

Effect of plastic deformation on ionic conduction in pure AgI and AgI–Al₂O₃ composite solid electrolytes

Su-II Pyun *, Joon-Sung Bae

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong Dong, Yusong Gu, Daejeon, 305-701 South Korea

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Abstract

The ionic conductivities of pure silver iodide and silver iodide–(10–40 mol%) alumina composites used as solid electrolytes are determined at room temperature by a.c. impedance spectroscopy as a function of compression pressure and annealing temperature. The ionic conductivities of both the pure and the composite silver iodide specimens increase with increasing compression pressure. This suggests that structural defects acting as conduction paths are generated in abundance by the plastic deformation. The mechanical strength of the as-deformed pure silver iodide specimen is decreased drastically by annealing at 413 K, whereas that of the as-deformed composite specimens remains virtually unchanged. This indicates that the deformation-induced defects are present largely as dislocations. The ionic conductivity of the as-deformed pure silver iodide specimen determined during annealing at 323 K decreases with annealing time, whereas the conductivities of the as-deformed composite specimens are practically unchanged. It is concluded that the removal of the deformation-induced dislocations during annealing is impeded by dispersed alumina particles.

Keywords: Solid-state batteries; Composite solid electrolytes; Plastic deformation; Silver iodide

1. Introduction

Composite solid electrolytes with appreciably high ionic and negligible electronic conductivity are attractive materials for solid-state batteries and sensors. Their higher ionic conductivities as compared with the pure electrolyte phase are believed to originate essentially from the electrolyte matrix/dispersoid interface [1–3]. Two general types of models have been proposed for this behaviour in terms of (i) an increased concentration of charge carriers in the space-charge region near the interface between the electrolyte matrix and dispersed oxide particles [2,4], and (ii) an enhanced ionic mobility along the interface [5].

The ionic conductivities of AgI–oxide composites are enhanced by the incorporation of insulating dispersed oxide particles below the α/β transformation temperature of 420 K [6]. Although the above two models have been adopted widely, they cannot account clearly for the abnormally high

ionic conductivity observed in an AgI–Al₂O₃ composite solid electrolyte.

It has been reported that the dislocation generated by the plastic deformation influences significantly the ionic conductivity of silver halides such as AgCl [7] and AgBr [8]. Since AgI has a relatively low yield-strength, the AgI phase contained in an AgI–Al₂O₃ composite undergoes a severe plastic deformation during compression.

The present study was undertaken to evaluate the ionic conduction in pure AgI and AgI–Al₂O₃ composite solid electrolytes prepared under compression as a function of the degree of plastic deformation. For this purpose, the ionic conductivities of both pure AgI and AgI–Al₂O₃ composite specimens previously subjected to plastic deformation were measured at room temperature (by using a.c. impedance spectroscopy) as a function of compression pressure and annealing temperature. The ionic conductivities of both the as-deformed pure and composite AgI specimens were also determined with a.c. impedance spectroscopy during annealing at 325 K. The crystal structure and mechanical strength of the as-deformed, annealed pure AgI and AgI–Al₂O₃ com-

* Corresponding author. Tel: (82) 42-869-3319; Fax: (82) 42-869-3310; e-mail: sipyun@sorak.kaist.ac.kr.

posite specimens were examined by both X-ray diffractometry (XRD) and compression testing.

2. Experimental

High purity AgI (Aldrich, USA, 99.999%) and α -Al₂O₃ (High Purity Chem., Japan, 99.9%, 0.3 μ m) powders were thoroughly mixed in a ball mill after accurately weighing the powders to have different alumina contents (0–40 mol% Al₂O₃). Each powder mixture was compressed in a steel die under a pressure of 100 to 550 MPa to form a disc of 1.2 cm in diameter and 0.1 to 0.15 cm in thickness. The as-deformed specimens were annealed at various temperatures below 420 K for 20 min in vacuum and then air-cooled; note, AgI is transformed from the β -phase to the α -phase (superionic conducting phase) at 420 K [6]. The annealed specimen was always previously subjected to plastic deformation. The XRD patterns of the powder mixture, as-deformed and annealed specimens were obtained for a scanning angle range of $2\theta=20^\circ$ to 50° by using an automated Rigaku X-ray diffractometer.

In order to investigate the mechanical behaviour of the as-deformed, annealed pure and composite AgI specimens, compression tests were made with cylindrical specimens of 1.0 cm in diameter and 0.6 to 0.8 cm in length by using an Instron universal testing machine at a constant strain rate of 0.05 min^{-1} .

In order to determine the ionic conductivities at room temperature of both the pure and the composite AgI specimens, a.c. impedance measurements were carried out over a frequency range of 10^2 to 10^6 Hz by using an impedance analyser (Zahner IM 5D). For a.c. impedance measurements, a colloidal carbon paint was applied to both sides of the disc specimens. The variation in ionic conductivity of the as-deformed pure and composite AgI specimens was measured as a function of time during annealing at 323 K. This involved the use of a silicon oil bath that was maintained at the required temperature. The ionic conductivities at 323 K were determined from the value of the real impedance, Z' , obtained at a frequency of 10 kHz.

The specimen preparation, mechanical test and a.c. impedance measurements were made under dark conditions, in order to prevent photo-decomposition of the AgI.

3. Results and discussion

The XRD patterns of the powder mixture, as-deformed and annealed AgI composite specimens containing 20 mol% (13 vol.%) Al₂O₃ are presented in Fig. 1(a)–(c), respectively. The XRD peaks of the dispersed Al₂O₃ particles do not appear for this comparatively low content of Al₂O₃. The XRD pattern of the powdered composite AgI specimen revealed that the hexagonal β -AgI and cubic γ -AgI phases co-exist in the specimen. The XRD peaks of β -AgI are found to disappear from the as-deformed composite AgI specimen. This indicates that the phase transformation of β -AgI to γ -AgI occurs via the

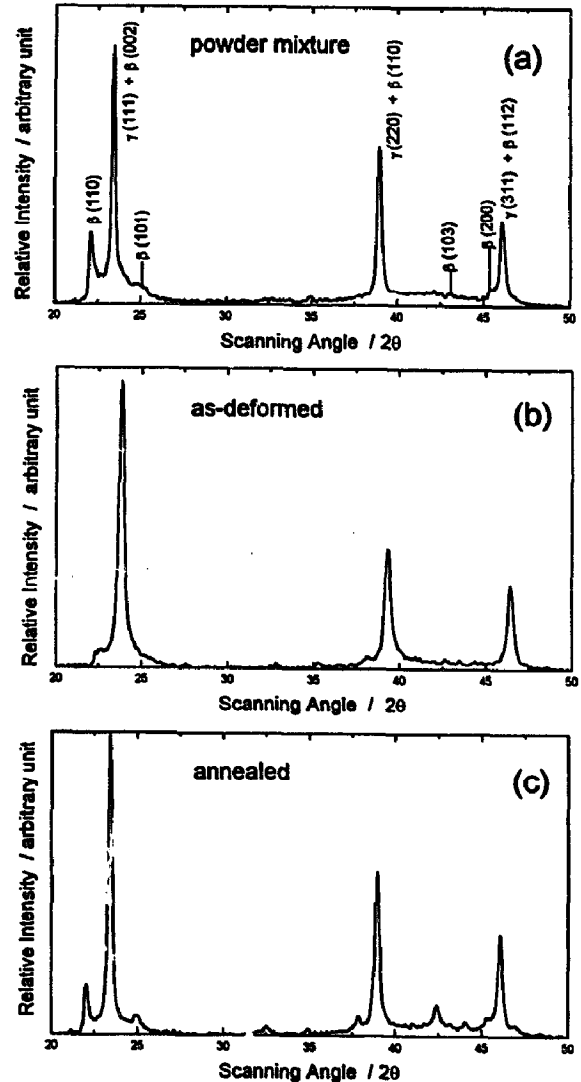


Fig. 1. X-ray diffraction patterns for AgI containing 20 mol% Al₂O₃: (a) powder; (b) as-deformed at 550 MPa, and (c) annealed at 413 K for 20 min. The annealing treatment was preceded by plastic deformation at 550 MPa.

plastic deformation of AgI particles, as previously reported by Mrgudich [6]. The XRD peaks of the as-deformed specimen move to higher diffraction angles (2θ) and become broader as compared with those of the powdered and annealed specimens. This suggests that the AgI particles within the AgI–Al₂O₃ composite have been subjected to a non-uniform deformation.

Typical impedance plots measured at room temperature for the as-deformed, annealed pure AgI and AgI–20mol% Al₂O₃ composite specimens are presented in Fig. 2(a) and (b), respectively. Each impedance spectrum exhibits a high-frequency arc due to an ionic conduction through the solid electrolyte and a low-frequency line that arises from blocking of ionic movement at the solid–electrolyte/carbon–electrode interface.

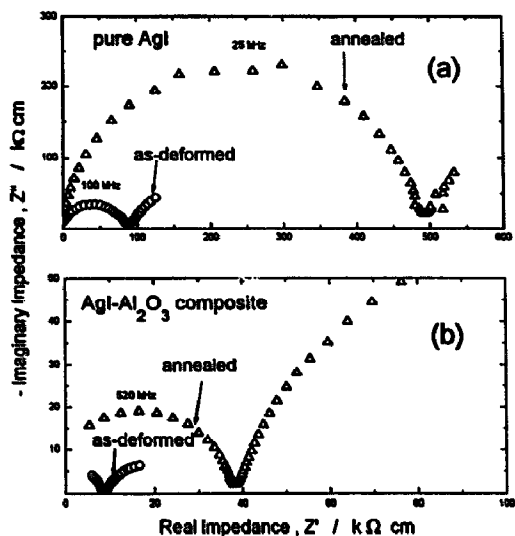


Fig. 2. Typical impedance plots obtained at room temperature from: (O) as-deformed at 550 MPa, and (Δ) annealed at 413 K for 20 min. (a) Pure AgI specimen, and (b) AgI-20mol%Al₂O₃ composite specimen. The annealing treatment was preceded by plastic deformation at 550 MPa.

The ionic conductivities of pure and composite AgI containing 20 mol% Al₂O₃ were determined at room temperature from the magnitude of the high-frequency arc. The result is presented in Fig. 3 as a function of compression pressure. The ionic conductivities of both specimens increase markedly with increasing compression pressure.

It is generally known [9] that the conduction mechanism in pure AgI involves the motion of Frenkel defects that consist of Ag⁺ ion vacancies and interstitial Ag⁺ ions. During compression of a powder mixture of AgI and Al₂O₃, a number of deformation-induced defects such as dislocations and point defects around the dislocations are produced by the plastic deformation of the AgI particles. The dislocations are known to provide the high ionic conductive paths [4,8] and the point defects around the dislocations act as the charge carriers for

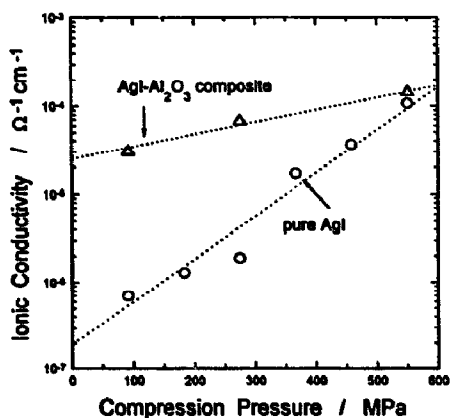


Fig. 3. Ionic conductivity at room temperature vs. compression pressure: (O) as-deformed pure AgI specimen, and (Δ) as-deformed AgI-20mol%Al₂O₃ composite specimen.

ionic conduction. Hence, these deformation-induced defects enhance the ionic conductivities of the as-deformed AgI specimens.

According to Cochrane and Fletcher [9], if the compression pressure exceeds about 10 MPa, the lower conductive β -AgI phase is entirely transformed to the higher conductive γ -phase, irrespective of the proportion of the β - and γ -phase contained in the original AgI powder specimen. Thus, the phase transformation that occurs under 10 MPa compression may raise the ionic conductivities of both the pure and the composite AgI specimens. In fact, the ionic conductivities of both kinds of AgI specimens increase with increase in compression pressure even above 10 MPa. This means that the increase in ionic conductivities of the pure and composite AgI specimens is due to appreciable generation of structural defects by the plastic deformation rather than to the phase transformation of the less conductive β -AgI phase to the more conductive γ -AgI phase.

It should be noted that the ionic conductivities of the pure and composite AgI specimens deformed at a compression pressure of 550 MPa have almost the same value, viz., about $1 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$. This suggests that the deformation-induced defects play a principal role in the ionic conduction in the as-deformed specimens, irrespective of the content of the dispersed Al₂O₃ particles.

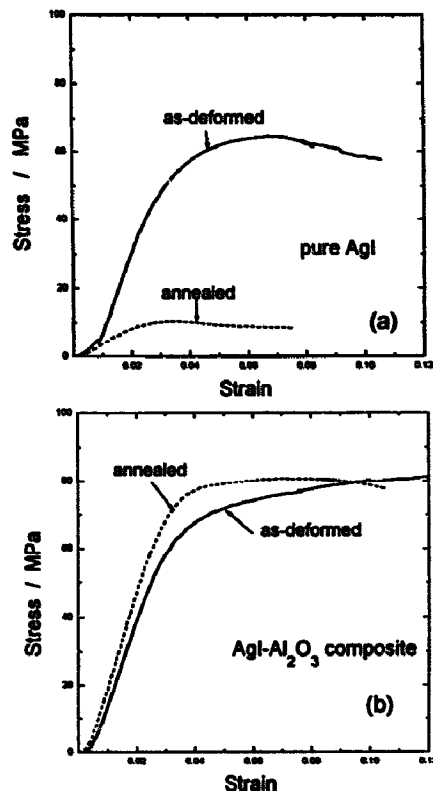


Fig. 4. Compressive stress-strain curves for pure AgI and AgI-20mol%Al₂O₃ composite specimens: (—) as-deformed at 550 MPa, and (---) annealed at 413 K for 20 min. The annealing treatment was preceded by plastic deformation at 550 MPa.

The compressive stress-strain curves obtained from pure and from composite AgI specimens that contain 20 mol% Al_2O_3 are presented in Fig. 4(a) and (b), respectively. The ultimate compression strength of the as-deformed pure AgI specimen decreased from 65 to 10 MPa by annealing at 413 K for 20 min. By contrast, the strength of the AgI–20mol% Al_2O_3 composite specimen was virtually unaffected by the same annealing procedure. This suggests that the deformation-induced defects are composed largely of dislocations and the removal of these dislocations within the AgI– Al_2O_3 composite specimens is impeded by the dispersed Al_2O_3 particles.

The ionic conductivities of the as-deformed, annealed pure and composite AgI specimens measured at room temperature are given as a function of the Al_2O_3 content in Fig. 5. The ionic conductivities of the as-deformed pure and composite AgI specimens are reduced markedly on increasing the annealing temperature from 318 to 413 K. The ionic conductivity of the specimen annealed at 413 K increased with increasing Al_2O_3 content and then showed a maximum value for an Al_2O_3 content in the range of 20 to 30 mol%. The contribution to the ionic conductivity of the highly conductive interfacial region between the AgI matrix and the dispersed Al_2O_3 particles competes with the contribution of the insulative conduction path by the dispersed Al_2O_3 particles. In the lower Al_2O_3 content range, the improved ionic conductivity of the annealed composite specimen with increasing Al_2O_3 content arises from the extended defective region, e.g. a high density of dislocations around the dispersed Al_2O_3 particles. For an Al_2O_3 content higher than 30 mol%, however, the reduced ionic conductivity with increasing Al_2O_3 content is due to a reduction in the cross-sectional area for the ion conduction by the insulative Al_2O_3 particles.

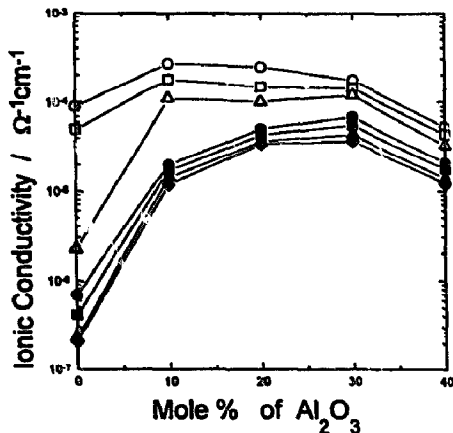


Fig. 5. Ionic conductivity for pure AgI and AgI– Al_2O_3 composite specimens as a function of the Al_2O_3 content, measured at room temperature: (○) as-deformed at 550 MPa, (□) annealed at 318 K; (△) annealed at 338 K; (●) annealed at 353 K; (■) annealed at 373 K; (▲) annealed at 393 K, and (◆) annealed at 413 K. The annealing treatment at each temperature for 20 min was preceded by plastic deformation at 550 MPa.

The reduced amount of the room-temperature ionic conductivity ($\Delta\sigma$) of the as-deformed pure and composite AgI specimens by annealing at 413 K is presented as a function of Al_2O_3 content in Fig. 6. The magnitude of $\Delta\sigma$ decreases with increasing content of Al_2O_3 , except for the pure AgI specimen. This indicates that removal of the deformation-induced dislocations is impeded by the dispersed Al_2O_3 particles. It is noted that the pure AgI specimen displayed a value of $\Delta\sigma$ that was lower than those for the other composite AgI specimens. Provided the ionic conductivity had been measured at room temperature very quickly, i.e. within a few

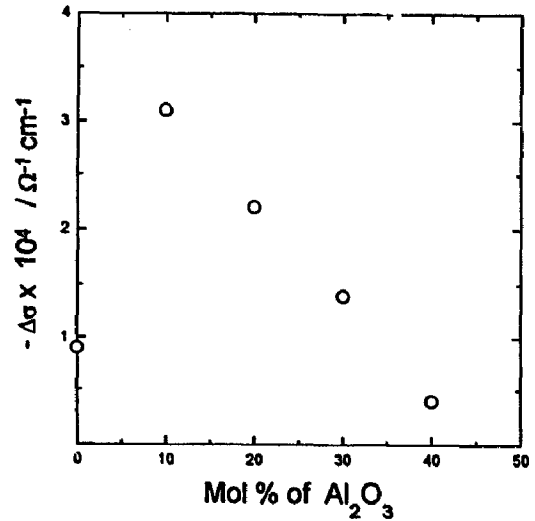


Fig. 6. Decrease in room-temperature ionic conductivity ($\Delta\sigma$) of as-deformed pure AgI and AgI– Al_2O_3 composite specimens by annealing at 413 K as a function of Al_2O_3 content (mol%). The relative value $\Delta\sigma$ relates to the absolute value σ_1 , i.e. $(\sigma_1 - \sigma_r)$ where σ_1 is the ionic conductivity of the as-deformed specimen measured at room temperature and σ_r is that of the corresponding annealed specimen.

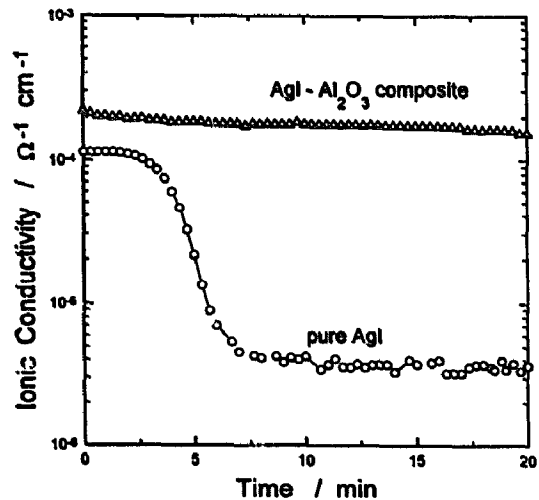


Fig. 7. Ionic conductivity during annealing at 323 K against annealing time for: (○) pure AgI specimen, and (△) AgI–20mol% Al_2O_3 composite specimen. The annealing was preceded by plastic deformation at 550 MPa.

minutes, the real absolute value, σ_1 , and hence the relative value, $\Delta\sigma$, for the pure AgI specimen should have been higher than those for the other composite AgI specimens. As expected, the disappearance of the deformation-induced dislocations in the pure AgI specimen proceeds very quickly, even at room temperature.

The variation in ionic conductivity of pure AgI and AgI–20mol%Al₂O₃ composite specimens with time during annealing at 323 K is shown in Fig. 7. The ionic conductivity of the pure AgI specimen decreases drastically from 1×10^{-4} to $3 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ within 7 min. By contrast, the ionic conductivity of the composite AgI specimen was practically unchanged after 20 min. The dislocations generated by the plastic deformation are readily annealed from the pure AgI specimen, even at a relatively low temperature of 323 K, whereas the movement of dislocation in the AgI–Al₂O₃ composite specimen is impeded by the dispersed Al₂O₃ particles and, thus, a high density of dislocations is stabilized around the Al₂O₃ particles.

4. Conclusions

The present work examines the ionic conduction as a function of plastic deformation for pure AgI and AgI–(10–40mol%) Al₂O₃ composites used as solid electrolytes. The major findings are as follows:

(i) A compression pressure of 100 to 550 MPa raises considerably the ionic conductivity, measured at room temperatures, of both the pure and the composite AgI specimens. Structural defects that provide conduction paths are produced in abundance by the plastic deformation.

(ii) The mechanical strength of the as-deformed pure AgI specimen was considerably diminished by annealing at 413 K, whereas that of the as-deformed composite specimens remained practically unchanged. This result indicates that the

deformation-induced defects are composed almost completely of dislocations.

(iii) The ionic conductivities of the as-deformed composite AgI specimens were substantially reduced by annealing the as-deformed specimens at 318 to 413 K. The higher the annealing temperature, the greater the reduction in ionic conductivity. The ionic conductivity of the as-deformed pure AgI specimen measured during annealing at 323 K for 20 min diminished substantially with annealing time, whereas that of the as-deformed composite specimens stayed virtually constant. It is concluded that during the annealing the annihilation of the deformation-induced dislocations is impeded by dispersed alumina particles and, hence, the dislocations are stabilized by the alumina particles.

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