Measurements of Ionic•Conductivity of Silver Fluoride-doped Silver Phosphate

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Summary: The present work deals with the study of electrical conductivity of the system $(AgPO_3)_{1-x}-(AgF)_x$ in the range $0.2 \leqslant x \leqslant 0.9$ mole fraction by method of complex impedance. Conductivity measurements were carried out between 70°C & 240°C. We observed a large increase of conductivity due to the doping effect by AgF. A maximum conductivity appears at X=0.8 mole fraction corresponding to a minimum activation energy(E =0.548 ev). Similar behaviour of maximum conductivity corresponding to a minimum activation energy has been observed in other solid electrolytes based on AgI [1,2,7,12,13].

Introduction

The electrolytes obtained from silver compounds exhibit high ionic conductivity at low temperatures for silver ions [1,5]. The most important use of these silver conductors in found in the development of solid-state batteries [6,7]. In a recent work, J.P. Malugani et. al. [8] have studied the ionic conductivity of silver phosphate doped with various concentrations of silver halides in their glassy states and have provided some interesting results. It will be equally interesting to investigate the ionic conductivity of silver phosphate doped with AgF in the crystalline form.

Experimental

Materials preparation

The preparation of samples of crystalline silver phosphate is based on the method described by Bouille [9]. Powdered silver phosphate is mixed with different quantities of powdered AgF within the concentration limits of 0.2-0.9 mole fraction. The mixture so obtained is pressed in to different cylindrical sizes at 400°C for 48 hours. The preliminary indications of X-ray analysis, using X-ray powder technique at room temperature, have shown the existence of a crystalline solid solution.

Method of measurements

The complex impedance method [10] which allows a clear separation of ionic conductivity of electrolyte from the effects of the electrode polarization has been used here to find the values of ionic conductivity for different samples in argon. The metallic electrodes used for the measurements are made of platinum from commercial paints. The conductivity measurements are made in the frequency range of 5Hz to 500 KHz using an Impedancemeter of Alcatal, type 2531.

Results and Discussion

The results of impedance measurements for symmeterical cell P_t/electrolyte/P_t are shown in figure (1). At high frequencies, the results are shown by an arc which is characteristic to the conduction of electrolyte. The impedance complex is obtained by the analytical relation [11].

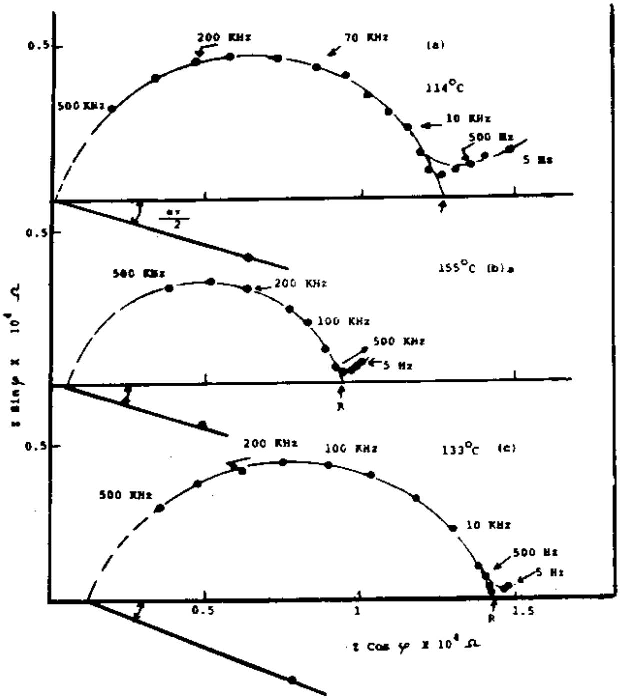

Fig.1 Complex impedance diagrams for the symmetrical cells: (c)pt/0.8 $AgPO_3$-0.2 AgF/Pt, (b) Pt/0.4 $AgPO_3$-0.6 AgF/Pt, (a) Pt/0.2 $AgPO_3$-0.8 AgF/Pt.

$$Z = \frac{Zo}{1 + (jwc_o)^{1-\alpha}}$$

Where Zo is the value of the impedance which is given by the intersection of the arc with the real axis. This Zo is equivalent to the ohmic resistance of the electrolyte, τo can be obtained from the value of the angular frequency w at the top of the arc where $w\tau o = 1$. The centres of arc lie on a straight line which makes an angle $\alpha\pi/2$ with the real axis. This angle is characteristic of the material and can be attributed to scattering of the local conductivity [11]. The results at low frequencies are represented by the begining of another arc. This part is due to the polarization of the electrodes. The results of ionic conductivity measure-

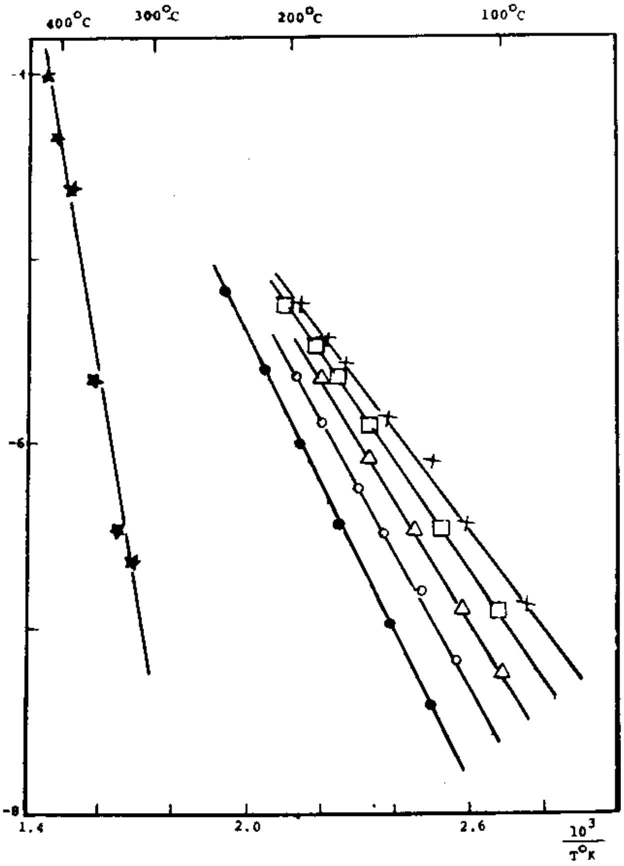

Fig.2 Temperature dependance of the ionic conductivity of various doped Samples : (0) 0.2 mole fraction AgF, (△)0.4 mole fraction AgF, (□) 0.6 mole fraction AgF, (x) 0.8 mole fraction AgF, (o) 0.9 mole fraction AgF, (★) pure $AgPO_3$.

ments, made for various doped samples, are shown in figures (2) as a function of temperature. Our results can be expressed by the following equation:

$$\sigma=A\exp(\frac{E\sigma}{RT})$$

Where σ is the conductivity of the material, A the preeexponential term, E, the activation energy of the electrical conductivity and R is the gas constant. The various values of activation energy obtained in the present work are listed in table I. The variation of the conductivity with the mole fractions of AgF are shown in figures [3]. These results show a maximum conductivity at 0.9 mole fraction of AgF, where the activation energy is lowest for this composition. A similar observation is reported by several workers in the case of solid electrolytes based on AgI [1,2,12,13]. Successful interpretation of the conductivity results has not yet been found out. These workers have spoken only about the formation of intermediate compounds in these materials. However we have not observed formation of such compounds by X-ray anyalysis. The classical attempt to interpret the conductivity results in crystalline solid electrolyte attributes the experimental results to the interaction of defects or ions responsible for conductivity. The electrical conductivity must increase with the concentration of charge carriers; but one has to take into account the influence of the concentration of charge carriers on their mobility. This property is very sensitive to concentration and therefore it is very difficult to estimate its effect.

The electronic conduction in these electrolytes is checked by number of measurements carried out under dc conditions and found that dc electronic resistance is at least 7 order of magnitude greater than the ionic resistance.

The large enhancement in conductivity of silver phosphate at low temperature due to the presence of AgF makes good silver electrolytes which may find many applications in industry.

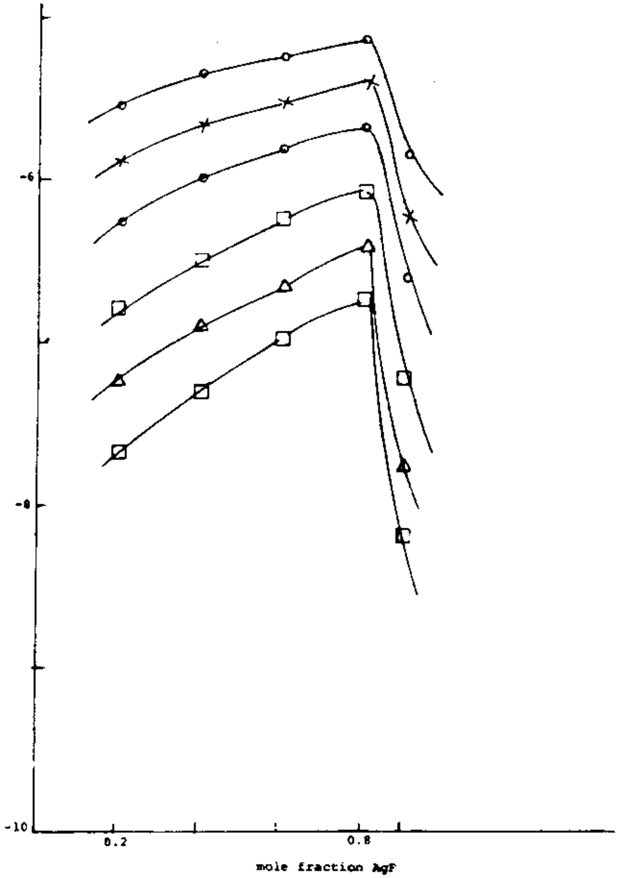

Fig.3 Composition dependance of the ionic conductivity at different temperatures.( ) 97°C,(Δ) 114°C,(o) 136°C, (O) 161°C,(x) 181°C, ( ) 203°C.

Table.1. Ionic conductivity data at 100°C and the values of activation energy of the samples.

Mole fraction AgF	Conductivity at 100°C($ohm^{-1}.cm^{-1}$)	Activation energy E (e.v)	Temperature Range K
0.2	2.5×10^{-8}	0.702	390 - 469
0.4	5.7×10^{-8}	0.627	373 - 456
0.6	1.2×10^{-7}	0.581	374 - 476
0.8	1.95×10^{-7}	0.548	363 - 468
0.9	7.0×10^{-9}	0.719	400 - 518
Pure $AgPO_3$	1.8×10^{-18}	2.1	590 - 690

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