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Structural and electrical studies on thin films of solid electrolyte $Ag_6I_4WO_4$

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An electrolytic method of preparation of thin films of solid electrolyte $Ag_6I_4WO_4$ on a silver substrate is described. Films of different quality were obtained when the electrolysis was carried out at different temperatures and current densities. X-ray diffraction studies were carried out to confirm the compound formation. Scanning electron micrographs were taken in order to study the surface characteristics of these films. Investigations on the a.c. electrical conductivity of films prepared at different electrolysis temperatures (10 to 80° C) and two current densities (2 and 10 mA cm^{-2}) are also reported in the temperature range 30 to 130° C. The films deposited at 65° C gave values of room temperature conductivity and the activation energy for Ag^+ ion conduction as $0.04\ \Omega^{-1}\ cm^{-1}$ and 0.132 eV, respectively.

1. Introduction

In recent years there have been many fascinating studies on superionic conductors. It is due to the fact that they could be used as solid electrolytes in solid state batteries and in other electrochemical devices which would overcome some of the problems associated with conventional liquid electrolyte systems. AgI is a superionic solid having a silver ion conductivity of $1\ \Omega^{-1}\ cm^{-1}$ at 150° C, while in its β-phase (i.e. below 147° C) it exhibits a low conductivity of $10^{-4}\ \Omega^{-1}\ cm^{-1}$. Many attempts have been made to substitute either the cation or the anion in silver iodide. Anions such as WO_4^{2-}, CrO_4^{2-}, MoO_4^{2-}, PO_4^{3-} and AsO_4^{3-} have been successfully introduced into the lattice of AgI [1].

Takahashi *et al.* [2] have reported a few solid electrolytes such as $Ag_4I_2WO_4$, $Ag_5IW_2O_8$ and $Ag_6I_4WO_4$, in the complex salt system AgI–Ag_2WO_4 having electrical conductivities in the range of 10^{-6} to $10^{-2}\ \Omega^{-1}\ cm^{-1}$ at 25° C. There are many reports on the compound $Ag_6I_4WO_4$ in the bulk form [3–6]. Before attempting to use this material in thin film devices, it is important to understand its properties in thin film form. In general, the electrodeposition technique is a simple one and this technique was extensively used by Chandra and co-workers to prepare films of KAg_4I_5 [7], $Ag_7I_4PO_4$ [8] and $NH_4Ag_4I_5$ [9]. This paper deals with the deposition of the solid electrolyte $Ag_6I_4WO_4$ by the above technique. Films were deposited onto a pure silver substrate when electrolysis was carried out at different temperatures. The structural and electrical characteristics of these films are also discussed.

2. Experimental methods

2.1. Deposition of films

Analar grade $Na_2WO_4 \cdot 2H_2O$ and a 55% solution of hydriodic acid (HI) were used as starting materials. Two thoroughly cleaned silver plates of 99% purity were used as electrodes. An electrolyte solution was prepared by mixing $Na_2WO_4 \cdot 2H_2O$ and HI in the molar ratio of 1:4 in water. The experimental arrangement for the deposition was the same as described in our earlier work [10] for the compound $Ag_5IW_2O_8$. The electrolysis was carried out at various temperatures, namely, 10, 32, 50, 65 and 80° C. Current densities of 2, 4, 6 and 10 mA cm^{-2} were employed. The films were deposited on the anode plate. The thickness of the films was measured using a travelling microscope with an accuracy of ± 10 μm.

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2.2. Characterization of the compound

The films were annealed at 100° C for 3 h. They were ground into fine powder and X-ray diffraction studies were carried out using a Philips X-ray Diffraction unit with Cu*K*α radiation ($\lambda = 0.15418$ nm). Surface characteristics of these films were analysed using a Cambridge Scanning Electron Microscope (model stereoscan).

2.3. Measurement of electrical conductivity

The silver plate containing film acted as one electrode and the other electrode was made by the application of silver paint on a portion of the film. Details of the experimental set-up were described earlier [10]. The resistance of the films at various temperatures was measured using a General Radio Impedance Bridge (165OB) operating at a frequency of 1 kHz. A precalibrated copper–constantan thermocouple was used to measure the sample temperature.

3. Results and discussion

3.1. Formation of films

Figs. 1a and b indicate the variations in the front side film thickness with respect to time, temperature and current density. Two silver plates immersed in the aqueous solution of $Na_2WO_4 \cdot 2H_2O$ with HI were surrounded by water molecules as well as anions (I^- and WO_4^{2-}) and cations (Na^+ and H^+) in the solution. When the electric field was applied, hydrated cations and anions would move towards the cathode and anode, respectively. (Compounds which are chemically favourable and thermodynamically stable would be formed at the electrodes after electrolysis.) At the anode both I^- and WO_4^{2-} ions would have reacted with Ag^+ ions supplied by the anode to form the compound $Ag_6I_4WO_4$, while the H^+ ions formed hydrogen molecules and evolved as gas at the cathode.

Once a layer of $Ag_6I_4WO_4$ was formed, the thickness was controlled by the diffusion of Ag^+ ions through this layer which should be available for the formation of successive layers of the compound. In the beginning the film growth rate should be fast and then slow down as the thickness was increased.

3.2. Structural studies

3.2.1. X-ray analysis

In order to confirm the formation of the compound, powder X-ray diffraction studies were carried out on typical films (removed from the anode) using Cu*K*α radiation. Our results were compared with the earlier data [2] and it was found that the films deposited at 65° C contained $Ag_6I_4WO_4$ as their major content (see Table I).

TABLE I X-ray diffraction results for $Ag_6I_4WO_4$

Reported data [2]		Present results	
d(nm)	*I*	*d*(nm)	I/I_0(%)
0.444	W	–	–
0.425	VW	–	–
0.413	VW	0.415	29
0.379	MWB*	0.375	46
0.368	MB	0.371	50
0.348	MSB*	0.345	54
–	–	0.344	96
0.318	MB	0.3198	63
0.296	MB	–	–
0.292	M	0.292	58
0.287	M	0.287	67
0.271	SB*	0.276	83
–	–	0.262	71
0.256	WB	0.256	100
0.246	W	0.246	50
0.238	WB	0.237	46
0.231	WB	–	–
0.218	MB	0.218	54
–	–	0.214	71
0.193	WB	0.194	46
–	–	0.187	50

*MB, MWB, MSB and SB; B means that the peak is rather broad.

3.2.2. SEM analysis

The films of $Ag_6I_4WO_4$ were examined by scanning electron microscopy in order to know about their surface characteristics. SEM pictures of films deposited at various temperatures 32, 50, 65 and 80° C and at a constant current density of 2 mA cm^{-2} were taken. From Fig. 2a it is seen that even in the same film the grain size varies from 1 to 7 μm and that from room temperature (RT) to 80° C the grain size increases with increasing temperature of electrolysis; moreover a 65° C film exhibits a rather smooth surface and contains a small number of voids. Accordingly we should expect the conductivity of a 65° C film to be the maximum compared to others. Although a 32° C film too shows a fairly smooth surface, due to the smaller grain size and the presence of voids, its conductivity value is expected to be relatively lower than the 65° C film. Conductivity studies to be discussed in the next section agree with this. Fig. 3a suggests

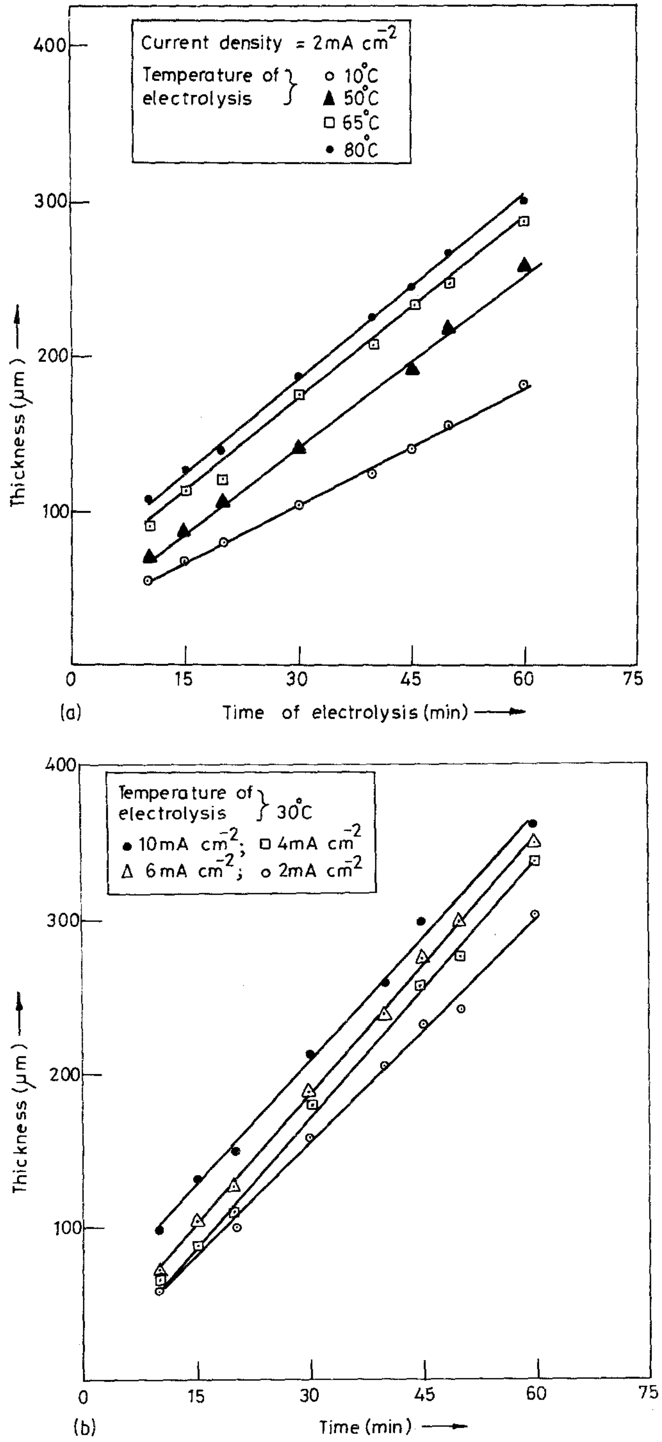

Figure 1 (a) Thickness of $Ag_6I_4WO_4$ films as a function of time for various electrolysis temperatures. (b) Thickness variations of $Ag_6I_4WO_4$ films with respect to current density.

that when the current density is increased to 10 mA cm^{-2} the grain size decreases, incorporated by lots of voids which account for its low value of electrical conductivity. Similar arguments hold good for a thinner film as shown in Fig. 3b.

3.3. Characterization of films

The properties of the electrodeposited films obtained in our study were found to depend on many important parameters such as electrolysis temperature, the current density, the pH of the solution and the presence of mechanical stress,

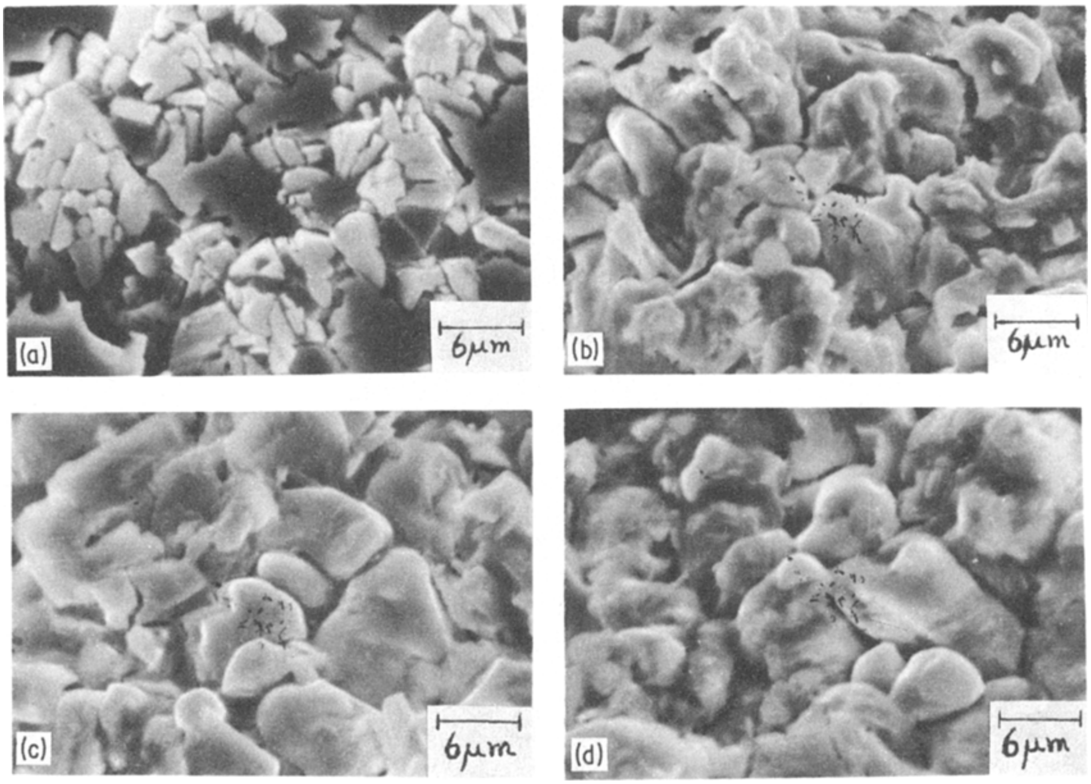

Figure 2 SEM pictures of $Ag_6I_4WO_4$ films deposited at different temperatures (film thickness, 100 μm; current density, 2 mA cm^{-2}): (a) 32° C, (b) 50° C, (c) 65° C, (d) 80° C.

voids and the impurities. Fig. 1a indicates that the thickness increases linearly with time, showing a constant growth rate. It is also seen that the thickness behaviour is similar in both 65 and 80° C films and that the thickness is a maximum in the case of a 80° C film for any time interval (e.g. 30 min). The reason for such behaviour can be understood on the basis of stress in these films.

During all our depositions we have also observed considerably thick films on the rearside of the substrate. In general, mechanical stress in films depends on the temperature of the substrate. With this in mind, the temperature dependence of the backside film thickness is studied for a frontside film thickness of 100 μm. The back side film thickness is studied proportional to the mech-

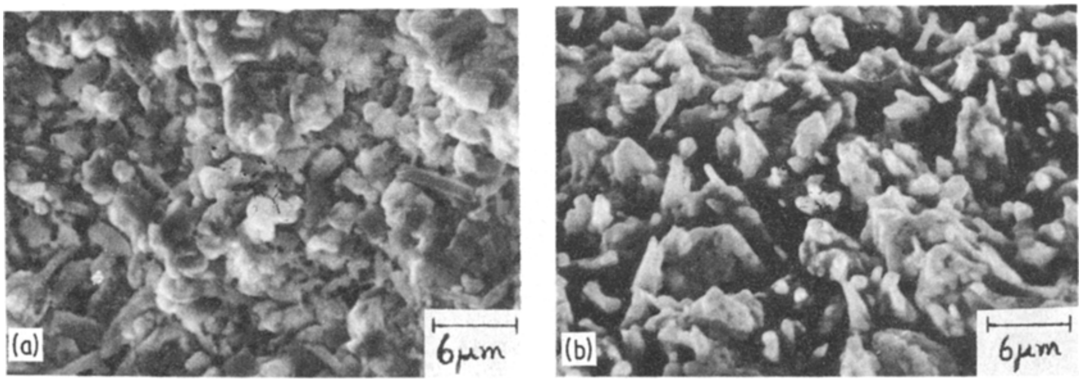

Figure 3 (a) SEM pictures of $Ag_6I_4WO_4$ film deposited at a current density of 10 mA cm^{-2} (film thickness, 100 μm; electrolysis temperature, 32° C). (b) SEM picture of $Ag_6I_4WO_4$ film of thickness 50 μm (electrolysis temperature, 32° C; current density, 2 mA cm^{-2}).

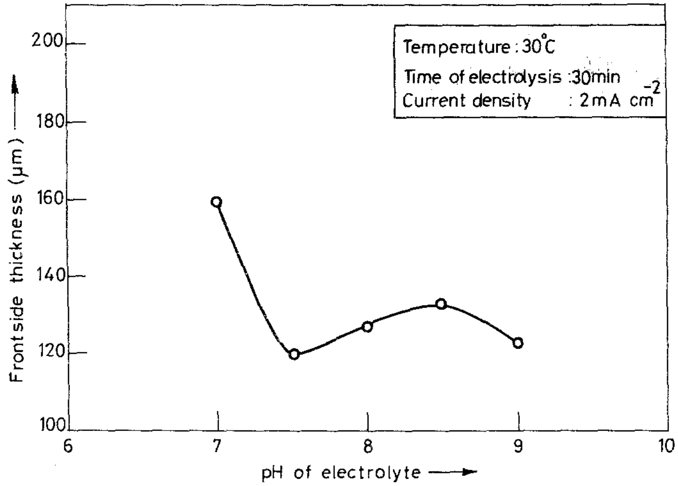

Figure 4 Variation in the front side film thickness with respect to the pH of electrolysis.

anical stress. From these studies it has been found that among the five temperatures (namely, 10, 32, 50, 65 and 80° C) chosen, only at 65° C was the stress the least. Since the stress is small the electrical conductivity is expected to be large in this film. Nevertheless, the fastest growth rate at 80° C could be due to the presence of voids, because even voids of microscopic dimensions would increase the film thickness by leaving hollow spaces within the films. This process would lead to low electrical conductivity and large mechanical stress. The X-ray results and SEM analysis discussed earlier indicate that this explanation is valid for films deposited at 80° C, while at 65° C the least built-in mechanical stress prevails and it is responsible for the formation of thicker films at 65° C. Chandra and Mohabey [7] also have observed similar behaviour in the case of KAg_4I_5.

From Fig. 1b it is found that as the current density is increased the growth rate also increases. This is due to the fact that the migration of ions in an electrolyte solution and hence the rate of film deposition are influenced by the current density.

In addition, Fig. 4 shows the thickness of the front side film deposited at a current density of 2 mA cm^{-2} as a function of the pH of electrolyte. It is clear from Fig. 4 that the pH of the solution has very little effect on the film thickness.

3.4. Electrical conductivity studies

3.4.1. *Temperature dependence of conductivity*

Fig. 5 gives the temperature dependence of the electrical conductivity of films deposited at various temperatures, namely 10, 32, 50, 65 and 80° C for a film thickness of 150 μm. This figure shows that the films obtained at 65° C have the maximum conductivity, a typical value being 0.04 Ω^{-1} cm^{-1} at 28° C, which agrees with the reported value of 0.047 Ω^{-1} cm^{-1} at 25° C [2]. The activation energy was found to be 0.132 eV for the silver ionic conductivity, whereas the reported value was 0.158 eV. The highest conductivity of films deposited at 65° C is due to the least stress, the least number of voids and their being of best quality. This is supported by X-ray and SEM analysis.

It is also seen that a 32° C film shows a conductivity value of 10^{-3} Ω^{-1} cm^{-1} which is an order of magnitude less than that of the reported one, while giving an activation energy value of 0.161 eV. This may be attributed to the presence of voids in a 32° C film as discussed earlier. Low values of electrical conductivity of films prepared at 10, 50 and 80° C may be attributed to the presence of low conducting β-AgI [8]. Fig. 6 shows the electrical conductivity of films deposited at three different temperatures as a function of the film thickness. This figure has been considered only as supporting evidence to prove that for any thickness 65° C is the most suitable temperature for obtaining $Ag_6I_4WO_4$.

3.4.2. *Current density dependence of conductivity*

The quality of the electrodeposited film is also affected by the current density. Fig. 7 gives the electrical conductivity of 65° C films deposited at 2 and 10 mA cm^{-2}. It is clear from Fig. 7 that for

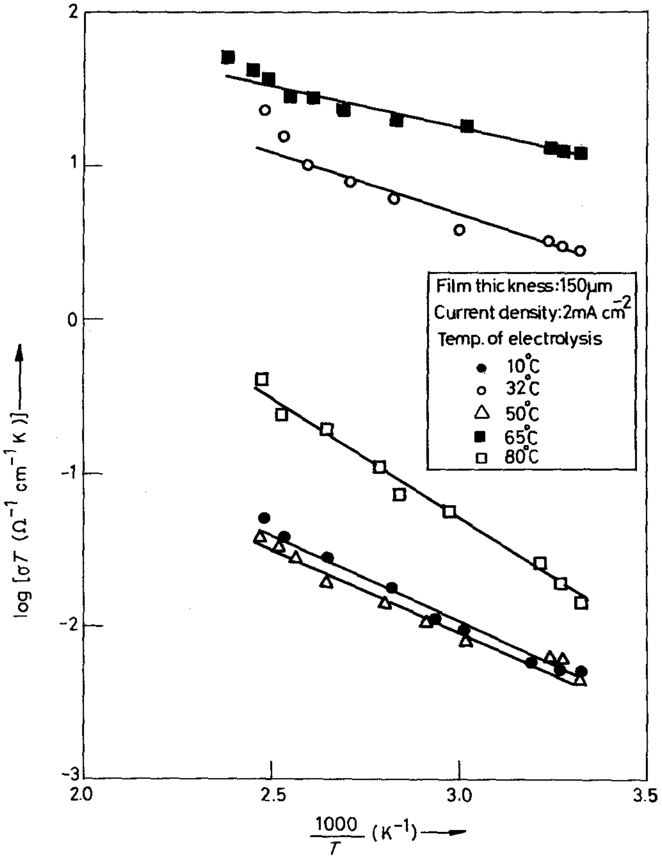

Figure 5 Log (σT) against $1/T$ plot for $Ag_6I_4WO_4$ films deposited at various temperatures.

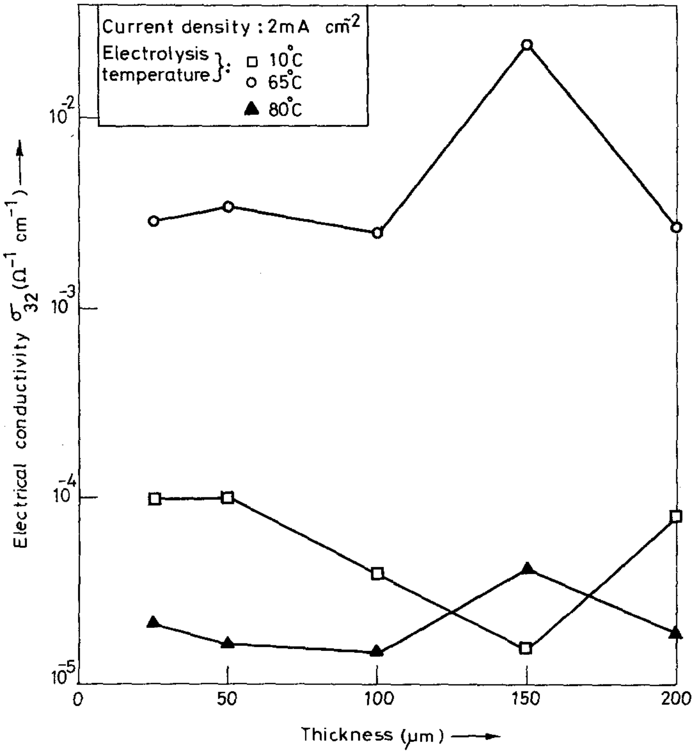

Figure 6 The room temperature conductivity of $Ag_6I_4WO_4$ films as a function of film thickness for various electrolysis temperatures.

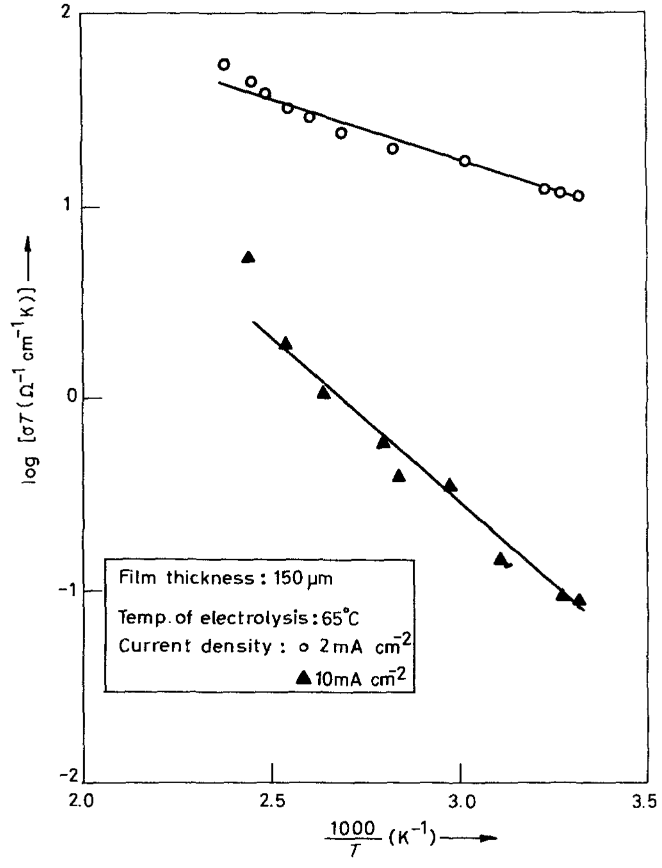

Figure 7 Log (σT) against $1/T$ plot for $Ag_6I_4WO_4$ films deposited at two different current densities.

the 65° C films a current density of 2 mA cm^{-2} may be preferred to higher values since the former leads to a higher electrical conductivity.

4. Conclusion

Thin films of the solid electrolyte $Ag_6I_4WO_4$ were successfully deposited onto silver substrates by the electrodeposition technique. From X-ray and SEM analysis it was possible to arrive at the optimum experimental conditions which would yield films having $Ag_6I_4WO_4$ material as their major constituent. Good quality films were obtainable at a temperature of 65° C and at a current density of 2 mA cm^{-2}. This is due to the presence of the least built-in mechanical stress in these films. These films showed an electrical conductivity of 0.04 Ω^{-1} cm^{-1} at 28° C and an activation energy of 0.132 eV for Ag^+ ion transport. SEM analysis showed that 65° C films had a rather smooth surface containing a smaller number of voids. The pH of the electrolyte solution did not have any considerable effect on film thickness.

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