

## Synthesis and characterization of polyethylene oxide based nano composite electrolyte

M MALATHI\* and K TAMILARASAN

Department of Physics, Kongu Engineering College, Perundurai 638 052, India  
e-mail: mal\_kongu@yahoo.com; dr.k.tamilarasan@gmail.com

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**Abstract.** Polyethylene oxide (PEO) – montmorillonite (MMT) composite electrolytes were synthesised by solution casting technique. The salt used for the study is Lithium perchlorate ( $\text{LiClO}_4$ ). The morphology and percentage of crystallinity data were obtained through X-ray Diffraction and Differential Scanning Calorimetry. The ionic conductivity of the polymer electrolytes was studied by impedance spectroscopy. The addition of MMT resulted in an increase in conductivity over the temperature range of 25–60°C. The ionic conductivity of a composite polymer electrolyte containing 1.2 wt% MMT was  $1 \times 10^{-5} \text{ S cm}^{-1}$  at 25°C, which is at least one order of magnitude higher than that of the polymer electrolyte ( $4 \times 10^{-7} \text{ S cm}^{-1}$ ). The increase in ionic conductivity is explained on the basis of crystallinity of the polymer electrolyte.

**Keywords.** Polymer electrolyte; polyethylene oxide; composite electrolyte; montmorillonite; conductivity.

### 1. Introduction

Polymer electrolytes are becoming increasingly important because of their potential use in several electrochemical devices: ‘smart’ windows, displays, sensors, and more importantly, rechargeable solid-state lithium batteries (Armand *et al* 1978). Their high energy densities combined with the potential for low-cost manufacturing technologies render solid-state lithium batteries with polymer electrolytes extremely attractive for usage in portable consumer electronics products. These batteries are also likely to be important power sources for pollution-free electric vehicles. Compared to liquid electrolytes, solid polymer electrolytes would eliminate electrolyte leakage, limit electrolyte-electrode reactions and allow tremendous flexibility in design (Sun *et al* 1999a). However, the successful use of these materials requires them to be mechanically strong but processable and have conductivities higher than  $10^{-5} \text{ S/cm}$  at room temperature. Studies on polymer electrolytes have primarily focused on polyethylene oxides (PEO)

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\*For correspondence

and PEO copolymers since these materials form stable complexes with lithium salt (Sun *et al* 1999b). These materials conduct well ( $10^{-4} > S/cm$ ) for temperatures above  $60^{\circ}C$  but poorly ( $10^{-5} < S/cm$ ) at room temperature because of the formation of a poorly-conducting crystalline phase. Numerous synthetic approaches were developed to eliminate the PEO-based systems, and now amorphous crystallinity polymers are available with room-temperature Li ion conductivities greater than  $10^{-5} S/cm$  (Yang *et al* 2000). Unfortunately, most of these polymers have poor mechanical properties and exhibit creeping behaviour. The addition of inert fillers to the polymer to improve its mechanical characteristics was first suggested by Boyd *et al* (2000) and Weston & Steele (1982) reported a nanocomposite polymer electrolytes composed of a PEO-LiClO<sub>4</sub> electrolyte and a nano-sized titanium oxide (TiO) or alumina (Al<sub>2</sub>O<sub>3</sub>) filler, where addition of the ceramic fillers increased the ionic conductivities of the electrolytes to  $10^{-6} S/cm$  at room temperature. The nano-sized fillers kinetically inhibited crystallization of the ionic conductive amorphous phases. The effect was explained by the high surface area of the dispersed fillers. Similar behaviour was also reported in other studies for composite polymer electrolytes based on linear PEO in Croce *et al* (1998), Appetecchi *et al* (1998) and Munichandraiah *et al* (1995). On the other hand, the filler provides a solid polymer electrolyte like support matrix, allowing the amorphous polymer to maintain its liquid-like characteristics at the microscopic level. Recently, significant work has been carried out in PEO–MMT based composite electrolytes (Choudary & Sengwa 2011, 2012; Pradhan *et al* 2011; Manoratna *et al* 2006; Zhng *et al* 2007). The presence of MMT in PEO matrix increases amorphous phase. In this work, the structure of the PEO–MMT composites were investigated by small angle X-ray scattering (SAXS) and to find the optimized loading of MMT in PEO matrix to achieve maximum ionic conductivity.

## 2. Experimental

The PEO-based composite polymer electrolytes were obtained by a solvent casting technique using acetonitrile (AN) as a solvent. High molecular weight PEO (Aldrich Chemical,  $4 \times 10^5$  average molecular weight), LiClO<sub>4</sub> (Aldrich Chemical) were used as received. MMT (Aldrich Chemicals, average particle size) was dried under vacuum at  $120^{\circ}C$  for 24 h. Preparation of the composite electrolytes involved the dispersion of the MMT powder and lithium salt in AN, then followed the addition of PEO. The slurry was completely homogenized and then cast onto a flat Teflon substrate. The solvent in the slurry was allowed to evaporate slowly under the flow of nitrogen gas for 24 h at room temperature. Finally, the composite polymer electrolyte films were dried at  $55^{\circ}C$  under vacuum for 48 h. These procedures yield mechanically stable membranes with an average thickness of about  $250 \mu m$ . The polymer composite of five different composition were prepared and is shown in table 1. The X-ray diffraction patterns were recorded using a X'PERT PRO MRD diffractometer at a scan rate of  $10^{\circ}/min$ . Thermal analysis of the polymer gel electrolytes was carried out with NETZSCH 200PC Differential Scanning Calorimeter (DSC). The samples sealed in aluminum pans were scanned from  $-125$  to  $150^{\circ}C$  at the heating rate of  $10^{\circ}C \text{ min}^{-1}$ . Frequency dependent conductivities of these electrolytes were measured with an Alpha high resolution analyzer [Novo control GmbH, Germany] system in the frequency range of  $10^{-1}$  Hz to  $10^6$  Hz and the temperature range of  $-80^{\circ}C$  to  $+50^{\circ}C$  in steps of  $10^{\circ}C$ . The data was analysed using impedance spectroscopic tools to extract the dc conductivity at each temperature. Polymer electrolyte of uniform thickness was placed between two gold electrodes to ensure the good contact between the electrolyte and electrodes.

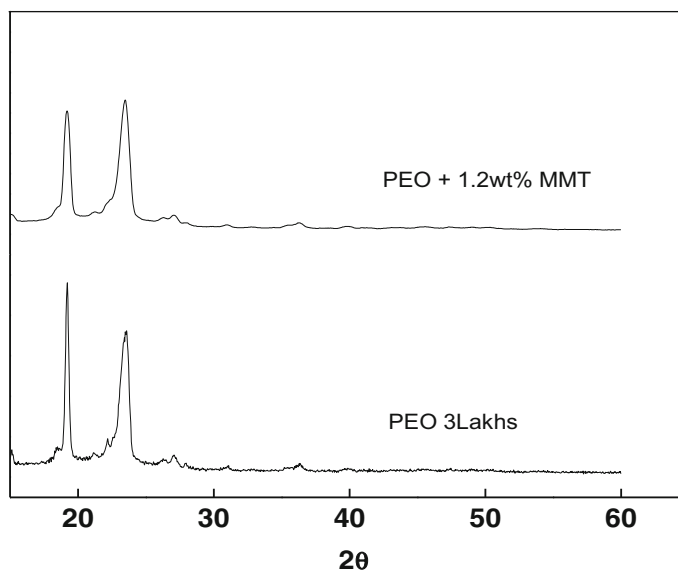
**Table 1.** Composition of composite polymer electrolyte.

PEO (wt %)	MMT (wt%)	Code	LiClO <sub>4</sub> (wt %)
93	0	PEO	7
92.4	0.6	PEO1	7
92.1	0.9	PEO2	7
91.8	1.2	PEO3	7
91.5	1.5	PEO4	7

### 3. Results and discussions

Figure 1 shows the XRD patterns for PEO polymer electrolyte and MMT reinforced PEO polymer electrolyte (1.2 wt% of MMT). Two prominent peaks at  $2\theta = 19^\circ$  and  $2\theta = 23^\circ$  correspond to PEO present in the electrolyte. The presence of peaks confirms the crystalline phase of PEO polymer electrolyte. It is clearly seen from the figure that, slight shift in two prominent peaks with broadening indicates that the inclusion of MMT in the polymer phase exerts a strain in the crystalline phase of PEO. However, the crystalline phase of polymer matrix still not vanished. Similar results were observed in all composition of PEO–MMT based nano composite electrolyte.

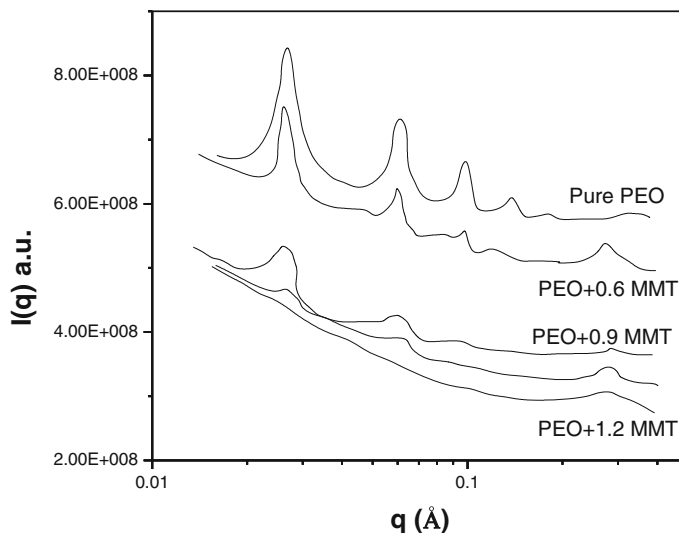
Experiments of small angle X-ray scattering on polymer gel electrolytes were performed in pinhole geometry, using SAXS camera (Anton Paar GmbH). The Cu  $K\alpha$  line was used as incident radiation from PANalytical X-ray source at 40 kV (40 mA). Image plate reader, (Packard

**Figure 1.** XRD pattern of PEO-based composite electrolyte.

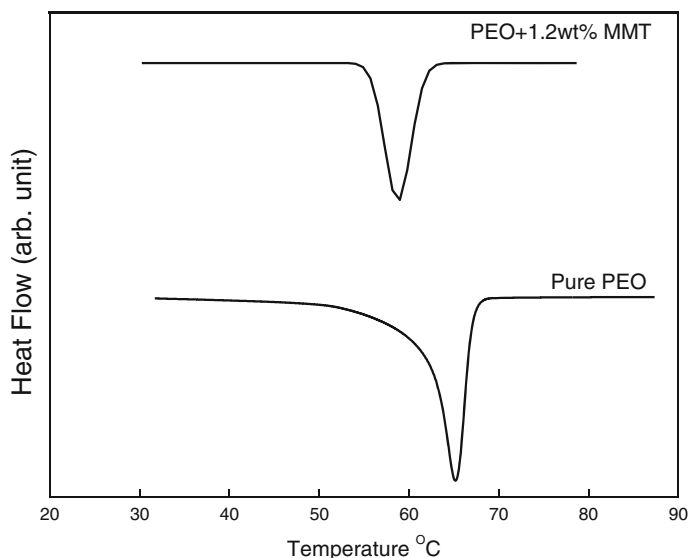
Bioscience, Inc.) was used to record the scattering rays. The scattering intensities were presented as a function of the magnitude of the scattering vector  $q = (4\pi/\lambda) \sin \theta$ , where  $\lambda$  is the wavelength of the radiation and  $2\theta$  is the scattering angle.

Figure 2 shows the SAXS patterns for pure PEO and MMT reinforced PEO polymer electrolyte. For pure PEO, SAXS pattern exhibits five strong peaks at  $q$  value of 0.02, 0.06, 0.09, 0.14 and  $0.18 \text{ \AA}^{-1}$ . Such type of sequence is characteristic of mesoscopic periodic arrangement of lamellae with  $d$ -spacing of  $128 \text{ \AA}$ . The diffracting peak (not shown) corresponding to the inter-layer distance of the as received MMT is not apparent in the SAXS pattern because the first order of the diffraction peak occurs at  $q = 0.053 \text{ \AA}^{-1}$  being out of the maximum  $q$ -value probed in the experimental set-up. It is seen that increase in MMT content in these composites leads to decrease in intensity of the characteristics peaks of PEO. The height at the peak is related to the volume of the mesoscopic phase. At 1.2 wt% of MMT, all the characteristic peak in the SAXS pattern vanishes which indicates that the amorphous nature of PEO-based composite electrolyte. The effects of MMT incorporation on the nanoscopic structure of the studied nanocomposites is also evidenced by the appearance of a diffraction peak at  $q = 0.3 \text{ \AA}^{-1}$ . The presence of the peak indicates that the long-range period of the MMT separated by amorphous layer of PEO. The long-range period ( $d$ ) was calculated from  $d = 2\pi/q$  where  $q$  is the position of the peak. The calculated  $d$  spacing between MMT layer is found to be  $21 \text{ \AA}$ .

Figure 3 shows the DSC patterns (heating cycle) from  $30$  to  $100^\circ\text{C}$  for PEO polymer electrolyte and MMT reinforced PEO polymer electrolyte (1.2 wt% of MMT). A single endothermic peak is observed in both the samples. The melting temperature of pure PEO electrolyte is observed at  $67^\circ\text{C}$  and the corresponding  $\Delta H$  (enthalpy of melting) is  $132 \text{ J/g}$ . It is to be noted that the theoretical  $\Delta H$  value of PEO (100% Crystallinity) is  $205 \text{ J/g}$ . This indicates that 64% of crystallinity is present in the case of pure polymer electrolyte. In the case of MMT (1.2 wt %) reinforced nano composite electrolyte, the melting temperature is observed at  $58^\circ\text{C}$  and the corresponding  $\Delta H$ (enthalpy of melting) is  $88 \text{ J/g}$ . This indicates that 43% of crystallinity is present



**Figure 2.** SAXS patterns for pure PEO and MMT reinforced PEO polymer electrolyte.



**Figure 3.** DSC pattern of PEO-based composite electrolyte.

in the case of MMT reinforced nano composite electrolyte. Table 2 shows the melting temperature and enthalpy value of all mentioned composition of PEO–MMT nano composite. The table clearly shows that increase in wt% of MMT, increases the amorphous nature of PEO–MMT nano composite electrolyte.

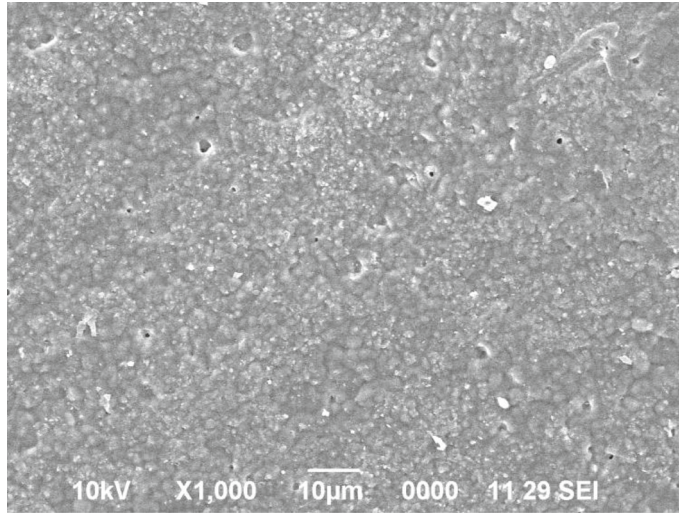
The morphology of composite electrolytes are studied using Scanning electron microscopy. Figure 4 shows the morphology of PEO electrolyte with 1.5 wt% MMT. The bright spots in the image represent MMT. The morphology clearly suggests that MMT is homogeneously distributed in the polymer matrix.

The real and imaginary parts of impedances measured for the composite electrolyte were used to obtain the Nyquist plots and these plots are shown in figures 5 and 6 for PEO-based composite electrolyte with 1.2 and 1.5 wt% MMT, respectively.

The inset of figures 5 and 6 represent the corresponding equivalent circuits. The components in the equivalent circuit, C2 is attributed to the double-layer capacitance at the electrode/electrolyte interface, R1 and C1 are attributed to the bulk electrolyte resistance and capacitance, respectively. It may be noted that the equivalent circuit was found to be applicable to other composites

**Table 2.** DSC data of composite polymer electrolyte.

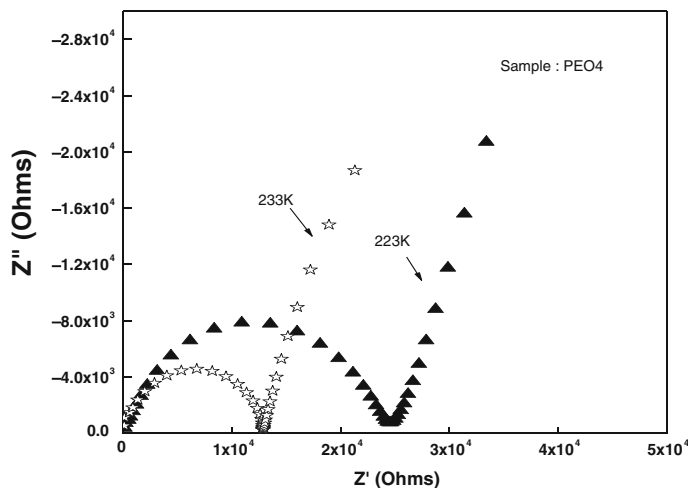
Code	$T_m(^{\circ}\text{C})$	$\Delta H$ (J/g)
PEO	67	132
PEO1	65	116
PEO2	63	108
PEO3	60	96
PEO4	58	88
PEO5	58	89



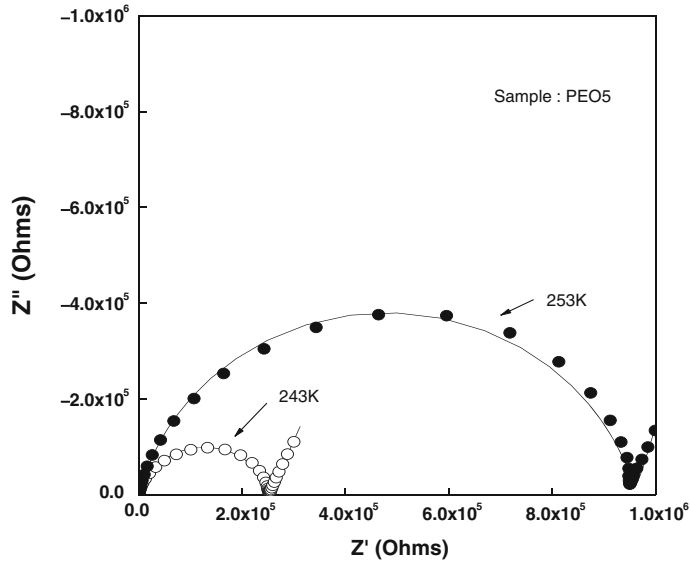
**Figure 4.** SEM morphology of electrolyte with 1.2 wt% MMT.

with various MMT content ( $X = 0, 0.6, 0.9$ ) and at all temperatures in the region  $-90$  to  $30^\circ\text{C}$ . The DC conductivity of the composite electrolyte is calculated from the bulk resistance  $R_1$ .

Table 3 shows the DC conductivity of the composite electrolytes with various MMT content ( $X = 0, 0.6, 0.9, 1.2$  and  $1.5$  wt%) at room temperature. The DC conductivity of composite is attributed to  $\text{Li}^+$  ions in electrolyte. Figure 7 shows the variation of DC conductivity with MMT content in the composite electrolyte. The conductivity increases with increase in wt% of MMT. At 1.2 wt% of MMT, the conductivity reaches to a maximum value of  $1 \times 10^{-5}$  S/cm



**Figure 5.** Cole–Cole plot for PEO electrolyte with 1.2 wt% MMT.



**Figure 6.** Cole–Cole plot for PEO electrolyte with 1.5 wt% MMT.

and thereafter remains constant. The increase in conductivity is attributed to the increase in amorphous nature of composite electrolyte. Figure 8 shows the variation of the DC conductivity with temperature for composite electrolytes of different MMT content. The experimental values were fitted to VTF relationship (Souquet *et al* 1994) given by

$$\sigma = AT^{-1/2} \exp \left[ -B / (T - T_0) \right]. \quad (1)$$

Here, A is a constant which is independent of temperature; B is the pseudo activation energy,  $T_0$  is the ideal glass transition temperature. The fit indicates that variation of logarithmic DC conductivity with inverse temperature obeys VTF. This confirms that Lithium ion migrates in the composite through amorphous phase of the polymer electrolyte.

**Table 3.** Conductivity data of composite polymer electrolyte.

Code	$\sigma_{DC}$ at RT (S/cm) ( $\times 10^{-5}$ )	Ea (kJ/mol)	$T_0$ (K)
PEO	0.05	12.09	178
PEO1	0.12	10.40	172
PEO2	0.65	9.61	160
PEO3	1.10	7.68	154
PEO4	1.01	7.58	153

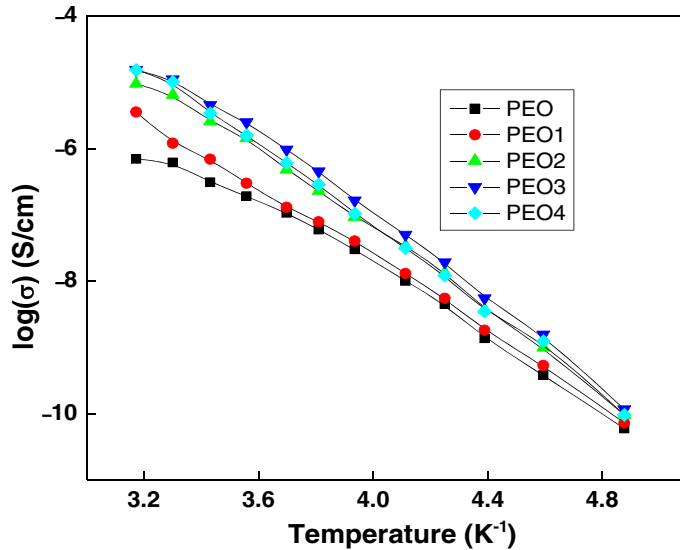


Figure 7. VTF plot for PEO based composite electrolyte.

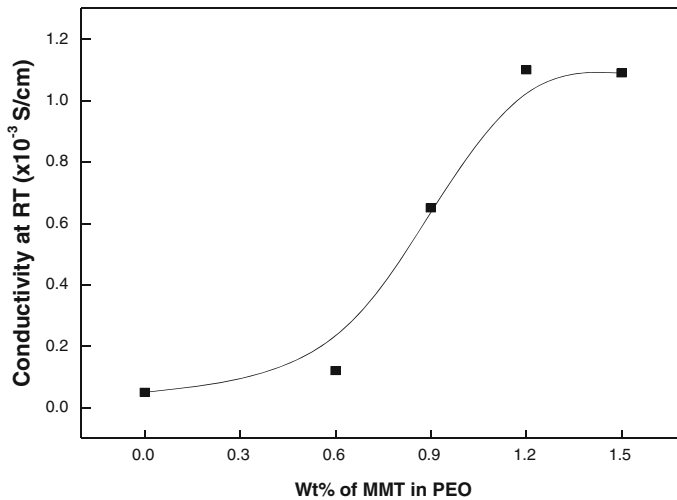


Figure 8. Variation of conductivity with wt% of MMT in composite polymer electrolyte.

#### 4. Conclusions

Nano composite PEO–MMT electrolytes were prepared through solution casting technique. XRD result confirms the presence of strained crystalline phase present in the composite electrolyte. DSC result indicates that crystalline phase decreases with increase in MMT content in composite electrolyte. The maximum conductivity at room temperature,  $1 \times 10^{-5}$  S/cm, is attained for composite electrolyte with 1.2 wt% of MMT. The increase in conductivity is due to the increase in amorphous nature of composite electrolyte.



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