

Preparation and study of conductivity in lithium salt complexes of mixed MEEP : PEO polymer electrolytes

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Abstract. Poly(ethylene oxide)–LiX complexes and poly[bis(methoxy ethoxy ethoxide) phosphazene]–LiX complexes of polymer thin films were prepared. Conductivity measurements were carried out and the values were found to lie between 10^{-8} and 1.7×10^{-5} (S/cm). MEEP : LiX salts showed higher conductivity than PEO–LiX salts despite lower dimensional stability. For enhancing stability and conductivity, MEEP–PEO : (LiX)_n systems were prepared and conductivity measurements carried out. Further the MEEP/PEO : (LiX)_n was doped with Al₂O₃ and TiO₂ nanocomposite ceramic fillers and the conductivity was studied. The conductivity vs temperature plots showed the enhancement of conductivity with TiO₂ added nanocomposite ceramic fillers. The enhanced conductivity is explained on the basis of the effect of local structural modification—promoting localized amorphous region—for enhancement of the Li⁺ ion transport.

Keywords. Complexes; conductivity; structural modification; amorphous region.

1. Introduction

Rechargeable solid-state Li batteries employing polymer electrolytes are being actively pursued as possible power sources for a variety of applications (Armand 1986; MacCullum and Vincent 1987). Although several theoretical models have been put forward to explain ionic motion in polymer electrolytes, present understanding of this phenomenon is rather incomplete (Papke *et al* 1982; Hibma 1983; Scrosati *et al* 2000; Chung *et al* 2001). A significant part of the current effort is concerned with developing mixed polymer electrolyte by using a novel class of plasticizers. Classical polymer electrolytes are composed of complexes of poly(ethylene oxide) or PEO, with Li salts (MacCullum and Vincent 1987). The low conductivity (i.e. $< 10^{-7}$ ohm⁻¹ cm⁻¹) of these poly[ethylene oxide] electrolytes at room temperature has limited their use in batteries operating at relatively high temperature of about 100°C. However, PEO–LiX polymer electrolytes are affected by some problems, viz. (i) a reactivity towards the lithium metal electrode and (ii) a low conductivity at ambient temperature. Later, there have been reports of organic solvents like sulfolane (SL), propylene carbonate (PC), acetonitrile (AN) and tetrahydrofuran (THF) in LiAsF₆ showing the conductivity to be around 10^{-3} ohm⁻¹ cm⁻¹ at 25°C. The conductivity of 35Ec/30Pc/25PVP/11LicF₃SO₃; 31Ec/26Pc/32PVP/11LicF₃SO₃; 54Pc/

35PVP/11LicF₃SO₃ etc compositions of organic solvent and polymer electrolytes, was reported to be around 10^{-4} ohm⁻¹ cm⁻¹ at 25°C. However, little information was given concerning their compositions (Abraham 1986; Rhoo *et al* 1995; Yoshino *et al* 1996).

Complexes of certain Li salts and inorganic poly[bis(methoxy ethoxy ethoxide) phosphazene] named as MEEP, belong to the class of high conductivity polymer electrolytes (Blonsky *et al* 1984). However, MEEP–(LiX)_n polymer electrolytes have shown poor mechanical properties and hence cannot be cast as free standing thin films for electrolyte in solid state Li batteries. For enhancing the mechanical as well as dimensional stability, the MEEP–(LiX)_n system was significantly improved by blending them with high molecular weight of PEO. The systematic studies on these lines were reported earlier (Abraham *et al* 1988, 1989; Best *et al* 2001).

Another technique to enhance the conductivity without affecting the morphological and mechanical properties at or near ambient temperature is to add a low molecular weight organic nonaqueous solvent such as ethylene carbonate, dimethyl carbonate, etc. These liquids can be used as plasticizers to enhance the conductivity (Sheldon *et al* 1989; Michael *et al* 1997). But when the systems were added with liquid plasticizers, it loses its solid state configuration due to loss of compatibility with lithium electrodes. This represents loss of the most important feature of the polymer electrolyte. Consequently liquid plasticizers such as PEO–(LiX)_n cannot be used in lithium batteries because of their limited processibility and

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high reactivity causes serious problems in terms of battery cyclability and safety. Thus work is needed to find out the proper approaches for solving or minimizing these drawbacks. In this paper, it is shown that the dispersion of selected ceramic powders in the polymer mass, produces composite PEO–MEEP:LiX polymer electrolytes which show improvement in both interfacial and transport properties as reported earlier (Weston and Steete 1982; Croce and Scrosati 1993; Borghini *et al* 1995).

2. Experimental

2.1 Polymer film preparation

PEO was obtained from BDH Limited (polyox WSR-301, MW $\sim 4 \times 10^6$) in powdered form and used without further purification. MEEP was synthesized according to a previously reported procedure (Allock *et al* 1986). The LiClO₄ and LiBF₄ were obtained from Fluka, Germany and Aldrich. The samples of MEEP:(LiClO₄)_n; PEO:(LiBF₄)_n; MEEP/PEO–(LiBF₄)_n and MEEP/PEO–(LiClO₄)_n and Al₂O₃ and TiO₂ doped composite ceramic fillers were prepared by using the usual technique (Abraham *et al* 1988, 1989). Here $n = 0.033, 0.07, 0.13, 0.18, 0.125$ and 0.25 . The MEEP/PEO samples were made in the ratio 55:45.

Differential scanning calorimeter (DSC) experiments were conducted to estimate the degree of crystallinity in the composites. The experiments were carried out in the temperature range -93 to 160°C using TA instruments, DSC (model 2910) at a heating rate of $10^\circ\text{C}/\text{min}$. The procedure for estimating the degree of crystallinity in the composites is described elsewhere (Allock *et al* 1986).

2.2 Conductivity measurements

The d.c. conductivity was measured using samples of 1 cm diameter sandwiched between two electrodes. The samples were coated with silver paint for good electrical contact. The electrodes were sealed with glass tube and the currents were measured using Keithley electrometer by varying temperature at the rate of $100^\circ\text{C}/\text{h}$.

3. Results and discussion

The DSC studies of PEO show an endothermic, melting point peak at 72°C . The MEEP did not show any DSC peak between room temperature and 150°C , implying that the entire MEEP is completely amorphous. MEEP/PEO–(LiX)_n mixed electrolytes with low salt concentrations ($X_{\text{Li}^+} < 0.13$) also showed endothermic peak around the melting point of PEO.

The DSC traces of MEEP/PEO–(LiBF₄)_{0.18} were made from -93°C to 200°C . The endothermic heat flow vs

temperature showed two peaks indicating the presence of two crystalline phases, crystalline PEO which melts at 64°C and a crystalline salt rich complex that melts at 137°C . Since MEEP:(LiBF₄)_n does not show any thermal peak in this temperature range, the peak at 137°C can be ascribed to LiBF₄ complexed PEO. It is concluded that the mixed MEEP/PEO–(LiBF₄)_n formed individual complexes of PEO:(LiBF₄)_n; MEEP:(LiBF₄)_n semicrystalline form of MEEP/PEO:(LiBF₄)_n in the mixed polymer electrolyte. The endothermic peak is observed at 124°C in the mixed electrolyte. Similar type of behaviour was observed in the case of MEEP/PEO:(LiClO₄)_n system and the results are similar to those previously reported (Abraham *et al* 1989; Robitaille and Fauteux 1986).

MEEP/PEO:(LiX)_n system containing 10% wt of Al₂O₃ and TiO₂ systems also exhibit two endothermic peaks indicating the presence of two crystalline phases at 58°C and 133°C . These two peaks are similar in behaviour as unplastified samples.

The Arrhenius plots of the conductivity of MEEP:(LiClO₄)_{0.25}; PEO:(LiClO₄)_{0.125}; MEEP:(LiBF₄)_{0.25} and PEO:(LiBF₄)_{0.125} are shown in figure 1. At room temperature, the PEO:(LiClO₄)_n and PEO:(LiBF₄)_n are partially crystalline, while MEEP:(LiBF₄)_n and MEEP:(LiClO₄)_n com-

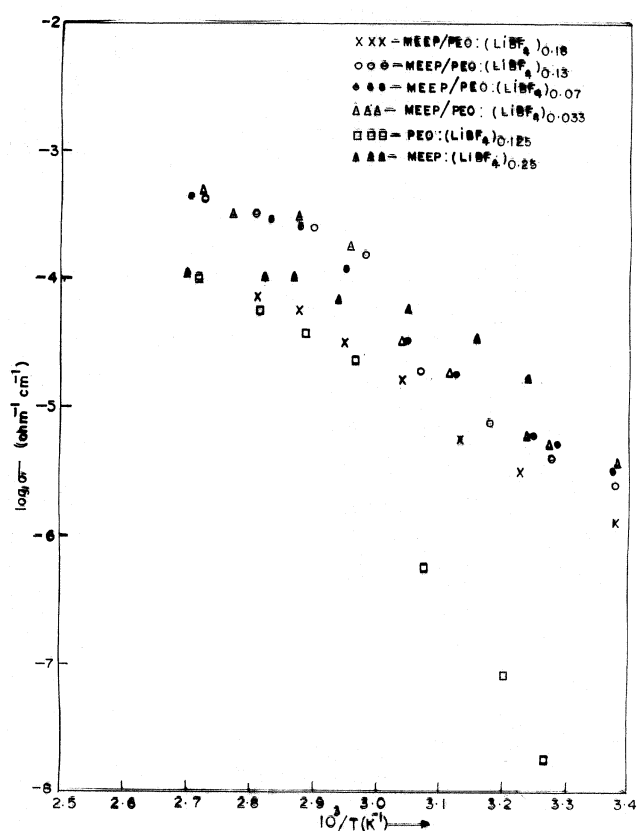


Figure 1. Conductivity vs temperature plots of MEEP/PEO:(LiBF₄)_n.

plexes are fully amorphous. From the plots, it is observed that the conductivity of Arrhenius plots of MEEP:(LiClO₄)_{0.25} and MEEP:(LiBF₄)_{0.25} exhibit higher conductivity than the PEO:(LiX)_n complexes. But above 60°C the conductivity increases abruptly in PEO-(LiX)_n and shows rather similar behaviour as that of MEEP:(LiX)_n. The Arrhenius plots for PEO:MEEP and MEEP/PEO:LiBF₄ where $n = 0.033, 0.07, 0.125, 0.13, 0.18$ and 0.25 are shown in figure 2. The Arrhenius plots of comparative studies of other compositions are shown in figure 3. The Arrhenius plots of MEEP/PEO:(LiClO₄)_{0.07} and MEEP/PEO:(LiClO₄)_{0.25} show higher and similar conductivity although the mechanical properties of MEEP:(LiClO₄)_{0.25} are poor.

Arrhenius plots of MEEP/PEO:(LiClO₄)_{0.07}, MEEP/PEO:(LiBF₄)_{0.07}, MEEP/PEO:(LiBF₄)_{0.07} + 10% wt of Al₂O₃ and MEEP/PEO:(LiBF₄)_{0.07} + 10% wt of TiO₂ are respectively shown in figure 3. The MEEP/PEO:(LiBF₄)_{0.07} + 10% wt of TiO₂ show higher conductivity than other composites.

The comparison studies on 55%–45% w/o MEEP:PEO (LiX)_n mixed electrolytes MEEP:(LiX)_n and PEO (LiX)_n of Arrhenius plots are shown in figures 2 and 3, respectively. From the plots it is clear that MEEP:(LiClO₄)_{0.25} and MEEP:(LiClO₄)_{0.07} exhibit similar conductivity than

other samples. In other compositions also MEEP:(LiBF₄)_{0.25} and MEEP/PEO:(LiBF₄)_{0.07} exhibit similar higher conductivity. The conduction mechanism in mixed polymer electrolytes of MEEP/PEO:(LiX)_n was explained earlier by various investigators (Abraham *et al* 1988, 1989; Abraham and Alamgiri 1991).

In an attempt to produce ceramic powders of nanoparticle size, solid state MEEP/PEO:(LiX)_n mixed polymer composite electrolyte was used. This electrolyte works in the temperature range 30–80°C with better mechanical stability, high ionic conductivity and good interfacial characteristics as reported earlier (Weston and Steete 1982; Croce and Scrosati 1993; Borghini *et al* 1995). From the review of the work, it is inferred that this method was never been used for promoting low temperature conductivity in mixed polymer electrolytes. So in the present investigation, an attempt has been made to study the effect of Al₂O₃ and TiO₂ of nanocomposite ceramic fillers in MEEP/PEO:(LiX)_n system and the corresponding activation energy values are calculated and shown in table 1. The Arrhenius plots of MEEP/PEO:(LiClO₄)_{0.07}, MEEP/PEO:(LiBF₄)_{0.07}, MEEP/PEO:(LiBF₄) + 10% wt of Al₂O₃ and MEEP/PEO:(LiBF₄) + 10% wt of TiO₂ shows that MEEP/PEO:(LiBF₄)_{0.07} + 10% wt of TiO₂ has higher conductivity than other systems. The heating scan of the ce-

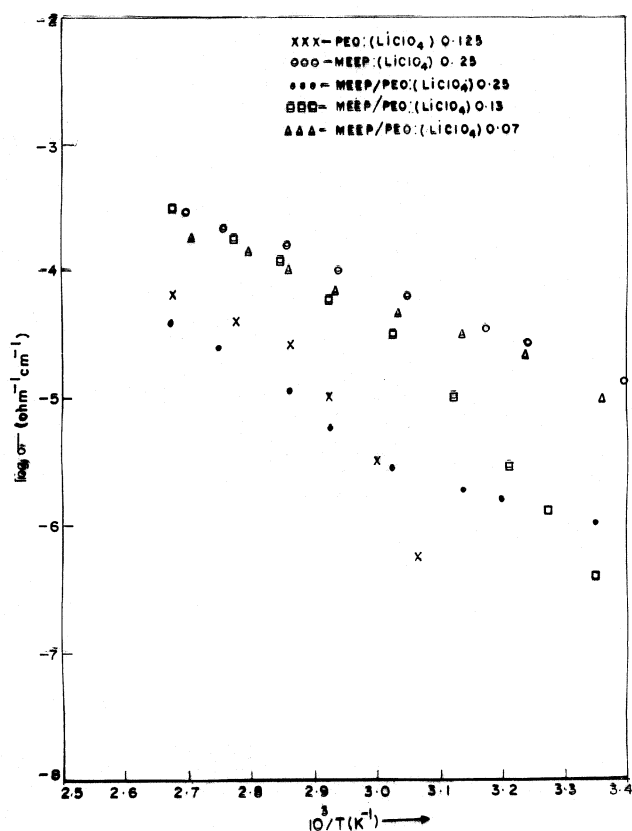


Figure 2. Conductivity vs temperature plots of MEEP/PEO:(LiClO₄)_n.

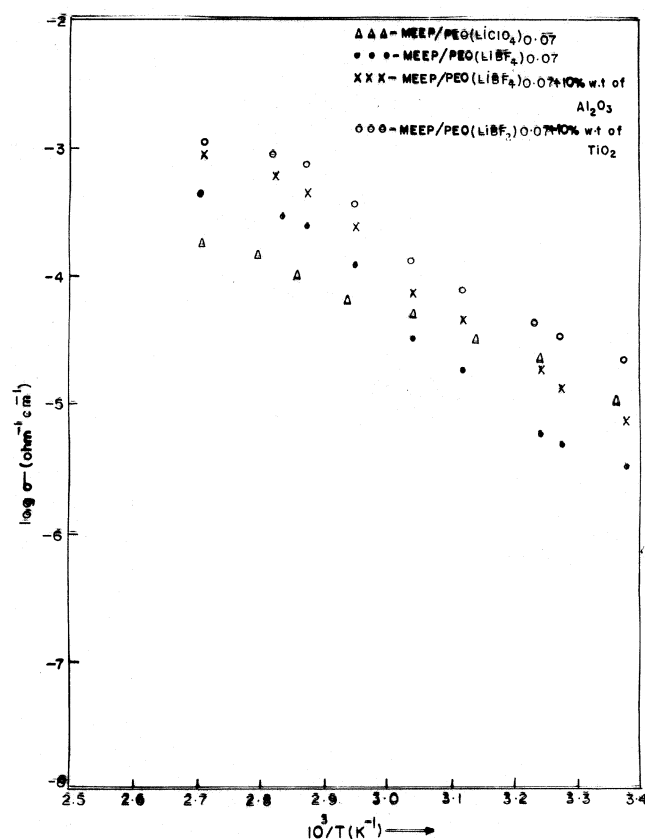


Figure 3. Arrhenius plots of MEEP:(LiClO₄)_{0.07}, MEEP/PEO:(LiBF₄)_{0.07}, MEEP/PEO:(LiBF₄)_{0.07} + 10% wt of TiO₂ and MEEP/PEO:(LiBF₄)_{0.07} + 10% wt of Al₂O₃.

Table 1. The activation energy values of different polymer electrolytes.

System	Corresponding activation energies (eV)	
	at 40°C	at 70°C
PEO : (LiBF ₄) _{0.125}	0.3114	0.6503
MEEP/PEO : (LiBF ₄) _{0.18}	0.5356	0.0300
MEEP/PEO : (LiBF ₄) _{0.13}	0.5892	1.707
MEEP/PEO : (LiBF ₄) _{0.07}	0.546	0.273
MEEP/PEO : (LiBF ₄) _{0.033}	0.4553	0.585
MEEP/PEO : (LiBF ₄) _{0.025}	0.7285	1.0408
MEEP/PEO : (LiClO ₄) _{0.13}	1.0927	0.4202
MEEP/PEO : (LiClO ₄) _{0.25}	0.3035	0.4202
PEO : (LiClO ₄) _{0.125}	1.5685	0.4047
MEEP/PEO : (LiClO ₄) _{0.07}	0.3749	1.707
MEEP : (LiClO ₄) _{0.25}	0.4138	
MEEP/PEO : (LiBF ₄) _{0.17} + 10% wt of Al ₂ O ₃	0.525	0.607
MEEP/PEO : (LiClO ₄) _{0.07}	0.3749	0.476
MEEP/PEO : (LiBF ₂) _{0.07} + 10% wt of TiO ₂	0.5098	0.2731

ramic free electrolyte and dispersion of nanocomposite ceramic did not show any break and is accompanied by increase in conductivity of dispersion ceramic fillers mixed electrolyte. This implies that the semicrystalline nature of PEO is reduced and it is in the form of amorphous state. This was already confirmed in DSC studies (Abraham *et al* 1989; Binod Kumar *et al* 1999).

From the DSC data the corresponding endothermic transition values are evaluated and the values are compared with the transition temperature of conductivity plots (with respect to change in slope value). The values of endothermic transition temperature and corresponding temperature of slope changes are shown below.

In case of PEO : (LiBF₄)_n, the DSC value is 65°C and 67°C from the conductivity plot. In MEEP/PEO : (LiBF₄)_n, DSC value is 58°C and 54°C from the conductivity plot. Similarly in PEO : (LiClO₄)_n the endothermic transition value is 64°C and from conductivity plot it is 62°C. In MEEP/PEO : (LiClO₄)_n, the DSC peak is at 64°C and from conductivity plot it is 58°C. From the above data it is clear that the endothermic transition values are nearly correlating with the conductivity plots change in slope values.

One possibility for the mechanism of enhanced conductivity in MEEP/PEO (LiX)_n containing nanocomposite ceramic fillers is as follows. When the MEEP/PEO mixed electrolytes was doped with LiBF₄ and LiClO₄, it favoured formation of complexes with ether or oxygen in PEO or in MEEP. In case of ceramic free mixed electrolytes it favoured to form more transient cross links with dimensional stable morphology due to large cation–anion association effects (Abraham 1993). Due to increase in transient cross links the mobility of Li⁺ increases so that conductivity is increased in mixed polymer electrolytes. When the systems were dispersed with nanocomposite ceramic

fillers like Al₂O₃ and TiO₂ with 10% wt, there is a possibility that conductivity enhancement is greater in TiO₂ than Al₂O₃ due to fast ion transport. This could have been related to dilution effect promoted by an excess of liquid adsorbed by the ceramic during casting and released in the heating scan. For this purpose, the samples were initially heated to 130°C after preparation. Due to this the crystalline phase is converted to amorphous phase. Simultaneously there was an enhancement of mechanical properties in these systems (Saibaba 2003).

These interactions originate a series of processes which work together to increase the fraction of free ions and to enhance their mobility. In fact, it is reasonable to assume that the acid sites on the surface of the ceramic particles may compete with acid lithium cations to form complexes with the basic oxygen [ether] on the MEEP and PEO chains. Thus the ceramics may act as cross linking centres for PEO and MEEP segments; thereby lowering the reorganization tendency of the polymer chain and promoting preferred Li⁺ transport routes at the boundaries of the ceramic particles. Under these conditions, a consistent enhancement of the cation transference number is expected (Evans *et al* 1987; Croce and Scrosati 1993).

The results obtained here on MEEP/PEO : (LiBF₄)_{0.07} + 10% wt of TiO₂ show higher conductivity than MEEP/PEO : (LiBF₄)_{0.07} + 10% wt of Al₂O₃. Further the conductivity of fillers of Al₂O₃ of mixed polymer electrolyte had pronounced towards temperature axes. That means the MEEP/PEO : (LiBF₄)_{0.07} + 10% wt of Al₂O₃ might get some disturbance in configuration [mechanical properties]. For this, further investigation is required.

We believe that a proper choice of the type and morphology of the ceramic filler could optimize the conduction. This might lead to the development of mixed polymer electrolytes having a true solid state configuration with high conductivity and high interfacial stability, which are ideal for rechargeable batteries (Scrosati 1995).

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