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1

Ionic Conductivity Measurements of Lithium Iodide-doped Lithium Phosphate

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Summary: Present work deals with ionic conductivity measurements of system $(LIPO3)_{1-x}$ - $(LiI)_x$ where $0.2 \leq x \leq 0.9$ mole. Measurements carried out between $100^{\circ}C$ and $500^{\circ}C$ using the method of complex impedance. Results obtained indicate a large increase of conductivity due to the doping effect by LiI. A maximum conductivity appears at $x = 0.8$ corresponding to a minimum activation energy $(E_0 = 0.42 \, eV)$.

Introduction

Earlier works shown that many electrolytes obtained from lithium compounds exhibit good ionic conductivity at low and moderate temperature[1,2]. Malugani et al.[3] have studied the ionic conductivity of silver phosphate containing different amount of silver iodide in their glassy states and have provided interesting results. In the previous work[4], we have shown the effect of LiF on the conductivity of lithium phosphate, ionic conductivity of the latter was found to rise several orders of magnitude with respect to the added amounts of LiF. The results obtained in this work have shown an enhancement of ionic conductivity of Lithium phosphate due to the presence of lithium iodide.

Experimental

Material preparation:

Prepared lithium phosphate doped with different amounts of LiI was obtained by Henri's method[5]. Lithium phosphate powder was mixed with different amounts of lithium iodide powder within the range limits of $0.2 \leq x \leq 0.9$ mole in the system $(LiPO3)_{1-x}$ - $(LiI)_x$. Obtained mixtures were pressed into different cylindrical sizes and sintered at $500^{\circ}C$ for 50 hours. X- ray analysis of the powder before sintering have shown the existence of a crystalline solid solution.

Method of measurements:

Measurements of electrical conductivity were made using the complex impedance method, which allows the clear separation of electrical conductivity of material from the electrode polarization effects[6,7]. Electrodes used for the measurements were made from suspension liquid platinum. Impedance measurements were taken in the frequency range of 5Hz to 500 KHz using an impedance meter of Alcatal type 2531.

Results and Discussion

Impedance measurements of symmetrical cells Pt/electrolyte/Pt are shown in Fig.(1). For all samples, the diagrams show two distinct curves. High frequency curve was a portion of circle which is characteristic of the electrolyte, with circle centres move along a straight line passing through the origin, which determines the $\frac{\pi}{2}$ angle, with the real axis. This angle is characteristic of the material and can be attributed to scattering of the local conductivity[8]. Ravaine and Souquet[8,9] have demonstrated the analytical expression of the frequency distribution of experimental points of a circle using a geometrical method described by Cole and Cole for dielectric constant[6]. This was also employed by Bauerle[7] and Shouler[10] for admittance complex in solid electrolytes. The expression of Ravaine and Souquet has been used in the present work as follows:

$$Z = \frac{Z_o}{1 + (JW_o \, \tau_o)^{1-\alpha}}$$

where Z_o is impedance value given by the interesection of the extrapolation of experimental points of the circle to zero frequency, with the real axis. τ_o is the relaxation time which can be obtained from the value of the angular frequency at the top of the circle W_o, at this point $W_o \tau_o = 1$. The value of Z_o is equivalent to the ohmic resistance of the electrolyte under dc current, and allow to determine the conductivity by the following relation[9].

$$\sigma = \frac{1}{Zo} \times \frac{1}{S}$$

where 1/s is the goemetrical factor of the specimen, Zo is the ohmic resistance of the electrolyte. At low frequencies the experimental value of Z does not tend to Zo as the analytical equation of the impedance is no longer satisfied. The new portion of the circle depends on
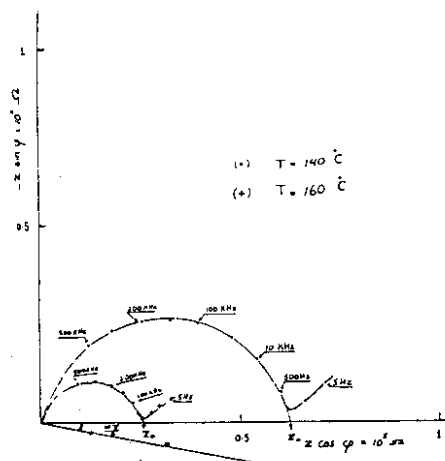

Fig. 1: Experimental curves obtained in a complex impedance diagrams at different temperature for the symmetrical cell: Pt/(LiPO3)0.4 - (LiI)0.6/Pt (●) at 140°C, (+) at 160°C.
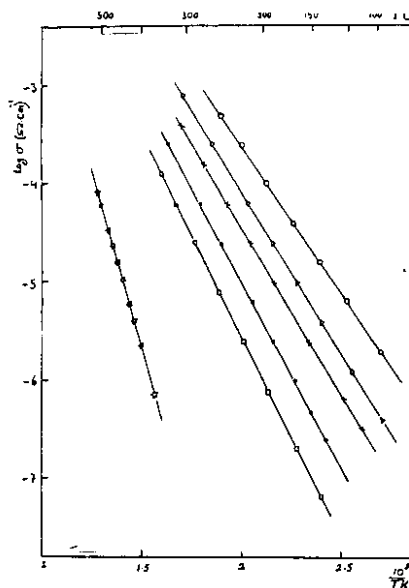

Fig. 2: Temperature dependence of conductivity for various doped samples.

(★) Pure LiPO3. (●) 0.2 mole LiI, (x) 0.4 mole LiI, (x) 0.6 mole LiI, (▲) 0.8 mole LiI. (▭) 0.9 mole.

the electrode polarization. Logarithm of conductivity for different samples are reported in the Fig.(2) as a function of temperature. Experimental points in the range of temperature investigated give straight lines which are characteristic of an activated mechanism of conduction and verified the following equation:

$$\sigma = A \exp^{(-Ea/RT)}$$

σ is the electrical conductivity of the electrolyte, A is the preexponential term, Ea the activation energy of ions responsible for the conduction, and R is the gas constant. Variation of conductivity with mole of LiI is shown in Fig.(3). Results have shown a maximum of conductivity of 10^{-6} Ω^{-1}. cm^{-1}, with sample containing 0.8 mole of LiI which corresponds to a minimum activation energy (Ea = 0.42 eV).
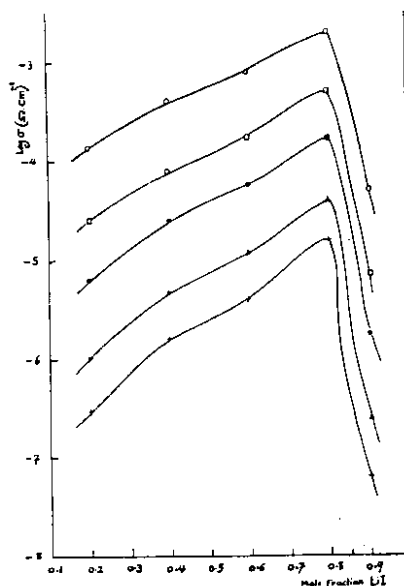

Fig. 3: Conductivity as a function of mole LiI for (LiPO3)1-x- (LiI)x.

Our results can be compared to those obtained in the previous work[4] based on lithium phosphate. Their results have shown a maximum conductivity of 10^{-7} Ω^{-1}. cm^{-1}, with 75% mole LiF at 100°C, also comparison can be made with work of Hu et, al[11] where they used lithium conductor based on lithium orthosilicate, their maximum conductivity was 10^{-4} Ω^{-1}. cm^{-1}, with 40% mole of

Li_3PO_4 at 100°C. Thus observed increase in conductivity upto 0.8 mole of LiI may be due to the increase of concentration of charge carriers of Lithium ions responsible for the conduction and distribution of Li^+ among the available sites as the conductivity must rise with increasing concentration of charge carriers. Higher increase of mole gives a sharp rise in activation energy with corresponding decrease in the conductivity. It can be interpreted due to the interaction of defects or ions in the lattice structure of electrolyte. Values of conductivity at 100°C and those of activation energy of pure and doped samples are listed in Table-1.

Table (I):

mole LiI	Conductivity at 100°C $(\Omega\ cm)^{-1}$	Activation energy Ea (eV)	Temperature range K°
0.2	2.76×10^{-8}	0.76	413-609
0.4	1.33×10^{-7}	0.63	384-588
0.6	4.17×10^{-7}	0.54	373-588
0.8	2×10^{-6}	0.42	373-520
0.9	4.17×10^{-9}	0.84	416-624
Pure $LiPO_3$	8.2×10^{-15}	1.46	636-781

Table 1: Values of ionic conductivity at 100°C and the values of activation energy of pure and doped samples.

Work was also carried out in order to check the electronic conductivity under d.c. current. It was found that the electronic resistance of these electrolyte is 8 order of magnitude higher than their ionic resistance. This confirms that the electrolyte is pure ionic conductor.

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