Preparation and Electrical Properties of $\text{MgO-M}_x\text{O}_y$ ($\text{M}=\text{Fe}, \text{Ni}$) Solid Solution for Magnesium Secondary Battery Cathode

Yu-Ting Siao, Tzer-Shin Sheu*

Department of Materials Science & Engineering, I-Shou University, Taiwan

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Abstract $\text{MgO-M}_x\text{O}_y$ ($\text{M}=\text{Fe}, \text{Ni}$) oxide powders were prepared by a direct drying technique and a co-precipitation method for comparing their physical properties. These dried nitrate precursors or hydroxide precipitates were subsequently calcined at 550°C to transform themselves into oxides, respectively. Calcined oxide powders were sintered at 1100°C to determine their crystal structures, microstructures, and electrical properties at room temperature. As to crystal structures, sintered $\text{Mg}_{1-x}\text{Fe}_x\text{O}_{1+y}$ and $\text{Mg}_{1-x}\text{Ni}_x\text{O}$ ($x=1/3, 1/2, 2/3$) specimens contained spinel and rock salt (NaCl or MgO) crystal structures separately. Electrical resistances of these sintered specimens decrease as the measuring frequency of LCR increases. Sintered specimens obtained from the co-precipitated powders had slightly lower electrical conductivities. At a low measuring frequency of 30-3000Hz, these polycrystalline grains have a grain electrical conductivity of $1.0\text{-}9.0 \times 10^{-4} \text{ S/m}^{-1}$ in the semiconductor range. As to microstructures, grain size of these sintered specimens was $0.1\text{-}1.0 \mu\text{m}$. Relationships between crystal structure, microstructure, and electrical properties were discussed. From this preliminary investigation, these magnesium-containing oxides were a possible cathode material for the secondary magnesium battery.

Keywords Magnesium Oxide Electrode, Electrical Properties, Phase, Crystal Structure, Transition Metal Oxide

1. Introduction

Different types of lithium batteries have been extensively used in our daily lives. But the resources of lithium element (Li) in our earth are very limited. Someday the lithium element is expected to use up, and instead its materials or alloys are probably dependent of its recycling sources. As to

magnesium element (Mg), it has a much higher content than the lithium element in our earth, and also has the same ionic radius as Li^+ . If higher electrical conductive (electronic or ionic) magnesium-containing materials can be developed, magnesium batteries probably can replace the lithium batteries in the coming future.

Currently magnesium batteries have been used as a primary battery like sea water battery, and most of their anode electrodes are magnesium metal alloys with higher corrosion resistance.[1,2] More recently, a few research works have suggested some oxides probably have higher electrical conductivities for the cathode materials in a secondary magnesium battery.[3-6] However, whether a secondary magnesium battery can be commercialized in the market is still under development.

For cheaper obtaining the finer magnesium-containing oxide initial powders, two synthesized methods are chosen to obtain their chemical precursors from the mixed nitrate aqueous solutions in this study. One is a so-called direct drying method, in which the mixed nitrate solution is directly heated to high temperature to let it become the dried nitrate powder, or further convert into oxides. Another method is a co-precipitation method, in which the mixed nitrate solution is titrated by a KOH basic solution up to $\text{pH}>11$ to form hydroxide precipitates. This is because $\text{Mg}(\text{OH})_2$ has a higher solubility product (K_{sp}), in which $K_{\text{sp}}=[\text{Mg}^{2+}]_{\text{aq}}[\text{OH}^-]_{\text{aq}}^2=5.61 \times 10^{-12}$. [7] For obtaining the exact Mg^{2+} composition in the hydroxide precipitates, and also preventing Na^+ in the polyhedral sites of the calcined oxide powders, the KOH basic solution are used instead of an NH_4OH or NaOH basic solution. After dried nitrate or hydroxide precursors being calcined, these calcined powders are sintered to examine and discuss their relationships between crystal structure, microstructure, and electrical property.

2. Materials and Methods

Table 1. Composition of initial nitrate solutions for preparing different magnesium-containing oxide specimens

Specimen*	Initial Composition	4M Mg(NO ₃) ₂ (ml)	1M Fe(NO ₃) ₂ (ml)	1.5M Ni(NO ₃) ₂ (ml)
MF11E	MgFeO _{2+x}	12	48	
MF12E	MgFe ₂ O _{3+x}	7	56	
MF21E	Mg ₂ FeO _{3+x}	17	34	
MN11E	MgNiO ₂	11		29.3
MN12E	MgNi ₂ O ₃	7		37.3
MN21E	Mg ₂ NiO ₃	16.5		22
MF11K	MgFeO _{2+x}	12	48	
MF12K	MgFe ₂ O _{3+x}	7	56	
MF21K	Mg ₂ FeO _{3+x}	17	34	
MN11K	MgNiO ₂	11		29.3
MN12K	MgNi ₂ O ₃	7		37.3
MN21K	Mg ₂ NiO ₃	16.5		22

*The last letter “E” for a direct drying process, and “K” for a co-precipitation method.

2.1. Powder Preparation

Starting chemicals were MgO (99% pure, Riedel-de Haen, Berlin, Germany), Fe(NO₃)₂ · 9H₂O (99% pure, Fullin Chemical Company LTD., Taipei, Taiwan), Ni(NO₃)₂ · 6H₂O (99% pure, Paneac Quimca, Germany), HNO₃ (69-70% pure, Union Chemical Works LTD., Hsinchu, Taiwan). Starting chemical MgO was firstly dissolved in HNO₃ acid and de-ionized water to prepare 4M Mg²⁺ aqueous solution. As to the starting chemicals Fe(NO₃)₂ · 9H₂O and Ni(NO₃)₂ · 6H₂O, they were separately dissolved in the de-ionized water to prepare 1M Fe²⁺ and 1.5M Ni²⁺ aqueous solution, respectively. According to the compositions listed in Table 1, these aqueous solutions were uniformly mixed together for a direct drying process and a co-precipitation method. Specimens were indexed by three letters and two digital numbers. The first two letters “M”, “N”, and “F” represent specimens containing elements Mg, Ni, and Fe separately. By following the first two letters, the first digital number represents the mole number of the first element, and the second one for the second element. As to the last letter, “E” or “K” represents the oxide powders from a direct drying method or a co-precipitation method, respectively.

For a direct drying method, a mixed nitrate solution was dried by a continuously stirring condition inside a beaker under an infrared light illumination, or was dried inside an oven at 100°C overnight. Each batch of dried nitrate powders were calcined at 550°C for 1h with a heating rate 5°C/min to transform into oxides. For a co-precipitation method, a basic KOH solution was put inside a beaker, and then a batch of mixed nitrate solution as shown in Table 1 was titrated with this basic solution to keep pH>11. After continuously filtering and washing with a pH>11 of water/alcohol two times, the filtered hydroxide precipitates was dried. Each batch of dried hydroxide powders were also calcined at 550°C for 1h with a heating rate 5°C/min to transform into oxides.

Calcined oxide powders were slightly grinded, and were then sieved to collect -200mesh powders. A batch of 0.5g -200mesh powders was poured into a cylindrical die to form a cylindrical disc with a diameter of 12mm, under a uniaxial compressive stress of 22MPa. Each cylindrical disc of green powder compact was sintered at 1100°C for 1h with a heat rate of 5°C/min. Sintered specimens were determined their phase existence, microstructures, and electrical properties.

2.2. Phase and Microstructure Observations

Phase existence of sintered specimens was determined from X-ray diffraction patterns (XRDs) at room temperature by an X-ray unit (X’Pert PRO, PANalytical Inc., Netherlands) with a Cu target at 2θ=10-70°, and with a scanning speed of 3°/min plus a sampling interval of Δθ=0.04°. For microstructure observations, a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi Inc., Germany) was used to observe the fracture surface of sintered specimen.

2.3. Electrical Property Measurement

Sintered specimens were determined their electrical properties by using an LCR meter (HP4284L, Kobe, Japan) from a frequency range 30Hz-30MHz at room temperature. Before electrical property measurements, sintered specimens were carbon-coated on both cylindrical top and bottom surfaces. After a reactance/resistance measurement, the electrical resistivity (ρ) is calculated by the following equation

$$R = \rho \cdot t/A$$

where R is electrical resistance (R), A and t are the cross section and thickness of a tested cylindrical specimen, respectively. As to electrical conductivity (σ), it is an inverse value of electrical resistivity, in which σ=1/ρ.

3. Results

3.1. Phase Existence

(a) In the MgO-Fe_xO_y system

As to directly dried powders, X-ray diffraction patterns of their sintered specimens in the MgO-Fe_xO_y system are shown in Fig. 1. All sintered specimens contain a spinel crystal structure MgFe₂O₄. Except for the spinel crystal structure MgFe₂O₄, specimen MF12E has an extra second phase, α -Fe₂O₃, as shown in Fig. 1(a). This α -Fe₂O₃ is referred to JCPDS 33-0664. It indicates the Fe ion probably exists with a trivalent state of Fe³⁺ not Fe²⁺.

As to the co-precipitated powders, X-ray diffraction patterns of their sintered specimens are shown in Fig. 2. All sintered specimens only contain a single phase, MgFe₂O₄ spinel crystal structure. Specimen MF21K has a trace diffraction peak at $2\theta \sim 25^\circ$.

Figure 1. X-ray diffraction patterns for sintered specimens (a) MF12E, (b) MF11E, (c) MF21E, (d) JCPDS 21-1152 (MgAl₂O₄), (e) JCPDS 21-0540 (MgFe₂O₄), and (f) JCPDS 75-0033 (Fe₃O₄). Symbols “▲” are for diffraction peaks of the spinel crystal structure, but symbols “○” are for α -Fe₂O₃.

(b) In the Mg-NiO system

X-ray diffraction patterns of sintered specimens are shown in Figs. 3 & 4. All sintered specimens from directly dried powders or from co-precipitated powders only contain a single phase, rock salt (NaCl) crystal structure like MgO or NiO, respectively. Except for a single rock salt crystal

structure, specimens MN11E, MN12K, MN11K, and MN21K all contain a trace diffraction peak at $2\theta \sim 25^\circ$, which is probably from the silica glass.[8]

3.2. Electrical Property

(a) In the MgO-Fe_xO_y system

Electrical properties of reactance versus resistance as a function of measuring frequency for sintered specimens in the MgO-Fe_xO_y system are shown in Figs. 5 & 6. These specimens were measured from a frequency of 30Hz to 30MHz. As a measuring frequency increases, the resistance of all sintered specimens decreases; however, the reactance of most specimens decreases first, then increases, and finally decreases again. It indicates that the minimum value of reactance appears at a specific measuring frequency. Sintered specimens from co-precipitated powders seem have a slightly higher electrical resistance or reactance than those from directly dried powders.

Figure 2. X-ray diffraction patterns for sintered specimens (a) MF12K, (b) MF11K, (c) MF21K, (d) JCPDS 21-1152 (MgAl₂O₄), (e) JCPDS 21-0540 (MgFe₂O₄), and (f) JCPDS 75-0033 (Fe₃O₄). Symbols “▲” are for diffraction peaks of the spinel crystal structure.

(b) In the MgO-NiO system

Electrical properties of reactance versus resistance as a function of measuring frequency for sintered specimens in the MgO-NiO system are shown in Figs. 7 & 8. The electrical properties of these sintered specimens are very similar to the specimens in the MgO-Fe_xO_y system. For directly dried powders, sintered specimens in the MgO-NiO

system have lower electrical resistances than those in the MgO-Fe_xO_y system. However, for co-precipitated powders, sintered specimens in MgO-NiO system do not show lower electrical resistances than those in the MgO-Fe_xO_y system.

3.3. Microstructures of Sintered Specimens

SEM micrographs of sintered specimens are selectively shown in Fig. 9. These microstructures were observed from their fracture surfaces perpendicular to the free surfaces. Grain size of sintered specimens is ranged from 0.1-1.0 μm, as listed in Table 2. Sintered specimens only contain a very small content of pores with a size smaller than ~0.2 μm.

Figure 3. X-ray diffraction patterns for sintered specimens (a) MN12E, (b) MN11E, (c) JCPDS 44-1159 (NiO), (d) JCPDS 45-0946 (MgO). Symbols “▲” are for rock salt diffraction peaks.

Table 2. Grain size of sintered specimens in the different systems.

Sintered specimen	Grain size (μm)
MF12E	0.3-0.5
MF21E	0.3-1.0
MN11E	0.1-0.5
MN12E	0.5-1.0
MF11K	0.1-0.2
MF12K	0.1-0.2
MN11K	0.5-1.0
MN21K	0.3-0.5

4. Discussion

4.1. Crystal Structure

From XRDs shown in Figs. 1 & 2, sintered specimens in MgO-Fe_xO_y have an MgFe₂O₄ crystal structure, which is an inverse spinel crystal structure. If it is the case, Fe element in this binary oxide system is probably transformed into Fe³⁺, not Fe²⁺. The valence state of Fe element can also be seen from specimen MF12E, in which it contains α-Fe₂O₃, as shown in Fig. 1(a). Based on an inverse spinel crystal structure, Mg²⁺ and 1/2 Fe³⁺ ions are located at the octahedral sites, and the other 1/2 Fe³⁺ ions are located at the tetrahedral sites.

Figure 4. X-ray diffraction patterns for sintered specimens (a) MN12K, (b) MN11K, (c) MN21K, (d) JCPDS 44-1159 (NiO), (e) JCPDS 45-0946 (MgO). Symbols “▲” are for rock salt diffraction peaks.

As to the MgO-NiO system, sintered specimens contain a single rock salt crystal structure (NaCl) like MgO or NiO, as shown in Figs. 3 & 4. From ionic size ratio, it indicates that O²⁻ ions are in the lattice sites, but Mg²⁺ and Ni²⁺ ions are all in the octahedral sites.

From the above cation locations, the electrical properties in the MgO-Fe_xO_y system are closely related with Fe³⁺ in both tetrahedral and octahedral sites. However, in the MgO-NiO system, its electrical properties are related with Ni²⁺ ions in the octahedral sites.

As to an X-ray diffraction peak at 2θ=~25° in specimens MF21K, MN11E, MN12K, MN11K, and MN21K shown in Figs. 2(c), 3(b), and 4(a)-(c), it belongs to silica phase (or glass).[8] This peak has a much larger broadening 2θ angle, which implies this phase having a very small grain size or an amorphous phase. From Sherrer equation $D = 0.9\lambda / (B \cos \theta)$, [9] the diameter of crystalline particle (D) of this phase is 6.5 nm

from the radian (B) of half-width of diffraction peak at $2\theta \sim 25^\circ$. The contamination of silica phase is probably from the glass beaker during powder preparation.

Figure 5. Reactance versus resistance as a function of measuring frequency (30 Hz to 30MHz) for sintered specimens from direct drying powders in the $\text{MgO-Fe}_x\text{O}_y$ system. Symbols “→” represent the directions of higher measuring frequency.

Figure 6. Reactance versus resistance as a function of measuring frequency (30 Hz to 30MHz) for sintered specimens from co-precipitated powders in the $\text{MgO-Fe}_x\text{O}_y$ system. Symbols “→” represent the directions of higher measuring frequency.

In the $\text{MgO-Fe}_x\text{O}_y$ system, from published phase equilibria,[10] specimens MF21E, MF11E, MF21K, and

MF11K should contain a second phase, MgO periclase phase. However, this MgO periclase phase is not found in these sintered specimens. Specimen MF12E but not MF12K contains an extra minor phase $\alpha\text{-Fe}_2\text{O}_3$, but not an exact MgFe_2O_4 . The above deviations of phase region are needed to further study.

Figure 7. Reactance versus resistance as a function of measuring frequency(30 Hz to 30MHz) for sintered specimens from direct drying powders in the MgO-NiO system. Symbols “→” represent the directions of higher measuring frequency.

Figure 8. Reactance versus resistance as a function of measuring frequency(30 Hz to 30MHz) for sintered specimens from co-precipitated powders in the MgO-NiO system. Symbols “→” represent the directions of higher measuring frequency.

Figure 9. SEM micrographs for sintered specimens (a) MF21E, (b) MN12E, and (c) MN21K.

As to MgO-NiO system, MgO and NiO oxides form a complete soluble solid solution at low temperatures.[11] Therefore, sintered specimens with different contents of NiO in MgO from directly dried powders have a rock salt (NaCl) structure like MgO or NiO .

4.2. Electrical Properties

From electrical properties of reactance versus resistance shown in Figs. 5-8, electrical resistance of sintered specimens decreases as the measuring frequency increases, but electrical reactance of most sintered specimens firstly decreases to a minimum value, then increases to a maximum value, and finally decreases again. The location of minimum electrical reactance is related with resonance of grain boundary electrical resistance and electrical capacitance. Therefore, the electrical resistance at the location of minimum electrical capacitance under a low measuring frequency is defined as the grain electrical resistance. Grain electrical resistances and conductivities of sintered specimens are listed in Table 3. Most sintered specimens have a resonance at 100Hz. As a result, sintered specimens have a grain electrical conductivity in the range of $1.0\text{--}9.0 \times 10^{-4} \text{ S/m}$, which is in the semiconductor range.

In most cases, MgO is an insulator; however, MgFe_2O_4 and $\text{Mg}_{1-x}\text{Ni}_x\text{O}$ solid solutions in $\text{MgO-M}_x\text{O}_y$ ($\text{M}=\text{Fe}, \text{Ni}$) are semiconductors. It indicates that Ni^{2+} in the octahedral site for a rock salt structure of $\text{Mg}_{1-x}\text{Ni}_x\text{O}$, and $1/2\text{Fe}^{3+}$ ions in the octahedral sites plus $1/2\text{Fe}^{3+}$ ions in the tetrahedral sites for an inverse spinel MgFe_2O_4 play very important roles for obtaining higher electrical properties.

For directly dried powders, sintered specimens (MF12E & MN12E) with a lower content of MgO in the $\text{MgO-Fe}_x\text{O}_y$ or MgO-NiO system have lower electrical resistances as shown in Figs. 5 & 7, even though specimen MF12E has a second phase $\alpha\text{-Fe}_2\text{O}_3$. Above correlations can also be seen from the corresponding electrical conductivity (from Table 3) versus mole fraction (x) of Ni^{2+} and Fe^{2+} or Fe^{3+} , as shown in Fig.10. The electrical conductivities of sintered specimens increases as the content of transition metal ions (Ni^{2+} , Fe^{3+} , or Fe^{2+}) increases, or alternatively increases as the number of transition metal ions in the polyhedral sites (octahedral or

tetrahedral) increases. If compared with specimen MN21E ($x=1/3$) in the $\text{Mg}_{1-x}\text{Ni}_x\text{O}$ system, specimen MN11E ($x=1/2$) has a lower electrical conductivity even with a lower Mg content. This is because MN11E has a minor content of silica glass at $2\theta \sim 25^\circ$, as shown in Fig. 3(b). Except for the effect of Mg content, sintered specimens in the $\text{Mg}_{1-x}\text{Ni}_x\text{O}$ system have higher electrical conductivities than those in the $\text{Mg}_{1-x}\text{Fe}_x\text{O}_{1+y}$ system, as shown in Fig. 10. It indicates that charge carriers are much easier to move for Ni^{2+} in the octahedral site than the case for the inverse spinel MgFe_2O_4 with $1/2\text{Fe}^{3+}$ in the octahedral site plus $1/2\text{Fe}^{3+}$ in the tetrahedral site.

Figure 10. Relationships between electrical conductivity (σ) and mole fraction (x) of transition metal ion in the $\text{Mg}_{1-x}\text{Fe}_x\text{O}_{1+y}$ and $\text{Mg}_{1-x}\text{Ni}_x\text{O}$ systems.

For co-precipitated powders, almost all sintered specimens contain an impurity diffraction peak at $2\theta \sim 25^\circ$, as shown in Figs. 2 & 4. This impurity diffraction peak is from silica contamination, which is the same as specimen MN11 shown in Fig. 3(b). If compared with the specimens from the directly dried powders shown in Figs. 5 & 7, sintered specimens from the co-precipitated powders have higher electrical resistances shown in Figs. 6 & 8. The same results also can be seen from the electrical conductivities listed in Table 3. Except for the silica contamination, for co-precipitated powders, whether the residue of K^+ affects the electrical properties of sintered specimens is needed to further study.

Table 3. Grain electrical resistances and conductivities of sintered specimens.

Specimen	Frequency (Hz)	Resistance (k Ω)	Conductivity (S/m)
MF11E	100	166.4	4.48*10 ⁻⁴
MF12E	100	120.5	5.51*10 ⁻⁴
MF21E	30	218.6	3.89*10 ⁻⁴
MN11E	100	166.7	5.37*10 ⁻⁴
MN12E	100	88.6	9.26*10 ⁻⁴
MN21E	100	121.1	7.86*10 ⁻⁴
MF11K	1000	558.6	1.54*10 ⁻⁴
MF12K	100	137.4	4.82*10 ⁻⁴
MF21K	3000	909.1	1.03*10 ⁻⁴
MN11K	30	410.4	1.19*10 ⁻⁴
MN12K	30	593.6	1.57*10 ⁻⁴
MN21K	1000	1181.1	2.09*10 ⁻⁴

Overall, sintered specimens in the MgO-NiO system have slightly lower electrical resistances or higher electrical conductivities than those in the MgO-Fe_xO_y system. Except for better electrical conductivities, sintered specimens in the MgO-NiO system also have the same crystal structure in the different content of Mg²⁺. Therefore, if these sintered specimens are used for the electrodes in the magnesium battery, they will not change their crystal structures during a charging/discharging cycle. As a result, this magnesium battery may have a longer performance life.

For electrochemistry property, olivine-type MgMSiO₄ (M=Fe, Mn, Co) cathode materials have been evaluated their performance under an anode and a liquid electrolyte.[12,13] It has shown some promising results of these particular cathode materials in a secondary magnesium battery. As to Mg_{1-x}MxO_{1+y} (M=Ni and Fe; x=1/3, 1/2, and 2/3) in this study, its electrochemical performance will be tested under a combination of a solid electrolyte and a different anode material in the next study.

5. Conclusions

A directly drying technique and a co-precipitation method were used to prepare Mg_{1-x}MxO_{1+y} (M=Ni and Fe; x=1/3, 1/2, and 2/3) oxide powders from mixed nitrate solutions. A basic solution KOH was used for the co-precipitation method, instead of NaOH and NH₄OH, to keep the mixed acid/basic solution up to pH>11 during titration. After drying, these nitrate powders and hydroxide precipitates were calcined at 550°C to transform themselves into oxides, respectively. Subsequently, calcined oxide powders were sintered at 1100°C for 1h. Most sintered specimens had a grain size of 0.1-1.0 μ m.

As to crystal structure, all sintered specimens in the MgO-Fe_xO_y system contained an inverse spinel structure MgFe₂O₄, except for one specimen from directly dried powders with a second phase α -Fe₂O₃. Sintered specimens in the MgO-NiO system had a rock salt crystal structure. Excluding these major phases, a trace silica contamination

was observed in most sintered specimens from co-precipitated powders, especially in the MgO-NiO system.

In the electrical property measurement, as the measuring frequency increased, electrical resistance of sintered specimens was decreasing. However, electrical reactance was firstly decreasing, then increasing to a maximum, and finally decreasing again. At a low measuring frequency of 30-3000Hz, grain electrical conductance of sintered specimen was 1.0-9.0*10⁻⁴S/m, which is in the semiconductor range. For directly dried powders, sintered specimens in the MgO-NiO system had slightly higher electrical conductivities than those in the MgO-Fe_xO_y system. Sintered specimens with a minor silica contamination had higher electrical resistances or lower electrical conductivities, especially for sintered specimens from co-precipitated powders in the MgO-NiO system.

Overall, from phase existence and electrical property, the MgO-NiO system was believed to be a better candidate for the electrode in the magnesium battery because of no phase changes during a charging/discharging cycle.

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