

Synthesis of Spinel-Type Magnesium Cobalt Oxide and Its Electrical Conductivity

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This work devotes to investigate synthesis and electrical properties of spinel MgCo_2O_4 that is considered as a candidate of the cathode materials of magnesium-ion batteries in future. Samples were synthesized by two types of techniques: solid-state reaction and wet process. The crystal structures of the samples were analyzed by X-ray diffraction, and their electrical conductivities were obtained through the dc resistance and ac impedance measurements. By solid-state reaction, sample of a single MgCo_2O_4 phase was not obtained; a sample synthesized at 800°C for 24 h after milling of Co_3O_4 and MgO powder was comprised of dual phases of spinel-type and rocksalt-type structures, and samples synthesized at temperatures higher than 880°C showed a single rocksalt-type phase without electrical conductance. The former sample showed p-type semiconducting behavior as well as spinel-type Co_3O_4 , but its electrical conductivity around room temperature was shown to exceed that of Co_3O_4 . In contrast, a sample consisting of a single spinel-type phase was successfully synthesized by wet process, which exhibited an electrical conductivity of the order 10^{-2} Scm^{-1} , being much higher than those of the samples synthesized by solid-state reaction. Thus, substitution of Co^{2+} in Co_3O_4 with Mg^{2+} is found to enhance the electrical conductivity of the spinel-type phase.

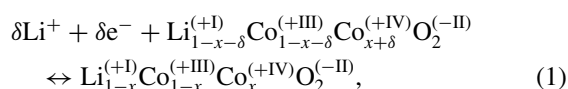
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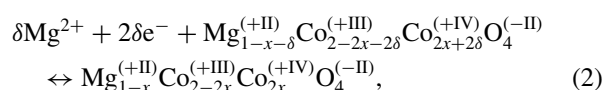
1. Introduction

Lithium-ion batteries are widely used in various mobile electronic devices, because they provide higher energy density, compared to other rechargeable battery systems. At present, LiCoO_2 is commercially available and utilized as an active material of the cathode. The charge-discharge process in a LiCoO_2 cathode proceeds via intercalation and deintercalation of Li. Through the Li-insertion process, the valence of lithium remains monovalent, but that of cobalt instead alters from $\text{Co}^{(+IV)}$ to $\text{Co}^{(+III)}$:



where superscripts (+I), (+IV), etc., denote the apparent valence of the respective ions. Although potential of the current Li-ion batteries are excellent, several problems on safety have been raised recently, for example, firing physiology, dendrite short circuit, reactions with air and water, etc. Hence, safer and comparable powerful rechargeable batteries are strongly demanded.

Magnesium-ion batteries are considered as a new rechargeable battery system comparable to lithium-ion batteries.¹⁻⁴⁾ Magnesium that would be used as an active material for an anode is possible to provide a considerably high energy density due to its high electrochemical equivalence and considerably negative electrode potential. Therefore, if an excellent cathode material can be sought somehow, rechargeable magnesium-ion batteries can be realized in future. In this work, we focus on a spinel-type MgCo_2O_4 as a candidate for a cathode material, in which the following cathode reaction is supposed:



where also in this case the valence of cobalt is expected to change as well as LiCoO_2 . Both of high electronic conductivity and high ionic conductivity are indispensable to be used as a cathode material. It has been reported that the crystal structure of MgCo_2O_4 is partially inverted spinel.⁵⁾ In this work, we devote to investigate the electrical properties of MgCo_2O_4 to examine the feasibility of its use as a cathode material.

2. Experimental

2.1 Sample preparation

MgCo_2O_4 samples were synthesized by two types of techniques: solid-state reaction and wet process. In the solid-state reaction process, powder of MgO and Co_3O_4 with diameter of about 100 μm was prepared as a starting material, then mechanically milled by a ball-mill apparatus (Fritsch Japan), subsequently pelletized by pressing uniaxially, and finally calcined in air. Samples with the atomic ratio of $\text{Mg}/\text{Co} = 1/2$ were calcined in various calcining conditions: at 700°C for 24 h, at 800°C for 24 h, at 880°C for 24 h, and at 1100°C for 1 h. In order to investigate how the cationic ratio affects the crystal structure and electrical conductivity, samples with other atomic compositions of $\text{Mg}/\text{Co} = 3/1$, $1/1$, $1/3$ were also prepared by calcining at 800°C for 24 h. In addition, each powder of MgO and Co_3O_4 was calcined at 800°C for 24 h.

Referring to the literature reported previously,⁶⁻⁹⁾ we have also employed a wet process. First, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used as starting materials. The mixture with the atomic ratio of $\text{Mg}/\text{Co} = 1/2$ was dissolved and stirred in deionized water. By heating the solution on a hotplate at approximately 250–300°C, H_2O and NO_2 were

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removed by evaporation. Then, deposit was washed in water and ethanol, subsequently dried to the powder. After pressing the powder into a pellet and calcining at 700°C or 800°C for 24 h in air, we obtained MgCo_2O_4 samples for the electrical conductivity measurement. The crystal structures were analyzed by X-ray diffraction (XRD) with $\text{Mo K}\alpha$ radiation.

2.2 Electrical conductivity measurements

The electrical conductivity was analyzed by two measurements: dc resistance and ac impedance. Using ionically blocking electrode, only the electronic conductivity contributes to the dc conductivity. By contrast, the ac conductivity involves both electronic and ionic conductivities. Thus, by subtracting the value of dc conductivity from that of ac conductivity, the value of ionic conductivity can be obtained in principle. The present ac impedance measurements were performed in the frequency range from 10 Hz to 7 MHz. The electrical conductivity of the samples synthesized by solid-state reaction was measured at room temperature in air; for the measurements, the top and bottom surfaces of each sample were painted with gold paste. The temperature dependence of electrical conductivity of the samples was measured up to approximately 500°C in a mixed gas atmosphere with the fraction of $\text{Ar}/\text{O}_2 = 4/1$. In addition, by controlling the partial pressure of Ar/O_2 in a mixed gas atmosphere, the dependence of the electrical conductivity on the partial pressure of oxygen was also examined. The electrical conductivity of samples synthesized by wet process was measured (at 80°C) in a mixed gas of $\text{Ar}/\text{O}_2 = 4/1$.

3. Results

3.1 Structure and electrical conductivity of samples by solid-state reaction

Figure 1(a) shows the X-ray diffraction (XRD) profiles of the samples of $\text{Mg}/\text{Co} = 1/2$ synthesized at various temperatures by solid-state reaction. The XRD profile of the sample calcined at 700°C for 24 h is almost unchanged from that of the as-milled sample. The samples calcined at or above 880°C, however, showed a single phase of rocksalt-type structure, in which the peak positions were intermediate between those of MgO and CoO . Thus, when the calcining temperature is above 880°C, the thermal decomposition of Co_3O_4 to CoO occurs; resultingly, an objective spinel-type phase is not obtained. Furthermore, also the sample calcined at 800°C possesses a dual phase composed of spinel-type and rocksalt-type structures, which indicates that the thermal decomposition tends to occur even at 800°C and a homogeneous solid solution of MgCo_2O_4 cannot be attained despite the occurrence of Co and Mg diffusion. Figure 1(b) shows the XRD profiles of the samples with various compositions of Mg/Co synthesized at 800°C by solid-state reaction. As seen in the profiles, the peak intensity ratio of the spinel-type phase to that of the rocksalt phase decreases with increase in the Mg content and, especially, the samples of $\text{Mg}/\text{Co} = 3/1$ and $1/1$ virtually possess a single rocksalt-type phase, and the objective spinel-type phase is not obtained.

The sample preparing conditions, dimensions and density of the samples subjected to the conductivity measurements are listed in Table 1. As shown in the Cole-Cole plots in

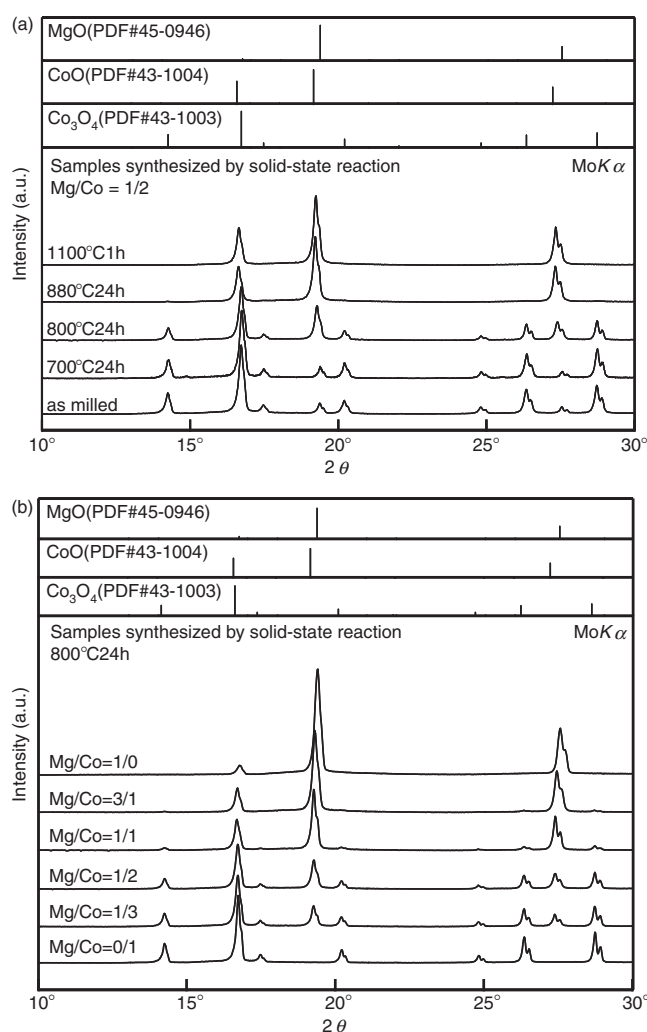


Fig. 1 The X-ray diffraction (XRD) profiles obtained for the samples synthesized by solid-state reaction; (a) for the samples with the atomic ratio of $\text{Mg}/\text{Co} = 1/2$ calcined at various temperatures and (b) for the samples with various atomic ratios of Mg/Co calcined at 800°C.

Fig. 2, among the samples synthesized by solid-state reaction, Sample A ($\text{Mg}/\text{Co} = 1/2$) and Sample B ($\text{Mg}/\text{Co} = 1/3$), have shown appreciable electrical conductance at room temperature. The electrical conductivities measured at room temperature of Sample A were $\sigma_{\text{dc}} = 7.51 \times 10^{-4} \text{ Scm}^{-1}$ in dc and $\sigma_{\text{ac}} = 8.24 \times 10^{-4} \text{ Scm}^{-1}$ in ac, and those of Sample B were $\sigma_{\text{dc}} = 2.44 \times 10^{-3} \text{ Scm}^{-1}$ in dc and $\sigma_{\text{ac}} = 3.36 \times 10^{-3} \text{ Scm}^{-1}$ in ac. As to the other samples with a single rocksalt structure (*i.e.*, with larger Mg/Co ratios), electrical conductance was hardly observed.

Figure 3 shows the Arrhenius plots of electrical conductivity of Sample A ($\text{Mg}/\text{Co} = 1/2$) and Sample C (a pure Co_3O_4 pellet prepared by calcining at 800°C for 24 h). The electrical conductivities of both the samples were elevated with increasing temperature, and such a feature is typical of semiconductor. From the Arrhenius plots, we have obtained the activation energies (band gaps in this case) were evaluated to be $E = 0.0803 \text{ eV}$ for Sample A and $E = 0.123 \text{ eV}$ for Sample C. Figure 4 shows the change in the electrical conductivity by changing the partial pressure of oxygen during the conductivity measurement upon sweeping temper-

Table 1 Sample synthesis conditions (upper table) and sample dimensions, density and porosity of four conductive samples (lower table). Sample A and Sample B were synthesized by solid-state reaction in the ratio of Mg/Co = 1/2, 1/3 at 800°C, respectively. Sample C was Co₃O₄ simply calcined at 800°C. Sample D having an atomic ratio of Mg/Co = 1/2 was synthesized by wet process and subsequently calcined at 700°C. The porosity was evaluated with the theoretical density of MgO (3.56 gcm⁻³), Co₃O₄ (6.054 gcm⁻³) and MgCo₂O₄ (4.96 gcm⁻³). For Sample A and B, the proportions of spinel phase to rocksalt phase were substituted with those before calcining.

Sample	Atomic ratio Mg/Co	Process	Calcining temperature	Phases
Sample A 1/2	1/2	Solid-state reaction	800°C	Spinel & Rocksalt
Sample B 1/3	1/3	Solid-state reaction	800°C	Spinel & Rocksalt
Sample C 0/1 (Co ₃ O ₄)	0/1	Solid-state reaction	800°C	Spinel
Sample D 1/2	1/2	Wet process	700°C	Spinel

Sample	Basal area, S/cm	Thickness, L/cm	Density, ρ/gcm ⁻³	Porosity
Sample A	0.757	0.486	3.13	0.5894
Sample B	0.741	0.468	3.68	0.6692
Sample C	0.420	0.199	3.06	0.5041
Sample D	0.785	0.121	3.48	0.7033

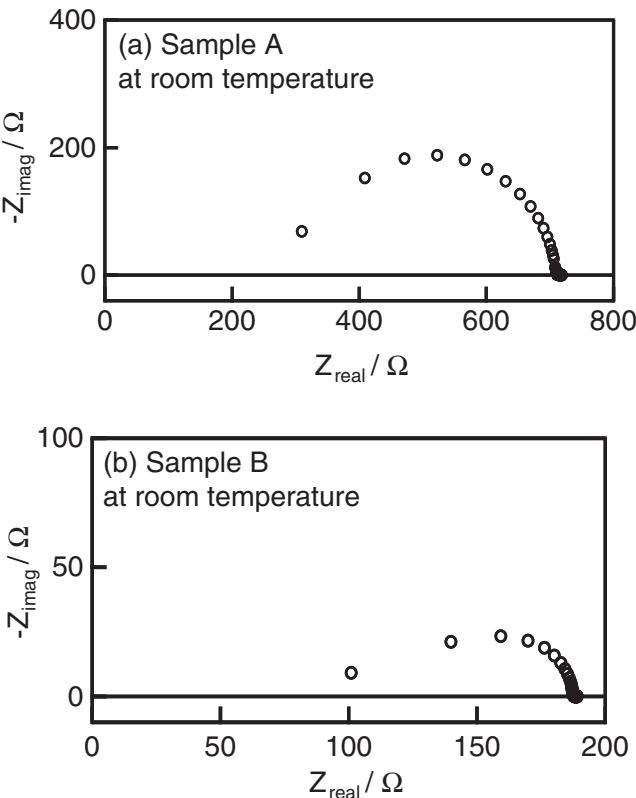


Fig. 2 The Cole-Cole plots of the ac impedance measured for the samples synthesized by solid-state reaction, (a) Sample A (Mg/Co = 1/2) and (b) Sample B (Mg/Co = 1/3). These were measured at room temperature, in the frequency range from 10 Hz to 7 MHz. The ac conductivity is determined as a value of Z_{real} at the cross point with the horizontal axis of $Z_{\text{imag}} = 0$.

ature (the measurement temperature was around 300°C for Sample A and around 500°C for Sample C). It is found that the electrical conductivities of both the two samples are raised in response to increase of partial pressure of oxygen.

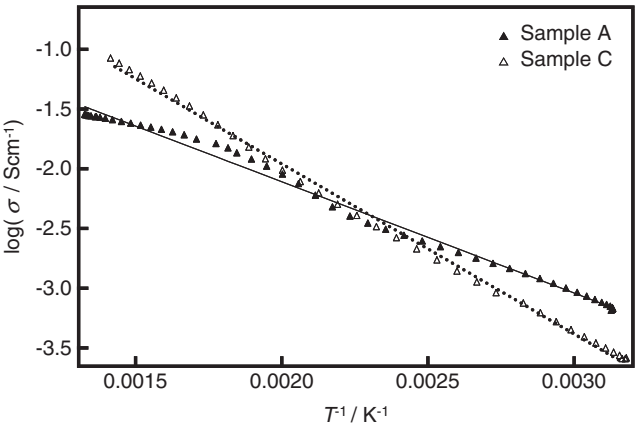


Fig. 3 The Arrhenius plots of the electrical conductivities for Sample A (Mg/Co = 1/2) and Sample C (Co₃O₄). The apparent activation energies (band gaps in this case) are estimated to be 0.0803 eV for Sample A and 0.123 eV for Sample C. At higher temperatures, the electrical conductivity of Sample A deviates from the Arrhenius behavior, which may be due to the lattice vibration effects.

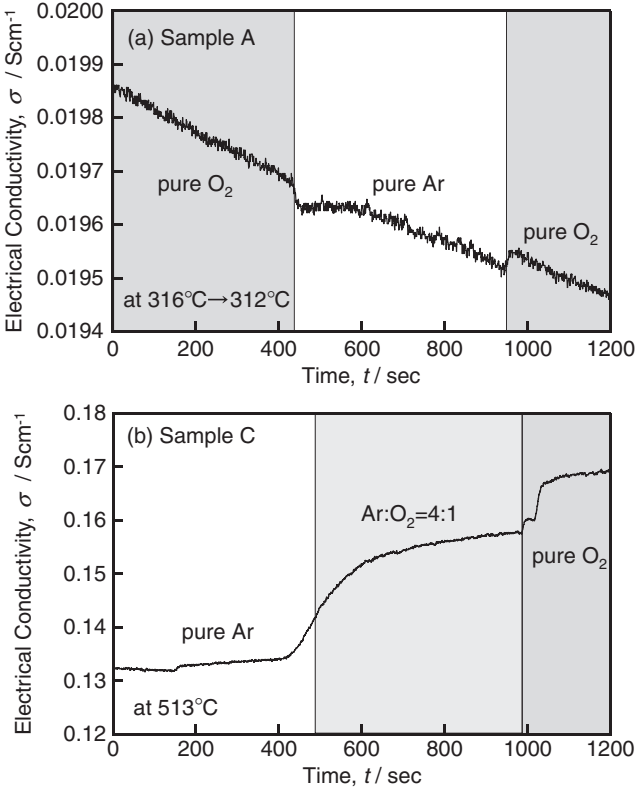


Fig. 4 The dependence of the electrical conductivity on the partial pressure of oxygen for (a) Sample A (Mg/Co = 1/2) and (b) Sample C (Co₃O₄). (a) Partial-oxygen dependence Sample A was measured during slowly decreasing temperature from 316°C to 312°C. (b) Sample B was measured at stable temperature, at 513°C.

3.2 Structure and electrical conductivity of samples by wet process

Figure 5 shows the XRD profiles of the samples synthesized by wet process. The as-synthesized sample is found to have a single spinel-type structure, and also the sample annealed at 700°C after the synthesis (Sample D) shows little change from the profile of the as-synthesized sample. It is

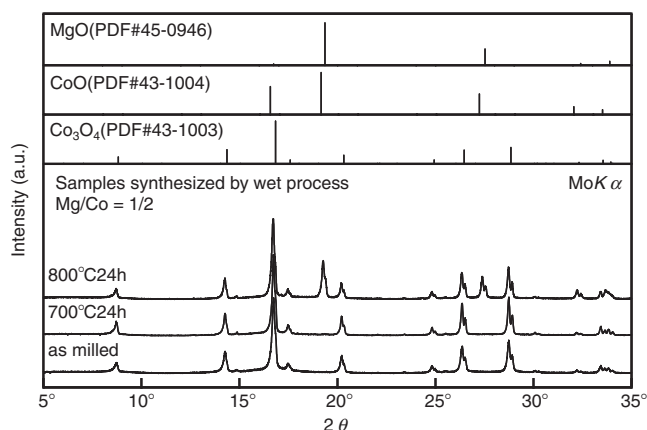


Fig. 5 The X-ray diffraction (XRD) profiles of the samples synthesized by wet process; the as-milled samples and the samples annealed at 700 and 800°C for 24 h.

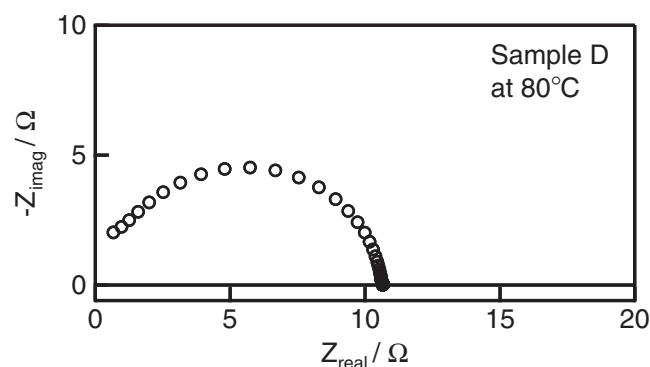


Fig. 6 The Cole-Cole plot of the ac impedance measured for Sample D synthesized by wet process. This was measured at room temperature in the frequency range from 10 Hz to 7 MHz.

noted that the XRD peak positions of the spinel phase of these samples are located at slightly lower 2θ angles compared to those of Sample A, B and C. The lattice parameter of the sample of a single MgCo_2O_4 is determined to be $a = 0.811$ nm, which is slightly larger than the value ($a = 0.808$ nm) of Co_3O_4 . In contrast, the XRD profile of the sample annealed at 800°C shows the dual phases of spinel-type and rocksalt-type structures. Thus, the spinel phase of MgCo_2O_4 is found to be unstable any longer at 800°C. Then, we have measured the ac electrical conductivity of Sample D with a single spinel-type structure. The electrical conductivity of Sample D (measured at 80°C) was $\sigma_{\text{ac}} = 1.45 \times 10^{-2} \text{ Scm}^{-1}$ (see the Cole-Cole plot in Fig. 6), which is much higher than those of Sample A ($\text{Mg/Co} = 1/2$) and Sample C (pure Co_3O_4) measured at the same temperature.

4. Discussion

The samples synthesized higher than 880°C by solid-state reaction have a single rocksalt-type structure; this feature is similar to the thermal decomposition of the spinel-type Co_3O_4 to rocksalt-type CoO occurring at about 900°C.^{9–11)} The fact that the XRD peaks of the obtained rocksalt phase (Fig. 1) are located at intermediate positions between those

of MgO and CoO suggests that Mg^{2+} and Co^{2+} are substituted mutually due to inter-diffusion in these phases. Thus, although inter-diffusion occurs even at about 800–900°C, such temperatures may not be sufficiently high to synthesize an objective spinel MgCo_2O_4 by the solid-state diffusion process, that is, it is actually impossible to obtain a single spinel phase by the solid-state reaction process due to the limitation of the thermal decomposition at about 800°C, as is found from Fig. 1.

Although the samples with a single rocksalt-type structure hardly exhibited electrical conductance, Sample A and Sample B with a spinel-type phase have shown considerable electrical conductance, despite containing an insulative rocksalt phase. The XRD peak positions (in Fig. 1) of the spinel-type phase in these conductive samples is almost the same as those of Co_3O_4 (Sample C), but the electrical conductivities of these samples ($\sigma_{\text{ac}} = 8.24 \times 10^{-4} \text{ Scm}^{-1}$ for Sample A and $\sigma_{\text{ac}} = 3.36 \times 10^{-3} \text{ Scm}^{-1}$ for Sample B markedly exceed that of Co_3O_4 at room temperature ($\sigma_{\text{ac}} = 2.89 \times 10^{-4} \text{ Scm}^{-1}$). Therefore, the spinel-type phase of these samples obtained by solid-state reaction should be different from the starting material Co_3O_4 and probably be a spinel phase of $(\text{Mg}, \text{Co})_3\text{O}_4$. (The reason of the higher electrical conductivity of Sample B with $\text{Mg/Co} = 1/3$ than that of Sample A with $\text{Mg/Co} = 1/2$ is unclear, but this is probably due to the sample porosity difference between the samples; see Table 1.) Moreover, the dependence of electrical conductivity on partial pressure of oxygen (Fig. 4) indicates that Sample A is judged to be also a p-type semiconductor similar to Co_3O_4 (Sample C), because intrinsic oxygen vacancies in oxide substances were generally occupied with oxygen atoms by raising the oxygen pressure for a thermodynamic equilibration, so that the hole carrier increases.

Although the preparation of single spinel MgCo_2O_4 sample by solid-state reaction is practically impossible, it can be attained by wet process. The reason of successful preparation of spinel MgCo_2O_4 is considered to be owing to homogeneous mixture of Mg and Co at ionic or atomic level at low temperature (250–300°C). Sample D with a single spinel MgCo_2O_4 phase shows an excellent electrical conductivity of the order 10^{-2} Scm^{-1} in comparison with Sample A, B, and C. Furthermore, it is emphasized here that the electrical conductivity of MgCo_2O_4 (Sample D) is comparable to that of LiCoO_2 and sufficiently high for use as an electrode of batteries.¹²⁾ Thus, by substituting Mg for Co, the electrical conductivity of spinel $(\text{Mg}, \text{Co})_3\text{O}_4$ is found to be markedly enhanced. The reason is now under investigation from the viewpoint of the electronic structure of the spinel phase.

Finally, we shall address some remarks on the ionic conductivity of magnesium ions. The difference in the ac and dc electrical conductivities, $\Delta\sigma = \sigma_{\text{ac}} - \sigma_{\text{dc}}$, of Sample A is $\Delta\sigma = 0.73 \times 10^{-4} \text{ Scm}^{-1}$ and that of Sample B is $\Delta\sigma = 0.92 \times 10^{-3} \text{ Scm}^{-1}$; the ratio of $\Delta\sigma/\sigma_{\text{ac}}$ of the former is about 9% and that of the latter is about 27%. Thus, since the differences between the ac and dc conductivities are detectable but not so large, only from these results we cannot conclude that the ionic conductivity is indeed present in the samples. In order to check the ionic conductivity

by magnesium ions in the spinel phase, it is necessary to perform further electrochemical experiments after establishing a reversible electrode to allow a redox reaction involving magnesium ion.

5. Concluding Remarks

In this work, we have tried to synthesize spinel-type MgCo_2O_4 by two methods of solid-state reaction and wet process, and have measured the electrical conductivities of the synthesized samples.

- (1) By the solid-state reaction process, a single spinel phase was not obtained; for example, the sample of $\text{Mg}/\text{Co} = 1/2$ synthesized by solid-state reaction at 800°C for 24 h showed a spinel-type phase and a rocksalt-type phase, but when samples are synthesized at higher temperature, only the rocksalt phase was obtained because of the thermal decomposition. The sample of $\text{Mg}/\text{Co} = 1/2$ was a p-type semiconductor as well as Co_3O_4 , but its electrical conductivity exceeds that of Co_3O_4 around room temperature, despite containing an insulative rocksalt-type phase.
- (2) The samples synthesized by wet process successfully showed a single spinel-type phase. Its electrical conductivity of the order 10^{-2} Scm^{-1} was very much higher than the sample synthesized by solid-state reaction, being comparable to that of LiCoO_2 . This sample is promising in terms of its high electrical

conductivity, but for the purpose of use as a cathode, it is necessary to investigate the presence of ionic conductivity.

In future, we will conduct cell performance tests using MgCo_2O_4 samples to examine the feasibility of magnesium-ion batteries, and will further investigate the presence of diffusion of magnesium ions and details of the hole conductivity of the MgCo_2O_4 spinel structure.

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