Solid State Ionics 180 (2009) 497–500

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

The interfacial effect on ionic conduction of AgI–anatase TiO_2 composites

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ARTICLE INFO

Article history:
Received 18 January 2008
Received in revised form 13 August 2008
Accepted 4 December 2008

Keywords:
Ionic conduction
Interfacial effect
AgI-based solid electrolytes

ABSTRACT

AgI–anatase TiO_2 nanoparticle composites, (x)AgI–$(1-x)$anatase, with different porosities were fabricated over a wide range of 0–1 of AgI content. The electrical conductivity was measured at room temperature as function of AgI content (x) and porosity (p). The conductivity varies considerably with both x and p. In the vicinity of $x=0.4$ and $p=0.31$, the conductivity attains a maximum (2.5×10^{-3} S/cm). The conductivity is enhanced by three orders of magnitude in comparison with that of pristine AgI. The mechanism of the observed conductivity enhancement is discussed in the light of the scanning electron microscope images and X-ray diffraction patterns of the different (x)AgI–$(1-x)$anatase composites.

1. Introduction

In recent years, there are numerous reports on various kinds of solid ionic conductors, working as electrolytes. Among these conductors, silver iodide (AgI)–oxide glass and AgI–oxide nanoparticle composite show high ionic conductivity of ~10^{-4} S/cm at room temperature [1–3]. We synthesized different kinds of AgI–oxide nanoparticle composites, for example, AgI–anatase TiO_2 [4], AgI–ZnO [5], AgI–ZrO_2 [6], etc. and have measured the conductivity at room temperature. In particular, AgI–anatase composite, (x)AgI–$(1-x)$anatase, showed a high ionic conductivity (~10^{-4} S/cm) at $x=0.4$ [4], which was the highest value among those reported for AgI–oxide particle composites by the authors. The starting materials of the composite were nominally pure AgI (99% in purity) and amorphous TiO_2 nanopowder (99.7% in purity, ~50 nm). Very recently, we fabricated (x)AgI–$(1-x)$anatase composite with different porosities over a wide range of 0–1 of AgI content, using purer AgI (99.999% in purity) and crystal anatase nanoparticle (~13 nm). Since the dispersion of the oxide with smaller particle size enhances the conductivity more than that with larger particle size [7], it is expected that the composite fabricated in the present may yield the higher conductivity than the composite reported in previous. In addition, the comparison the structural and morphological properties with the electrical one of different composites with different porosities may give new information of the mechanism for the conductivity enhancement. In the present paper, the electrical conductivity, morphology and crystal structure of the AgI–anatase composite were studied in detail as function of porosity (p) and AgI content (x). The results clarify well the conductivity enhancement in the (x)AgI–$(1-x)$anatase composite.

2. Experimental

AgI powder (Alfa Aesar, 99.999% in purity) and anatase TiO_2 nanoparticles (Aldrich, 99.7% in purity) with an average diameter of 13 nm, which was calculated by the Scherrer formula [8], were used as starting materials of the (x)AgI–$(1-x)$anatase composite. AgI powder and anatase TiO_2 nanoparticles were mixed in an agate mortar, and then the mixture was compressed in a conventional piston–cylinder apparatus under different pressures between 0.05 and 0.55 GPa to fabricate pellets (13 mm in diameter). The pellets were then heated in the lidded crucible at 673 K in air for 12 h. The apparent density ($\rho_{ap.}$) was calculated from the measured values of mass (m) and volume (V) of the pellet as $\rho_{ap.}=m/V$, and the theoretical density ($\rho_{th.}$) of the composites was estimated from the Eq. (2) in Ref. [2], as follow.

$$\rho_{th.}(x)=\rho_A\cdot[1-x\cdot(1-\alpha)]/[\gamma-x\cdot(\gamma-\alpha)]$$

where $\alpha=M_A/M_{AgI}$ and $\gamma=\rho_A/\rho_{AgI}$. M_A and M_{AgI} are molecular weights of anatase and AgI, respectively, ρ_A and ρ_{AgI} are densities of anatase (3.88 g/cm^3) and AgI (5.96 g/cm^3), respectively. The porosity (p) was estimated by an equation: $p=(1-(\rho_{ap.}/\rho_{th.}))$.

The crystal structure of the composite was characterized by X-ray diffraction (XRD) analysis with Cu Ka radiation (Rigaku: RINT 2500). The morphology of the composite was studied by a field emission scanning electron microscope (FE-SEM) (HITACHI: S-4500). Electrical contact with the pellet was obtained by evaporating silver onto both sides of the pellet and the complex impedance measurement was then performed by an impedance analyser (Kokuyo: KC-605), which was operated at frequency range from 42 up to 3×10^6 Hz, at room temperature. Assuming that the resistive component is in parallel with capacitive component, the conductivity was extracted from the impedance spectra obtained. Since the conductivity obtained was hardly changed against frequency until about 100 kHz, we adopted the

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doi:10.1016/j.ssi.2008.12.012

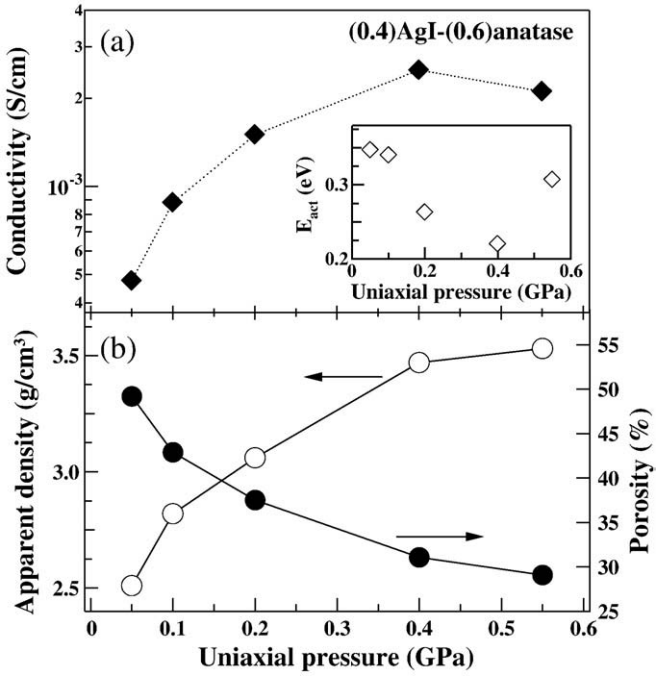

Fig. 1. (a) Conductivity and (b) apparent density and porosity of the (0.4)AgI–(0.6) anatase TiO_2 nanoparticle composites are plotted against the uniaxial pressure to fabricate. In the inset of panel (a) shows the variation of the activation energy (E_{act}).

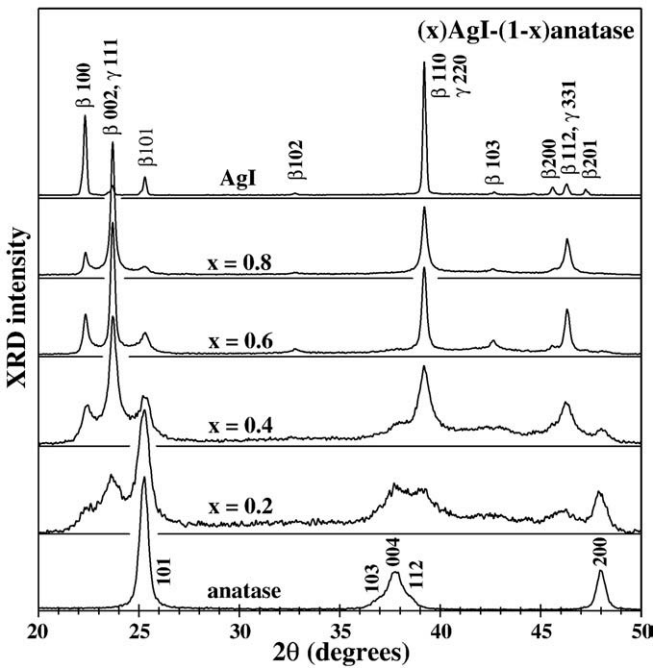

Fig. 2. XRD patterns of different (x)AgI–$(1-x)$anatase TiO_2 nanoparticle composites.

conductivity value at 1 kHz. Since AgI has the electron transference number of 0.008 [9] and the conductivity of anatase was measured about 10^{-6} S/cm, which is small about three orders of magnitude in comparison with the conductivity of the composite, the electronic conductivity may be able to neglect for this system.

3. Results and discussion

Fig. 1 shows (a) the conductivity variation with compaction pressure and (b) the apparent density and porosity variations with compaction pressure, for the (0.4)AgI–(0.6)anatase. In the inset of Fig. 1(a), the activation energy (E_{act}) (estimated from $\ln(sT)$ vs. $1/T$ representation below ~373 K) is shown against compaction pressure. With increasing compaction pressure, the apparent density increases monotonously and the porosity decreases monotonously. However, the conductivity shows a maximum of 2.5×10^{-3} S/cm and E_{act} displays a minimum of 0.22 eV, at a compaction pressure (0.4 GPa). This shows that the conductivity is changeable even the same AgI content and suggests that the optimum condition to fabricate the pellet may exist.

XRD patterns of different (x)AgI–$(1-x)$anatase composites which were compressed by 0.2 GPa to pellets are shown in Fig. 2. All XRD patterns in this figure are normalized at the peak intensity. Anatase shows broad diffraction lines and the average particle size of anatase particle was determined as 17 nm. With increasing x from 0 to 0.4, the reflections due to βAgI phase emerge followed by extra broad reflection backgrounds in two 2θ ranges ($27°<2\theta<36°$ and $40°<2\theta<45°$). In these 2θ regions, several workers observed broad reflection lines for pristine βAgI crystal [10,11] and AgI–γAl_2O_3 composites [1]. AgI and AgI–γAl_2O_3 composites which display the extra broad reflection lines are known to have high ionic conductivities [1,11]. The observed extra lines may be assigned to 7-layer polytype AgI (7H-AgI) structure [12], which is one of the heterolayer stacking structure of βAgI and γAgI, though it can not exclude the attribution of the existence of other AgI polytypes, e.g. 4H-, 9R-AgI, etc. The full width at half maximum of the diffraction lines from AgI ($x\leq0.4$) is broader than that of the diffraction lines from AgI ($x\geq0.6$), which may arise from the lower crystallinity of AgI domain as well as the smallness of AgI domain size. Therefore, both the broad reflection backgrounds and the broadness of the line width due to AgI shown in Fig. 2 prove the existence of the randomly stacked β-/γAgI heterostructure, which is responsible for high ionic conductivity [1,13], in the present (x)AgI–$(1-x)$anatase composites. With further increasing x (>0.4), the extra broad reflection backgrounds become decreased in intensity and the line width from AgI sharpens, which indicates that the relative amount of the β-/γAgI heterostructure against the AgI-rich domain decreases. Incidentally, no distinct reflections due to other compounds composed of constituent atoms, e.g., TiI_4, Ag_2O, etc, were observed.

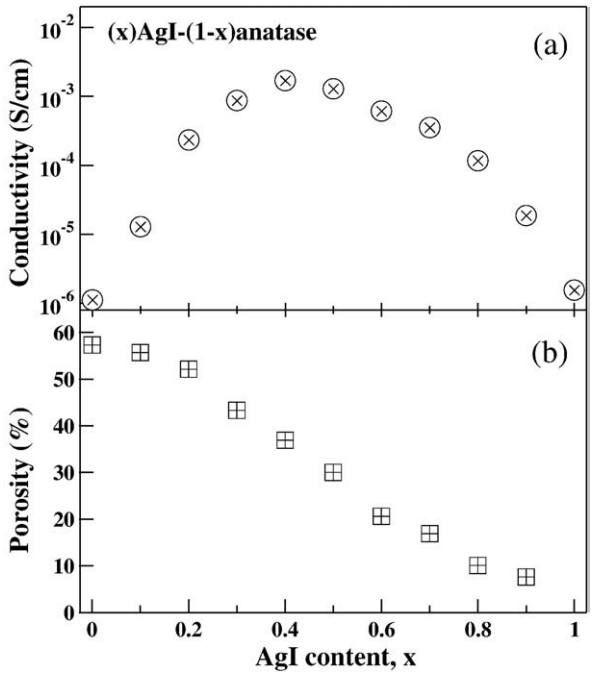

Fig. 3. (a) Conductivity and (b) porosity of different (x)AgI–$(1-x)$anatase TiO_2 nanoparticle composites.