

Ionic Transport and Surface Morphological Studies on SbI_3 - Ag_2WO_4 Mixed System for Solid State Battery Applications

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Abstract: Detailed experimental data pertaining to ionic transport and micro structural investigations on new superionic materials formed in the mixed system $(\text{SbI}_3)_x - (\text{Ag}_2\text{WO}_4)_{1-x}$ ($0.1 \leq x \leq 0.5$) have been described in this paper. Temperature-dependent electrical conductivity analysis yielded the activation energy values for various compositions as confirmed by means of frequency-dependent conductivity results as well. Evaluation of transport properties carried out in terms of ionic transport number (t_i) measurements by Wagner's dc polarization method and silver ionic transport number (t_{Ag^+}) measurements by EMF method has revealed that a typical t_i value of 0.99 along with a silver ionic transport number of 0.95 would be exhibited by the best conducting composition $(\text{SbI}_3)_{0.4} - (\text{Ag}_2\text{WO}_4)_{0.6}$ having the room temperature electrical conductivity of $5.7 \times 10^{-2} \text{ Scm}^{-1}$. The surface morphological results obtained by scanning electron microscopy (SEM) have suggested the presence of AgI micro-crystals as dispersoids within the silver oxysalt matrix formed as a result of probable solid state ion exchange reactions occurring between SbI_3 and Ag_2WO_4 in accordance with hard and soft acids and bases (HSAB) principle. The measured open circuit voltage, OCV for an all-solid-state electrochemical cell fabricated using the best conducting composition $(\text{SbI}_3)_{0.4} - (\text{Ag}_2\text{WO}_4)_{0.6}$ as solid electrolyte is found to be 603 mV at room temperature.

Keywords: Solid electrolytes, Complex impedance, Solid state battery, Ionic transport number

Introduction

Although most of today's global energy needs are met by fossil fuels, it is becoming increasingly clear that due to their finite reserves there is a likelihood that these systems would in due course become in short supply for the mankind. By the year 2050, the global population on the other hand is alarmingly anticipated to have grown into 10 billion and therefore future energy generation must also be sustainable in terms of cost, fuel resource availability and environmental acceptability. In addition, energy must be generated and supplied in the desired form and quality in order to meet the end-user requirements. Solid State Ionics (SSI) technologies that are set to play increasingly important roles in sustainable energy systems include: fuel cells, advanced batteries, super capacitors, ionic-transport membranes (gas separation and chemical reactors), advanced sensors for process control and safety, electro chromic smart windows for optical modulation and energy-efficient buildings¹.

Silver batteries or micro batteries can be attractive as power sources for portable electronic devices operating under ambient conditions, taking into account high Ag^+ -ion conductivity (up to $10^{-2} \text{ S cm}^{-1}$) of a range of solids, amorphous or crystalline, which may serve as electrolytes in such batteries².

Whereas a large number of binary, pseudobinary and ternary mixed systems were reported to exhibit silver ion transport at ambient conditions, recent research findings on silver oxysalt systems with different dopants other than AgI , have demonstrated the feasibility of obtaining appreciably high silver ion conductivity values over a wide range of temperatures. During the course of our experimental investigations concerning the synthesis of new superionic solids for ambient temperature applications it was understood that certain mixed systems such as $\text{CuI}-\text{Ag}_2\text{MoO}_4$, $\text{CuI}-\text{Ag}_2\text{CrO}_4$, $\text{CuI}_{1-x}\text{Ag}_x\text{I}-\text{Ag}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{CdI}_2-\text{Ag}_2\text{O}-\text{MoO}_3$ would possess solid electrolytic behavior due to silver ionic migration³. As an attempt towards developing new series of silver ion conducting solid electrolytes as cost-effective systems, antimony triiodide SbI_3 was considered as a different dopant salt replacing AgI . In our previous work, we have demonstrated the role of SbI_3 in developing new solid electrolytes in the mixed system $(\text{SbI}_3)_x-(\text{Ag}_2\text{CrO}_4)_{1-x}$ with ionic conductivity values of $3.2 \times 10^{-2} \text{ Scm}^{-1}$ in the case of composition namely $(\text{SbI}_3)_{0.3} - (\text{Ag}_2\text{CrO}_4)_{0.7}$ at room temperature. The role of the silver oxysalt Ag_2WO_4 has also been well established in the literature by many researchers^{4,5} owing to its applications in oxygen sensors, chemical sensors and as an electron beam recording material⁶. Encouraged by these reports, we have undertaken the present study on the preparation of $(\text{SbI}_3)_x - (\text{Ag}_2\text{WO}_4)_{1-x}$ mixed system, its transport properties and surface morphological aspects characterized through scanning electron microscopy in addition to fabrication of a solid state battery employing the best conducting composition as identified earlier⁶.

Experimental

Analar grade chemicals of antimony triiodide, SbI_3 and silver tungstate, Ag_2WO_4 were used as raw materials. Appropriate amounts of these raw materials were taken as per the stoichiometric composition of the binary system $(\text{SbI}_3)_x-(\text{Ag}_2\text{WO}_4)_{1-x}$ where $x = 0.1, 0.2, 0.3, 0.4$ and 0.5 mole fraction respectively. Samples were prepared by melting appropriate amounts of these starting materials in vacuum sealed quartz tubes (in order to prevent the starting materials from reacting with atmospheric oxygen) placed in ceramic boats at 873 K for 6 h in a high temperature furnace and rapidly quenching the molten mixture into a liquid nitrogen bath. The resultant mixture was then finely powdered using pestle and mortar and stored in darkened desiccators for further investigation.

Ionic transport number (t_i) measurements

The room temperature ionic transport number (t_i) measurements were carried out on all the synthesized samples by Wagner's dc polarization method⁷ wherein a circular pellet of the sample was sandwiched between an ion-blocking electrode (graphite) and a non-blocking electrode (silver) and a constant direct current (dc) potential of 100 mV was applied across the sample. The steady-state current measurements were made with the aid of a Keithley model 6517A Electrometer and the variation of current in the circuit was noted as a function of time for about 7 h till the current became constant, indicating the fully depleted condition of the blocking electrode. Ionic transport number (t_i) data for the various compositions of the present system were determined by using the relation:

$$t_i = (I_{\text{initial}} - I_{\text{final}}) / I_{\text{initial}} \quad (1)$$

Where I_{initial} is the initial current due to the mobile species *i.e.* ions and electrons and I_{final} is the steady- state current indicating the fully-depleted condition of the blocking electrode corresponding to the electronic current.

Silver ionic transport number (t_{Ag^+}) measurements

The electromotive force (EMF) method was also employed for the estimation and reconfirmation of ionic transport number in each composition of the present system at room temperature. Accordingly, a galvanic cell was fabricated with a configuration⁸



Where a powder mixture of metallic silver powder and the sample taken in the weight ratio 2:1 was used as anode and iodine as cathode. The cell components were cascaded and pressed together at a pelletizing pressure of 5 ton cm^{-2} in order to fabricate the galvanic cell. The values of the open circuit voltage of the cells were measured and compared with the thermodynamic value of 687 mV at room temperature reported for the Ag / I_2 couple for arriving at the room temperature silver ionic transport number (t_{Ag^+}) data corresponding to each composition of the present mixed system⁹.

Electrical conductivity studies

Complex impedance studies were carried out on the pelleted samples of various compositions of the present mixed system SbI_3 - Ag_2WO_4 using a computer - controlled Hewlett-Packard model HP4284A Precision LCR Meter in the frequency range 20 Hz–1 MHz and over the temperature region 298-435 K. The temperatures of the samples were measured using a chromel- alumel thermocouple attached to the sample compartment.

Morphological characterization studies

Micro structural features of all the freshly prepared samples were observed using a Hitachi model-S3400N scanning electron microscope (SEM) with an accelerating voltage of 15kV. A thin layer of platinum was coated on the polished surfaces of the SEM specimen in order to avoid sample charging when exposed to the electron beam.

Fabrication of a solid-state cell

The primary requirement of a solid cell is an electrolytic medium characterized by high ionic conductivity with negligible electronic mobility¹⁰. The chosen system indicated that the best conducting composition $(\text{SbI}_3)_{0.4}-(\text{Ag}_2\text{WO}_4)_{0.6}$ would exhibit an electrical conductivity of $5.7 \times 10^{-2} \text{ Scm}^{-1}$ at 298 K⁷. Hence, the above solid electrolyte having the composition $(\text{SbI}_3)_{0.4}-(\text{Ag}_2\text{WO}_4)_{0.6}$ has been employed as an electrolytic medium for the fabrication of the present solid state electro chemical power cell. Analar grade phenothiazine ($\text{C}_{12}\text{H}_9\text{NS}$) and molecular iodine (I_2) were taken in the molar ratio 2:3 and mixed together and the above mixture was ground thoroughly and allowed to react directly in an agate mortar for two hours at room temperature. Since the reaction between iodine and phenothiazine is instantaneous, the sublimation of iodine is most significant. The formation of the charge transfer complex (CTC) was indicated by the appearance of a dark complex¹¹.

Cell design

Powder mixtures comprising of silver powder and the solid electrolyte (E) in the weight ratio 2:1 served as the anode material and solid-state cells were fabricated with the following configuration,





The anode and the electrolyte were pressed together at a pressure of 5 ton cm⁻² into a single pellet of 8 mm diameter and the cathode was subsequently incorporated over it. The entire pellet assembly was stacked between two ebonite plates and sealed with an epoxy resin in order to avoid any iodine sublimation.

Results and Discussion

Ionic transport number measurements

Table 1 presents the values of ion transport number, t_i , evaluated by Wagner's dc polarization method as well as the silver ion transport number, t_{Ag^+} , data obtained by the EMF method for the reconfirmation of mobile species in various compositions of the chosen mixed system. From Table 1, it is evident that those compositions having $x = 0.2, 0.3, 0.4,$ and 0.5 would exhibit large ionic transport number (t_i) values of 0.99, 0.9, 0.99, and 0.9 respectively. This means that the active mobile species in this system are ionic in nature and that the electronic contribution to the total electrical conductivity would be negligible as compared to the ionic conductivity of these new compositions. However, the t_i value obtained for the composition $x = 0.1$ is found to be as low as 0.37 which may be due to the presence of pure metallic silver as seen from the XRD analysis and hence responsible for the electronically conducting nature of this composition as well¹².

Table 1. Ionic transport number data

Composition (x)	Ionic transport number (t_i)	Silver ionic transport number (t_{Ag^+})
0.1	0.37	0.91
0.2	0.99	0.91
0.3	0.9	0.92
0.4	0.99	0.95
0.5	0.9	0.91

Figure 2 shows the current versus time plot obtained for the composition containing 0.4 mole fraction of SbI_3 by the Wagner's polarization technique. It is clear from Figure 2 that the initial total current (I_{initial}) which is nearly 2.16 mA, decreases with time due to the depletion of the ionic species in the electrolyte and becomes constant in the fully-depleted situation. At this stage the residual current is found to be only 0.07 mA, *i.e.*, the electronic current (I_{final}), after 8 h.

It is also obvious from Table 1 that the set of t_{Ag^+} values obtained by the EMF method are 0.91 or greater for all the five different samples of the present system corresponding to $x=0.1, 0.2, 0.3, 0.4$ and 0.5 respectively. These observed features strongly indicate that the major contribution to the electrical conductivity in the present system may be due to silver ions only. In other words, electronic transport in these materials seems negligible as compared to the ionic migration. The ionic migration is likely to exist due to the ion exchange reaction occurring between SbI_3 and Ag_2WO_4 in the molten state resulting in the formation of AgI according to hard and soft acids and bases (HSAB) principle¹³ which states that soft acids would prefer to bind to soft or polarizable bases and that hard acids would prefer to bind to hard or non polarizable bases as a result of various degrees of ionic and covalent bonding.

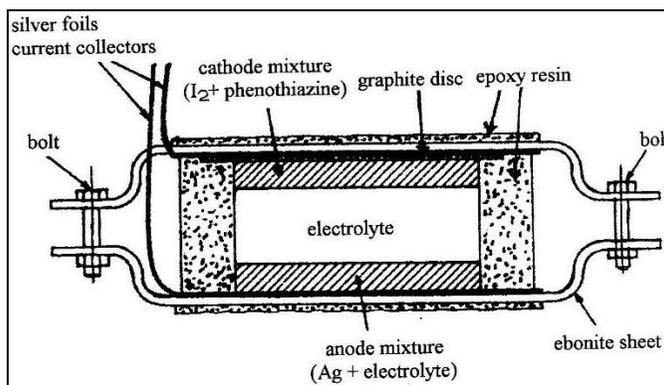


Figure 1. Cell assembly

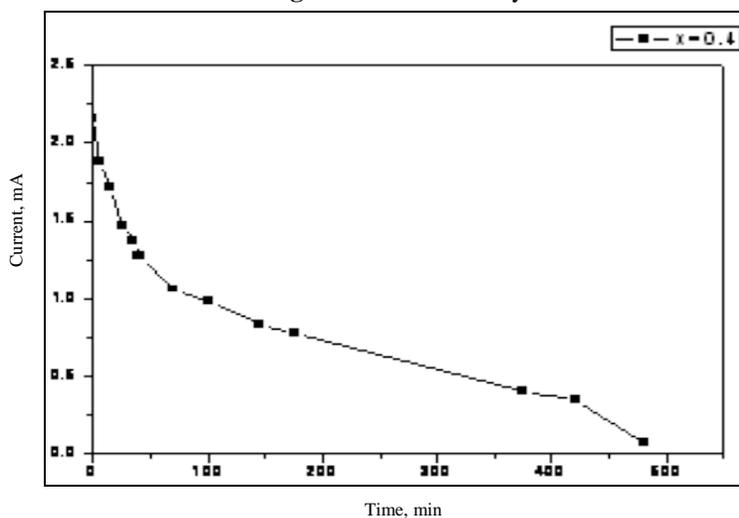


Figure 2. Current versus time plot used for the estimation of ionic transport number in the case of $(\text{SbI}_3)_{0.4}(\text{Ag}_2\text{WO}_4)_{0.6}$ specimens

From the present investigation on the new mixed system $(\text{SbI}_3)_x(\text{Ag}_2\text{WO}_4)_{1-x}$, ($0.1 \leq x \leq 0.5$), it is evidenced that the silver ionic conduction improves linearly with the content of SbI_3 from $x=0.1$ and gets optimized at $x=0.4$ associated with an appreciably high ionic conductivity value of $5.7 \times 10^{-2} \text{ Scm}^{-1}$ owing to the formation of a relatively high concentration of AgI . With further increase in SbI_3 content, the tendency of crystallization was found to increase leading to a decrease in ionic conduction. Above $x = 0.4$, the concentration of AgI formed as a reaction product in the solid state reaction is expected to decrease and hence result in a decreased electrical conductivity value¹⁴.

Temperature-and frequency- dependent conductivity studies

The room temperature electrical conductivity values obtained from the present system were found to be 4.1×10^{-4} , 5.5×10^{-3} , 1.7×10^{-3} , 5.7×10^{-2} and $6.4 \times 10^{-4} \text{ Scm}^{-1}$ respectively for $x=0.1, 0.2, 0.3, 0.4$ and 0.5 mole fraction respectively during our previous work⁶ wherein the

composition with $x=0.4$ was identified as the best conducting specimen. Figure 3 depicts the typical complex impedance Nyquist plots obtained for the best conducting composition having $x=0.4$ at six different temperatures *viz.*, 301, 316, 346, 356, 376 and 396 K respectively. The value of the real part of impedance (Z') corresponding to the intersection of the low frequency side of the arc pertaining to the bulk resistance R_b was obtained using Boukamp equivalent circuit software for each temperature and such R_b values were used to determine the d.c conductivity (σ_{dc}) values at different temperatures. It is clear from Figure 3 that with the increase in temperature, the intersection of the impedance plot on the real axis is shifted towards the origin, i.e. with the increase in temperature, the bulk resistance of the sample decreases and the electrical conductivity thus shows a gradual enhancement¹⁵.

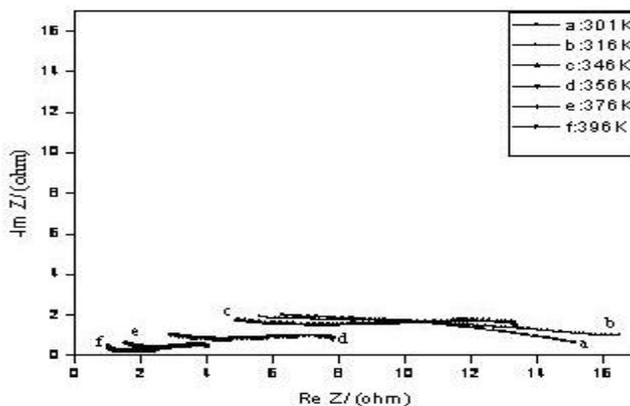


Figure 3. Complex impedance plots obtained for the best conducting composition $(SbI_3)_{0.4} - (Ag_2WO_4)_{0.6}$ at six different temperatures

Generally, the temperature dependence of conductivity (σ) in the case of an ideal superionic glassy material below its glass transition temperature may be expressed by the Arrhenius equation¹⁶

$$\sigma_{(T)} = (\sigma_0/T) \exp(-E_a/kT) \quad (2)$$

Where σ_0 is the pre-exponential factor, the activation energy for ionic migration within the solid, k , the Boltzmann constant and T is the absolute temperature. Though no glass transition temperature has been observed for any of those compositions of the present system over the temperature range 298-446 K, the characteristic β to α phase transition of AgI is found¹⁷ to occur at around 420 K in the case of compositions having $x=0.4, 0.3$ and 0.2 as is evident from the variation of electrical conductivity observed for all these compositions of the mixed system and shown as plots of $\log \sigma T$ as a function of temperature in Figure 4. The increase in the observed dc conductivity with temperature may be attributed to the increase in the thermally activated drift mobility of ions. From Figure 4, it is seen that in the temperature range 301-403 K, all the above compositions obey the Arrhenius relation. Usually, the activation energy for the conduction phenomenon represents the energy required for mobile ions to hop from one site to another within the solid¹⁸. Though no glass transition temperature has been observed for any of these systems over the temperature range 301-437 K, the characteristic β to α phase transition of AgI is found to occur with a change in slope at 420 K in the case of three different compositions having $x=0.4, 0.3$ and 0.2 . This feature may be due to the formation of AgI in these samples, as already revealed by DSC and XRD studies. The activation energies (E_a) evaluated from best-fit lines in the

temperature range 301-413 K along with appropriate conductivity equations are summarized in Table 2. Table 2 shows that the value of activation energy (E_a) is minimum (0.22 eV) for the best conducting composition $(\text{SbI}_3)_{0.4}(\text{Ag}_2\text{WO}_4)_{0.6}$.

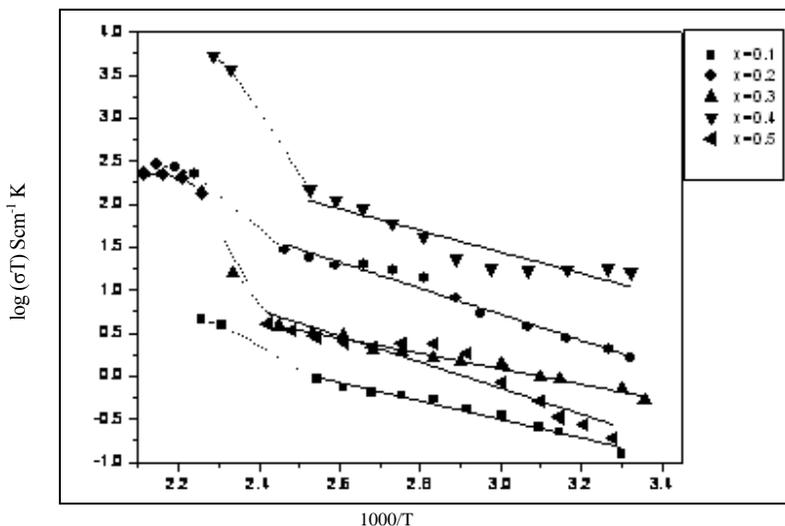


Figure 4. Variation of $\log(\sigma T)$ vs. $(1000/T)$ for $(\text{SbI}_3)_x(\text{Ag}_2\text{WO}_4)_{1-x}$ ($0.1 \leq x \leq 0.5$) specimens

Table 2. Temperature-dependent electrical conductivity data for the system $(\text{SbI}_3)_x(\text{Ag}_2\text{WO}_4)_{1-x}$

Composition (x)	Activation energy E_a (eV)	Conductivity equation $\log_{10}\sigma T = \log_{10}\sigma_0 - E_a / kT$
0.1	0.22	$\log_{10}\sigma T = 2.857 - 1.121 (10^3/T)$
0.2	0.24	$\log_{10}\sigma T = 4.433 - 1.187 (10^3/T)$
0.3	0.22	$\log_{10}\sigma T = 3.391 - 1.100 (10^3/T)$
0.4	0.21	$\log_{10}\sigma T = 4.68 - 1.061 (10^3/T)$
0.5	0.27	$\log_{10}\sigma T = 3.966 - 1.367 (10^3/T)$

The variation of frequency-dependent electrical conductivity (σ) in the form of plots of $\log\sigma T$ vs. $1000/T$ for the best conducting composition $(\text{SbI}_3)_{0.4}(\text{Ag}_2\text{WO}_4)_{0.6}$ is shown in Figure 5. It is obvious from Figure 5 that the Arrhenius relation is obeyed over the entire range of temperature (*i.e.*, 298-435 K) at different frequencies¹⁹. In the above temperature range of investigation, it is interesting to note that a constancy of activation energy (E_a^*) at all frequencies has also been observed. Table 3 presents the summary of frequency-dependent conductivity results obtained along with the value of activation energy for silver ion conduction (E_a) evaluated by complex impedance analysis for comparison. Table 3 also suggests the constancy of activation energies E_a^* derived from the least square curve fitting method for the best conducting composition. Frequency-dependent σ values also indicated that low activation energy is associated with the characteristic composition having the highest conductivity value²⁰. It is interesting to note from Table 3 that the value of activation energy (E_a^*) obtained from frequency-dependent Arrhenius plots also agree well with that of (E_a) (*i.e.* 0.21 eV) calculated during the complex impedance analysis.

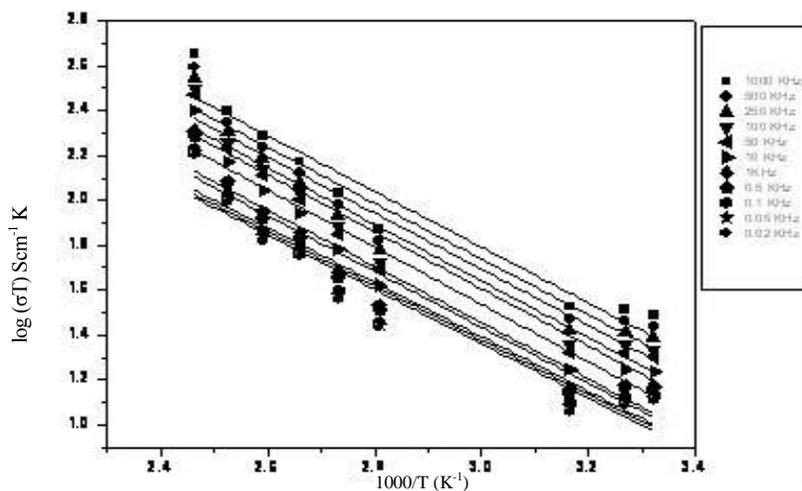


Figure 5. Plots of $\log(\sigma T)$ vs. $(1000/T)$ at various frequencies for the best conducting composition $(\text{SbI}_3)_{0.4}-(\text{Ag}_2\text{WO}_4)_{0.6}$

Table 3. Frequency-dependent conductivity results on the best ionic conducting composition $(\text{SbI}_3)_{0.4}-(\text{Ag}_2\text{WO}_4)_{0.6}$

Frequency (Hz)	Frequency-dependent conductivity equation $\log_{10}\sigma T = \log_{10}\sigma_0 - E_a^*/kT$	Frequency-dependent activation energy E_a^* (eV)	Activation energy calculated from dc conductivity E_a (eV)
1000000	$\log_{10}\sigma T = 5.173 - 1.131 (10^3/T)$	0.23	0.21
500000	$\log_{10}\sigma T = 5.128 - 1.133 (10^3/T)$	0.23	
250000	$\log_{10}\sigma T = 5.107 - 1.141 (10^3/T)$	0.23	
100000	$\log_{10}\sigma T = 5.094 - 1.155 (10^3/T)$	0.23	
50000	$\log_{10}\sigma T = 5.088 - 1.171 (10^3/T)$	0.23	
10000	$\log_{10}\sigma T = 5.038 - 1.171 (10^3/T)$	0.23	
1000	$\log_{10}\sigma T = 4.884 - 1.147 (10^3/T)$	0.23	
500	$\log_{10}\sigma T = 4.832 - 1.136 (10^3/T)$	0.23	
50	$\log_{10}\sigma T = 4.657 - 1.097 (10^3/T)$	0.22	

Scanning electron microscopic (SEM) results

Figure 6 shows the set of SEM micrographs obtained for three different SbI_3 -rich compositions corresponding to $x=0.9$, 0.5 and 0.4 respectively in the case of the mixed system $(\text{SbI}_3)_x-(\text{Ag}_2\text{WO}_4)_{1-x}$. Figure 6(a) indicates the polycrystalline nature of the sample having $x=0.9$ with little scope for the agglomeration process to occur probably due to its low conducting nature. In the case of yet another sample having 0.5 mole fraction of SbI_3 as shown in Figure 6(b). AgI clusters are dispersed with other rod-like structures which may be attributed to the remaining constituent phases present and the feasibility of formation of AgI . On the other hand, Figure 6(c) depicts the SEM micrograph of the $(\text{SbI}_3)_{0.4}-(\text{Ag}_2\text{WO}_4)_{0.6}$ specimen, revealing the formation of AgI as agglomerates with an amorphous background. As is evidenced from the present SEM analysis, SbI_3 tends to combine with Ag_2WO_4 in order to form AgI dispersed clusters on rapid quenching thereby enhancing the observed electrical conductivity of the superionic system. Furthermore, the amount and size of such AgI clusters may reach an optimum level at $x=0.4$ mole fraction of SbI_3 and contribute

towards enhancement of ionic conductivity. Beyond the concentration of 0.4 mole fraction of SbI_3 , the formation of large crystallites may occur thus resulting in a reduced silver ionic transport²¹.

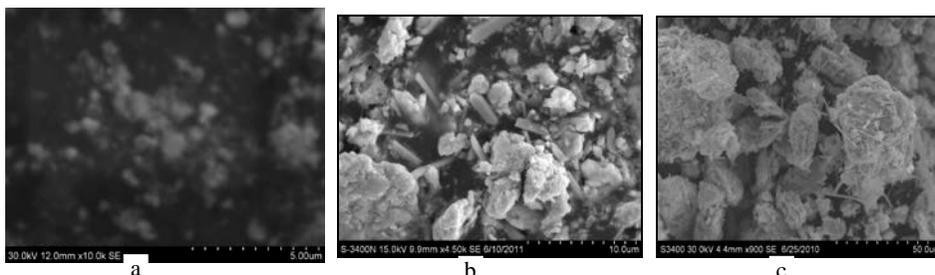
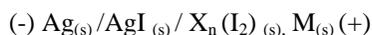


Figure 6. SEM micrographs of $(\text{SbI}_3)_x-(\text{Ag}_2\text{WO}_4)_{1-x}$ (a) $x = 0.9$ (b) $x = 0.5$ (c) $x = 0.4$

Solid state cell properties

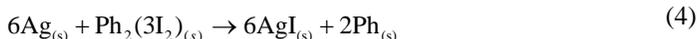
According to McKechnie *et al.*²², the overall cell reaction for a solid-state cell of the type,



In which AgI acts as solid electrolyte, M denotes an inert electronic conductor (e.g., graphite) and $\text{X}_n(\text{I}_2)_{(s)}$ an iodine molecular complex used as the source of iodine in the cathode, may be written as,



Therefore, the cell reaction occurring in the case of the above solid-state cell may be expressed as,



Where $\text{Ph}_2(3\text{I}_2)_{(s)}$ represents the 2:3 molar ratio I_2 -phenothiazine charge-transfer complex. The values of open circuit voltage (OCV) and short circuit current density of the freshly fabricated all solid-state electrochemical cell were found to be 603 mV and 1.38 mAcm^{-2} respectively at room temperature in good agreement with that of other silver batteries reported earlier²³. The above OCV is found to be comparable to the thermodynamically estimated value of 646 mV for a solid-state cell having silver as anode and phenothiazine-iodine (CTC) as the cathode element. In order to investigate the electrochemical stability of these newly fabricated cells and to identify their shelf life, the OCV was carefully monitored over a period of several months. The invariance of the measured OCV values tends to indicate an excellent electrochemical stability of the electrolytic medium against iodine diffusion at ambient conditions.

Conclusion

The occurrence of an enhancement in electrical conduction as a result of incorporation of the dopant SbI_3 into the matrix of silver oxysalt system, Ag_2WO_4 has been identified as due to the formation of AgI as a consequence of probable solid state exchange reactions taking place between SbI_3 and Ag_2WO_4 and confirmed by the relevant SEM analysis which has also revealed the presence of clusters of AgI within an amorphous background. The detailed analysis of ion transport properties has shown that the observed charge transport phenomenon is essentially ionic in nature, due to the Ag^+ ionic motion as evidenced by the ionic transport number (t_i) and silver ion transport number (t_{Ag^+}) data as well. The temperature

and frequency-dependent electrical conductivity results were found to reveal the Arrhenius type of behavior. The performance evaluation of all-solid-state cells fabricated with the best conducting composition $(\text{SbI}_3)_{0.4}-(\text{Ag}_2\text{WO}_4)_{0.6}$ has suggested their suitability for low-power device applications.

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