Measurements of Ionic Conductivity of Lithium Fluoride-Doped Lithium Phosphate

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Summary: The ionic conductivity of the system $(LiPO_3)_{1-x}-(LiF)_x$ where $0.25 < x < 0.90$ mole fraction have been measured using the method of complex impedance. Conductivity measurements were carried out between 100°C and 400°C. The results obtained show a large increase of lithium ion conductivity due to the presence of lithium fluoride. A minimum of the activation energy (E_a = 0.489 eV) appears at x = 75% mole fraction of LiF.

Introduction

Many works [1-3] have shown that some lithium electrolytes are a good lithium conductor electrolytes at low temperature. In an earlier work, Malugani et al [4] studied the ionic conductivity of lithium phosphate doped by different amounts of lithium halides in glassy state giving interesting results. The main purpose of this work is to show that the ionic conductivity of lithium phosphate can be greatly enhanced by doping with LiF in the crystalline state.

Experimental

Preparation of samples:

Henri's procedure was used [5] for the preparation of samples of crystalline lithium phosphate. The resulting powder is mixed with different quantities of powdered LiF in the range limits of 25% $\leqslant x \leqslant$ 90% mole fraction. The mixtures so obtained are pressed in the form of discs having a geometrical factor 1/s of 0.209 cm^{-1}, and sintered at 550°C for 70 hours. X-Ray analysis has shown the existence of a crystalline solid solution.

Method of measurements:

The complex impedance method [6,7] has been used to characterize the electrical properties of solid electrolytes. Surface conductivity can be prevented by a flow of dry nitrogen in the cell. Impedance measurements were taken in the frequency range 5Hz to 500 KHz with an impedancemeter (Alcatel 2531 Type). The metallic electrodes used for the conductivity cells were made of platinum from commercial paints.

Results and Discussion

In earlier papers it was reported [8-10] that the complex plane representation of the impedance of symmetrical cells Pt/electrolyte/Pt can be used to characterize the electrical conductivities of solid electrolytes by avoiding the effect of electrods polarization. Figure (1) gives an example of the obtained complex impedance diagrams. The complex impedance plots lead to only one semi-circle in the investigated frequency range. The results of ionic conductivity measurements for pure lithium phosphate and

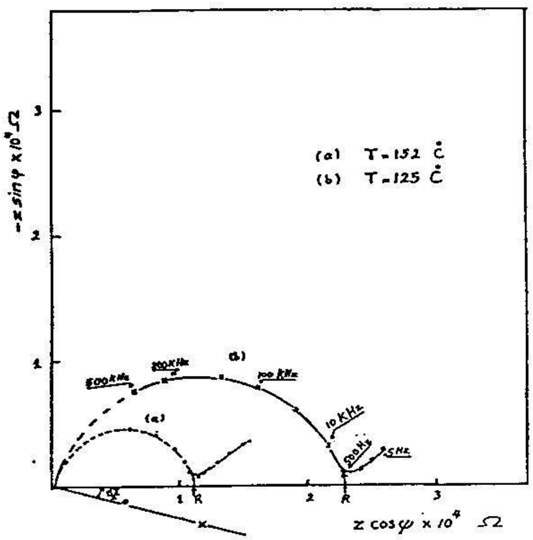

Fig.I: Complex impedance diagrams for the symmetrical cells: P_t/ 0.25 $LiPO_3$-0.75 LiF/P_t (x) at; 25°C. ( ) at 152°C.

for various doped samples are shown in figure (2) as a function of temperature (100-400°C). The results can be expressed by the following equation:

$$\sigma = A \exp \frac{-E_\sigma}{RT}$$

where σ is the bulk electrical conductivity of the material, A the pre-exponential term, E_σ the activation energy of the electrical conductivity and R the gas constant.

The results show a decrease of activation energy with LiF content. It appears that the maximum conductivity and the minimum of activation energy (E_σ=0.489 ev) occur in the sample containing about 75% mole LiF. The large effect of increase the conductivity due to the concentration of charge and distribution of lithium ions

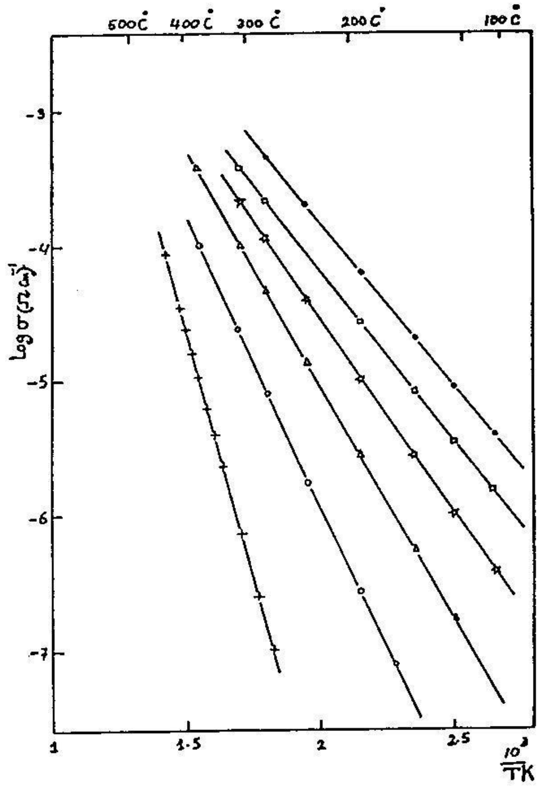

Fig.II: Temperature dependence of the ionic conductivity of various doped samples: (+) pure $LiPO_3$, ( ) 0.25 mole fraction Lif. ( ) 0.45 mole fraction LiF, ( ) 0.65 mole fraction LiF, ( ) 0.75 mole fraction LiF, (O) 0.90 mole fraction LiF.

within the available sites as the electrical conductivity must increase with the increasing of charge carriers. The values of conductivity at 100°C and values of activation energy of pure and doped sample are listed in table (I).

The results cited in this work can be compared to those obtained in the Li_4SiO_4-Li_3PO_4 system by Hu et.al [11], where they observed a maximum of electrical conductivity at 40 mole% of Li_3PO_4. At 100°C the corresponding

Table-I: Values of conductivity at 100°C and the values of activation energy of pure and doped lithium phosphate.

mole fraction LiF	Conductivity at 100°C (ohm^{-1}, cm^{-1})	Activations energy Ea (eV)	Temperature range K°
0.25	2.55×10^{-9}	0.68	399-423
0.45	3.17×10^{-8}	0.59	378-588
0.65	7.99×10^{-7}	0.53	378-588
0.75	2.89×10^{-7}	0.49	378-553
0.90	5.76×10^{-10}	0.79	423-643
Pure $LiPO_3$	6.4×10^{-15}	1.46	546-703

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

value is equal to $10^{-4}\ \Omega^{-1}.\ cm^{-1}$ with an activation energy equal to 0.555 eV. In both $LiPO_3$ and Li_4SiO_4 the massive doping by LiF and Li_3PO_4 respectively leads to an enhancement of the electrical conductivity. The magnitude of this enhancement is greater the lower the temperature and amounts several orders of magnitude at 100°C. Inspite of that, one cannot think to use these electrolytes in solid state batteries using lithium as negative electrode. It is not presently known whether the vast observed effects of doping $LiPO_3$ by LiF are primarily due to changes in the concentration and distribution of lithium among the available sites between the tetrahedral anionic groups or to the modification of the lattice through which ions move.

Many experiments were carried out to check the electronic conduction under dc conditions. We found that electronic resistance is at least 8 order of magnitude greater than the ionic resistance.

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