Studies on ionic transport properties of a new Ag^+ ion conducting composite electrolyte system $(1-x)[0.75 \text{ AgI} : 0.25 \text{ AgCl}] : x\text{SnO}_2$

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Abstract. A new Ag^+ ion conducting composite electrolyte system $(1-x)[0.75 \text{ AgI} : 0.25 \text{ AgCl}] : x\text{SnO}_2$ using a quenched/annealed $[0.75 \text{ AgI} : 0.25 \text{ AgCl}]$ as host compound in place of conventional host AgI, has been investigated. The effects of various preparation methods and soaking time are reported. The composition $0.8[0.75 \text{ AgI} : 0.25 \text{ AgCl}] : 0.2\text{SnO}_2$ exhibited optimum conductivity ($\sigma = 8.4 \times 10^{-4} \text{ S/cm}$) with conductivity enhancement of $\sim 10^1$ from the annealed host at room temperature. Transport property studies such as electrical conductivity (σ) as a function of temperature using impedance spectroscopy technique, ionic transference number (t_{ion}) using Wagner's d.c. polarization method and ionic mobility (μ) by transient ionic current technique were carried out on the optimum conducting composition. The mobile ion concentration (n) was calculated from ' σ ' and ' μ ' data.

Keywords. Ag^+ ion conductor; composite solid electrolyte; two-phase composite system; ionic conductivity; ionic mobility.

1. Introduction

Composite electrolytes are a new class of fast ion conductors which have attracted widespread interest in the recent years due to their possible technological applications in solid state batteries, electrochromic display devices, fuel cells etc. They are mostly two-phase systems in which conductivity enhancements $\sim 10^1$ – 10^3 have been achieved at room temperature by dispersing ultrafine particles of a chemically inert and insoluble material (termed as second phase or dispersoid) viz. Al_2O_3 , SiO_2 , Fe_2O_3 , SnO_2 , Fly-ash etc into a first phase host material such as AgI, AgBr, AgCl, LiI, CuCl, CaF_2 etc. A large number of two-phase composite electrolyte systems with Ag^+ , Li^+ , Cu^+ , F^- etc ion conduction have been reported and studied so far (Liang 1973; Liang *et al* 1978; Shahi and Wagner 1981; Poulsen 1985; Dudney 1989; Maier 1989, 1992; Wagner 1989; Shukla and Sharma 1992). Several phenomenological models have been suggested to explain the conductivity enhancement in these systems (Bunde *et al* 1985; Blender and Dieterich 1987; Dudney 1989; Maier 1989, 1992; Wagner 1989; Shukla and Sharma 1992; Uvarov *et al* 1992). Majority of these models have many common themes to explain the transport mechanism in these systems e.g. the increase in the mobile ion concentration at the host/dispersoid interfacial space charge region and/or increase in the ionic mobility due to the creation of high conducting paths connecting these regions, are predominantly responsible for the conductivity enhancement. Moreover, the volume fraction and size of the dispersoid particles play very vital roles in controlling the conductivity enhancement in these systems.

We report here the preparation and transport property studies of a new Ag^+ ion conducting composite electrolyte system $(1-x)[0.75 \text{ AgI} : 0.25 \text{ AgCl}] : x\text{SnO}_2$ using

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SnO_2 particles of size $\sim 10\ \mu\text{m}$. In majority of the Ag^+ ion conducting composite electrolyte systems, reported earlier, a relatively larger room temperature enhancement has been obtained when AgI is used as a host matrix. In the present investigation, however, we replaced the conventional AgI by a new host: a quenched/annealed $[\text{0.75 AgI:0.25 AgCl}]$ mixed system. The new host compound investigated by us recently (Agrawal *et al* 1994), exhibited many transport properties superior to AgI along with an identical $\beta \rightarrow \alpha$ -like transition of AgI at a reduced temperature ($\sim 135^\circ\text{C}$).

In this paper, the following experimental investigations on $(1-x)[\text{0.75 AgI:0.25 AgCl}]:x\text{SnO}_2$ composite electrolyte systems are reported: (i) the electrical conductivity (σ) as a function of composition 'x', preparation routes, soaking time to find out the optimum conducting composition; (ii) temperature variation of ' σ ' for the optimum conducting composition to evaluate the activation energy (E_a) for the ion transport; (iii) determination of ionic transference number (t_{ion}) to know the extent of ionic contribution to the total conductivity; and (iv) direct determination of ionic mobility (μ) at room temperature on the optimum conducting composition and evaluation of mobile ion concentration (n) from ' σ ' and ' μ ' data.

2. Experimental

2.1 Sample preparation

Commercially available chemicals AgI, AgCl [purity $> 98\%$, Reidel (India) Chemicals] and SnO_2 [purity $> 99\%$, CDH, India] were used without further purification. Homogeneous mixtures of $(1-x)[\text{0.75 AgI:0.25 AgCl}]:x\text{SnO}_2$, in different wt(%) ratios $0 \leq x \leq 50$, were heated at $\sim 600^\circ\text{C}$ for 15 min (soaking time) then cooled rapidly to $\sim 10^\circ\text{C}$ with the quenching rate $\sim 10^2\ \text{K}\cdot\text{sec}^{-1}$ (this is referred to as preparation route no. 1). Similar mixtures were also annealed at $\sim 200^\circ\text{C}$ for 24 h (this is referred to as preparation route no. 2). In addition to this, composite electrolyte system $(1-x)\text{AgI}:x\text{SnO}_2$ using conventional AgI as host were also prepared following preparation route no. 1. The finished products were thoroughly ground then pressed at $\sim 2\ \text{ton}\cdot\text{cm}^{-2}$ to form pellets of diameter $\sim 1.185\ \text{cm}$ and thickness $0.75\text{--}2\ \text{mm}$. Colloidal silver paint was used as electrodes for conductivity measurements.

2.2 Transport property studies

2.2a Electrical conductivity (σ): The electrical conductivity measurements were carried out using impedance spectroscopy (IS) technique with the help of a computer controlled HIOKI LCR bridge (Model 3520 – 01, Japan) in the frequency range 40 Hz to 100 kHz. The true bulk resistances were computed from $Z' - Z''$ impedance plots.

2.2b Ionic mobility (μ) and transference number (t_{ion}): The ionic mobility and the transference number were measured using transient ionic current (TIC) technique (Chandra *et al* 1988; Agrawal *et al* 1994; Agrawal and Kumar 1994) and Wagner's d.c. polarization method (Chandra 1981) respectively. A Graphtec X-Y-t recorder (Model WX 2300-1L, Japan) was employed for both the measurements [For details of the experimental techniques, please see the referred papers].

Figure 1. Log σ vs x plot for composite system $(1-x)[0.75 \text{ AgI}:0.25 \text{ AgCl}]:x\text{SnO}_2$ using different preparation routes: (1) Quenched sample and (2) annealed sample. (●) composite system $(1-x) \text{ AgI}:x\text{SnO}_2$.

3. Results and discussion

3.1 Compositional variation of room temperature conductivity: Effect of preparation routes and soaking time

Figure 1 shows the variation of the room temperature conductivity (σ) as a function of wt(%) ratio ' x ' for the composite electrolyte system $(1-x)[0.75 \text{ AgI}:0.25 \text{ AgCl}]:x\text{SnO}_2$, prepared by routes (1 and 2), mentioned in § 2. Similar plot for the composite system $(1-x) \text{ AgI}:x\text{SnO}_2$ with conventional host AgI, prepared by route (1), is also drawn in figure 1 for direct comparison. The σ vs x variation follows the usual behaviour of solid electrolyte systems reported in the literature (Maier 1989, 1992; Wagner 1989; Shukla and Sharma 1992). It is obvious from the figure that the quenched sample $0.8[0.75 \text{ AgI}:0.25 \text{ AgCl}]:0.2\text{SnO}_2$ prepared by route (1) exhibits highest enhancement in the conductivity with $\sigma = 8.4 \times 10^{-4} \text{ S/cm}$ at 27°C . An enhancement: $\sim 10^1$ from the annealed host and ~ 3 times from the quenched host was obtained at room temperature which can be explained on the basis of proposed models for two-phase composite electrolyte systems, referred in § 1. The existence of two separate phases has been confirmed by X-ray diffraction (XRD) studies. We also note from the figure that the conductivity enhancements in all the ratios of the composite system prepared using new host compound are $\sim 10^1$ higher as compared to those using AgI as host. Hence, on the basis of this study, as well as the results reported by us earlier (Agrawal and Kumar 1994; Agrawal *et al* 1994, 1995; Gupta and Agrawal 1994; Agrawal and Gupta 1995), we conclude positively that better solid electrolyte composite/glass systems can be prepared with the new host than the conventional host AgI.

Soaking time i.e. the time for which the two-phase mixture is heated at $\sim 600^\circ\text{C}$ during the sample preparation, significantly affects the physical property of the composite system (Uvarov *et al* 1990; Shastry and Rao 1992). To examine this effect, samples of the optimum composition were prepared following route (1) for different

Figure 2. Room temperature conductivity as a function of soaking time for the optimum conducting composition 0.8[0.75 AgI:0.25 AgCl]:0.2SnO₂ (prepared by route 1).

Figure 3. Log σ vs $1/T$ plot: (○) optimum conducting composition 0.8[0.75 AgI:0.25 AgCl]:0.2SnO₂; (Δ) host compound [0.75 AgI:0.25 AgCl].

soaking times. Figure 2 shows the conductivity variation for the optimum composition at different soaking times viz. 5, 10, 15, 30 min and 24 h. It is obvious from the figure that the highest conductivity was obtained for the soaking time ~ 15 min. Lower conductivity values obtained at 15 min > soaking time > 15 min, are possibly due to incomplete dispersal reaction at lower soaking times and stoichiometric changes due to liberation of iodine at higher soaking times.

3.2 Transport property studies

Figure 3 shows the temperature variation of the conductivity for the optimum conducting composition 0.8[0.75 AgI:0.25 AgCl]:0.2SnO₂. For direct comparison, a similar

Figure 4. Transient ionic current vs time plot for ionic mobility measurement of the optimum conducting composition $0.8[0.75 \text{ AgI}:0.25 \text{ AgCl}]:0.2 \text{ SnO}_2$. Inset shows the basic circuit used for TIC measurements.

plot for the annealed host $[0.75 \text{ AgI}:0.25 \text{ AgCl}]$ is also drawn in figure 3. This obviously indicates the conductivity enhancements in the composite system from the host specially in the lower temperature region. Arrhenius equations governing the $\log \sigma$ vs $1/T$ variation in the two regions of temperatures indicated below, can be expressed as:

$$\sigma = 0.255 \exp(-0.147/kT) \rightarrow (27-110^\circ\text{C});$$

$$\sigma = 0.674 \exp(-0.052/kT) \rightarrow (145-205^\circ\text{C}),$$

where 0.147 and 0.052 eV are the activation energy values in the above two regions of temperatures.

Ionic transference number close to unity was obtained at room temperature using Wagner's d.c. polarization method, mentioned in § 2. This indicates that the current carriers in this system are Ag^+ ions only and the electronic contribution to the total current is negligibly small.

Table 1. Comparison of some important transport parameters of annealed and quenched host [0.75 AgI:0.25 AgCl] and composite system 0.8[0.75 AgI:0.25 AgCl]:0.2SnO₂.

Material	Ionic conductivity σ at 27°C (S/cm)	Ionic mobility μ at 27°C (cm ² /V·s)	Transference number t_{ion}	Activation energy E_a (eV)	Mobile ion concentration n at 27°C (cm ⁻³)
[0.75 AgI:0.25 AgCl] (annealed)	1×10^{-4}	$(1.5 \pm 1) \times 10^{-2}$	~ 1	0.243(< 140°C) 0.025(> 140°C)	4×10^{16}
[0.75 AgI:0.25 AgCl] (quenched)	3.14×10^{-4}	$(2.4 \pm 1) \times 10^{-2}$	~ 1	0.234(< 135°C) 0.050(> 135°C)	8×10^{16}
0.8[0.75 AgI:0.25 AgCl]: 0.2SnO ₂	8.40×10^{-4}	$(1.4 \pm 1) \times 10^{-1}$	~ 1	0.147(< 135°C) 0.052(> 135°C)	3.7×10^{16}

Figure 4 shows the transient ionic current vs time plot to determine the ionic mobility in the optimum conducting composition at room temperature using TIC technique mentioned in § 2. If the applied voltage V and the thickness d of the sample, are known, the mobility can be calculated with the help of following expression:

$$\mu = d^2/V \cdot \tau \quad [\text{cm}^2/\text{V} \cdot \text{s}],$$

where τ is the time of flight and is obtained from the TIC plot (figure 4). We obtained $\mu \sim (1.4 \pm 1) \times 10^{-1} \text{ cm}^2/\text{V} \cdot \text{s}$ at 27°C. Using room temperature values of σ and μ , we calculated the mobile ion concentration $n \sim 3.7 \times 10^{16} \text{ cm}^{-3}$ with the help of a well-known equation:

$$\sigma = nq\mu.$$

Table 1 lists the values of the ionic transport parameters obtained above for the composite electrolyte system 0.8[0.75 AgI:0.25 AgCl]:0.2SnO₂. The values of similar parameters for the annealed and quenched hosts [0.75 AgI:0.25 AgCl] obtained earlier by us (Agrawal *et al* 1994) are also included in table 1. On comparing the activation energy of the composite system with that of the host in the lower temperature region (27–110°C), we clearly note a substantial decrease in the value. This indicates that the ion transport in the composite system takes place relatively with ease. This has got further support by mobility measurements. We obtained an increase of $\sim 10^1$ in the mobility value of the composite system from the host. However, the number of mobile ion concentration remained almost unaltered in both host and composite systems. Hence, on the basis of these studies we conclude that the conductivity enhancement in the composite system is predominantly due to the increased ion mobility, as mentioned in § 1. Detailed investigations on this system are currently under way in our laboratory.

4. Conclusion

A new Ag⁺ ion conducting two-phase composite electrolyte system $(1-x)[0.75 \text{ AgI}:0.25 \text{ AgCl}]:x\text{SnO}_2$ has been synthesized using a new host compound in place of conventional host AgI and a second phase SnO₂ particles of size $\sim 10 \mu\text{m}$. Conductivity enhancements $\sim 10^1$ from the annealed and ~ 3 times from the quenched host

were obtained at room temperature. Effect of various preparation routes and soaking times were studied. Transport characterization studies were carried out on the optimum conducting composition and the results were compared with those of the host. These studies clearly indicated that the enhancement in the conductivity is predominantly due to the increased ionic mobility in the composite system whereas, the number of mobile ion concentration remained unaltered.

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