

Conductivity Enhancement and Thermal Properties of $AgI-MO_2$ (M = Zr, Si) Composites Using Sol-Gel Derived Aerogels

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AgI-ZrO₂ and AgI-SiO₂ composites were prepared using sol-gel derived aerogels. The conductivity at room temperature showed a maximum for the composition of 0.4AgI·0.6ZrO₂ or 0.4AgI·0.6SiO₂ and was 3.3×10^{-3} S cm⁻¹ for the composite using ZrO₂ aerogels and 1.2×10^{-4} S cm⁻¹ for the composite using SiO₂ aerogels. The diffusion of AgI into the micropores of the aerogel was observed for the ZrO₂ system, suggesting that the diffusion caused a decrease of the crystallinity of AgI and the formation of a high conductive phase of AgI at the AgI-ZrO₂ interface. In the SiO₂-containing system, however, the diffusion was not observed and, hence, the conductivity was an order of magnitude lower than that of the ZrO₂-based system. (© 2002 The Electrochemical Society. [DOI: 10.1149/1.1475687] All rights reserved.

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In recent years there has been much interest in materials which show high ionic conductivity at room temperature, because they have potential application in various electrochemical devices such as all solid-state batteries, sensors, etc.¹ Several approaches have been tried to increase the ionic conductivity of solid electrolytes. For example, the conductivity enhancement in the two-phase composites, which consist of ionically conducting and inorganic oxide (insulator) fine particles, has been studied since Liang reported the effect in LiI-Al₂O₃ composites in 1973.² Among these composites, AgI-based systems, such as AgI-MxOy (MxOy = Al₂O₃,SiO₂,ZrO₂,CeO₂,Fe₂O₃), have been studied extensively.³⁻¹¹

The mechanism of conductivity enhancement is unclear even now, but some models have been proposed. Most of them are based on the fact that the interface of ionic conductors and inorganic oxides plays an important role in conductivity enhancement.⁹⁻¹¹ From this point of view, further conductivity enhancement is expected by controlling ionic conductor-oxide interfaces.

The sol-gel process is known to be a practical method for preparing oxides with a variety of characteristics.¹² In the sol-gel process, wet gels are prepared by hydrolysis of an alcoholic solution of metal alkoxides, and dried gels are porous materials with high porosity and large specific surface area. Thus, sol-gel derived oxides are expected to bring higher conductivity than the usual oxides in two-phase composites, because the large specific surface area of the gels can increase the area of ionic conductor-oxide interfaces, and micropores of the gels must be used as ion conduction pathway.

Aerogels, which are formed by drying wet gels under a supercritical condition of the solvent used, have larger pore size and porosity than xerogels which are formed by drying wet gels under an ambient atmosphere.¹² We have already reported that the pore size of gels influences the conductivity and thermal properties of composites in the AgI-Al₂O₃ system prepared using Al₂O₃ aerogel and xerogel.¹¹ These results indicated that the microstructure of aerogels was more effective than that of xerogels for enhancing the ionic conductivity of the composites. In other AgI-based systems, such as AgI-MxOy (MxOy = SiO₂,ZrO₂,CeO₂,Fe₂O₃), oxides with such large specific surface area or large pore volume have not been used for the preparation of the ion conducting composites.

In the present study, $AgI-ZrO_2$ and $AgI-SiO_2$ composites were prepared using ZrO_2 and SiO_2 aerogels prepared through the sol-gel method. This paper reports their microstructure, electrical, and thermal properties. By comparing the results with the $AgI-Al_2O_3$ aerogel system, the difference in the magnitude of conductivity enhancement in the AgI-ZrO₂ and AgI-SiO₂ systems is discussed.

Experimental

Zirconium tetra-*n*-butoxide, $Zr(O-n-Bu)_4$, was used as a starting material for ZrO_2 aerogel. $Zr(O-n-Bu)_4$ and ethyl alcohol, EtOH, were mixed and stirred at room temperature for 30 min. Ethyl acetoacetate, EAcAc, was added to the solution as a chelating agent and the solution was stirred for 3 h. A water-EtOH mixture was added subsequently drop by drop to the solution for hydrolysis. The sols prepared were kept in closed containers for gelation at 50°C. The molar ratios of EtOH, EAcAc, and H₂O to $Zr(O-n-Bu)_4$ were kept at 10, 1, and 4, respectively. For the preparation of aerogels, the wet gels were aged in EtOH for at least 1 week at 50°C, and the alcohol was renewed several times to wash out the remaining water in the aging process. The aged wet gels were then supercritically dried in an autoclave at about 10 MPa at 270°C, in which the initial pressure of 4 MPa was established with nitrogen gas. In SiO₂ aerogels, tetraethoxysilane, $Si(OC_2H_5)_4$, was used as a starting material. Si(OC₂H₅)₄, EtOH, and 0.01 wt % HCl were mixed and stirred at room temperature for 3 h. The selected molar ratios of EtOH and HCl to $Si(OC_2H_5)_4$ were 5 and 6, respectively. The sols were kept in closed containers at 50°C for gelation. After aging and washing out using the same process for ZrO₂ aerogels, the wet gels were supercritically dried in an autoclave. ZrO₂ and SiO₂ aerogels were heat-treated in air at 400°C for 3 h, at 500°C for 7 h, respectively, and used for the preparation of the composites.

AgI was mixed in an agate mortar with ZrO_2 or SiO_2 aerogels and ground in a planetary ball mill for 15 min. Then the mixture was pelletized to bar shape at a pressure of 400 kg cm⁻². The pellets of the AgI-ZrO₂ composite were heat-treated at 400°C for 3 h and those of the AgI-SiO₂ composite at 500°C for 3 h.

The conductivity was measured on the pellets with Ag pasted electrodes by use of an impedance analyzer (Solartron 1260) in the frequency range from 10 Hz to 8 MHz. All the measurements were carried out under a flow of dry nitrogen atmosphere. The intercept of a semicircle or arc at the real axis of the complex impedance plot was adopted as bulk impedance, including interfacial impedance between particles.

Differential scanning calorimetry (DSC) measurements were carried out by heating and cooling cycles from 30 to 200°C with a Rigaku TA100 DSC. X-ray diffraction (XRD) patterns were obtained using a Rigaku RINT 1100. The Brunauer-Emmett-Teller (BET) specific surface area and pore-size distribution of the heattreated aerogels were studied by the nitrogen adsorption method.

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Figure 1. Pore distribution of ZrO₂ and SiO₂ aerogels.

Results and Discussion

Figure 1 shows the pore size distribution of the ZrO_2 and SiO_2 aerogels prepared in this study. The aerogels have pores with a wide range of size from 1 to 30 nm. The 10-30 nm pores observed in the aerogels are due to the supercritical drying.¹² The specific surface areas of ZrO_2 and SiO_2 aerogels were 150 and 950 m² g⁻¹, respectively. Since ZrO_2 aerogels were partially crystallized during the supercritical drying, the specific surface area of ZrO_2 aerogels was smaller than that of SiO_2 aerogels. Pores of 20-30 nm in size in the aerogel were confirmed to disappear partly with the mechanical



Figure 3. Temperature dependence of the ionic conductivity for the (1-x)AgI·xSiO₂ composites.



Figure 2. Temperature dependence of the ionic conductivity for the (1-x)AgI·xZrO₂ composites.



Figure 4. Composition dependence of the conductivity at 25° C for the (1-x)AgI·xMxOy (MxOy = ZrO₂, SiO₂) composites using oxide aerogels. Conductivity of the AgI-Al₂O₃ aerogel composites is also shown for comparison.

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Figure 5. DSC curves of the (1-x)AgI·xZrO₂ composites and of AgI.

grinding. However, the feature of pore size distribution of the aerogel was basically maintained after the mechanical grinding; the aerogels have pores with a wide range of size, up to 20-30 nm.

Temperature dependences of conductivity for some compositions in the systems (1-x)AgI·xZrO₂ and (1-x)AgI·xSiO₂ are presented in Fig. 2 and 3, respectively. The conductivity of an AgI pellet is also shown for comparison in both figures. In 0.6AgI · 0.4ZrO2 composite (x = 0.4) a jump of conductivity is observed near the α - β transformation temperature of 147°C during heating. The magnitude of the conductivity jump decreased with an increase in x, and almost no jump is observed at x = 0.7, as shown in Fig. 2. During cooling, however, no change in conductivity is observed at 147°C, and the conductivity decreases suddenly at around 130°C in the case of x= 0.4. No drop is observed in the case of x = 0.7. The jump in conductivity during heating and the drop during cooling are due to the α - β transformation of AgI crystals in the matrices. The disappearance of the jump and drop of conductivity during heating and cooling at x = 0.7 is discussed later. At temperatures above 147°C, the conductivity continuously decreased with x. This behavior of conductivity in these composites is basically similar to that of conductivities in the AgI-Al₂O₃ system using an Al₂O₃ aerogel and commercial γ -Al₂O₃.¹¹

In the AgI-SiO₂ system, the jump and drop in conductivity were clearly observed in all the samples. The observation of the jump and drop in conductivity at high AgI contents indicates that the character of the composite in the AgI-SiO₂ system is different from that of the AgI-Al₂O₃ aerogel system we reported so far¹¹ or the AgI-ZrO₂ system prepared in this study.



Figure 6. DSC curves of the (1-x)AgI·xSiO₂ composites and of AgI.



Figure 7. XRD patterns of the 0.4AgI·0.6MxOy (MxOy = ZrO₂, SiO₂, Al₂O₃) composites and of AgI.

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Figure 8. FE-SEM photographs of 0.4AgI $\cdot 0.6$ ZrO₂ composites (a) before and (b) after heat-treatment and 0.4(1-x)AgI $\cdot 0.6$ SiO₂ composites (c) before and (d) after heat-treatment.

The composition dependences of the conductivity at 25°C of AgI-MO₂ (M = Zr, Si) composites are shown in Fig. 4. Results of the AgI-Al₂O₃ system with Al₂O₃ aerogel¹¹ are also shown for comparison. The maximum conductivity is observed at around x = 0.6 in all the systems. The maximum conductivities in the AgI-ZrO₂ and AgI-SiO₂ system are 3.3×10^{-3} and 1.2×10^{-4} S cm⁻¹, respectively. The conductivity of the AgI-ZrO₂ system is about two orders of magnitude higher than that already reported for the same system.⁸ The conductivity of the AgI-SiO₂ system is also about one order of magnitude higher than that of the system reported so far.⁶ The large specific surface area and large pore volume of aerogels must contribute to higher defect densities in space charge regions¹³ and thus these higher values of conductivity were observed.

Figure 5 shows the DSC heating and cooling curves for (1-x)AgI xZrO₂ composites using a ZrO₂ aerogel together with data for AgI crystal for comparison. The DSC curves for the AgI

crystal show the endothermic (at 147°C) and the exothermic peaks (140°C) due to the α - β transformation during heating and cooling, respectively. At x = 0.4, a shoulder at the endothermic peak at 143°C in the heating run and a small exothermic peak at 140°C in the cooling run are observed in addition to the main peaks. These small shoulder and peaks were also observed in AgI-Al₂O₃ composites using an Al₂O₃ xerogel.¹¹ These peaks probably indicate the presence of free AgI, because the ZrO₂ aerogel has a relatively small pore volume compared with Al₂O₃ aerogel in the AgI-Al₂O₃ composite as shown in Fig. 1. Compared with pure AgI crystals, the endothermic peaks for the composites are located at slightly higher temperatures and the exothermic peaks are located at lower temperatures.

Figure 6 shows the heating and cooling curves of DSC for (1-x)AgI·xSiO₂ composites using a SiO₂ aerogel together with data for AgI crystals for comparison. Compared with AgI crystal, the

endothermic peaks during heating are located at slightly higher temperatures and the exothermic peaks during cooling at lower temperatures. In the cooling curve of the SiO₂-based composite, only a large peak with the onset temperature at around 135°C is observed and the onset temperature is not changed with an increase in AgI contents. The peaks observed in the SiO₂-containing composites at around 135-147°C during heating and cooling are due to the α - β transition of free AgI, indicating that most of the AgI crystals are present as free AgI in the composites. The presence of free AgI in the SiO₂ composites corresponds to the large jump in conductivity at around the phase transformation temperature as shown in Fig. 2.

Figure 7 shows XRD patterns of the 0.4 AgI \cdot 0.6 MxOy composites (MxOy = Al₂O₃, ZrO₂, and SiO₂), together with data for AgI crystals for comparison. All the diffraction peaks due to β -AgI are broad in the samples with Al₂O₃ and ZrO₂, while the peaks are sharp for SiO₂-containing composites. This indicates that the average crystallite size or crystallinity of AgI decreases by spreading of AgI along a large surface of Al₂O₃ or ZrO₂ during sintering.¹⁰ In the composites, AgI may present as the mixture of very small crystals, crystals with strong mechanical stress, and amorphous phase of AgI.

Figure 8 shows field emission-scanning electron microscopy (FE-SEM) photographs of the cross-section of the composites based on ZrO₂ aerogels, (a) before and (b) after heat-treatment, and the composites using SiO₂ aerogels, (c) before and (d) after heat-treatment. Before the heat-treatment, AgI grains of 1 μ m in size are observed in the ZrO₂ or SiO₂ matrix and the composite has a dense structure. After the heat-treatment of the ZrO₂-containing composite, some small holes of about 1 μ m in diameter are observed and the AgI grains disappear. This indicates that AgI diffuses into pores of the ZrO₂ aerogels with the heat-treatment, and holes are formed at the location where AgI crystals were originally present. Similar behavior was already observed for the composites in the AgI-Al₂O₃ system using Al₂O₃ aerogel.¹¹ Only a small number of holes are present and AgI grains remain after the heat treatment in the AgI-SiO₂ system.

From these photographs and other results described, the difference in enhancement of the conductivity between Al₂O₃, ZrO₂, and SiO₂ can be explained as follows. In the Al₂O₃ and ZrO₂ aerogels, AgI easily diffuses into the pores upon heat-treatment at 400°C. This diffusion of AgI into pores gives rise to the coverage of Al₂O₃ or ZrO₂ surfaces with AgI, which means the formation of large areas of interface between AgI and the aerogels. This interaction can be explained by the adsorption of Ag^+ cations on the Al_2O_3 or ZrO_2 surface.¹⁰ Since Al_2O_3 or ZrO_2 are ionic crystals, defect concentration in the space-charge region¹³ is rather high, and the highly conductive region is thus formed at the interface between AgI and Al₂O₃ or ZrO₂, respectively. The formation of such large interface areas between AgI and Al2O3 or ZrO2 should lead to a decrease of the average crystallite size or crystallinity of AgI. Due to the decrease in the crystallite size or crystallinity, the XRD pattern of the composites with smaller amounts of AgI showed broad peaks, as shown in Fig. 7. An interaction between AgI and Al₂O₃ or ZrO₂

should result in the suppression of the phase transformation from the α - to β -AgI phase, and thus, the bulk properties of AgI were not observed in the DSC and conductivity measurements.

In the composites with SiO₂ aerogels, AgI did not diffuse into the pores, and free AgI, which does not form effective interface with SiO₂ aerogels, remains in the composites despite the fact that the specific surface area of SiO₂ aerogels is larger than that of ZrO₂ or Al₂O₃, respectively. Since the Si-O bond has more covalent character than the Al-O or Zr-O bonds, defect concentration in the space-charge region is rather small and also AgI, which is an ionic crystal, may have small interactions with the SiO₂ surface. Thus, highly conductive regions do not form at the interface between AgI and SiO₂. This induces the appearance of the bulk properties of AgI in DSC and conductivity measurements, and the enhancement of the conductivity is smaller than Al₂O₃- or ZrO₂-containing composites.

Conclusions

AgI-MxOy (MxOy = ZrO_2 , SiO₂) composites were prepared using the sol-gel derived aerogels. The conductivity of the composites was about one or two orders of magnitude higher than that of reported composites. The diffusion of AgI into the micropores of the aerogel was observed in the ZrO_2 -containing composites and the diffusion brought decrease of crystallinity of AgI and the formation of a highly conductive phase of AgI, probably at around the interface between AgI and ZrO_2 . In the SiO₂-containing system, however, the diffusion was not observed and thus the conductivity was lower by an order of magnitude compared with that of the ZrO_2 system.

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