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XRD AND THERMAL STUDIES OF AgI CONFINED IN nm-SIZE PORES BY FORMING POROUS SILICA–AgI COMPOSITES

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Abstract

To investigate the nm-size dependence of structural and thermal properties for AgI, the formation of composites between AgI and porous silica with controlled pore diameters of 10, 15, 30, and 50 nm was examined. The introduction of AgI within the micropores of the porous silica was performed successfully by a salt-bridge precipitation method with using $AgNO_3$ and KI aqueous solutions. The AgI formed within the micropores was identified to be β/γ-AgI, independent of the pore size of 10–50 nm, by powder X-ray diffractometry. In differential scanning calorimetry, the composites showed thermal anomaly at around 150°C on heating due to the phase transition from β/γ-AgI to α-AgI as in the case of bulk crystalline AgI (T_{trs}=147°C). However, the transition temperature from α-AgI to β/γ-AgI on cooling decreased remarkably with the decrease of the pore size from 50 to 10 nm. The result indicates the possibility for AgI particles with diameter less than 10 nm to exist as α-AgI even below 100°C.

Keywords: AgI, DSC, phase transition temperature, porous silica, powder X-ray diffractometry

Introduction

When the size of materials is restricted to be in nm-order, the temperatures of fusion and of order–disorder type phase transitions are expected to be lowered by the increase of the ratio of atoms, ions, or molecules on the particle surface resulting in the increase of the interfacial energy. Such the decrease of the phase transition temperatures has been observed actually for nm-sized metal and metal-oxide particles [1–3] and for materials confined to micropores of porous substrates [4–6]. This fact suggests the possibility for the materials, which has a useful property at higher temperatures than the ambient temperature as a bulk, to be in the high-temperature disordered phase even at room temperature, which make possible to use the valuable property of the material at room temperature.

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AgI in α-phase is a typical crystalline fast ion conducting material. However, the -AgI is stable only above 147°C [7], and transforms at the temperature to β- or γ-phase, which has no fast ion conducting property. By confining AgI in micropores of porous substrate and restricting the particle size to be in nm-order, the phase transition temperature of the AgI particle might be lower than that of the bulk AgI and the high-temperature phase of α-AgI will possibly be brought to room temperature making AgI as a valuable material for solid-state battery, solid sensor, and so on.

Therefore, at first, we tried to insert AgI in the micropores of porous silica with different pore sizes from 50 to 10 nm by a salt-bridge precipitation method. The composites between AgI and porous silica were successfully formed by the method, and then the structural and thermal properties were investigated of AgI particles confined in the micropores by powder X-ray diffractometry and by differential scanning calorimetry with using the porous silica–AgI composites.

Experimental

Granular porous silica particles in the size of ca. 4 mm with controlled pore diameters of 10, 15, 30 and 50 nm were purchased from Fuji Silysia Chemical Ltd., and were used as porous substrates in this work. The formation of AgI in the micropores of the porous silica was performed by a salt-bridge precipitation method with using $AgNO_3$ and KI aqueous solutions in the following procedure. The apparatus used in the method is shown in Fig. 1. A particle of granular porous silica was set between two glass vessels and fixed by a thermally shrink Teflon tube, forming a cell for the precipitation reaction. Then the

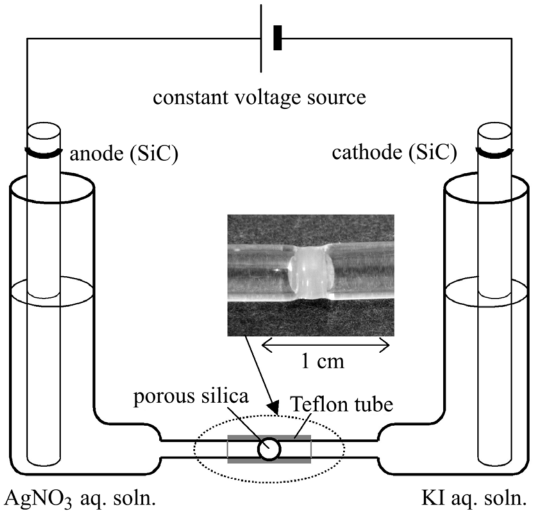

Fig. 1 Schematic drawing of the apparatus used in the salt-bridge precipitation method for the formation of AgI in the micropores of the porous silica particle

cell was steeped in water, boiled gently for 10 min, and cooled to room temperature. This treatment makes the micropores of the porous silica filled with water. After the treatment, the water in the cell was poured out, and 0.1 mol dm^{-3} $AgNO_3$ and 0.1 mol dm^{-3} KI aqueous solutions were put immediately into the two glass vessels, respectively. In the cell, each of the solution penetrates through the micropores of the porous silica and reacts with the other, resulting in the precipitation of AgI in the pores. An electric field was applied between the solutions to accelerate the formation of AgI in the pores. The electric field strength was controlled between 15 and 25 V m^{-1} dependent on the pore sizes for effective formation of AgI precipitate within the porous silica particle. After the formation of AgI within the micropores, the porous silica particle was taken off from the cell, washed in boiled water for the exclusion of unreacted $AgNO_3$ and KI from the pores, then dried in an outgassed desiccator, and used as the sample for powder X-ray diffractometry and differential scanning calorimetry (DSC).

The powder X-ray diffractometry was performed at room temperature by Rigaku Denki RAD-2C diffractometer with using CuK_α line. DSC was carried out by Perkin Elmer Pyris1 differential scanning calorimeter in the temperature range between 20 and 200°C with heating and cooling rates of 10°C min^{-1}.

Results and discussion

Figure 2 shows the time development of AgI formation within the porous silica particle after filling the glass vessels with $AgNO_3$ and KI aqueous solutions, respectively, and applying the electric field between them. After several minutes from the start of the reaction, AgI precipitation layer began to be observed, as seen in Fig. 2b, in the middle of the particle, then the AgI precipitation layer developed in its thickness to the KI solution side with time. Figure 3 is a photograph of the cross section of the porous silica particle after the precipitation reaction of AgI. A band-shaped AgI precipi-

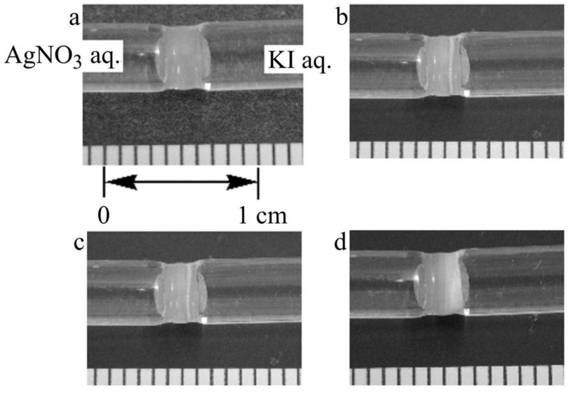

Fig. 2 Time development of AgI formation within the porous silica particle with controlled pore diameter of 30 nm in the salt-bridge precipitation reaction: a – just after the start of the reaction; b – 10 min after the start of the reaction; c – 60 min after the start of the reaction; d – 4 h after the start of the reaction

tation region was observed inside of the particle, clearly indicating the successful formation of AgI in the micropores of the porous silica by the present salt-bridge precipitation method. In porous silica with different pore sizes, AgI formation was observed to proceed in the same manner, and AgI was confirmed to form in the micropores of the porous silica.

Since the AgI precipitation region had the band shape in the porous silica particle, the particle was filed to the AgI precipitation region with sandpaper and tried on the

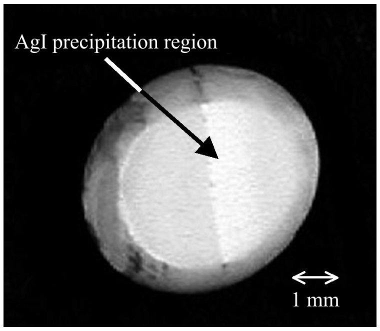

Fig. 3 Photograph of the cross section of the porous silica particle with controlled pore diameter of 50 nm after the salt-bridge precipitation reaction of AgI

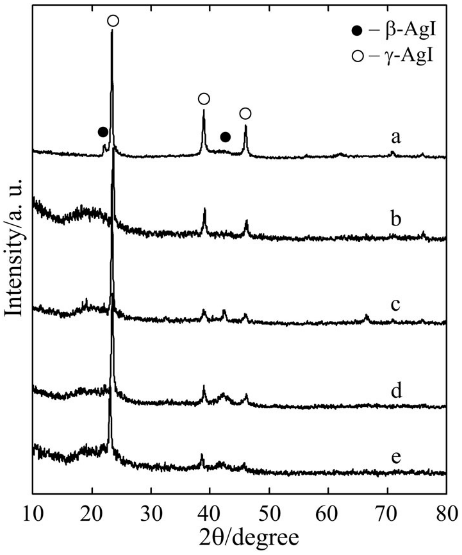

Fig. 4 Powder X-ray diffraction patterns of AgI crystallites (a) and of the AgI precipitation region in the porous silica particles (b – e): a – AgI crystallites formed by the precipitation reaction between $AgNO_3$ and KI aqueous solutions with the concentration of 0.1 mol dm^{-3}; b – AgI precipitation region in the porous silica particles with controlled pore diameter of 50 nm; c – with controlled pore diameter of 30 nm; d – with controlled pore diameter of 15 nm; e – with controlled pore diameter of 10 nm

powder X-ray diffractometry. All the samples with different pore sizes exhibited the diffraction peaks attributable to β- and γ-AgI, as shown in Fig. 4. No other significant peak was observed in the X-ray diffractions, although the peaks due to β/γ-AgI were overlapped with halo pattern due to amorphous silica of the porous silica substrates.

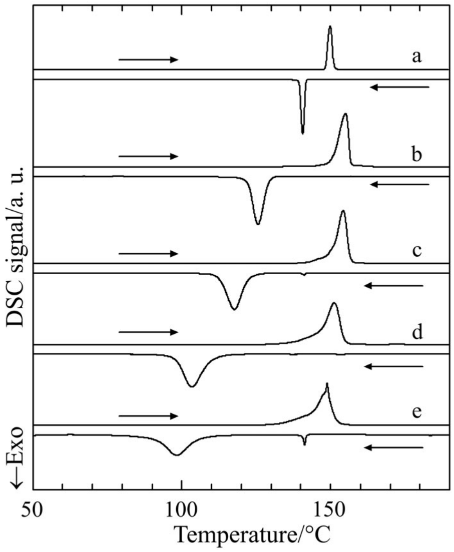

Fig. 5 DSC results for AgI crystallites (a) and for the porous silica–AgI composites (b – e): a – AgI crystallites formed by the precipitation reaction between $AgNO_3$ and KI aqueous solutions with the concentration of 0.1 mol dm^{-3}; b – the composite of the porous silica with controlled pore diameter of 50 nm; c – with controlled pore diameter of 30 nm; d – with controlled pore diameter of 15 nm; e – with controlled pore diameter of 10 nm

DSC measurements were also performed to the samples used in the X-ray diffractometry. The sample was put in an aluminum pan, and the pan was crimped with an aluminum cover gently without crushing the sample in it. Figure 5 shows the DSC results for the samples with different pore sizes along with that for bulk AgI crystallites.

In heating run, all the samples exhibited endothermic effect at around 150°C. This thermal anomaly is reasonably considered due to the order–disorder phase transition from β/γ- to α-phase of crystalline AgI confined in the micropores of the porous silica [7]. The endothermic anomaly was observed to broaden in temperature with the decrease of pore sizes from 50 to 10 nm, with a small decrease of the peak temperature. In the sample with the pore size of 10 nm, a sharp endothermic peak was observed overlapping to the broad peak. A sharp exothermic peak was also observed on cooling as a companion to the endothermic peak on heating. These are well corresponding to the thermal anomaly of bulk AgI crystallites, and thus considered to be due to the AgI crystallites formed on the surface of granular silica particle. In the samples with pore sizes of 50, 30 and 15 nm, the endothermic peak was observed at slightly higher temperature than that in the bulk AgI crystallites. In the case of AgI crystallites formed in the micropores of porous silica, thermal conduction is rather hindered by the amorphous silica surrounding them due to the low thermal conductivity of amorphous silica, resulting in the delay of temperature increase at the position of AgI crystallites in the micropores on heating. The slight increase of the peak temperatures of the endothermic effect in those samples is considered to be due to the delay of the temperature increase, and the actual phase transition temperatures of AgI in the porous silica–AgI composite might be lower than that for the bulk AgI crystallites or the same.

In cooling runs, on the other hand, all the samples showed exothermic anomaly due to the phase transition of AgI crystallites from α- to β/γ-phase. The exothermic peak temperature was observed to become lower remarkably with the decrease of pore sizes and thus the particle sizes of AgI crystallites. It should be contrasted with the small change of the endothermic peak temperatures in heating runs with the change of the AgI particle size. The broadening of the exothermic anomaly in temperature was also observed with the decrease of AgI particle size.

In the DSC for the porous silica–AgI composites, the thermal anomaly due to the phase transition of AgI was observed as the broadened endo or exothermic peak. Thus the phase transition temperature, T_{trs}, was decided as the peak temperature of the thermal anomaly in the DSC curve, and plotted in Fig. 6 as the function of the AgI particle size.

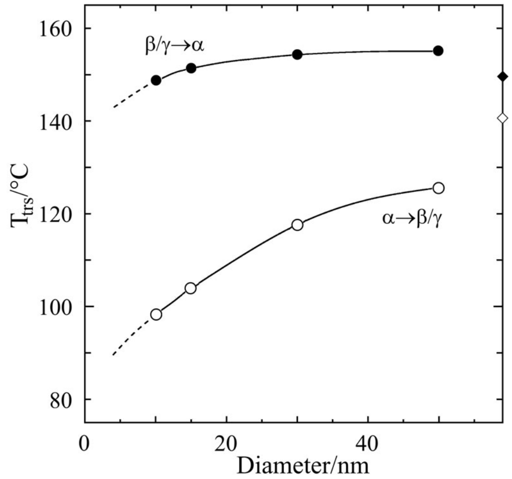

Fig. 6 Particle size dependence of the phase transition temperature, T_{trs}, of AgI confined in the micropores of porous silica with controlled pore diameters (●,○) and of AgI crystallites formed by the precipitation reaction between $AgNO_3$ and KI aqueous solutions with the concentrations of 0.1 mol dm^{-3} (◆,◇) determined from the DSC measurements; closed marks represent the results for β/γ to α phase transition observed in heating runs, and open marks for α to β/γ phase transition in cooling runs

In this work, we tried to insert AgI inside of micropores of porous silica by the salt-bridge precipitation method, and succeeded to fill the micropores with AgI crystallites. After the formation of AgI precipitation layer within the particle of porous silica in the precipitation reaction, the AgI precipitation region was observed to develop as a thickening of the layer into the KI solution side. Similar precipitation manner of AgI crystallites has been reported in the formation of porous Al_2O_3–AgI composites [8], and it can be concluded that Ag^+ ions diffuse more efficiently than I^- ions from $AgNO_3$ solution side to that of KI in the AgI precipitate formed within the micropores, even though the Ag^+-ion conductivity of β- and γ-AgI is low in the order of 10^{-5} S cm^{-1} at room temperature [9]. The salt-bridge precipitation method employed here is considered to be useful not only for AgI but also for other salts with low solubility to the used solvent for the insertion into the micropores of porous substrates.

The powder X-ray diffraction patterns observed for AgI confined in the micropores of the porous silica were almost identical to that of bulk AgI crystallites independently of the pore size, and no other diffraction peak, e.g. due to α-AgI which is the high-temperature disordered phase of crystalline AgI, was exhibited. This result shows that the AgI crystallite with the diameter of 10 nm still has the same structural property as bulk AgI crystal, even though such the small AgI crystallite includes only ~10^4 of Ag^+ and I^- ions, respectively, and is formed by only ~10^{-20} mol of AgI.

In the heating run of DSC for β/γ to α phase transition of AgI within the micropores of the porous silica, the phase transition temperature, T_{trs}, was observed to decrease slightly with decrease of the pore size and thus the AgI particle diameter from 50 to 10 nm. However, T_{trs} for α to β/γ phase transition was observed, in the cooling run of DSC, to be brought lower with the decrease of the AgI particle size from bulk to the diameter of 50, 30, 15 and 10 nm. This result exhibits that α-AgI particles restricted in their size of nm-order can be supercooled easily below T_{trs} of the bulk. The facility of supercooling α-AgI largely depends on the particle size of AgI becoming easier with decrease of the particle size from 50 to 10 nm. The AgI-particle size dependence of T_{trs}, shown in Fig. 6, indicates that α-AgI is stabilized even below 100°C as the supercooled phase in AgI particles with diameter of 10 nm, and suggests the possibility for AgI with the particle size less than 10 nm to be existed as α-AgI much lower temperatures. The α to β/γ phase transition is a typical disorder–order type one, and proceeds through the nucleation of the ordered phase and the growth of the nucleus in its size. The nucleation rate is defined as a frequency for emergence of nuclei in a unit volume of materials, and thus the increase of the facility in the supercooling of α-AgI is considered to be owing to the retardation of the nucleation of the ordered phase of β/γ-AgI with the decrease of the AgI particle size.

Conclusions

In this work, we tried to insert AgI inside of micropores of porous silica by the salt-bridge precipitation method in order to investigate the nm-size dependence of structural and thermal properties for AgI. The attempt resulted in a successful formation of the porous silica–AgI composites, with exhibiting the usefulness of the salt-bridge precipitation method.

The AgI formed within the micropores was identified to be β/γ-AgI by powder X-ray diffractometry independent of the pore size of 10–50 nm, and no significant change was observed in the phase transition temperature, T_{trs}, of β/γ to α phase transition on heating in DSC. However, T_{trs} from α-AgI to β/γ-AgI on cooling decreased remarkably with the decrease of the pore size, indicating the possibility for AgI particles with diameter less than 10 nm to exist as α-AgI even below 100°C.

It is interesting that T_{trs} of β/γ to α phase transition did not change so much with the change of AgI particle size, differently from that of to β/γ phase transition. The origin of this difference is not clear at present. To give an explanation for the difference, investigations are needed for precise information about the interaction between silica and AgI at the wall of the micropores. Such the studies are in progress in our laboratory by chemical modifications of the surface in micropores of porous silica.

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