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Transport studies on thin films of $Ag_7I_4VO_4$ solid electrolyte

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Deposition of thin films of the solid electrolyte $Ag_7I_4VO_4$ by an electrodeposition technique is discussed. The X-ray diffraction technique has been used for the characterization of the films. Measurement of a.c. electrical conductivity in the temperature range 300–400 K showed that films deposited at 313 K and at a current density of $8\,mA\,cm^{-2}$ are of the best quality, having a typical conductivity of $1.5 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$ at room temperature (305 K) with an activation energy of 0.2 eV. Dielectric studies carried out on the best quality films showed that $Ag_7I_4VO_4$ possesses a high value of dielectric constant ($\sim 10^5$). The frequency dependence of the dielectric constant is explained as due to an interfacial polarization phenomenon. The behaviour of the dielectric ion suggests a Debye-type relaxation.

1. Introduction

In the past few decades a new category of solid material, known as solid electrolytes or superionic conductors (SIC), has instigated interest because of their high ionic conductivity under ambient conditions. These materials are particularly useful in designing solid state batteries and other electrochemical devices. Furthermore, use of solid electrolytes overcomes most of the problems associated with liquid electrolytes. AgI is one of the few SICs with a silver ion conductivity of $1\,\Omega^{-1}\,cm^{-1}$ at 420 K (α-phase). For it to be useful commercially, however, this high conducting phase must occur near room temperature. In order to achieve this, AgI has been doped both with cations such as Cd^{2+}, Hg^{2+} etc. and anions such as CrO_4^{2-}, MoO_4^{2-}, VO_4^{3-}, etc. [1]. The main effect of these dopants is to stabilize the α-phase at or near room temperatures.

Scrosati *et al.* [2] reported briefly on AgI–Ag_3XO_4 (X = V, As) as possible solid electrolytes. Studies on AgI–Ag_2O–V_2O_5 glassy and polycrystalline systems have been carried out [3, 4]. The present work deals with investigations of thin films of the silver iodo-vanadate system by an electrodeposition technique. This method is a simple one and, moreover, it is the one best suited for these compounds as they dissociate at temperatures greater than 120° C. This technique has been used to prepare films of $Ag_7I_4XO_4$ (X = As, P) [5, 6]. In the present studies, films of $Ag_7I_4VO_4$ were deposited onto a pure silver (99.99%) substrate by carrying out electrolysis at different current densities and temperatures. The structural and transport characteristics of the best quality films obtained are discussed here.

2. Experimental methods

2.1. *Deposition of films*

Analar grade NH_4VO_3 and a 48% solution of hydroiodic acid were used as starting materials. Two thoroughly cleaned silver plates of 99.99% purity were used as electrodes. The electrolyte solution was prepared by mixing 0.35 g of NH_4VO_3 in 300 cm^3 of distilled water, and ten drops of HI acid were added to the solution. These values were arrived at after a trial and error method to obtain the best quality films which had a composition nearest to that of the stoichiometric compound, i.e. $Ag_7I_4VO_4$. These films were coated at room temperature and at a constant current density of $2\,mA\,cm^{-2}$. The experimental arrangement for the deposition has been described elsewhere [7]. Once these values were determined, the most ideal current density was found by coating films at room temperature and varying the current density at 4, 6, 8, 12 and 16 mA cm^{-2}. It was found that there was a large porosity in films prepared at 4 and 6 mA cm^{-2}, while the adhesion of films prepared at 12 and 16 mA cm^{-2} was poor. In the latter case it was also observed that during electrolysis a black compound with yellow particles started collecting around the silver anode in the electrolysis solution and the film formed was of a different colour. This means that these current densities are much higher than required for film preparation and its bonding to the substrate. However, at an electrolysis current density of 8 mA cm^{-2}, films showing good adhesion and texture (smooth surface) could be obtained. In this case, also, very thick films had a tendency to develop cracks. Therefore, for all further experiments a current density of 8 mA cm^{-2} was used to obtain films of 70–80 μm. The best temperature was established by varying the temperature for the most suited current density at 305, 313 and 318 K. The films were deposited on the anode plate. The thicknesses of the films deposited were measured using a travelling microscope with an accuracy of $\pm 10\,\mu$m. This method was used because the other common optical techniques such as interference, photometric or polarimetric methods cannot be applied, since the films are opaque.

2.2. *Characterization*

The films were scraped off the silver substrate and ground into fine powder, and powder X-ray diffraction studies were carried out using a Phillips X-ray diffraction unit with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å).

2.3. *Transport studies*

Measurements of a.c. electrical conductivity (σ) were made on the electrodeposited films using the technique described elsewhere [7]. The resistance of the samples at different temperatures (300–400 K) was measured using a GR impedance bridge (1650 B) operating at a frequency of 1 kHz. The sample temperature was measured by a pre-calibrated copper–constantan thermocouple. For dielectric measurements a parallel plate capacitor was constructed using the thin film as the dielectric. The silver substrate was used as one plate while silver paint applied over a known area of the thin film was used as the other plate. The thickness of the film was measured before applying the paint. The dielectric parameters studied were the variation of the capacitance and dielectric loss of the above capacitor with frequency at different temperatures (300–400 K). The measurements were carried out on the bridge mentioned above in conjunction with an Electronic Corporation (India) Function Generator type FG 6025. Only a sinusoidal wave form was used, and the voltage applied across the specimen was kept constant at 2 V over the entire frequency range (10^3 to 10^5 Hz). All the above measurements were carried out in vacuum.

3. Results and discussion

3.1. *Formation of films*

The two silver plates immersed in the aqueous solution of NH_4VO_3 with HI are surrounded by water molecules as well as anions (I^- and VO_4^{3-}) and cations (NH_4^+ and H^+) in the solution. When the electric field is applied, hydrated cations and anions move towards the cathode and anode respectively. The reactions at the electrodes are:

Anode

$$Ag \longrightarrow Ag^+ + e \text{ (oxidation)} \qquad (1)$$

$$7Ag^+ + 4I^- + VO_4^{3-} \longrightarrow Ag_7I_4VO_4 \qquad (2)$$

Cathode

$$H^+ + e \longrightarrow H \text{ (reduction)} \qquad (3)$$

$$H + H \longrightarrow H_2 \text{ (gas)} \qquad (4)$$

$Ag_7I_4VO_4$ is deposited as a film on the silver anode while H_2 is evolved as gas from the cathode.

Once a layer of $Ag_7I_4VO_4$ is formed, the thickness is controlled by the diffusion of Ag^+ ions through this layer. This is why, initially, the film

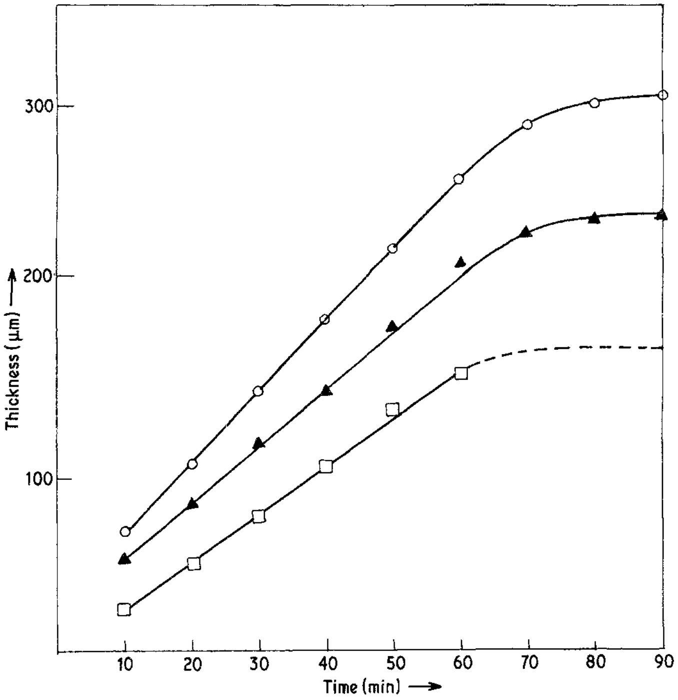

Fig. 1. Variation of the film thickness with deposition time for a constant current density of 8 mA cm^{-2} and different deposition temperatures (K): ▲, 305; ○, 313; □, 318.

growth rate is faster and then slows down as the thickness increases, as is evident from the thickness versus time plots (Fig. 1).

3.2. *Characterization studies*

The thin films obtained under various electrolysis conditions were scraped off the substrate, ground into a fine powder and subjected to X-ray diffraction (XRD). The XRD data obtained for films deposited at 313 K and at a current density of 8 mA cm^{-2} did not contain any strong peaks corresponding to AgI [8], and Ag_3VO_4 [2]. In fact, they correspond to the $Ag_7I_4VO_4$ data [2] (Table 1). Further, the sharpness of the bands indicates that the films formed are not amorphous. These observations suggest that good quality films of $Ag_7I_4VO_4$ are formed at a current density of 8 mA cm^{-2} and at a temperature of 313 K.

Table 1. X-ray diffraction data for films deposited at 313 K and a current density of 8 mA cm^{-2}

Reported data						*Present data*	
AgI [8]		Ag_3VO_4 *[2]*		$Ag_7I_4VO_4$ *[2]*		$Ag_7I_4VO_4$	
d *(Å)*	I/I_0 *(%)*	d *(Å)*	I/I_0 *(%)*	d *(Å)*	I/I_0 *(%)*	d *(Å)*	I/I_0 *(%)*
3.75	100	4.55	30	3.94	30	3.94	30
2.30	70	2.86	100	3.62	50	3.72	76
1.96	40	2.73	100	3.00	50	2.91	52
		2.54	45	2.83	50	2.78	52
				2.71	80	2.44	100
				2.58	100	2.28	66
						2.03	72
						1.95	40
						1.43	32
						1.22	32

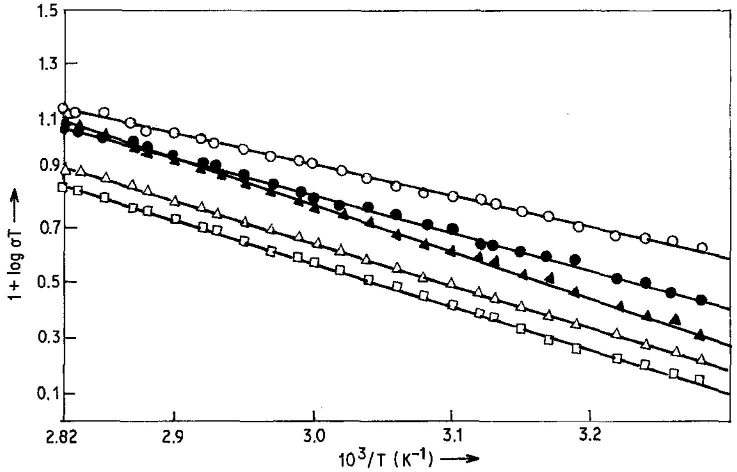

Fig. 2. Variation of log σT with temperature of films deposited at 305 K at different current densities (mA cm^{-2}): □, 4; ●, 6; ○, 8; ▲, 12; △, 16.

3.3. *Electrical conductivity studies*

3.3.1. Current density dependence of conductivity. Current density plays a major role in determining the quality of the deposited films. Fig. 2 gives the electrical conductivity of films deposited at a constant temperature of 305 K at different current densities of 4, 6, 8, 12 and 16 mA cm^{-2}. From this figure it is clear that the current density of 8 mA cm^{-2} is most suitable for film deposition because it gives the highest value of conductivity at any temperature. The changes in the bulk properties may be explained as follows. The lower conductivity value of the films obtained at current densities below 8 mA cm^{-2} may be attributed to

(i) the presence of voids,

(ii) the formation of low conducting β-AgI [5].

The porous nature of the films confirms the presence of voids. The presence of β-AgI is confirmed by the formation of a yellow layer on the substrate, the X-ray diffractogram of which showed peaks corresponding to β-AgI. At these current densities, i.e. 4 and 6 mA cm^{-2}, this layer of β-AgI inhibits the formation of the desired compound. The formation of β-AgI could be due to the I$^-$ ions arriving at the substrate in a greater concentration than required. This was further confirmed by depositing a layer of AgI on the silver plate by electrolysis using KI as the electrolyte solution. This film, together with the substrate was then put in the electrolytic solution for obtaining $Ag_7I_4VO_4$. It was found that at these current densities (4 and 6 mA cm^{-2}) no significant formation of $Ag_7I_4VO_4$ took place. However, when the current density was increased to 8 mA cm^{-2} a reddish brown film was observed, which was the colour of the required compound. However, this could not be confirmed by the XRD owing to the small quantity and contamination from the AgI layer.

At current densities greater than 8 mA cm^{-2} the formation of the low conducting compound could be attributed to:

(i) formation of AgOH, which decomposes to Ag_2O by a photochemical effect,

(ii) faster dissolution of silver in the solution, resulting in the precipitation of AgI,

(iii) exceeding the oxygen overvoltage value of silver in water.

The formation of the black deposit at the bottom of the silver anode, substantiates (i) to a certain extent, but the XRD of this substance gave peaks which were not unique to Ag_2O. Peaks corresponding to AgI and Ag_3VO_4 and some additional peaks were also observed. The presence of AgI peaks in the deposits could be explained on the basis of (ii), while the chipping off of the films on the substrate could be due to the formation of a thin oxygen layer (iii) on the substrate, which reduces the adhesive properties of the film.

The formation of good films at 8 mA cm^{-2} can be attributed to the right kinetic equilibrium existing for the I$^-$ and VO_4^{3-} ions arriving in the correct ratio at the substrate to form the

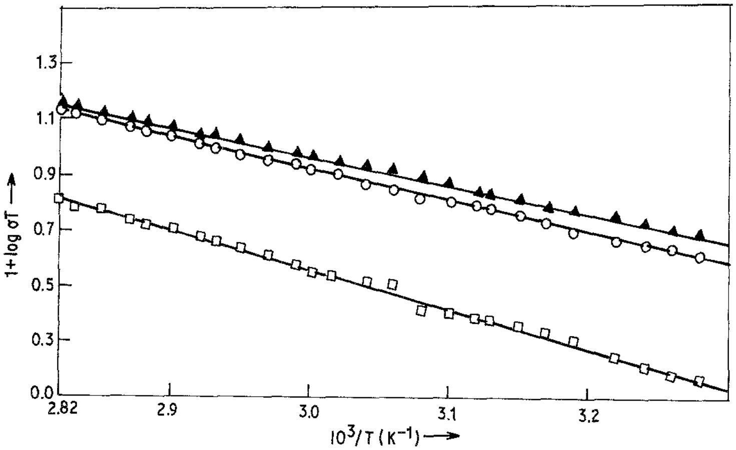

Fig. 3. Variation of log σT with temperature of films deposited at 8 mA cm^{-2} at different temperatures (K): ○, 305; ▲, 313; □, 318.

stoichiometric compound with the dissolving silver ions.

3.3.2. Temperature dependence. Once the best current density was established, the films were coated at different temperatures at this value of current density to obtain the best temperature value. Fig. 3 gives the typical log σT versus $10^3/T$ of these films deposited at 305, 313 and 318 K. The figure shows that the films deposited at 313 K show the highest conductivity at room temperature ($1.53 \times 10^{-3} \Omega^{-1} cm^{-1}$), which agrees well with the value of the bulk sample given elsewhere [4]. The activation energy obtained was 0.2 eV for silver ion migration in thin films, whereas in bulk it was reported to be 0.17 eV [4]. The thickness versus time plot (Fig. 1) indicates that initially the thickness increases linearly with time of deposition and then attains a constant value at any given time (x-axis); the film deposited at 313 K has the largest thickness as compared with those deposited at other temperatures.

The fastest growth rate (i.e. increase in thickness per unit time) at 313 K indicates that the films deposited at this temperature have the least built-in mechanical stress. However, even voids of microscopic dimensions would result in an apparent increase in the film thickness (owing to hollow spaces within the films). However, this would result in a large built-in mechanical stress and low conductivity. The conductivity results, however, indicate the absence of voids and low built-in mechanical stresses. Regarding the stress effects in electrodeposited films, the suggestions of Chandra and Mohabey were followed [9]. From the log σT versus thickness plot (Fig. 4) it is seen that, for any thickness, 313 K is the most suitable temperature for obtaining $Ag_7I_4VO_4$.

3.4. *Dielectric studies*

3.4.1. Dielectric constant. Fig. 5 gives the variation of the dielectric constant with frequency. The ε' values are observed to be fairly high, which is attributed to the high ionic conductivity in the material. Most of the solid electrolytes are known to possess high values of dielectric constant [10–12]. It is seen that initially ε' decreases rather sharply with increase in frequency and then tapers off to a constant value for higher frequencies. The variation at any temperature is similar, with the difference being only in the values of ε'. For any given frequency, ε' is

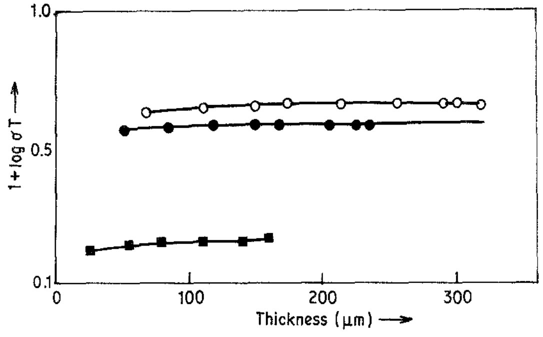

Fig. 4. Variation of log σT with thickness of the films deposited at different temperatures (K): ●, 305; ○, 313; ■, 316.

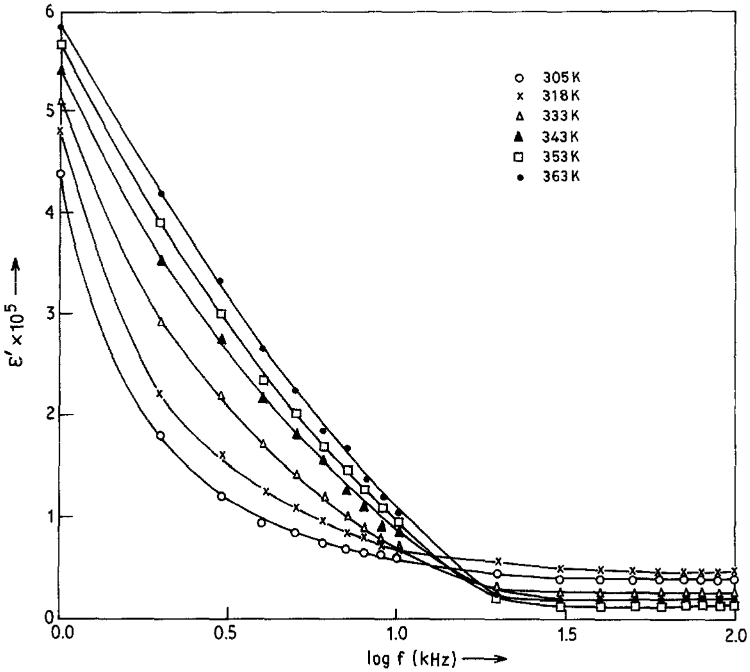

Fig. 5. Variation of the dielectric constant of the films deposited at $8\,\mathrm{mA\,cm^{-2}}$ at a temperature of 313 K with frequency.

greater at higher temperatures except in the region of higher frequencies where the variation at different temperatures is rather difficult to differentiate. The high values of ε' obtained may be attributed to the space charge layers created due to the ionic migration at low frequencies and high temperatures. These conform to the observations made by earlier workers [12–14]. It is also interesting to note that at higher temperatures the jump frequency of the mobile ions is large and matches the frequency of the applied electric field.

3.4.2. Dielectric loss. The variation of the dielectric loss with frequency is shown in Fig. 6. It is seen that for any given temperature the loss increases with frequency, reaches a peak at a characteristic frequency and then decreases. It is also observed that the characteristic frequency at which the loss peak occurs increases with the

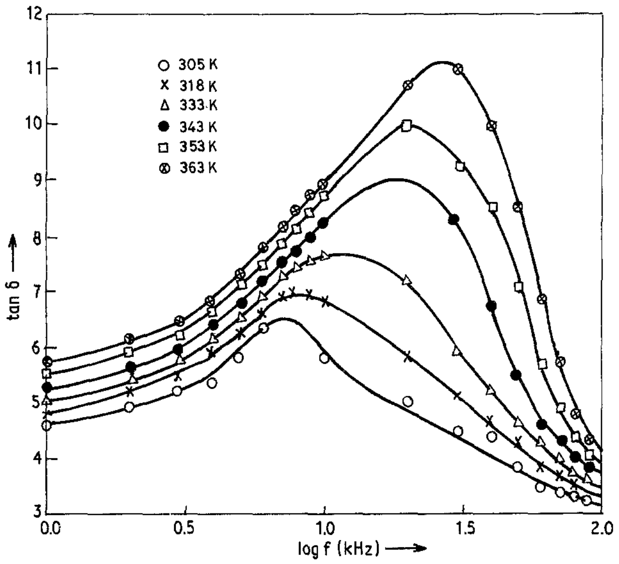

Fig. 6. Variation of the dielectric loss with frequency of the films deposited at $8\,\mathrm{mA\,cm^{-2}}$ at a temperature of 313 K.

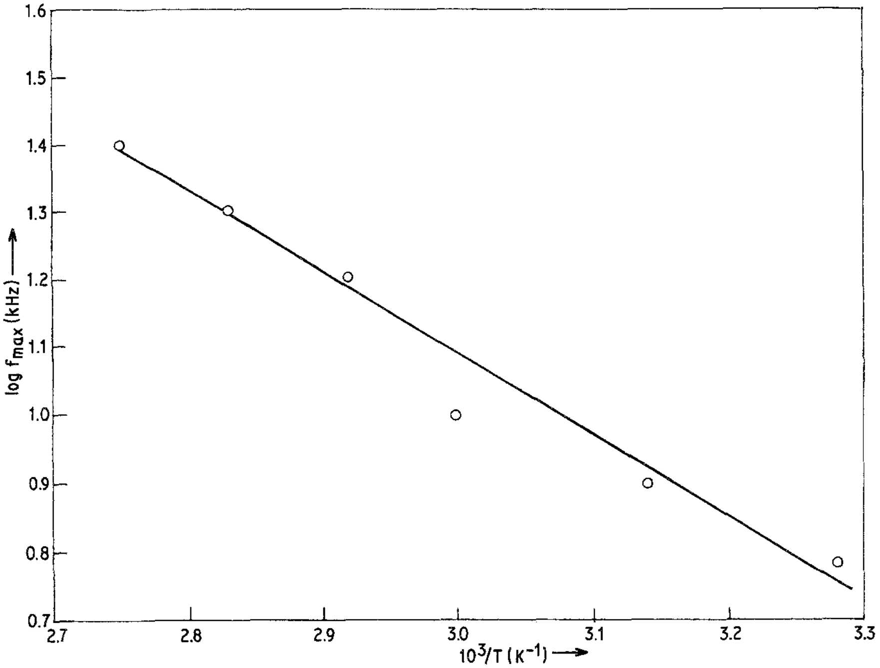

Fig. 7. Variation of log f_{max} with temperature for the film deposited at $8\,mA\,cm^{-2}$ at a temperature of 313 K. Activation energy = −0.23 eV.

temperature and that the rate at which the loss decreases after the peak also increases. The occurrence of a loss peak suggests a relaxation mechanism in the solid electrolyte, while the peak shifting with temperature signifies a behaviour similar to a Debye-type relaxation.

The most conventional equation relating the relaxation time (τ) and frequency (f_{max}) at which the loss peaks for a Debye-type relaxation is given by

$$2\pi f_{max}\tau = 1 \tag{5}$$

The relaxation time is a temperature-dependent factor and it decreases as the temperature increases. Thus, when the temperature rises, f_{max} becomes larger. Similar behaviour is observed in the present investigation as indicated in Fig. 6.

For a Debye process, f_{max} is given by

$$f_{max} = f_0 \exp\left(-\frac{\Delta E}{kT}\right) \tag{6}$$

where ΔE is the activation energy of the relaxation process, K is the Boltzmann constant and T the absolute temperature.

Fig. 7 shows the log f_{max} versus $10^3/T$ plot, i.e. the variation of f_{max} with inverse temperature, which gives a straight line of negative slope. From the graph the value of E_a is 0.23 eV which is comparable to that obtained from conductivity studies. The similarity in activation energy for ionic migration and that of the relaxation process indicates that the observed relaxation arises from the ionic migration which relaxes the space charge layer at the electrode. Such a relaxation is anticipated for solid electrolytes [15].

4. Conclusions

1. A simple electrodeposition method was used to obtain thin films of solid electrolyte $Ag_7I_4VO_4$. The optimum conditions required for preparing good quality films were established from structural and electrical studies.

2. Best quality films were obtained at a current density of $8\,mA\,cm^{-2}$ at a temperature of 313 K. These films show a typical electrical conductivity of $1.5 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$ at 300 K with an activation energy of 0.2 eV.

3. Dielectric studies were performed for the best quality films (i.e. at 313 K and $8\,mA\,cm^{-2}$). The results indicated a Debye type of relaxation

mechanism in the system due to hopping of Ag^+ ions. The value $\sigma_{300\,K}$, as obtained from dielectric studies, is $1.2 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$ with an activation energy of 0.23 eV. These values are comparable with those obtained from conductivity studies.

References

[1] T. Takahashi, 'Applications of Solid Electrolytes', SEC Inc., Cleveland, Ohio (1980) p. 8.

[2] B. Scrosati, F. Papaleo and G. Pistoia, *J. Electrochem. Soc.* **122** (1975) 339.

[3] K. Hariharan and Rajiv Kaushik, 'Materials for Solid State Batteries', World Scientific Publishing Co., Singapore (1986) p. 325.

[4] K. Hariharan, C. V. Tomy and Rajiv Kaushik, *J. Mater. Sci. Lett.* **4** (1985) 1379.

[5] S. Chandra, R. C. Agarwal and R. K. Panday, *J. Mater. Sci.* **37** (1980) 299.

[6] K. A. Murugesamoorthi, PhD Thesis, IIT, Madras (1986).

[7] S. A. Suthanthiraraj, B. V. R. Chowdari and S. Radhakrishna, *Thin Solid Films* **101** (1983) 131.

[8] ASTM card No. 9-399.

[9] S. Chandra and V. K. Mohabey, *Phys. Stat. Sol. A* **53** (1979) 63.

[10] R. Sudharsan, PhD Thesis, IIT, Madras (1983).

[11] A. Magestris and G. Chiodelli, *Electrochim. Acta* **26** (1981) 1241.

[12] R. D. Armstrong and K. Taylor, *J. Electronal. Interfacial Electrochem.* **63** (1975) 9.

[13] G. Cochrane and N. H. Fletcher, *J. Phys. Chem. Solids* **32** (1975) 2557.

[14] M. V. Susic and S. V. Mentes, *Electrochim. Acta* **28** (1983) 35.

[15] J. H. Andes, C. T. Moynihan and P. B. Macedo, *J. Phys. Chem.* **76** (1972) 3287.