

# Effect of plasticizer on structure—property relationship in composite polymer electrolytes

Dillip K. Pradhan, B.K. Samantaray, R.N.P. Choudhary\*, Awalendra K. Thakur

*Department of Physics and Meteorology, Indian Institute of Technology, Kharagpur 721302, India*

Received 18 February 2004; accepted 24 May 2004

Available online 28 October 2004

## Abstract

A new plasticized composite polymer electrolyte (PCPE) based on poly(ethylene oxide)–NaClO<sub>4</sub> dispersed with a ceramic filler (SnO<sub>2</sub>) and plasticized with polyethylene glycol (PEG<sub>200</sub>) is reported. The effect of plasticizer concentration on changes in structure/microstructure and their correlation with physical properties has been investigated and reported. A substantial enhancement in the electrical conductivity, by two orders of magnitude at room temperature, of the PCPE has been noticed when compared with that of composite polymer electrolyte (CPE) films without any plasticizer. This enhancement in electrical conductivity of the PCPE films agrees well with the changes in the local microstructure/structure on plasticizer addition. Grain boundary resistance ( $R_{gb}$ ) and glass transition temperature ( $T_g$ ) have been observed to decrease with increasing concentration of PEG<sub>200</sub>. Plasticizer addition has resulted in the suppression of crystallinity as observed from differential scanning calorimetry (DSC) and X-ray diffraction (XRD) studies. The DSC results indicate enhancement in the volume fraction of the amorphous phase, which appears to be consistent with the broadening in the polymer host peaks observed in X-ray diffractograms. The improvement in electrical conductivity has been achieved without any sharp deterioration in the thermal, electrochemical or mechanical stability of the PCPE thin films. These observations have been interpreted in terms of the action of plasticizer as a diluent/co-solvent. © 2004 Elsevier B.V. All rights reserved.

*Keywords:* Plasticization; Glass transition; Crystallinity; Impedance; Ion transport; Energy storage/conversion devices

## 1. Introduction

Ionically conductive solid polymers have recently received considerable attention in view of their technological importance in a wide variety of energy storage/conversion devices such as batteries, fuel cells, supercapacitors, and hybrid power sources [1–8]. The essential requirements of a material for such applications are: high ambient ionic conductivity, thermal, chemical, electrochemical, mechanical and interfacial stability in addition to dimensional flexibility of design [2–6]. Composite polymer electrolytes (CPEs) satisfy these criteria. The CPEs can be prepared by dispersing ceramic fillers (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>,  $\gamma$ -LiAlO<sub>2</sub>, Na<sub>2</sub>SiO<sub>3</sub>, SnO<sub>2</sub>, etc.) into the matrix of polymer–salt complexes [9–18]. The new idea of composite formation by dispersing inert ceramic fillers is an attractive approach to enhance the stability properties by modifying: (i) local structure/morphology, (ii) degree of crystallinity, (iii) glass transition temperature, (iv) flexibility of polymeric segments, (v) chemical nature

of filler particles, and (vi) the nature of the interaction in a heterogeneous polymer–salt–filler system [19–24]. The enhancement in mechanical properties is normally explained on the assumption that the filler particles act as a supporting matrix for the conductive polymer electrolyte so as to retain an overall solid structure, even at elevated temperature. The chemical nature (acidic/alkaline/amphoteric) of the filler particles also plays a major role in governing the nature of interaction in a heterogeneous composite system. Investigations on the mechanical properties of CPEs, using vibrational spectroscopy techniques, has indicated the possibility of polymer–ion–filler interaction and consequential stiffening of the polymeric network on filler addition [25–27]. Although this approach appears to be attractive, the enhancement in mechanical stability of CPEs occurs at the cost of their electrical conductivity [13]. In general, the electrical conductivity of CPEs lies normally in the range of 10<sup>–7</sup> to 10<sup>–5</sup> S cm<sup>–1</sup> at ambient temperature. Almost all the CPEs possess this inherent drawback which arises out of their partial crystalline nature that hinders their overall ionic conductivity and thereby imposes limitations on their utility.

\* Corresponding author. Tel.: +91 3222 283814.

E-mail address: [crnpfl@phy.iitkgp.ernet.in](mailto:crnpfl@phy.iitkgp.ernet.in) (R.N.P. Choudhary).

In order to overcome these limitations and to bring a desirable enhancement in the electrical conductivity of CPEs without affecting their stability properties to an undesirable level, various approaches are currently in vogue such as copolymerization and plasticization [28–36]. The essence of plasticization is to enhance the conductivity of solid polymer electrolytes by means of additives of low molecular weight and high dielectric constant such as propylene carbonate (PC), ethylene carbonate (EC) and polyethylene glycol (PEG). These additives tend to dissociate ion-pairs into free cations and anions, which leads to an overall enhancement in conductivity. The magnitude of conductivity is governed by the intrinsic nature of the plasticizer and plasticizer/salt ratio. The dielectric constant of the plasticizer acts as a controlling factor in modifying the ionic conductivity of the CPEs. A plasticizer is expected to induce important intrinsic modifications in the heterogeneous polymer composite system such as: (i) significant changes in local structure/microstructure; (ii) enhancement in the fraction of amorphous phase; (iii) increasing flexibility in the polymeric segments; (iv) release of mobile charge carriers due to ion dissolution effect and (v) changes in the local electric field distribution in the composite polymeric matrix. The overall effect leads to an increase in the number of mobile charge carriers ( $n$ ) and results in an enhancement of the net electrical conductivity in accordance with the relation:

$$\sigma = nq\mu \quad (1)$$

where:  $\sigma$  = electrical conductivity;  $q$  = magnitude of charge;  $\mu$  = mobility of the charge carrier. The mechanism of conductivity enhancement and other related properties in crystalline–crystalline composite has been studied extensively and suitable models have been reported by Maier et al. [37,38] and Bunde et al. [39]. Recently, we have also proposed a model to explain the changes in electrical and mechanical properties of CPEs in terms of polymer–ion–filler interactions [13,25,26]. Several explanations relating conductivity changes in CPEs exist in literature [19–24]. The enhancement in electrical conductivity in plasticized electrolytes has normally been explained in terms of ion association/dissociation effects and increase in the amorphous content of the system [16,40–42]. A complete description of the effect of plasticizer concentration on the structure of conductive polymer films is not available in the literature except for one reference [41] and this is restricted to a plasticized polymer–salt complex.

In this paper, we report results of systematic investigations of the effect of plasticizer concentration on the properties of a new plasticized composite polymeric system:  $(\text{PEO})_{25}\text{-NaClO}_4 + 10 \text{ wt.}\% \text{SnO}_2 + x \text{ wt.}\% \text{PEG}_{200}$ . The role of plasticizer concentration in changing the basic properties of CPEs such as electrical conductivity, ion transport behaviour and stability (thermal, mechanical, electrochemical) has been investigated. The observed change in physical properties has been interpreted in terms of the modification

of the microstructure/local structure of the host polymer on plasticizer addition.

## 2. Experimental

### 2.1. Materials preparation

Plasticized composite polymer electrolyte (PCPE) films of thickness ( $\sim 350 \mu\text{m}$ ) were prepared by a standard solution-cast technique using AR grade precursor materials. Commercial grade polyethylene oxide, PEO (M/S Aldrich, M.W.  $\sim 6 \times 10^5$ ) was used as the polymer host matrix,  $\text{NaClO}_4$  (M/S Fluka) as the salt for complexation, and  $\text{SnO}_2$  (with purity M/S BDH) as the ceramic filler. The precursors were vacuum dried and then used without any further purification. The appropriate ratio of polymer host (PEO) and salt ( $\text{NaClO}_4$ ) was dissolved in dehydrated methanol ( $\text{CH}_3\text{OH}$ ) and the solutions were then stirred vigorously for 10 h to facilitate proper mixing and complexation. Subsequently, an optimized ratio (10 wt.%) of the ceramic filler ( $\text{SnO}_2$ ) [25] was added followed by continuous stirring for 10 h. This was followed by the addition of a low molecular weight polymer, polyethylene glycol ( $\text{PEG}_{200}$ ) in different ratio by weight (in relation to polymer host) into the polymer–salt–filler solutions. The resulting solution mixture was finally stirred for 10 h. It was then cast in polypropylene dishes and allowed to evaporate slowly at room temperature ( $25^\circ\text{C}$ ) followed by vacuum drying. Next, the films were heated at  $45^\circ\text{C}$  under vacuum to remove residual solvent, if any. The entire operation was carried out in an inert atmosphere inside a glove-box. Finally, freestanding and dynamically stable thin films of plasticized composite polymer electrolyte were obtained. The plasticizer composition may be expressed as:  $(\text{PEO})_{25}\text{-NaClO}_4 + 10 \text{ wt.}\% \text{SnO}_2 + x \text{ wt.}\% \text{PEG}$  ( $x = 0, 5, 10, 20, 30, 40$  and  $50$ ).

### 2.2. Materials characterization

The morphological features and surface properties of different plasticized composite polymer electrolyte (PCPE) films were studied using an automated scanning electron microscopy (SEM JOEL-JSM Model 5800). The film surfaces were gold coated under an argon (Ar) atmosphere at a vacuum of  $\sim 10^{-2}$  Torr prior to being scanned in a high resolution, field emission, gun scanning, electron microscope. The thickness of the gold coating was approximately  $200 \text{ \AA}$ . The X-ray diffraction (XRD) pattern of the plasticized polymer films was recorded at room temperature using an X-ray diffractometer (Philips, Model 1710) with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in the  $2\theta$  (Bragg angles) range of  $9^\circ \leq 2\theta \leq 60^\circ$  at a scan speed of  $3^\circ$  per minute. Differential scanning calorimetry (DSC) studies of the different plasticized polymer films were carried out with a DSC unit (Perkin Elemer-Pyris Diamond). Approximately 3 mg samples of each composition was heated in the temperature

range  $-100$  to  $150$  °C at a scan rate of  $10^\circ$  per minute under an inert (helium) atmosphere. Thermal properties such as glass transition temperature ( $T_g$ ), enthalpy change ( $\Delta H$ ) and crystalline melting ( $T_m$ ) were obtained for each sample.

Complex impedance measurements were performed with a computer-controlled impedance analyzer (HIOKI LCR Hi-Tester Model 3532, Japan) in the frequency range of 100 Hz to 1 MHz using a cell of configuration SS|PCPE|SS (SS stands for stainless steel) and at an a.c. signal level of 20 mV. The complex impedance spectrum was used to evaluate the bulk d.c. conductivity and other related electrical properties. The ionic transport number ( $t_{ion}$ ) was measured using a polarization technique and evaluated using the relationship:

$$t_{ion} = \frac{i_T - i_e}{i_T} \quad (2)$$

where  $i_T$  = total ionic current and  $i_e$  = residual electronic current. The electrochemical stability of PCPE was determined by a simple d.c. voltammetry technique in which the variation of residual electronic current of the symmetrical cell, SS|PCPE|SS was monitored as a function of applied voltage. The current–voltage characteristics provide an estimate of the maximum working voltage (i.e., decomposition potential) of the plasticized solid electrolyte films in terms of the point of intercept of the suddenly rising current on the voltage axis.

### 3. Results and discussion

#### 3.1. X-ray diffraction

The XRD patterns for PCPEs with different plasticizer concentrations are shown in Fig. 1(a). The XRD pattern has typical features, namely a background hump followed by several characteristic diffraction peaks that are attributed to the host polymer (i.e., polyethylene oxide, PEO). This agrees well with the results of Takahashi et al. [43], and indicates that the solid polymeric films are composed of a combination of crystalline and amorphous phases, as demonstrated by Liquan and coworkers [44] for a polymeric conductor (Fig. 1). Further, the appearance of a small peak at  $\sim 26.5^\circ$  may possibly be related to the existence of  $\text{SnO}_2$  as a separate phase [45]. This suggests that the diffraction peaks of PCPE films are of composite nature. The addition of plasticizer brings substantial changes in the XRD patterns of CPE films with increasing concentration of plasticizer, as observed in Fig. 1(a) and (b). The main XRD peaks (due to PEO) that appear at  $\sim 19^\circ$  and  $23^\circ$  are characterized by a shift in position and significant broadening on addition of plasticizer. The peaks are sharp and well resolved for PEG = 30% and have maximum broadening for PEG = 50% (Fig. 1(b)). This suggests that the sample with PEG = 50% has maximum disorder. This observation is also corroborated by the value of the Scherrer length of the PEO peak (Table 1).

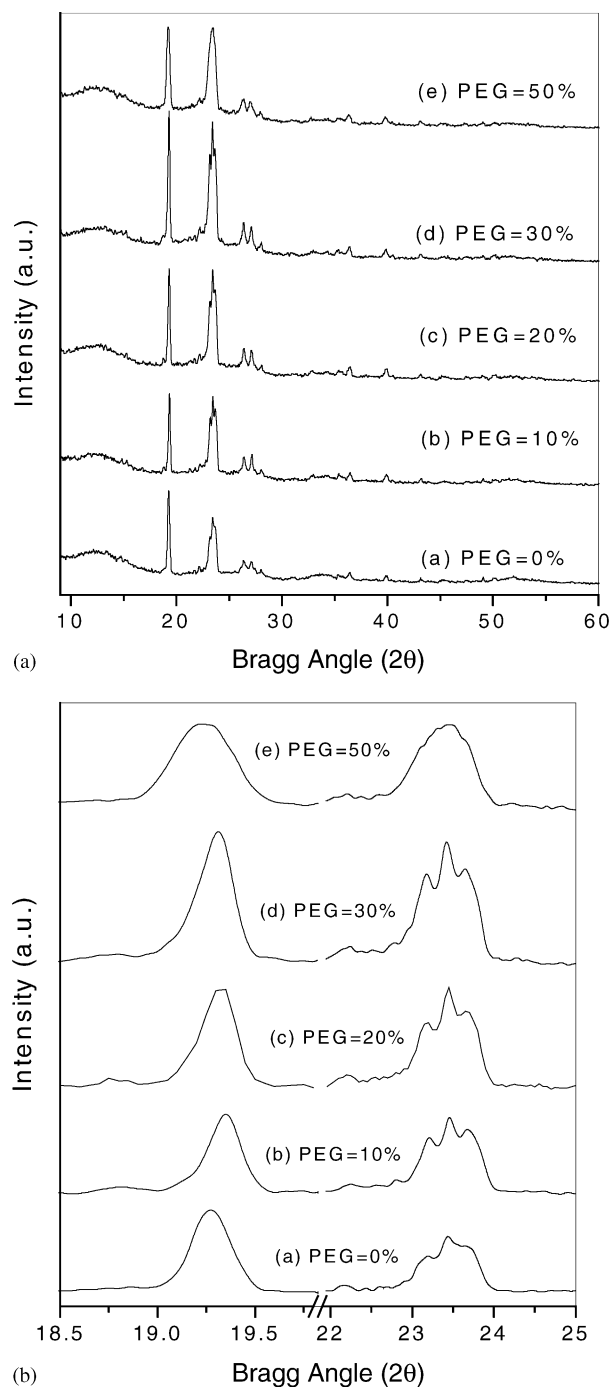


Fig. 1. (a) X-ray diffraction (XRD) pattern of PCPE thin films with different concentration ( $x$ ) of PEG (a)  $x = 0\%$ , (b)  $x = 10\%$ , (c)  $x = 20\%$ , (d)  $x = 30\%$ , (e)  $x = 50\%$ . (b) Amplified XRD patterns of PCPE thin films with different concentration ( $x$ ) of PEG (a)  $x = 0\%$ , (b)  $x = 10\%$ , (c)  $x = 20\%$ , (d)  $x = 30\%$ , (e)  $x = 50\%$ .

Comparison of the Scherrer lengths of the PEO peaks indicates that the crystallite size of PEO has become smaller on increasing plasticizer concentration. This suggests a possible decrease in crystallinity that results in an enhancement in the amorphous fraction in PCPE films on addition of plasticizer.

Table 1  
X-ray diffraction data for plasticized composite polymer electrolyte thin films (PEO<sub>25</sub>-NaClO<sub>4</sub> + 10 wt.% SnO<sub>2</sub> + *x* wt.% PEG<sub>200</sub>)

Composition (%PEG)	Main PEO peak		
	<i>d</i> -spacing	<i>I</i> / <i>I</i> <sub>0</sub>	<i>L</i> (nm)
0	4.5996	100	38
10	4.5859	100	46
20	4.5859	98	40
30	4.5996	100	40
40	4.5996	100	–
50	4.6244	100	23

### 3.2. Scanning electron micrographs

Scanning electron micrographs (SEM) of plasticized composite polymer electrolyte (PCPE) films (PEO<sub>25</sub>-NaClO<sub>4</sub> + 10 wt.% SnO<sub>2</sub> + *x* wt.% PEG) with *x* = 0, 10, 30 and 50 are presented in Fig. 2(a)–(d). A comparison of the surface morphology shows a marked change in the surface properties and texture of the composite polymeric thin films on addition of plasticizer. Surface roughening, crystalline texture and agglomeration of internal morphology appear to change gradually on increase of plasticizer concentration. These effects ultimately result in the appearance of a smooth texture of the surface. Such changes may be attributed to the fact that plasticization causes a reduction in the crystallinity of the host polymer (i.e., polyethylene oxide) and subsequent

enhancement in the overall amorphous fraction in the material. This observation appears to be in good agreement with the XRD results (Fig. 1(b) and Table 1).

### 3.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) curves for PCPE with different plasticizer concentrations are shown in Fig. 3(a) and (b) over a wide range of temperature i.e., –95 to 150 °C. The curves show two-step changes (Fig. 3(a)) that can be attributed to glass transition temperatures *T*<sub>g1</sub> at approximately –72 °C and *T*<sub>g2</sub> in the range of –56 to –27 °C. The *T*<sub>g1</sub> may possibly be related to the glass transition temperature of the host polymer (PEO) and the *T*<sub>g2</sub> to the glass transition temperature of the composite polymer electrolyte (CPE) system. The step change in each DSC curve is followed by a predominant endothermic peak (Fig. 3(b)) whose onset begins at approximately 66 °C (Table 2). This, in turn, is followed by a small but broad endothermic peak at 120 °C in the case of plasticizer-free composite polymeric (CPE) system. With the addition of plasticizer, these endothermic peaks shift towards lower temperatures. The two characteristic endotherms are assigned to the melting of the crystalline fraction of the uncomplexed and complexed PEO, respectively. The effect of plasticizer addition on the properties of CPE is clearly visible in the DSC data (Table 2). Further, it appears that the

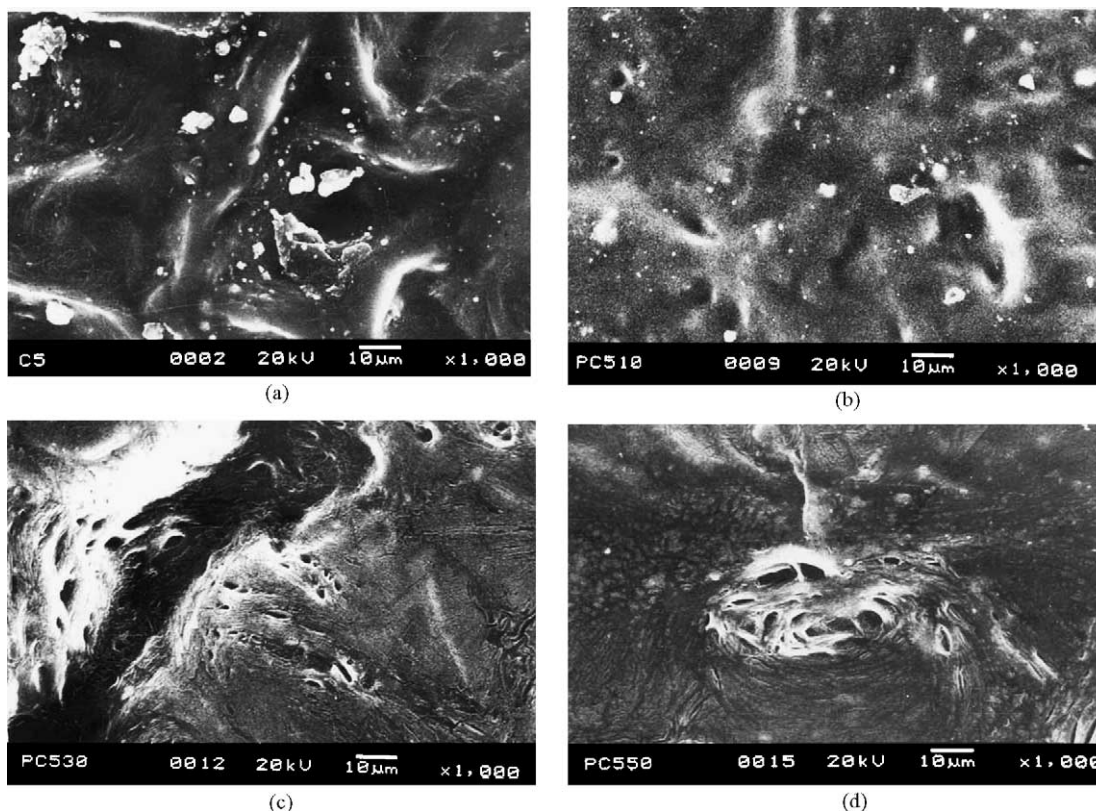


Fig. 2. SEM micrographs of PCPE thin films with different concentration (*x*) of PEG (a) *x* = 0%, (b) *x* = 10%, (c) *x* = 30%, (d) *x* = 50%.

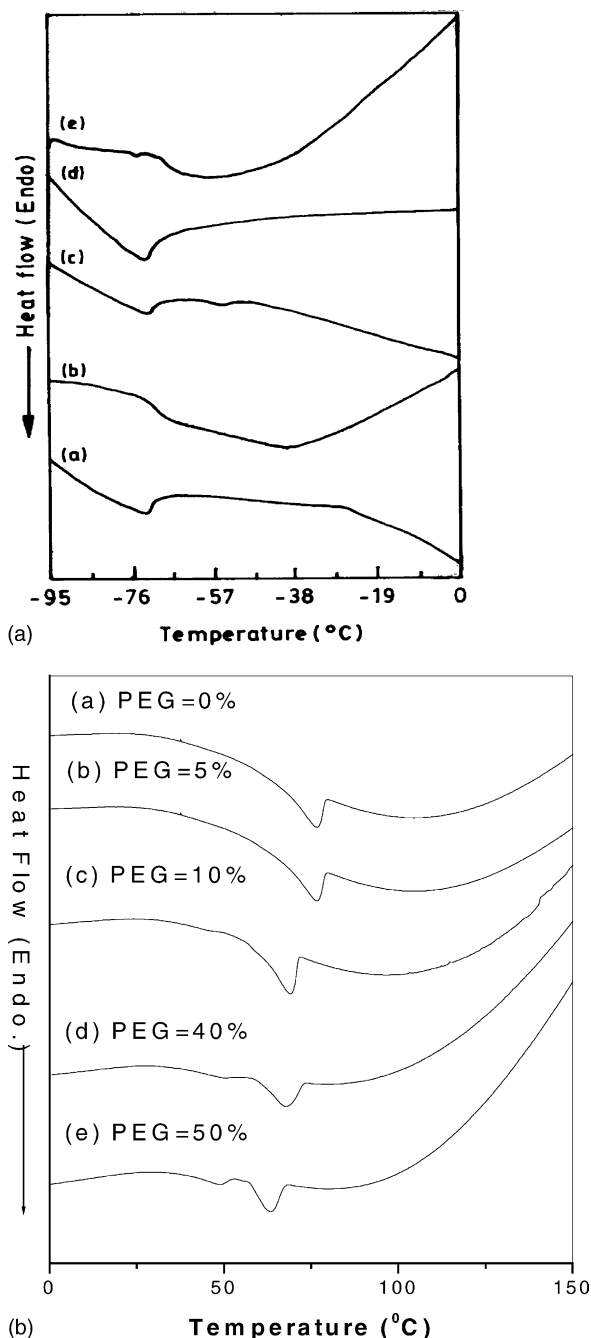


Fig. 3. (a) Variation of DSC pattern in temperature range  $-95$  to  $0$  °C with different concentration ( $x$ ) of PEG (a)  $x = 0\%$ , (b)  $x = 10\%$ , (c)  $x = 20\%$ , (d)  $x = 30\%$ , (e)  $x = 50\%$ . (b) Variation of DSC pattern in temperature range  $0$  to  $150$  °C with different concentration ( $x$ ) of PEG (a)  $x = 0\%$ , (b)  $x = 5\%$ , (c)  $x = 10\%$ , (d)  $x = 40\%$ , (e)  $x = 50\%$ .

glass transition temperature  $T_{g2}$  decreases with increasing plasticizer concentration. Since the glass transition temperature is related to the flexibility in the polymeric segments, the result may be related to a possible enhancement in the flexibility of polymeric chains of the PCPE films on addition of plasticizer. The relationship between increase in the elastomeric properties of the PCPE films on addition of

PEG is also indicated by the change in crystalline melting temperature ( $T_m$ ) and enthalpy ( $\Delta H_m$ ) value (Table 2). The relative percentage of crystallinity ( $\chi_c$ ) is calculated from DSC data by taking pure PEO as 100% crystalline and using the equation  $\chi_c = \Delta H_m / \Delta H_f^0$  ( $\Delta H_f^0 = 162 \text{ J g}^{-1}$  is heat of fusion of PEO) [35]. The calculated crystallinity and melting temperature are summarized in Table 2. It appears that there is a significant reduction in PEO crystallinity on plasticizer addition. This observation is consistent with the line-broadening effect in the XRD pattern with increasing concentration of plasticizer.

### 3.4. Complex impedance spectrum

The impedance spectrum analysis of plasticizer-free (pure CPE) and plasticized CPE has been carried out with an aim to observe the role of plasticizer in governing the electrical properties of solid PCPE films. The complex impedance spectra of plasticized composite polymer electrolytes with various plasticizer concentrations at room temperature are presented in Fig. 4. Each spectrum comprises of a semi-circle ( $x = 0$ ) in the high-frequency region followed by a trend of another semi-circle or spike in the low-frequency region. This feature appears to be common for plasticizer-free and plasticized composite polymer electrolyte. The magnitude of the impedance appears, however, to be drastically reduced in plasticized CPE when compared with plasticizer-free CPE. The high-frequency semi-circle may be attributed to the bulk properties of the material, whereas the low-frequency semi-circle to the grain-boundary effect, which is representative of the presence of an inhomogeneous crystalline phase in the films [13].

The intercept of the high-frequency semi-circle with the real axis gives an estimate of the bulk (d.c.) resistance ( $R_b$ ), whereas the intercept of the low-frequency semi-circle provides an estimate of grain-boundary resistance ( $R_{gb}$ ). There is a substantial reduction in the grain-boundary resistance of the plasticized sample when compared with that of plasticizer-free CPE. This provides a convincing evidence of the role of plasticizer in the reorganization of the physical structure of PCPE films and reduction of the crystallinity of the polymer host that favours long-term stability of the amorphous phase.

### 3.5. Electrical conductivity

The d.c. electrical conductivity of the plasticized composite polymer electrolyte has been evaluated from complex impedance spectrum data and expressed as a function of plasticizer concentration and temperature. The variation of the conductivity of  $(\text{PEO})_{25}\text{-NaClO}_4 + 10 \text{ wt.}\% \text{ SnO}_2 + x \text{ wt.}\% \text{ PEG}$  as a function of plasticizer concentration is shown in Fig. 5(a). Substantial enhancement in electrical conductivity of the PCPE films is observed on addition of up to 20 wt.% of plasticizer. A maximum enhancement in

Table 2

Differential scanning calorimetry data for plasticized composite polymer electrolyte thin films (PEO<sub>25</sub>-NaClO<sub>4</sub> + 10 wt.%SnO<sub>2</sub> + x wt.%PEG

Plasticizer concentration (PEG%)	$T_g$ (°C)		$T_m$ (°C)			$\Delta H_m$ (J g <sup>-1</sup> )	$X_c$ (%)
	$T_{g1}$	$T_{g2}$	Onset	Peak	End		
0	-72.5	-27.5	66.457	76.37	79.094	85.116	57.73
5	–	–	60.450	70.275	73.411	75.694	53.73
10	-72.9	-41.5	59.756	68.913	71.354	–	–
20	-72.98	-56.0	68.112	78.900	81.954	58.600	47.03
30	-72.76	-44.2	65.424	77.880	81.152	66.339	57.57
40	-72.7	–	60.015	67.715	72.775	60.427	55.91
50	-72.89	-44.9	57.213	63.300	67.357	47.081	46.5

electrical conductivity by two orders of magnitude at room temperature (RT) is found for films containing 20 wt.% PEG. This behaviour may be attributed to the combined effect of several factors such as reduction in crystallinity, increase in the elastomeric amorphous phase of the host PEO, and lowering of the  $T_g$  and grain-boundary resistance as observed in the present investigations.

The variation of electrical conductivity of (PEO)<sub>25</sub>-NaClO<sub>4</sub> + 10 wt.%SnO<sub>2</sub> + x wt.% PEG as a function of temperature for different values of x is presented in Fig. 5(b). The temperature dependence of the conductivity of plasticizer-free films (i.e., CPE) displays typical Arrhenius behaviour with a sharp jump in conductivity above the crystalline melting temperature (i.e.,  $T > 65$  °C). The two distinct and well-separated regions of electrical conductivity below and above  $T_m$  is characteristic of a semi-crystalline to amor-

phous phase transition in conductive polymeric films. The electrical conductivity of the PCPE films changes drastically with substantial enhancement in conductivity (nearly two order of magnitude), even at room temperature, on addition of plasticizer. The temperature-dependent conductivity of PCPE films exhibits typical VTF (Vogel–Tamman–Fulcher) behaviour, as expressed by the empirical relation:

$$\sigma = \sigma_0 \exp \frac{[-E_a]}{k_B [T - T_0]} \quad (3)$$

where:  $\sigma_0$  is the pre-exponential factor,  $k_B$  = Boltzmann constant,  $E_a$  is the activation energy,  $T_0$  is a reference temperature identified as the glass transition temperature of the host polymer (i.e., 216 K for PEO). It is clear that VTF behaviour of electrical conduction extends to the low-temperature region on increase in plasticizer concentration. This may

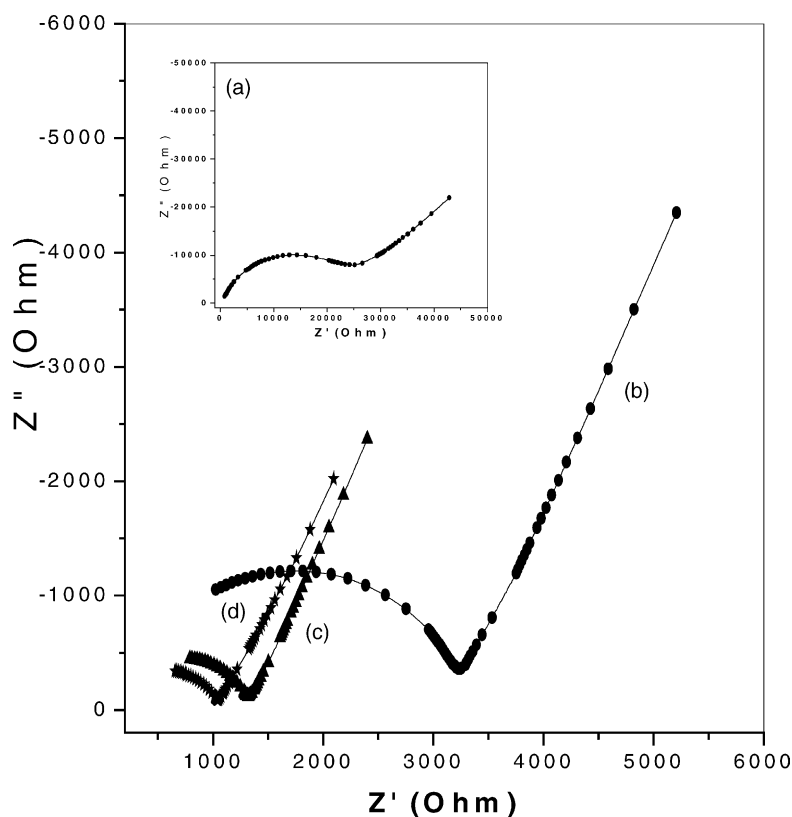


Fig. 4. Variation of real and imaginary part of impedance with different concentration (x) of PEG (a) x = 0%, (b) x = 10%, (c) x = 30%, (d) x = 50%.

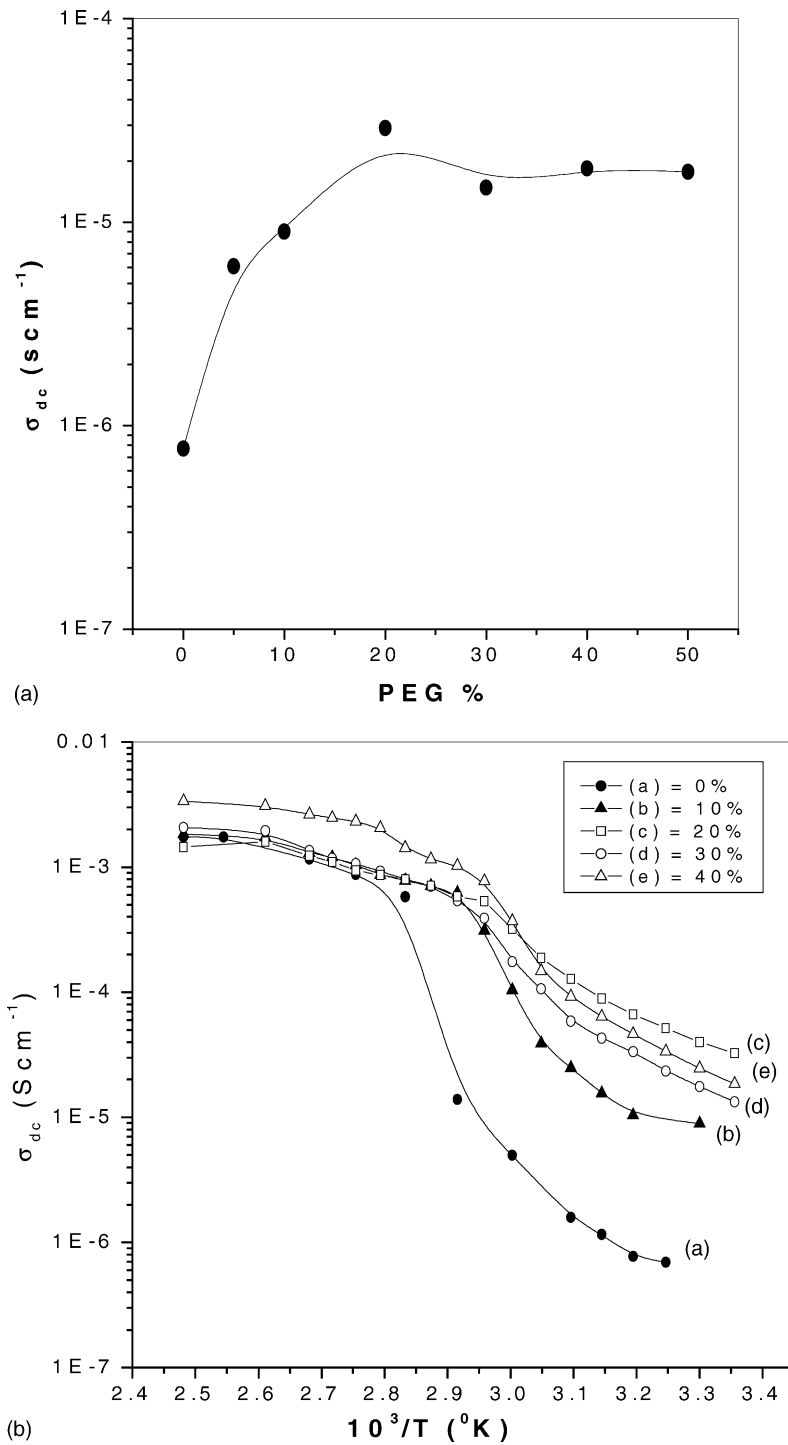


Fig. 5. (a) Variation of d.c. conductivity (RT) as a function of plasticizer concentration. (b) Variation of d.c. conductivity as function of temperature with different concentration ( $x$ ) of PEG (a)  $x = 0\%$ , (b)  $x = 10\%$ , (c)  $x = 20\%$ , (d)  $x = 30\%$ , (e)  $x = 40\%$ .

be interpreted as preferential interaction of plasticizer with crystalline PEO, which thereby reduces the concentration of crystalline phase and leads to an enhancement in the amorphous content. The last-mentioned effect has also been confirmed by DSC and impedance spectrum analysis (Tables 2 and 3).

### 3.6. Ionic transport properties

The ionic transport behaviour of the polymeric film has been investigated using a polarization technique. The results have been used to evaluate the transport number of the ions by using Eq. (2). The estimated values of the ionic transport

Table 3

Effect of plasticizer concentration on electrical and stability properties of plasticized composite polymeric thin films (PEO<sub>25</sub>-NaClO<sub>4</sub> + 10 wt.%SnO<sub>2</sub> + x wt.%PEG

% PEG	Electrical properties			Ionic transport number ( $t_{ion}$ )	Stability properties	
	d.c. conductivity ( $\sigma_{dc}$ ) at RT (S cm <sup>-1</sup> )	Activation energy (eV)			Dimensional stability	Voltage stability (V)
		Below $T_m$	After $T_m$			
0	$7.73 \times 10^{-7}$	0.69	0.39	0.99	Fairly good <sup>a</sup>	3.7
10	$9 \times 10^{-6}$	0.76	0.26	0.99	Good	2.7
20	$3 \times 10^{-5}$	0.52	0.25	–	Good	2.5
30	$1.5 \times 10^{-5}$	0.49	0.34	0.99	Good	2.5
40	$1.8 \times 10^{-5}$	0.53	0.46	–	Good	2.5
50	$1.8 \times 10^{-5}$	0.63	–	0.99	Good	2.5

<sup>a</sup> Dimensional stability observed in terms of tensile strength  $\sim 2.5$  MPa and % elongation at breakage (approximately three times) confirms fairly good mechanical properties [18].

numbers are shown in Table 3. These values indicate that the polymeric films are predominantly ionic in nature with  $t_{ion} = 0.99$ .

### 3.7. Material stability

The stability properties of the plasticizer-free and plasticized composite polymer electrolytes have been investigated in terms of the electrochemical potential window (safe working voltage limit). The dimensional stability of the plasticizer-free composite polymer electrolyte (CPE) has been studied by a static mechanical analysis method, as reported elsewhere [18]. Freestanding films of plasticized composite polymer electrolytes (PCPEs) also appear more or less similar in toughness and flexibility when compared with those of pure CPE (Table 3). A comparative visual observation suggests that even after addition of plasticizer the mechanical stability of the PCPE films remains fairly good and in an acceptable limit for all practical purposes.

The electrochemical potential window (break-down voltage limit) of PCPE films has been estimated by linear sweep voltammetry. The result has been expressed in terms of variation of residual electronic current as a function of applied voltage for different plasticizer concentrations (Fig. 6). It is clear that the threshold voltage (above which the material start breaking down) is higher for plasticizer-free (CPE) films than for plasticized composite polymer electrolyte (PCPE) films. Further, for plasticized films of different concentration (ranging from 5 to 50%), the sample break-down voltage is nearly the same. This indicates that the potential window of the PCPE films, although lower than the plasticizer-free CPE film, is still of interest and significance in view of the high electrical conductivity of these films.

### 3.8. Effect of plasticizer concentration on structure–property relationship

A composite polymer electrolyte comprising of polymer host, inorganic salt and ceramic filler can be visualized as a multiphase heterogeneous system that consists of crys-

talline, amorphous and an agglomeration of both. Such systems normally have a spherulitic microstructure in which grains are separated by dark-spaced amorphous regions [13,14]. The properties of such materials are governed by both the bulk material (grain interior) and the grain boundary, which ultimately depends on the fraction of crystalline phase present in the material. The addition of plasticizer to a composite polymeric (CPE) matrix is expected to bring substantial modification in the properties such as (i) increased ion solvation by interaction with the host polymer, (ii) increased flexibility in the polymeric chain by lowering the  $T_g$ , (iii) enhancement in the amorphous phase of polymer matrix at the cost of its crystallinity, (iv) enhancement in the electrical conductivity of the amorphous phase by acting as a co-solvent for the salt. These changes are largely dependent on the chemical nature and intrinsic properties of the plasticizer, such as molecular weight and permittivity.

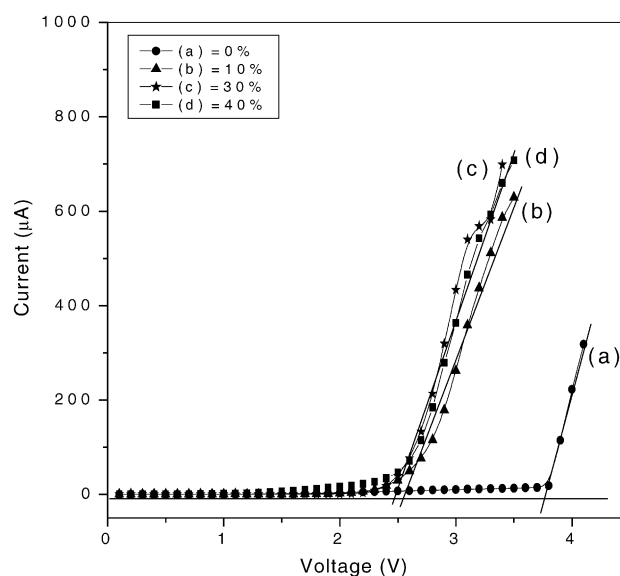


Fig. 6. Variation of residual electronic current as function of applied d.c. voltage with different concentration ( $x$ ) of PEG (a)  $x = 0\%$ , (b)  $x = 10\%$ , (c)  $x = 30\%$ , (d)  $x = 40\%$ .



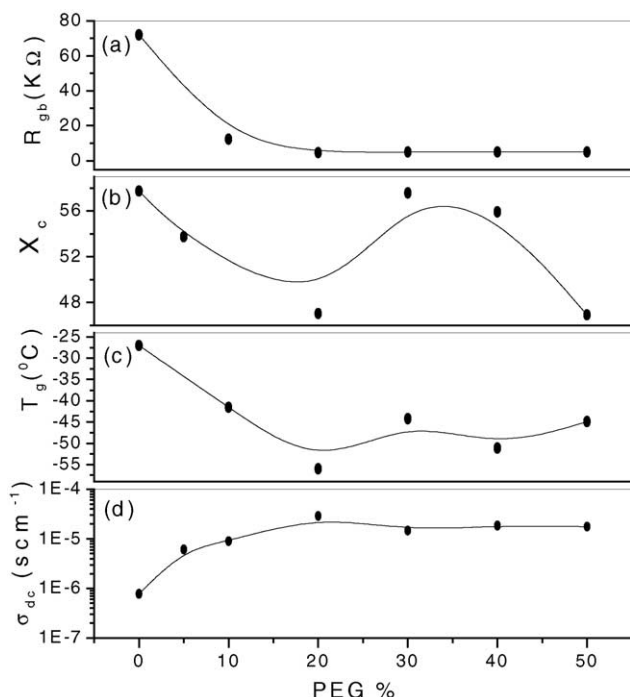


Fig. 7. Effect of plasticizer concentration on changes in: (a) grain-boundary resistance ( $R_{gb}$ ), (b) % crystallinity ( $X_c$ ), (c) glass transition temperature ( $T_g$ ), (d) d.c. conductivity of plasticized composite polymer electrolyte system (PEO<sub>25</sub>-NaClO<sub>4</sub> + 10 wt.% SnO<sub>2</sub> +  $x$  wt.% PEG<sub>200</sub>).

The variation of grain-boundary resistance ( $R_{gb}$ ) (as evaluated from Fig. 4), % degree of crystallinity ( $X_c$ ) of the polymer host (PEO) and glass transition temperature ( $T_g$ ) (evaluated from the DSC data of Fig. 3(a)) as a function of plasticizer concentration is shown in Fig. 7 and correlated to the variation of electrical conductivity with the varying concentration of plasticizer. The  $R_{gb}$  decreases monotonically at low concentrations of PEG and reaches a saturation value at high PEG concentrations (Fig. 7(a)). The decrease in grain-boundary resistance with increasing plasticizer concentration is testimony to a decrease in the crystallinity of the material with increase in PEG content. The variation of  $X_c$  as a function of plasticizer concentration Fig. 7(b)) also agrees with the above observation. It is well established that the broadening of XRD peaks corresponding to PEO (Fig. 1(b)) is associated with enhancement of the disorder/amorphous phase in the material on plasticizer addition [43].

Further, the glass transition temperature ( $T_g$ ) in a polymeric system is associated with the motion of polymeric segments in the amorphous phase without any change in its structure. It governs the flexibility of polymeric segments and chain motion. The addition of plasticizer in the present studies has resulted in substantial variation in  $T_g$  (Fig. 7(c)), i.e., an initial linear decrease at low PEG concentration and a plateau at high PEG concentrations. Since the value of  $T_g$  is directly associated with the segmental motion of the polymeric chains in the amorphous phase of the electrolyte, the lower the value of  $T_g$  the higher the mobility of the poly-

meric segments [15]. This explains the enhancement of the conductivity in accordance with Eq. (1).

The variation of crystallinity ( $\%X_c$ ),  $T_g$  and  $R_{gb}$  matches well with the pattern of conductivity as a function of plasticizer concentration. It is generally believed that ionic motion in the polymeric electrolyte takes place in the amorphous phase, so the increase in the volume fraction of amorphous phase (i.e. decrease in degree of crystallinity) and the reduction in grain-boundary resistivity that arises through suppression of the crystalline fraction is closely linked with the enhancement in ionic conductivity on plasticizer addition. The enhancement in conductivity is permitted by increased flexibility in the motion of the polymeric segments as indicated by the decrease in  $T_g$  on plasticizer addition. Finally, the mechanical properties of the polymeric films have been more or less retained on plasticizer addition (Table 3). This may be attributed to the prevention of any substantial degradation of mechanical properties by partial cross-linking.

The enhancement of ionic conductivity of CPEs may be attributed to the action of plasticizer as a diluent/co-solvent. This possibly brings substantial modification in the microstructure/structure in terms of the suppression of the crystallinity, dilution in the rigidity of the polymeric chains and ion dissociation paving the way for the release of more mobile charge carriers.

#### 4. Conclusion

A plasticized composite polymer electrolyte (PCPE) that has a heterogeneous composition (polymer–salt–filler–plasticizer) is studied. The effect of plasticization on the change in the electrical and the stability properties has been investigated. A substantial enhancement in the electrical conductivity (about two orders of magnitude at room temperature) has been found on plasticization. A maximum electrical conductivity of  $\sim 3 \times 10^{-5} \text{ S cm}^{-1}$  at 27 °C has been observed for 20 wt.% of plasticizer. The electrical conduction behaviour of the PCPE films is of the VTF type in sharp contrast to the Arrhenius behaviour displayed by unplasticized CPE films. The electrical transport is purely ionic in nature. The substantial improvement in the electrical properties on plasticization has taken place without much loss of thermal, electrochemical and mechanical stability; the values are in the acceptable limits for application in energy-storage devices. The change in physical properties of the CPE films on plasticizer addition is related to the change in the local microstructure/structure of the films and is governed by the chemical nature/intrinsic properties of the plasticizer. The effect of plasticizer on the CPE matrix manifests itself in terms of: (i) observed broadening of PEO peaks and hence decrease in crystallite size; (ii) decrease in the degree of crystallinity leading to enhancement in the amorphous fraction; (iii) decrease in the grain-boundary resistance resulting in more bulk conduction; (iv) a possible

modification in the local electric field distribution causing release of mobile charge carriers.

## Acknowledgements

The authors are grateful to Mr. Raj Kumar Yadav, Department of Physics, North Eastern Hill University (NEHU), Shillong, India for assistance with preparation of the samples.

## References

- [1] J.R. MacCallum, C.A. Vincent (Eds.), *Polymer Electrolyte Review—I and II*, Elsevier, London, 1987.
- [2] D.A.J. Rand, R. Woods, R.M. Dell, *Batteries for Electric Vehicles*, Wiley, 1998.
- [3] R.G. Linford (Ed.), *Electrochemical Science and Technology of Polymer—1*, Elsevier, London, 1987.
- [4] B. Scrosati (Ed.), *Application of Electroactive Polymers*, Chapman and Hall, London, 1993.
- [5] C.A. Vincent, *Prog. Solid State Chem.* 88 (1989) 109.
- [6] F.M. Gray, *Solid Polymer Electrolytes, Fundamentals and Technological Applications*, VCH, New York, 1991.
- [7] D.F. Shriver, P.G. Bruce, in: P.G. Bruce (Ed.), *Solid State Electrochemistry*, Cambridge University Press, UK, 1995.
- [8] B.E. Conway, *Electrochemical Supercapacitors: Scientific Fundamental and Technological Applications*, Kluwer Academic/Plenum, 1999.
- [9] J.E. Weston, B.C.H. Steele, *Solid State Ionics* 7 (1982) 75.
- [10] F. Capuano, F. Croceaad, B. Scrosati, *J. Electrochem. Soc.* 38 (1991) 1981.
- [11] B. Kumar, L.G. Scanlon, *J. Power Sources* 52 (1994) 261.
- [12] W. Wiczorek, Z. Florjanczyk, J.R. Stevens, *Electrochim. Acta* 40 (1995) 2251.
- [13] S.A. Hashmi, A.K. Thakur, H.M. Upadhyaya, *Euro. Polymer J.* 34 (1998) 1227.
- [14] A.K. Thakur, H.M. Upadhyaya, S.A. Hashmi, A.L. Verma, *Ind. J. Pure Appl. Phys.* 37 (4) (1999) 302.
- [15] B.-k. Choi, K.-H. Shin, *Solid State Ionics* 86–88 (1996) 303.
- [16] M.J. Reddy, T. Sreeknath, U.V. Subbarao, *Solid State Ionics* 126 (1999) 55.
- [17] W. Wiczorek, P. Lipka, G. Zukowska, B. Wycislik, *J. Phys. Chem. B* 102 (36) (1998) 6968.
- [18] S.A. Hashmi, H.M. Upadhyaya, A.K. Thakur, A.L. Verma, *Ionics* 6 (2000) 248.
- [19] C. Liquan, in: B.V.R. Chowdari, S. Radhakrishna (Eds.), *Materials for Solid State Batteries*, World Scientific Publishing Co., 1988, Singapore, p. 69.
- [20] W. Wiczorek, K. Such, J. Plochanski, J. Przulski, in: B. Scrosati (Ed.), *Proceedings of the Second International Symposium on Polymer Electrolytes*, Elsevier, Amsterdam, 1990, p. 339.
- [21] F. Crook, F. Bonino, V. Panero, B. Scrosati, *Philos. Mag. B* 59 (1989) 161.
- [22] F. Capuano, F. Croce, B. Scrosati, *J. Electrochem. Soc.* 138 (1991) 1918.
- [23] D. Brinkmann, W. Gang, F. Croce, B. Scrosati, *Solid State Ionics* 53–56 (1992) 1202.
- [24] L.W. Krawiec, L.G. Scanlon, J.P. Fellner, R.A. Vaia, S. Vasudevan, E.P. Giannelis, *J. Power Sources* 54 (2) (1995) 310.
- [25] Awalendra K. Thakur, Ph.D. Thesis, North Eastern Hill University (NEHU), Shillong, India, 2001.
- [26] Awalendra K. Thakur, R.N.P. Choudhary, *J. Mater. Chem. Phys.*, under revision.
- [27] F. Capuano, F. Croce, B. Scrosati, US Patent No. 5,576,115 (1996).
- [28] C.A. Vincent, *Progress Solid State Chem.* 17 (1987) 145.
- [29] M.B. Armand, *Annual Rev. Mater. Sci.* 16 (1986) 245.
- [30] M.A. Ratnar, D.F. Shriver, *Chem. Rev.* 88 (1988) 109.
- [31] W.J. Lee, H.R. Jung, S.M. Lee, J.H. Kim, K.S. Yang, *Solid State Ionics* 164 (2003) 17.
- [32] T. Wang, F. Xu, Y. Cheng, Z. Jiang, *Chem. Phys. Lett.* 359 (2002) 303.
- [33] S. Rajendran, S. Shivkumar, R. Subedevi, *J. Appl. Polymer Sci.* 90 (10) (2003) 2794.
- [34] J.R. MacCallum, M.M. Silva, S.C. Barros, M.J. Smith, E. Fernandes, *Proc. Electrochem. Soc.* (2003) 2001.
- [35] C.J. Leo, G.V. Subbarao, B.V.R. Chowdari, *Solid State Ionics* 148 (2002) 159.
- [36] M.H. Sheldon, M.D. Glasse, R.J. Latham, R.G. Linford, *Solid State Ionics* 34 (1989) 135.
- [37] J. Maier, in: A.L. Laskar, S. Chandra (Eds.), *Superionic Solids and Solid Electrolytes—Recent Trends*, Academic Press, New York, 1989, p. 137.
- [38] J. Maier, *Prog. Solid State Chem.* 23 (1995) 137.
- [39] A. Bunde, W. Dietrich, E. Roman, *Solid State Ionics* 18/19 (1986) 14.
- [40] C. Wang, Q. Liu, Q. Cao, Q. Meng, L. Yang, *Solid State Ionics* 53–56 (1992) 1106.
- [41] D.R. MacFarlane, J. Sun, P. Meakin, P. Fasoulopoulos, J. Hey, M. Forsyth, *Electrochim. Acta* 40 (1995) 2131.
- [42] D. Golodnitsky, G. Ardel, E. Peled, *Solid State Ionics* 85 (1996) 231.
- [43] Y. Takahashi, I. Sumita, H. Tadakoro, *J. Polymer Sci.: Polymer Phys.* 11 (1973) 2113.
- [44] J. Li, X. Huang, K. Chen, *J. Electrochem. Soc.* 147 (7) (2000) 2653.
- [45] *JCPCS* 1999 No. 77-0450.