $\lambda\text{-MnO}_2$ was the fastest process. This may explain the difficulty in Mg extraction from MgMn_2O_4 using electrochemical methods.

Introduction

An insertion (or intercalation) material contains free space (vacant site) in its crystal structure for the insertion of given chemical species (atoms, ions, or molecules). Intercalation compounds having two-dimensional structures, such as graphite and transition metal dicalcogenides, are well known to accommodate a large number of atoms, ions, and molecules between the layers.^{1–4} One of the most important and common applications of insertion/intercalation materials is the electrodes in batteries. Examples include proton insertion materials (MnO_2 for Zn- MnO_2 batteries⁵ and NiOOH for nickel metal hydride batteries^{6,7}) and lithium insertion materials such as graphite, LiCoO_2 , LiNiO_2 , and LiMn_2O_4 for lithium-ion batteries.^{8–10} Insertion materials of transition metal oxides having a wide variety of crystal structures show similar manners of insertion. When guest cations (A^{n+}) are inserted into the host structure, transition metal ions in the framework are reduced to maintain the metal-oxygen framework¹¹:

where $\square$ is a vacant site in the host. According to Eq. (1), there is a correlation between the valence of the guest cation (n), the number of electrons per formula unit in the host, and the change in the oxidation number of transition metals during the reaction. Therefore, the n value strongly affects the nature of the insertion reaction.

In recent years, insertion materials accommodating a guest cation other than Li^+ (e.g., Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Zn^{2+} , or Al^{3+}) have been investigated as possible electrode materials for post Li-ion batteries.^{12–18} These batteries have several advantages over Li-ion batteries, including natural abundance, low cost, and high energy content, depending on the guest cation species. Among them, insertion materials using the divalent Mg^{2+} ions have a theoretical capacity twice that of monovalent ions like Li^+ or Na^+ . Therefore, there is growing interest in Mg insertion materials for Mg-ion batteries.^{15,19–21} The reported Mg insertion materials encompass a wide variety of chemical formula and crystal structures: vanadium oxide, Prussian blue analogue, Chevrel phase, MnO_2 , etc.^{21–25} However, the insertion and extraction of divalent ions in the solid matrix are difficult due to the slow diffusion and/or migration.²⁶

MgMn_2O_4 with a spinel structure is one of the most attractive Mg insertion materials. To improve its electrochemical reactivity, researchers have modified it by nano-sizing to lower the crystallinity, incorporating conductive additives, and other methods.^{27–31} Most of the previous research focused on Mg insertion reaction into MgMn_2O_4 :

This step was reported to proceed as the solid state redox reaction of $\text{Mn}^{3+}/\text{Mn}^{2+}$, and its operating voltage is ca. 3 V vs. Mg metal electrode. Although MgMn_2O_4 can be reversibly cycled in the $\text{MgMn}_2\text{O}_4/\text{Mg}_2\text{Mn}_2\text{O}_4$ reaction, the Mg extraction reaction from MgMn_2O_4 is more attractive,

Reaction (3) is expected to show a higher potential, because of the solid-state redox reactions of $\text{Mn}^{3+}/\text{Mn}^{4+}$ as well as $\text{LiMn}_2\text{O}_4/\text{Mn}_2\text{O}_4$. Moreover, a reversible capacity of 500 mAh g^{-1} or higher could be achieved for the Mg insertion reaction of Mn_2O_4 up to $\text{Mg}_2\text{Mn}_2\text{O}_4$, if the Mg extraction reaction of MgMn_2O_4 were utilised. However, unlike Li ions, the Mg ions are difficult to dissolve into a nonaqueous solution. As a result,

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Electronic Supplementary Information (ESI) available: simulated XRD pattern of MgMn_2O_4 (Fig. S1), Rietveld refinement of MgMn_2O_4 (Fig. S2), Structural refinement of MgMn_2O_4 (Fig. S3), SEM images of MgMn_2O_4 (Fig. S4), XRD pattern of an intermediate phase (Fig. S5), Calibration curves for fraction estimates (Figs. S6 & S7), Fitting results of Mole fractions (Fig. S8), Summary of acid digestion (Table S1). See DOI: 10.1039/x0xx00000x

electrochemical Mg extraction/insertion reaction of MgMn_2O_4 has been reported in only a few papers^{32,33} to the best of our knowledge, while the following issues are still unclear: (1) whether all the Mg ions can be extracted, (2) the mechanism of Mg extraction reaction, and (3) how fast is the extraction.

In this study, the Mg extraction reaction of MgMn_2O_4 was examined using chemical extraction (acid digestion). Compared to the electrochemical method in a non-aqueous environment, this is an easier way to prepare $\text{Mg}_{1-x}\text{Mn}_x\text{O}_4$, and the extent of Mg extraction may be controlled by varying the acid concentration and digestion time. The extraction reaction of a guest ion from a host structure during acid digestion was firstly reported by Hunter³⁴ for Li extraction from LiMn_2O_4 forming $\lambda\text{-MnO}_2$. Nowadays, the acid digestion has been applied to a number of materials as a chemical extraction method for inserting materials.^{35–38} Among them, Mg insertion materials have been extensively investigated by acid digestion to clarify whether or not the Mg extraction reaction can proceed. Here, we investigate the reaction mechanism of chemical Mg extraction from MgMn_2O_4 from the structural, thermodynamic, and kinetic viewpoints.

Experimental

MgMn_2O_4 was prepared by heating a reaction mixture of $\text{Mg}(\text{OH})_2$ (Wako Chem.) and MnOOH (manganite, Tosoh Corp, Japan) at 1000°C for 16 h in air using a tubular electric furnace. The acid digestion of MgMn_2O_4 was performed by adding 1.00 g of MgMn_2O_4 powder into 30 ml of nitric acid aqueous solution of given concentration for a specific amount of time under magnetic stirring. After the acid digestion, the residual powder samples were collected by suction filtration, washed with distilled water several times, and dried at 60°C overnight. The residual samples were weighted, and their crystal structures were characterised by powder X-ray diffraction (XRD) measurements using an X-ray diffractometer (XRD-6100, Shimadzu Corp., Japan) with $\text{Fe-K}\alpha$ radiation ($\lambda = 1.9373 \text{ \AA}$) at 40 kV and 15 mA. The measurement range was $2\theta = 10^\circ\text{--}105^\circ$ at a scan rate of $0.5^\circ \text{ min}^{-1}$. The lattice parameters were calculated by the least squares method from the Miller index of the diffraction lines and the diffraction angles. The concentration of Mn ions dissolved in the filtrate after the acid digestion was determined by X-ray fluorescent (XRF) measurements using an energy dispersive XRF analyser (Rayny EDX-720, Shimadzu Corp., Japan). A Rh tube was used as the X-ray tube (tube voltage: 50 kV, current: 34 μA), and the measurement range was 0–40 keV. The concentration of Mn ions was determined from a calibration curve obtained using manganese acetate (II) tetrahydrate (Wako Chem.) solution at different concentrations ($R^2 = 0.9888$).

Results and discussion

Change in the Crystal Structure of MgMn_2O_4 During Acid Digestion

Figure 1 shows the XRD patterns of acid-digested MgMn_2O_4 using nitric acid solutions at different concentrations (0.1–1.0

M) for 16 h. The pattern of pristine MgMn_2O_4 is also shown in Fig. 1a for comparison. In the spinel structure, the Mn ions may occupy the tetrahedral sites, which results in the formation of a solid solution of $\text{Mg}[\text{Mn}_2]\text{O}_4$ and $\text{Mn}[\text{Mn}_2]\text{O}_4$. The occupation of tetrahedral sites by Mn ions affects the relative intensity of the diffraction lines because of the large difference between the scattering factors of Mg and Mn ions. Namely, the strongest peak for $\text{Mg}[\text{Mn}_2]\text{O}_4$ is the 101 diffraction line at $2\theta = 23^\circ$, in contrast to the 211 line at 46° for $\text{Mn}[\text{Mn}_2]\text{O}_4$. The relative intensity of XRD lines for pristine MgMn_2O_4 was very consistent with that calculated from a spinel structure (Fig. S1). In addition, the lattice parameters of pristine MgMn_2O_4 ($a = 5.726 \text{ \AA}$ and $c = 9.324 \text{ \AA}$) were very close to those for MgMn_2O_4 ($a = 5.72 \text{ \AA}$, $c = 9.31 \text{ \AA}$) rather than Mn_3O_4 ($a = 5.77 \text{ \AA}$ and $c = 9.47 \text{ \AA}$).³⁹ Structural refinement of MgMn_2O_4 was performed by classical Rietveld refinement using a program developed by the authors, in which only the oxygen positional parameters were variable (Fig. S2). The low R -value (11 %) indicates that the tetrahedral sites in pristine MgMn_2O_4 are almost all occupied by Mg^{2+} ions with a negligible amount of Mn^{2+} ions. Further, a structural refinement was performed on MgMn_2O_4 assuming the replacement of Mg ions with Mn at the tetrahedral sites and the replacement of Mn ions with Mg at the octahedral sites. The results indicate that no Mn ions occupy the tetrahedral sites (Fig. S3). Therefore, pristine MgMn_2O_4 can be assigned to the spinel structure with a space group symmetry of $I4_1/amd$, in which the Mg^{2+} ions are located at the tetrahedral 4a site, Mn^{3+} ions at the octahedral 8d site, and O^{2-} at the 16h site.

Figure 1. Powder XRD patterns of (a) as-prepared MgMn_2O_4 and MgMn_2O_4 after acid digestion using (b) 0.1 M, (c) 0.25 M, (d) 0.3 M, (e) 0.5 M, (f) 0.6 M, and (g) 1.0 M HNO_3 . Red arrows in (e) indicate new peaks that could not be assigned to MgMn_2O_4 or $\lambda\text{-MnO}_2$.

As seen in Figs. 1b-g, the XRD patterns of acid-digested $\text{Mg}[\text{Mn}_2]\text{O}_4$ changed drastically depending on the acid concentration. For acid concentrations below 0.4 M, the diffraction lines of MgMn_2O_4 remained, while new peaks appeared at higher diffraction angles than the main 101 line and grew at higher acid concentrations. At 0.5 M (Fig. 1e), the appearance of several additional diffraction lines indicates the formation of new phases other than the pristine $\text{Mg}[\text{Mn}_2]\text{O}_4$. At higher acid concentrations (Figs. 1f and g), diffraction lines indexed by a cubic lattice were mainly observed. The XRD pattern of the sample digested with 1.0 M nitric acid (Fig. 1g) is very similar to that of $\lambda\text{-MnO}_2$, and the lattice constant of 8.04 Å also agrees well with that of $\lambda\text{-MnO}_2$.⁴⁰ These results suggest that the amount of H^+ entering the crystal lattice via $\text{Mg}^{2+}/\text{H}^+$ exchange reaction is negligible,⁴¹ i.e., only the Mg extraction reaction takes place during the acid digestion of MgMn_2O_4 . For Mg extraction from MgMn_2O_4 by acid digestion, the diffraction lines broaden. To clarify the line broadening after acid digestion, the particle morphology was observed by SEM (Figure S4). The MgMn_2O_4 before acid digestion consisted of particles approximately 1 μm in size with a smooth surface. After acid digestion, the particles were cracked, and tiny particles adhered to their surface. Thus, the line broadening is probably due to particle destruction that reduces the crystallite size.

The drastic change in XRD patterns after the acid digestion is derived from the different crystal symmetries of MgMn_2O_4 and $\lambda\text{-MnO}_2$. The crystal lattice of MgMn_2O_4 is distorted to a tetragonal one by the cooperative Jahn-Teller effect caused by Mn^{3+} ions located at the octahedral sites.⁴² Mn-O bond distances are 1.953×4 Å and 2.235×2 Å, and MnO_6 is a distorted octahedron owing to the Jahn-Teller effect of Mn^{3+} ions, which is evidence that the Mn ions in MgMn_2O_4 are in the trivalent state. On the other hand, $\lambda\text{-MnO}_2$ has a cubic lattice because all Mn ions at the octahedral sites are oxidised to Mn^{4+} due to the Mg extraction reaction. Based on these results, MgMn_2O_4 was converted to $\lambda\text{-MnO}_2$ during the acid digestion in a topotactic manner, in which Mg^{2+} ions were extracted from the solid matrix without destroying the spinel framework consisting of Mn and oxygen ions.

In the XRD pattern of the sample treated with 0.5 M nitric acid (Fig. 1e), new diffraction lines (marked by red arrows) were observed that belong to neither MgMn_2O_4 nor $\lambda\text{-MnO}_2$, while Fig. S5 indicates the existence of an intermediate phase between MgMn_2O_4 and $\lambda\text{-MnO}_2$. The newly emerged XRD pattern could be assigned to a cubic structure, with the lattice parameter calculated to be 8.347 Å from the six diffraction lines. Figure 2 shows the lattice volume of the obtained intermediate phase, together with those of MgMn_2O_4 and $\lambda\text{-MnO}_2$. To compare the lattice volume of the three phases with different crystal systems (instead of the same spinel-framework structure), the cubic lattice with higher symmetry was converted to a tetragonal lattice with lower symmetry by using the following relations,

$$a_T = a_C / \sqrt{2}, \text{ and } c_T = a_C \quad (4)$$

where a_T and c_T represent lattice parameters of the tetragonal a -axis and c -axis, respectively, and a_C is that of the cubic lattice. The lattice volume for $A = \text{Mg}$ in Fig. 2 changes almost linearly with x between those of MgMn_2O_4 and $\lambda\text{-MnO}_2$. Therefore, the chemical composition of this intermediate phase was considered to be $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$, with a cubic lattice belonging to the space group of $\text{Fd}3\text{m}$, and only half of the Mg^{2+} ions were extracted from the tetrahedral sites of MgMn_2O_4 . The crystal system also changed from tetragonal MgMn_2O_4 to cubic $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ during the Mg extraction, because half of the trivalent Mn ions were oxidised to the tetravalent state. The presence of fewer Mn^{3+} Jahn-Teller ions results in a lattice transformation from tetragonal back to the cubic due to suppression of the cooperative Jahn-Teller effect. Considering the LiMn_2O_4 system (black in Fig. 2), the lattice volume of AMn_2O_4 ($A = \text{Li}$ and Mg) having a spinel structure mainly depends on the average oxidation state of Mn ions rather than cations at the tetrahedral site, because the ionic radii of Li^+ and Mg^{2+} at the tetrahedral sites are very similar (0.59 and 0.57 Å, respectively) with a coordination number of 4.⁴³

In addition, there was no continuous shift in these diffraction lines, indicating that Mg extraction proceeded in a heterogeneous two-phase manner. Therefore, the Mg extraction from MgMn_2O_4 consists of two-step topotactic two-phase reactions:

In a recent study⁴⁴, the intermediate $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ phase was generated by an electrochemical Mg extraction reaction. This result indicates that the disproportionation reaction mechanism underlying the acid digestion, in which $\lambda\text{-MnO}_2$ is produced through $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$, is the same in terms of the structural change, although this mechanism is different from that underlying the electrochemical Mg extraction.

Figure 2. Lattice volume of $A_x\text{Mn}_2\text{O}_4$ with a spinel structure as a function of x in $A_x\text{Mn}_2\text{O}_4$. $A = \text{Mg}$ (red) and Li (black).

Mechanism of Mg Extraction from MgMn_2O_4 During Acid Digestion

According to Manthiram et al.,³² the Mg extraction reaction of MgMn_2O_4 by acid digestion proceeds according to the following equation

which can be rewritten in a more rigorous form as described below, by considering the following two chemical facts: both MgO and MnO are soluble in the acid solution as Mg^{2+} and Mn^{2+} ions, and the H^+ ions are involved in the reaction of acid digestion.

This equation was validated by comparison to the experimental results of MgMn_2O_4 digested with excess nitric acid (1.0 M). When the ratio of H^+ to MgMn_2O_4 exceeds 4, which is the theoretical value in Eq. (7), Mg extraction is expected to be complete. Indeed, we observed that the solution pH remained greater than 1, and the residual samples only contained $\lambda\text{-MnO}_2$ (Fig. 1g). The weight of the residual powder (0.503 g) was half of that before the acid digestion (1.00 g). So the amounts of MgMn_2O_4 before and after the acid digestion (1.0 M) were calculated to be 5.38 and 2.89 mmol, respectively, based on the formal weights of MgMn_2O_4 (186.04) and $\square\text{Mn}_2\text{O}_4$ (173.88). Therefore, the molar ratio $\text{MgMn}_2\text{O}_4:\square\text{Mn}_2\text{O}_4 = 1.86:1$ agrees with the theoretical value of 2:1 from Eq. (7). In addition, the molar ratio of Mn^{2+} ions in the solution against MgMn_2O_4 is expected to be unity according to the equation, while the experimentally measured ratio (0.15 M Mn^{2+} in 30 mL solution) of 1:1.2 is in good agreement with the theoretical value.

Based on the above equation, the general chemical reaction during the acid digestion of MgMn_2O_4 at different acid concentrations can be expressed as follows:

where x is the amount of Mg extraction from MgMn_2O_4 , with $x = 1$ corresponds to full Mg extraction. To confirm Eq. (8), the amount of Mn^{2+} ions dissolved in the acid solution, the residual mass of the sample after acid digestion, and the amount of Mg ions in the residual material [(1- x) in $\text{Mg}_{1-x}\text{Mn}_2\text{O}_4$] were measured. The analytical results are summarised in Table S1. The residual amount of the samples after acid digestion is plotted against $[\text{H}^+]$ in the solution in Fig. 3a, showing good agreement with the theoretical line calculated from Eq. (8). The slight difference between the observed and theoretical values may be attributed to the loss of residues during the filtration process. Figure 3b shows the amount of dissolved Mn ions in the filtrate measured by XRF. The amounts of Mn^{2+} and H^+ are linearly correlated with the fixed ratio of $\text{Mn}^{2+}:\text{H}^+ = 4:1$, and this observed ratio agrees well with that calculated from Eq. (8). To determine the amount of Mg extraction from MgMn_2O_4 , the fraction of each phase was estimated by peak deconvolution of the strong XRD lines at $2\theta = 23^\circ$ into the 101 line for MgMn_2O_4 and 111 lines for $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ and $\lambda\text{-MnO}_2$. When a pseudo-Voigt function combined with Lorentzian and Gaussian functions is generally used to fit the peak of a diffraction line,⁴⁵ the proportion of Lorentzian component is extremely high, and

that of the Gaussian component is sufficiently low to be neglected. Therefore, the peak deconvolution was performed by using a Lorentzian function described below, instead of a pseudo-Voigt function.

$$I = I_0 + \frac{2A}{\pi} \frac{w}{4(y-y_c)^2 + w^2} \quad (9)$$

where I_0 represents the background intensity, w the half width, A the peak height, y the peak position, and y_c the peak position at A . Figure 4 shows the results of fitting the diffraction peaks for MgMn_2O_4 digested at various acid concentrations. For acid concentrations less than 0.4 M, pristine MgMn_2O_4 was the main phase. When the acid concentration increased, fractions of the intermediate phase $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ and final $\lambda\text{-MnO}_2$ phase increased simultaneously. At 0.5 M, the fractions of the three phases are almost the same. For acid concentrations greater than 0.6 M, the pristine MgMn_2O_4 phase disappeared, and $\lambda\text{-MnO}_2$ became the main component in addition to a tiny amount of the intermediate phase.

Figure 3. (a) The weight of the residual $\text{Mg}_{1-x}\text{Mn}_2\text{O}_4$ and (b) the amount of Mn^{2+} ions dissolved during acid digestion.

The fractions of each phase, $f(\text{MgMn}_2\text{O}_4)$, $f(\text{Mg}_{0.5}\text{Mn}_2\text{O}_4)$, or $f(\lambda\text{-MnO}_2)$, were estimated from the area of each diffraction line as determined by the product of A and w (Table S1) and the calibration curve shown in Fig. S7.

The extent of Mg extraction from MgMn_2O_4 was calculated as

$$x = 0.5 \times f(\text{Mg}_{0.5}\text{Mn}_2\text{O}_4) + 1.0 \times f(\lambda\text{-MnO}_2). \quad (10)$$

Fig. 5 plots x against the amount of H^+ . The solid line in the figure indicates theoretical values calculated from Eq. (10). It is in good agreement with the observed values, indicating that the Mg extraction is caused by a reaction between MgMn_2O_4 and H^+ ions. In other words, MgMn_2O_4 reacts with H^+ ions to form Mn_2O_4 , together with Mg extraction from the solid matrix and Mn^{2+} dissolution into the solution.

Figure 4. Peak fittings of the diffraction line for MgMn_2O_4 digested using HNO_3 solutions of (a) 0.1 M, (b) 0.25 M, (c) 0.3 M, (d) 0.4 M, (e) 0.5 M, and (f) 0.6 M. Black dots: experimental values. Coloured lines: simulated curves of MgMn_2O_4 (blue), $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ (red), and Mn_2O_4 (green).

According to the Eq. (8), a mechanism for Mg extraction from MgMn_2O_4 during acid digestion was proposed and shown in Fig. 6. Firstly, H^+ ions adsorb on the MgMn_2O_4 surface and combine with the surface oxygen ions, and the formed H_2O molecules enter the solution. Then, Mn^{3+} ions in the solid matrix disproportionate into ions with higher and lower oxidation states: Mn^{4+} in the solid matrix and Mn^{2+} in the solution. More specifically, Mn^{3+} ions at the crystal surface are reduced to Mn^{2+} and dissolve in the solution, while those in the solid matrix are oxidised to a tetravalent state. In this situation, two Mg^{2+} ions are extracted from the solid phase to maintain charge neutrality in the solid phase. As a result, $\lambda\text{-MnO}_2$ is formed by Mg extraction from MgMn_2O_4 to maintain the spinel framework. Overall, the solid phase is converted topotactically to $\lambda\text{-MnO}_2$, and two Mg^{2+} and two Mn^{2+} ions dissolve into the solution.

Figure 5. The amounts of Mg extraction from MgMn_2O_4 after acid digestion.

Figure 6. Schematic illustration of the extraction mechanism of Mg^{2+} from MgMn_2O_4 during the acid digestion.

Kinetics of Mg Extraction from MgMn_2O_4 During Acid Digestion

As described above, the Mg extraction reaction in the acid digestion of MgMn_2O_4 is expected to proceed as two-step topotactic two-phase reactions, i.e., the MgMn_2O_4 is converted to the intermediate $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ and then to the final $\lambda\text{-MnO}_2$ phase. According to this reaction scheme, the fraction of each phase should change proportional to the amount of Mg extraction (dashed lines in Fig. 7). The initial phase should disappear and the intermediate phase should increase in the range of $x < 0.5$. At $x = 0.5$, the sample should be completely converted to the intermediate phase, which is gradually converted to the final phase at $x > 0.5$.

However, when the fractions of each phase determined from the XRD patterns are plotted as a function of x (open symbols in Fig. 7), they deviate significantly from the theoretical values. While the amount of MgMn_2O_4 kept decreasing with increasing x , the decrease occurred more slowly than we expected. It is noticed that the final $\lambda\text{-MnO}_2$ phase was formed when $x < 0.5$. The fraction of the intermediate $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ phase was only 30% or less during whole the Mg extraction reaction.

To explain the mismatch between the calculated and observed fractions of each phase during Mg extraction, Mg extraction from MgMn_2O_4 via $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ to form $\lambda\text{-MnO}_2$ was analysed by taking into account the rates of the two reaction steps. We hypothesised that the reaction of MgMn_2O_4 to form $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ was slower than that from $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ to the final $\lambda\text{-MnO}_2$. In other words, the produced $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ was immediately transformed into $\lambda\text{-MnO}_2$. To confirm this hypothesis, acid digestion experiments for various periods of time were examined while fixing the concentration of nitric acid solution at 1.0 M. The fractions of the three phases (MgMn_2O_4 , $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$, and $\lambda\text{-MnO}_2$) were determined by peak deconvolution of the diffraction line at 23° (Fig. 8), as described previously. From the results, the intermediate phase of $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ hardly accumulated during the reaction, thus supporting our hypothesis about the rate-determining step. The initial MgMn_2O_4 disappeared after 5 h, indicating that the Mg

Figure 7. The mole fraction of MgMn_2O_4 (blue circles), $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ (red triangles), and Mn_2O_4 (green squares) as a function of the amount of Mg extraction. Dashed lines indicate the fraction of each phase calculated by assuming two-step two-phase reactions.

extraction reaction was almost complete at this point. The fraction of each phase was plotted against the digestion time in Fig. 9. After starting the reaction, the intermediate phase $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ grew to about 10% and remained that way for a long time without further accumulation. In contrast, the amount of $\lambda\text{-MnO}_2$ kept increasing and was almost linear to the digestion time.

Figure 8. Peak fitting of the diffraction lines for the acid-digested MgMn_2O_4 in 1 M HNO_3 after (a) 1 h, (b) 2 h, (c) 5 h, and (d) 16 h. Black circles: experimental values. Coloured lines: MgMn_2O_4 (blue), $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ (red), and Mn_2O_4 (green).

Figure 9. The mole fractions of MgMn_2O_4 (blue circles), $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ (red triangles), and Mn_2O_4 (green squares) as a function of the acid digestion time. Solid curves indicate the fraction of each phase calculated by assuming that the reaction proceeds in pathways shown in Figure 10.

To discuss the rates of these reactions more quantitatively, the following two pathways were considered: $\text{MgMn}_2\text{O}_4 \rightarrow \text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ (pathway 1) and $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4 \rightarrow \lambda\text{-MnO}_2$ (pathway 2). Pathway 1 represents Mg extraction from the initial MgMn_2O_4 to form the intermediate $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ phase, and pathway 2 represents that of the intermediate phase to the final Mn_2O_4 phase. According to the result of curve fitting (Fig. S8), the fraction of $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ phase was very low, while those of MgMn_2O_4 and Mn_2O_4 can be fitted without significant deviation. Thus, a new reaction pathway in which MgMn_2O_4 is directly converted to $\lambda\text{-MnO}_2$ (pathway 3: $\text{MgMn}_2\text{O}_4 \rightarrow \lambda\text{-MnO}_2$) was introduced in Fig. 9. The data shown in Fig. 9 were analysed based on the assumption that the $\lambda\text{-MnO}_2$ was also directly converted from MgMn_2O_4 .

$$\frac{df(\text{MgMn}_2\text{O}_4)}{dt} = -k_1f(\text{MgMn}_2\text{O}_4) - k_3f(\text{MgMn}_2\text{O}_4) \quad (11)$$

$$\frac{df(\text{Mg}_{0.5}\text{Mn}_2\text{O}_4)}{dt} = k_1f(\text{MgMn}_2\text{O}_4) - k_2f(\text{Mg}_{0.5}\text{Mn}_2\text{O}_4) \quad (12)$$

$$\frac{df(\text{Mn}_2\text{O}_4)}{dt} = k_2f(\text{Mg}_{0.5}\text{Mn}_2\text{O}_4) + k_3f(\text{MgMn}_2\text{O}_4) \quad (13)$$

In these differential equations, k_1 , k_2 , and k_3 are the rate constants for reaction pathways 1, 2, and 3, respectively. The three differential equations were solved numerically. By taking into account pathway 3, the calculated curve could fit the experimental data well, with the rate constants for pathways 1, 2, and 3 being $k_1 = 0.01$, $k_2 = 0.003$, and $k_3 = 0.07 \text{ mol s}^{-1}$, respectively. This indicates that the Mg extraction is fast for pathway 3 (direct extraction to form Mn_2O_4), slow for pathway 1 (MgMn_2O_4 to the intermediate $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$), and extremely slow for pathway 2 ($\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ to $\lambda\text{-MnO}_2$). Pathways 2 and 3 are slower by an order of magnitude than pathway 1. This probably explains the difficulty of Mg extraction by electrochemical methods, because direct reaction of pathway 1 cannot proceed in a topotactic manner due to the large dimensional change. Because the particle surface-area-to-volume ratio increases with the decreasing particle size, these rate constants depend on the particle size of MgMn_2O_4 ; specifically, smaller particles lead to higher rate constants. This suggests that scaling down MgMn_2O_4 particles to the nanoscale is an effective way to facilitate the complete electrochemical extraction of Mg ions from MgMn_2O_4 .

Conclusions

In this study, the mechanism of Mg extraction from MgMn_2O_4 with a tetragonal lattice was examined by chemical extraction (digestion in HNO_3 solution). From the results at various acid concentrations, the Mg extraction reaction proceeds in two-step topotactic two-phase reactions: tetragonal $\text{MgMn}_2\text{O}_4 \rightarrow$ cubic $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4 \rightarrow$ cubic $\lambda\text{-MnO}_2$ (Mn_2O_4). A Mg extraction mechanism during the acid digestion was proposed based on the disproportionation reaction of Mn ions:

The fraction of each phase with respect to x was estimated by peak separation in the XRD data. The results were significantly different from that expected from thermodynamic equilibrium assuming a two-phase reaction. The amount of intermediate $\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$ remained low, while the final product $\lambda\text{-MnO}_2$ was generated since the beginning of the reaction. In order to explain this discrepancy from a kinetic viewpoint, acid digestion experiments were conducted with various reaction times. Analysis of the Mg extraction kinetics was carried out based on the fraction of each phase with respect to the amount of Mg extraction. The results clarified that the Mg extraction reaction involved a direct oxidation reaction of MgMn_2O_4 to form $\lambda\text{-MnO}_2$, in addition to another two-step reaction pathway. The former direct pathway was an order of magnitude faster than the latter. This could explain the deviation of the fraction of each phase from thermodynamic equilibrium.

Conflicts of interest

There are no conflicts to declare.

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