

## Divalent Magnesium Ionic Conduction in the Magnesium Phosphate Based Composites

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By intentionally varying the mixing ratio to the nonstoichiometric region, spontaneous dispersion of the  $Zr_2O(PO_4)_2$  secondary phase was successfully achieved and the  $Mg^{2+}$  ion conductivity was greatly improved by considerably increasing the relative density of the composite and the  $Mg^{2+}$  ion conducting composite showing the highest ion conductivity among the  $Mg^{2+}$  ionic conductors reported was developed.

Monovalent ionic motions in solid electrolytes have been extensively well known and some of the solid electrolytes have been already prevailed in the market. In contrast, in the aspect of divalent ion migration in solids, solid electrolytes with divalent anion, oxide ion( $O^{2-}$ ), are commercially useful as the main constituent of oxygen sensors in various industrial fields. In the case of divalent cations, on the other hand,  $Mg^{2+}$ ,<sup>1-4</sup> alkaline earth cations such as  $Ca^{2+}$ ,<sup>5-7,9</sup>  $Sr^{2+}$ ,<sup>7-9</sup>  $Ba^{2+}$ ,<sup>7-9</sup> and transition metal ions like  $Cd^{2+}$ ,<sup>7,8</sup>  $Zn^{2+}$ ,<sup>7</sup>  $Mn^{2+}$ ,<sup>7</sup> with  $\beta''$ -alumina type structure, have been reported to show an ion conduction in the individual electrolyte. Among various types of divalent cations, magnesium ion has such a peculiar feature to hold a relatively small ionic size and to stably maintain the divalent state. In addition, magnesium metal is applicable for the electrode material of rechargeable batteries with  $Mg^{2+}$  ion conductors and its metal state is considerably stable in comparison to the alkali metal series. However, from the practical application point of view, there still remains such a disadvantage that the  $Mg^{2+}$  ion conductivity is still too low to use as practical electrolytes. This prompts us to develop divalent  $Mg^{2+}$  ion conducting solid electrolytes with higher ionic conductivity. In order to make it possible to install the solid electrolytes in a specific site for application in various practical fields, the electrolyte materials should be stable enough in various atmosphere. From these point of views, the phosphate based compounds with magnesium ions were chosen as the candidate materials for the practical solid electrolytes and its  $Mg^{2+}$  ion conducting properties were studied.

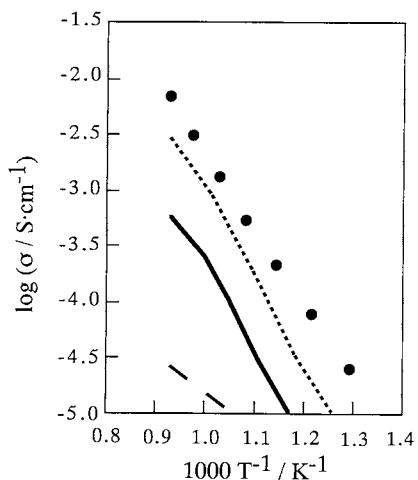
In this letter, the  $Mg^{2+}$  ion conducting solid composites were prepared in such a way to simultaneously disperse the secondary phase during the synthesis process by heating various mixing types of the starting material with a nonstoichiometric ratio.

The mixture of  $MgHPO_4 \cdot 3H_2O$ ,  $ZrO(NO_3)_2 \cdot 2H_2O$ , and  $NH_4H_2PO_4$  was mixed in a ratio of  $(1+x):(4+2x):(5+x)$  and heated at  $300\text{ }^\circ C$  for 5 h and then  $1200\text{ }^\circ C$  for 12 h in air atmosphere. By this heat treatment, zirconium oxide phosphate appears and is microscopically dispersed as a secondary phase in the heated sample and form a composite, since the stoichiometric ratio for the  $MgZr_4P_6O_{24}$  single phase preparation is 1:4:5. The composite powder was pressed and sintered at  $1200\text{ }^\circ C$  for 12 h in air atmosphere. The sample characterization was conducted by X-ray powder diffraction using Cu-K $\alpha$  radiation (M18XHF, Mac Science). The electrical conductivity of the samples was measured by a complex impedance method in the temperature range from 200 to  $800\text{ }^\circ C$ , using the sintered pellet with the Pt electrode on both surfaces with Pt paste. The polarization

measurements were carried out by applying a constant current of  $0.1\text{ }\mu A$  between the two Pt electrodes sandwiching the sample, and the voltage appeared was monitored as a function of time. The DC conductivity was calculated from the voltage, the applied current, the surface area and the thickness of the sample. In order to directly and quantitatively identify the mobile charge carrier in the composite, Tubandt method<sup>10</sup> was performed with two platinum plates as the electrode by applying a voltage of 6 V for 816 h at  $800\text{ }^\circ C$  in air. The relative density of the pellet was calculated by dividing sintered pellet density by the powder density by the Archimedes method.

From the X-ray powder diffraction(XRD) patterns of the composites with  $x=0.2$ , 0.4 and 0.5, all composites prepared were found to be a two phase mixture of  $MgZr_4P_6O_{24}$  and  $Zr_2O(PO_4)_2$  and no solid solution formation was recognized at all. By changing the mixing ratio from 1:4:5 to  $(1+x):(4+2x):(5+x)$  with increasing  $x$ , the intensities of the secondary  $Zr_2O(PO_4)_2$  phase in the X-ray pattern were monotonously increased. With the increase of the  $Zr_2O(PO_4)_2$  content in the  $Mg_{1+x}Zr_4P_6O_{24+x} + xZr_2O(PO_4)_2$  composite, the conductivity monotonously increased and a maximum value of  $6.92 \times 10^{-3}\text{ }\Omega^{-1} \cdot cm^{-1}$  at  $800\text{ }^\circ C$  was obtained for the composite with  $x=0.4$  in  $Mg_{1+x}Zr_4P_6O_{24+x} + xZr_2O(PO_4)_2$ . The relative density of  $MgZr_4P_6O_{24}$ , and the composites with  $x=0.4$  and 0.5 were 93.1, 99.3, 94.6%, respectively, and the Vickers hardness(Hv) of  $x=0$  and 0.4 are ca. 214 and 302, respectively. The considerable increase in the density occurs as the micro-dispersion effect of the  $Zr_2O(PO_4)_2$  sintering additive and increase the electrical conductivity. Further  $Zr_2O(PO_4)_2$  deposition from  $x=0.4$  deteriorates its conducting properties because of the decrease of the density and the increase of insulating  $Zr_2O(PO_4)_2$  volume in the composite. By dispersing the secondary phase simultaneously during the synthesis, the conductivity of the composite is enhanced almost one order of magnitude compared with that of the  $MgZr_4P_6O_{24}$  single phase of without any  $Zr_2O(PO_4)_2$  dispersion.

The temperature dependencies of the electrical conductivity for the composite of  $Mg_{1+x}Zr_4P_6O_{24+x} + xZr_2O(PO_4)_2$  ( $x=0.4$ ), which shows the highest conductivity in the composite series are presented in Figure 1. The electrical conductivity variations for the  $Mg^{2+}$  ion conductors reported before are also depicted in the same figure. The electrical conductivity of the present composite shows one order of magnitude higher in comparison to the single phase reported, in the whole temperature region examined.<sup>1</sup> Compared with the  $Mg_{1.15}Zr_4P_{5.7}Si_{0.3}O_{24}$  solid electrolyte,<sup>4</sup> which has been reported to show the highest  $Mg^{2+}$  ion conducting phosphate based solid electrolytes reported so far, the conductivity of the present composite prepared by a nonstoichiometric mixing method, is still 2.3 times larger. In addition, the conductivity of  $Zr_2O(PO_4)_2$  is also examined and depicted in Figure 1. The conductivity of the oxide phosphate is considerably lower than that obtained by the composite and this result clearly indicates that the  $Zr_2O(PO_4)_2$  particles exist as



**Figure 1.** The temperature dependencies of the electrical conductivity for the composite of  $Mg_{1+x}Zr_4P_6O_{24+x} + xZr_2O(PO_4)_2$  ( $x=0.4$ ) (●). Solid and dot lines are the data reported for  $MgZr_4P_6O_{24}$ <sup>1</sup> and  $Mg_{1.15}Zr_4P_{5.7}Si_{0.3}O_{24}$ ,<sup>4</sup> respectively. Broken line is the data for  $Zr_2O(PO_4)_2$ .

insulating secondary grains in the composite. The activation energy which exhibits the ease of the mobile ion conduction in solids were 135.8 kJ/mol and 141.5 kJ/mol, for the  $Mg_{1+x}Zr_4P_6O_{24+x} + xZr_2O(PO_4)_2$  ( $x=0.4$ ) composite and the  $MgZr_4P_6O_{24}$  single phase, respectively. The higher sinterability results in the relative density enhancement and also in the improvement of the electrical conducting characteristics in the grain boundaries and reduces the activation energy.

By the measurements of the time dependencies of the  $\sigma_{dc}/\sigma_{ac}$  ratio, an abrupt decrease in the ratio was similarly observed in both oxygen( $P_{O_2}$ :  $10^5$  Pa) and helium( $P_{O_2}$ : 4 Pa) atmosphere (Here,  $\sigma_{dc}$  and  $\sigma_{ac}$  represent the conductivity obtained by dc and by ac measurements, respectively.) The same polarization behavior clearly denies the probability of oxide ion conduction in the composites as demonstrated in our previous paper.<sup>11</sup> In addition, the considerable polarizing phenomenon indicates that the mobile species in the composite is neither electron nor hole.

For the purpose of directly and quantitatively identifying the mobile species in the composite, the Tubandt electrolysis method was carried out. After the electrolysis, the change of the weight in anodic part(A+Pt(Anode)), middle composite electrolyte(B), and cathodic part(C+Pt(Cathode)) was measured and tabulated in Table 1. From the phenomenon that the weight increase and decrease was observed in the cathodic and anodic part, respectively, the mobile ion is identified as a cation species. Since the cations in the electrolyte are  $Mg^{2+}$ ,  $Zr^{4+}$  and  $P^{5+}$ , the expected weight change can be calculated from the total coulomb of 4.7 C as listed in the table. From Table 1, the mobile cation species is identified as  $Mg^{2+}$  ion and by the weight change the  $Mg^{2+}$  ion transference number is estimated as a unity.

**Table 1.** The changes in weight after the electrolysis

Tablet	Change in weight of tablet/mg			
	Observed value	Calculated value for various charge carriers		
		$Mg^{2+}$	$Zr^{4+}$	$P^{5+}$
C+Pt(Cathode)	1.00	0.99	1.51	0.70
B	0.06	0	0	0
A+Pt(Anode)	-1.10	-0.99	-1.51	-0.70

From the above mentioned polarization and the Tubandt electrolysis results, the predominant mobile species in the  $Mg_{1+x}Zr_4P_6O_{24+x} + xZr_2O(PO_4)_2$  ( $x=0.4$ ) composite is definitely identified to the divalent magnesium cation in the composite and the conductivity enhancement is predominantly ascribed to the considerable enhancement in its relative density by microscopically dispersing the  $Zr_2O(PO_4)_2$  secondary phase in the composite.

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