Effect of polysorbate plasticizer on the structural and ion conduction properties of PEO–NH$_4$PF$_6$ solid polymer electrolyte

Kuldeep Mishra[1] · Saurabh Singh Pundir[2] · D. K. Rai[2]

Abstract Effects of a new plasticizer, polysorbate 80, on the structural and electrochemical properties of PEO–NH$_4$PF$_6$ polymer electrolyte system have been investigated. X-ray diffraction studies show significant increase in amorphicity of the solid polymer electrolyte on introduction of the plasticizer, which is also supported by lesser-dense spherulites observed in the SEM micrographs. The room temperature ionic conductivity of the electrolyte shows an increase of about two orders of magnitude ($\sigma_{max} \sim 10^{-5}$ S/cm) on plasticization. The frequency dependence of the conductivity has been found to obey the Jonscher's power law and slower backward ion hopping on plasticization. The polymer electrolyte shows protonic conduction as confirmed using cyclic voltammetry study. The studies show that polysorbate 80 is a promising plasticizer for semicrystalline polymer electrolytes.

Keywords Polymer film · Plasticization · Polysorbate 80 · Amorphicity

Introduction

Solid polymer electrolytes are the most extensively studied class of ion-conducting solids. These electrolytes possess properties like high shape versatility, flexibility, light weight, etc., which make them interesting choice for their use in electrochemical devices. Particularly, the polyethylene oxide (PEO)-based polymer electrolytes are the most widely studied polymer electrolytes because of the special properties like low glass transition temperature ($T_g = -67$ °C), high salt solvation capability, and good chemical and mechanical properties of PEO. The ether oxygen of PEO chains crosslink with cations of the ionic salts and facilitate ion conduction through the polymer matrix [1, 2]. The segmental motion of polymer chains in such polymer electrolytes is understood to help cations to jump from one site to the other. However, PEO is inherently a semicrystalline polymer; therefore, as a host, it offers only little flexibility of chains in the crystalline regions. As a result, PEO-based polymer–salt complexes offer poor ionic conductivity. A considerable amount of work, thus, has been focused on the modification of crystalline structure of the host PEO to enhance ionic conduction in the PEO-based polymer electrolytes [3, 4]. Among the existing methods, plasticization is the most effective one to reduce crystallinity of polymer electrolytes. In plasticization, commonly high dielectric constant organic liquids like ethylene carbonate (EC), propylene carbonate (PC), dimethylformamide (DMF), etc., are mixed with polymer electrolytes. These plasticizers are known not only to decrease the crystallinity of polymer electrolytes by dismantling the compact periodic arrangement of polymer chains but also to enhance ion dissociation and reduce T_g of the electrolytes. The increase in ion dissociation increases the number of mobile ions, and decrease in glass transition temperature enables the polymer electrolyte to become flexible at a reduced temperature. These effects on plasticization invariably result into higher ionic conductivity of polymer electrolytes [5–8]. The effect of plasticization by PC on PEO–NH$_4$PF$_6$ has been studied by Sharma and Sekhon [9]. They have obtained an increase of ~2 orders of magnitude in ionic conductivity (5.8×10^{-7} to 1.4×10^{-5} S/cm) of the polymer electrolyte films. But, for higher concentration of the plasticizer, electrolyte films have been found to show poor

✉ D. K. Rai
dk.rai@jiit.ac.in

1 Department of Physics, Jaypee University, Anupshahr 203390, India

2 Department of Physics and Materials Science and Engineering, Jaypee Institute of Information Technology, Noida 201309, India

mechanical strength. In an earlier study, we have reported effect of EC + PC on the ionic conductivity of PEO–NH_4PF_6 polymer electrolyte films wherein plasticized films show higher coordination between dissociated salt cation (NH_4^+) and ethylene oxide group of PEO [10]. Low molecular weight polymer like polyethylene glycol (PEG) has also been reported by several authors as plasticizer in different polymer electrolyte systems [11–13]. The PEG has been observed to increase amorphicity and ion mobility in the polymer electrolytes. The plasticizer PEG–borate ester has also been reported to enhance the ionic conductivity of the poly(ethylene glycol) methacrylate + lithium bis-trifluoromethanesulfonimide (LiTFSI) solid polymer electrolyte system [14]. According to the report, higher number of ethylene oxide chains in the plasticizer results into higher number of coordinating sites in the host polymer which helps in increasing the ionic conductivity of the electrolyte system. In another study, Yahya and Arof [15] have reported that small molecules of oleic acid plasticizer in Chitosan + lithium acetate polymer electrolyte system decrease the cohesive force between polymer chains and hence increase the segmental motion in the polymer.

Figure 1a shows the structure of PEO–NH_4PF_6 complex, in which cation (NH_4^+) of the salt is attached with the ether oxygen of PEO through hydrogen bonding, and Fig. 1b shows the molecular formula of polysorbate 80, also known as Tween 80, which is a non-ionic viscous liquid polymer carrying oxyethylene group (–CH_2CH_2O–) with Oleic acid end. Polysorbate 80 is a kind of branched polymer which may plasticize and upset the crystalline arrangement of PEO chains and thus increase the amorphicity of the polymer electrolyte further. The availability of ethylene oxide chains may also support higher ionic conductivity of the electrolyte system. The present paper reports structural, thermal, and electrochemical properties of PEO–NH_4PF_6 solid polymer electrolyte plasticized with polysorbate 80.

Experimental

Reagents and preparation of polymer electrolyte membranes

PEO ($M_w = 5 \times 10^6$), ammonium hexafluorophosphate (NH_4PF_6), and polysorbate 80 (Tween 80) were purchased from Aldrich. Water-free acetonitrile (AR grade) was obtained from Fisher scientific and was used as a common solvent. The chemicals were used as received.

Polymer electrolyte membranes were prepared by solution-cast technique. In an earlier study reported elsewhere by us, it has been observed that polymer electrolyte membrane of PEO–NH_4PF_6 shows highest ionic conductivity (2.5×10^{-7} S/cm at room temperature (RT) = 27 °C and relative humidity (RH) = 55 %) for the PEO–salt composition 88:12 by weight

[10]. Therefore, this very composition of the polymer electrolyte, i.e., 88 wt% PEO + 12 wt% NH_4PF_6 (henceforth written as PE), was chosen for the plasticization with polysorbate 80. The amounts of the PE and polysorbate 80 were taken according to the compositional formula (100-x) PE + x polysorbate 80 for x = 0, 10, 20, 30, 40, 50 wt%. The electrolyte membranes for the compositions x > 50 wt% could not be considered for study as the membranes were sticky and difficult to handle. The constituents taken in the desired ratios were dissolved separately in acetonitrile and then were mixed together by continuous stirring for 24 h. The mixed homogeneous solutions were casted on Petri dishes and left for slow evaporation of solvent at RT and membrane formation. The solid membranes so obtained were 200–300 μm thick, freestanding, flexible, and non-sticky.

Instrumentation

To study structural and morphological changes due to plasticization by polysorbate 80, the electrolyte membranes were characterized using X-ray diffractometer (XRD-6000, SHIMADZU, Japan) with CuKα radiation in the range of 2θ = 5°–60° and scanning electron microscope (SEM, LEO 435 VP, UK), respectively. The ionic conductivity of the polymer electrolyte membranes was evaluated by complex impedance spectroscopy using HIOKI 3522-50 LCR HiTESTER over the frequency range from 100 kHz to 10 Hz with a signal level of 100 mV. All the electrochemical measurements were performed using a cell: stainless steel (SS)/electrolyte/SS held in a sample holder. For temperature dependence of ionic conductivity, cells were left for 5 min for achieving saturation at each temperature before taking measurement. The electrochemical stability of the electrolyte system was evaluated by cyclic voltammetry using electrochemical analyzer (CHI 608C, CH Instruments, USA). A sweep voltage was applied across the cell SS/polymer electrolyte/SS with a scan rate of 5 mV/s to record the cyclic voltammogram. In order to establish H^+ ion conduction in the electrolyte system, a comparative cyclic voltametric measurement was carried out on symmetrical cells, SS |electrolyte| SS, and Zn + $ZnSO_4·7H_2O$ |electrolyte| Zn + $ZnSO_4·7H_2O$ where SS and Zn + $ZnSO_4·7H_2O$ were taken as blocking and reversible electrodes, respectively.

Results and discussion

SEM studies

SEM is an important technique to study crystalline structure and morphology of polymer electrolyte membranes. PEO is a semicrystalline polymer. Its crystallinity in polymer electrolyte membranes appears in the form of spherulites [10, 16]. Spherulites consist of aggregate of chain-folded lamellar

Fig. 1 Structures of PEO–
NH_4PF_6 complex (a) and
polysorbate 80 (b)
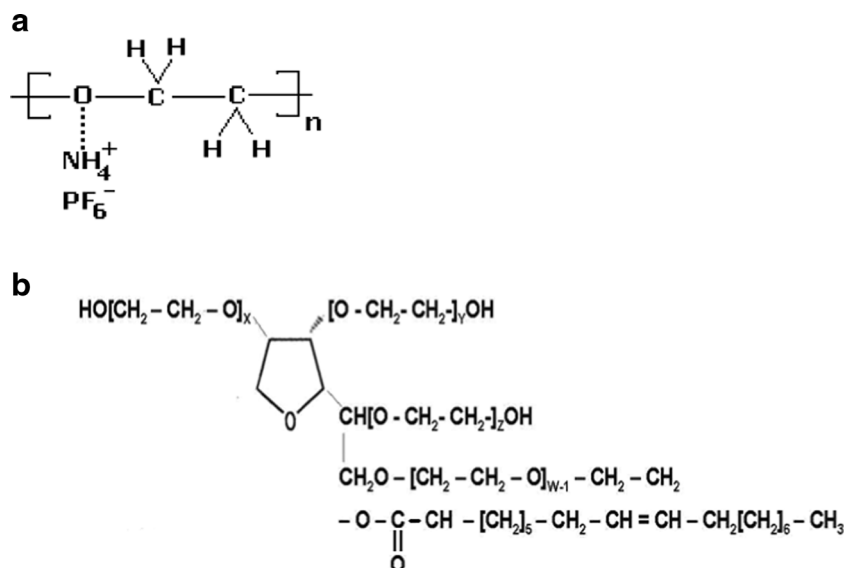
crystallites. In the present case, SEM is used to see the changes in crystalline structure by observing the distribution of spherulites and morphology of PE membranes on plasticization with polysorbate 80. Figure 2 shows SEM images of (100-x) PE + x polysorbate 80 polymer electrolyte membranes with x = 0, 30, and 50 wt%. The micrograph of the unplasticized PE membrane (x = 0 wt%) shows presence of crystalline regions imitated as nearly circular and densely arranged small spherulites of average size ~20 μm (Fig. 2a). In the plasticized PE membrane with 30 wt% polysorbate 80, a comparatively flat morphology with lesser density of spherulites has been observed as shown in Fig. 2b. The density of spherulites reduces further on further increase in the plasticizer concentration as observed in the SEM image of the electrolyte membrane with 50 wt% plasticizer (Fig. 2c). In the plasticized PE, the size of spherulites becomes substantially small, and spherulites are surrounded by larger amorphous regions. These observations show that plasticization of the PE membrane by polysorbate 80 results into reduction of crystallinity of the polymer electrolyte.

XRD studies

In the solid polymer electrolytes, amorphous matrix of polymers supports higher segmental motion which enhances ion mobility and ionic conductivity. In view of this, XRD is an important technique as it provides information about the structure of the polymer electrolyte membranes. The XRD patterns of (100-x) PE + x Polysorbate 80 polymer electrolyte are shown in Fig. 3 for x = 0 and 50 wt%. The XRD pattern of the electrolyte with x = 0 wt% shows semicrystalline nature of the polymer electrolyte, in which amorphous phase of the electrolyte system co-exists with crystalline regions reflected by predominant peaks at 2θ~19.6° (120) and 23.8° (032 + 112) and by small peaks at 13.6°, 16.3°, 18.8°, 21.8°, 22.4°,

and 37.7°. On plasticization with polysorbate 80, almost all the crystalline peaks are observed to have been disappeared except the two prominent peaks appearing at 2θ~18.8° and 23°. The disappearance of the crystalline peaks is accompanied with appearance of a broader hump ranging from ~10° to 28°. The shifting of the predominant crystalline peaks toward the lower 2θ values is attributed to the increase in the interplaner separation in the crystalline region of the host polymer matrix on introduction of the polysorbate 80. The disappearance of the smaller crystalline peaks and the appearance of the broader hump in the diffraction pattern indicate increase in the amorphicity of PE on plasticization with polysorbate 80. The percentage crystallinity of the polymer electrolyte has been evaluated with the help of following formula:

$$\%\text{crystallinity} = \left(\frac{\chi_p}{\chi}\right) \text{x } 100\% \qquad (1)$$

where χ_p and χ are the areas covered under crystalline peaks and the whole diffractogram, respectively. The crystallinity of the unplasticized polymer electrolyte is obtained as ~67 %, while that of the plasticized polymer electrolyte with 50 wt% polysorbate 80 as ~33 %. This shows a considerable decrease in the crystallinity of the polymer electrolyte on plasticization with polysorbate 80; however, electrolyte still remains slightly crystalline. These results corroborate fully with the SEM results described above.

Conductivity studies

Figure 4 shows complex impedance plots for the unplasticized (x = 0 wt%) and different compositions (x = 10–50 %) of plasticized (100-x) PE + x polysorbate 80 polymer electrolyte obtained at RT 26 °C and RH 50 %.
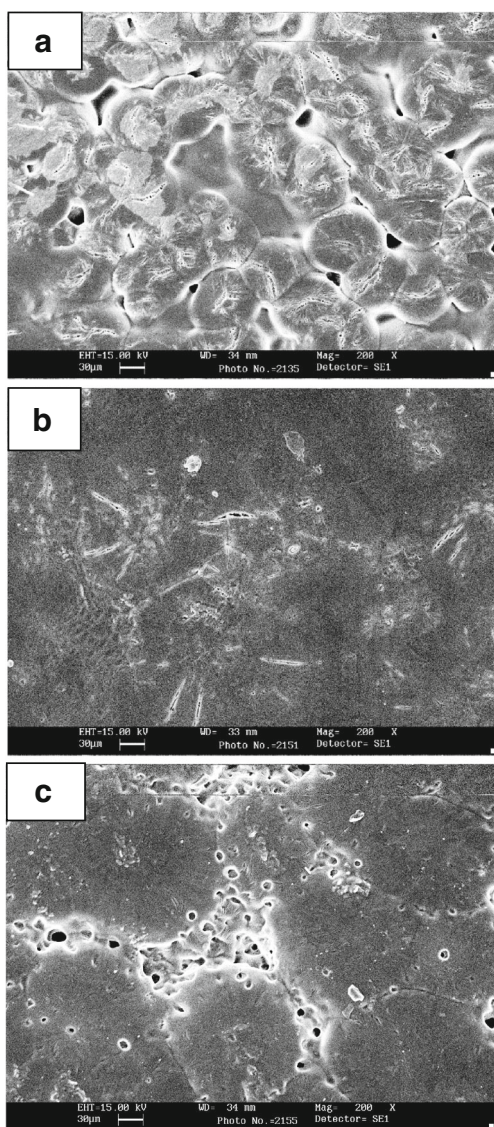
Fig. 2 SEM micrographs of (100-x) PE + x polysorbate 80 polymer electrolyte membranes for the compositions x = 0 wt% (**a**), x = 30 wt% (**b**), and x = 50 wt% (**c**)

Fig. 3 XRD patterns of (100-x) PE + x polysorbate 80 polymer electrolyte membrane for the compositions x = 0 wt% (unplasticized) and x = 50 wt%

The plots consist of a compressed semicircle in high-frequency range which corresponds to charge transfer process through bulk of the polymer electrolyte. The semicircle is followed by an inclined line in the low-frequency region which is characteristic of capacitive nature of electrode–electrolyte interface. The equivalent circuit of the impedance plots is shown in Fig. 4a (inset). In this circuit, R_b corresponds to the polymer electrolyte resistance (bulk resistance). The constant phase element CPE1 signifies the effect of dipolar relaxation inside the polymer electrolyte. The semicircle in the high-frequency range is due to the combined effect of R_b and CPE1, while the straight line in the low-frequency range is due to the CPE2 representing the double layer between electrode–polymer electrolyte interface. As shown in Fig. 4b, with increasing
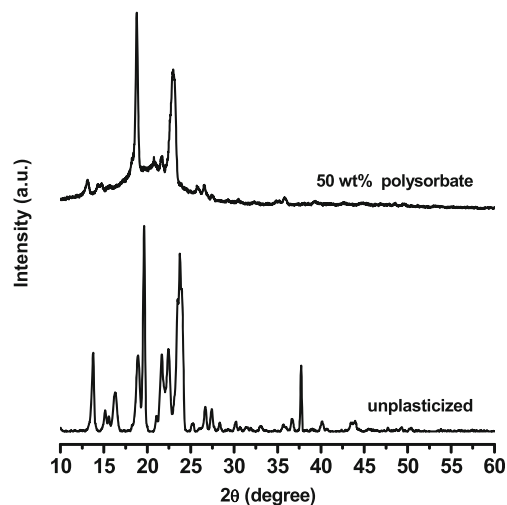
concentration of the polysorbate 80, the semicircle in the high-frequency range continuously disappears. This is attributed to the dominant contribution of resistive nature of the plasticized polymer electrolytes, while capacitive nature due to the polymer backbone diminishes at higher concentration of the plasticizer [17]. In addition, the slope of the curve at low-frequency side has been found to be independent to the plasticizer concentration, which suggests that the interfacial resistance at the low-frequency side is mainly due to the ion motion at electrode–electrolyte interface [18].

The ionic conductivity of the polymer electrolyte membrane has been obtained by using bulk resistance (R_b) of the polymer electrolytes estimated from the complex impedance plots with the help of the following formula:

$$\sigma = \left(\frac{1}{R_b} \frac{d}{A} \right) \tag{2}$$

where d is the thickness of the sample and A is the area. Figure 5 shows composition dependence of ionic conductivity of (100-x) PE + x polysorbate 80 polymer electrolyte membranes. The conductivity is found to increase continuously with the plasticizer concentration. This is attributed to the lowering of crystallinity of the membranes with increasing concentration of the plasticizer as observed in the structural studies above. Addition of plasticizers, in general, increases the mobility of ions by providing low viscosity surrounding to the ions and by higher segmental motion in the polymer matrix produced by increased disordered fraction of the polymer backbone. Additionally, in the polysorbate 80, the plasticizer used in the present study, availability of extra ether oxygen can provide extra sites for the salt complexation and may contribute to the enhanced conductivity by preventing ion association.
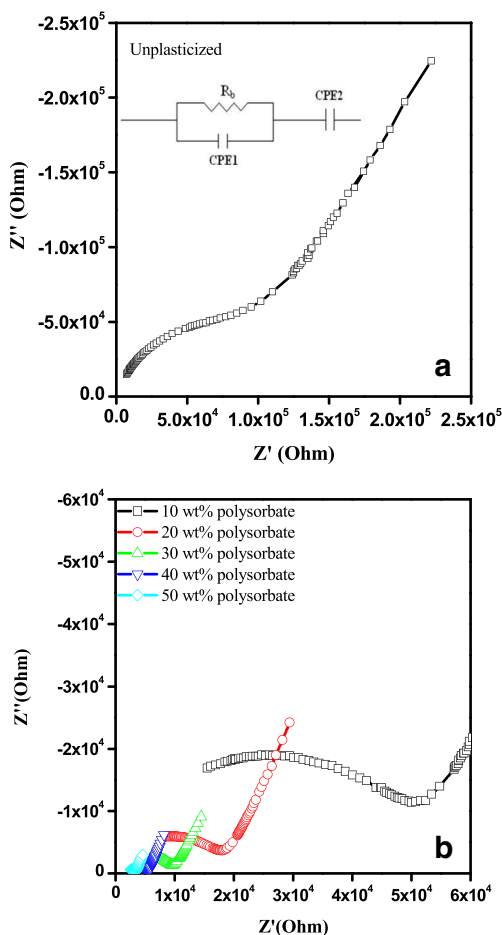
Fig. 4 Complex impedance plot for (100-x) PE + x polysorbate 80 polymer electrolyte membrane with x = 0 wt% (**a**) and x = 10–50 wt% (**b**)

Figure 6 shows temperature dependence of ionic conductivity of (100-x) PE + x polysorbate 80 polymer electrolyte membranes with x = 0, 30, and 50 wt%. For all the compositions, conductivity is found to increase with temperature. A change in
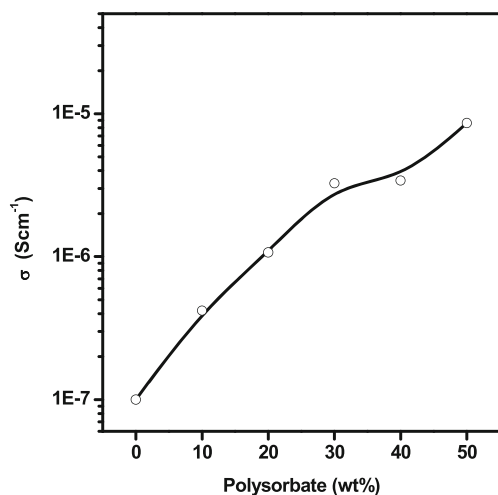

Fig. 5 Variation of ionic conductivity with composition of (100-x) PE + x polysorbate 80 polymer electrolyte membranes at RH = 50 % and RT = 26 °C
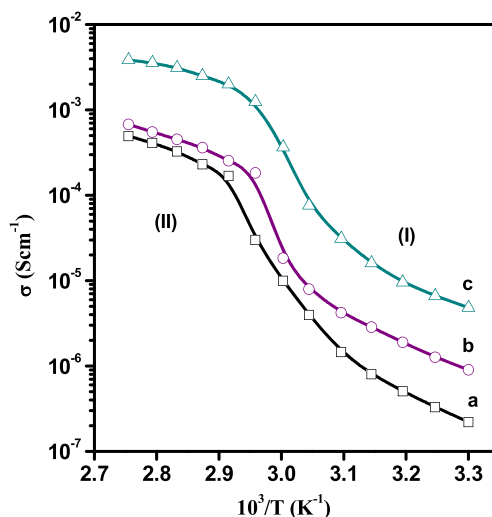

Fig. 6 Temperature dependence of ionic conductivity of (100-x) PE + x polysorbate 80 polymer electrolyte membrane with x = 0 wt% (**a**), x = 30 wt% (**b**), and x = 50 wt% (**c**)

the slope is observed in each conductivity curve at about 338 K which is associated with melting of the polymer matrix leading to the crystalline to amorphous phase transition of the electrolyte. The conductivity curve has been divided into two regions, I and II, below and above the melting point, respectively. In the region I, where polymer electrolyte possesses semicrystalline phase, conductivity linearly increases with the temperature showing the Arrhenius behavior and suggesting the conductivity to be thermally activated. In the region II, where polymer electrolyte possesses amorphous phase as a result of melting, EO chains receive fast bond rotation and support higher segmental motion favoring fast ion motion through the polymer matrix and hence higher ionic conductivity. Conductivity in this region increases with slower rate as compared to the region I; this is because of the fact that the ion migration depends mainly on the segmental motion of the polymer chains assisted by the amorphous nature of the polymer matrix above the melting point. The linear region of the plot can be expressed by the following Arrhenius relation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{K_b T}\right) \qquad (3)$$

where σ_0 is the pre-exponential factor, K_b the Boltzmann constant, E_a is the activation energy, and T is the temperature in Kelvin. The activation energy for linear region I has been calculated for all the compositions of (100-x) PE + x polysorbate 80. The values have been found to be within the range of typical solid polymer electrolytes. Activation energy of the unplasticized polymer electrolyte membrane (x = 0 wt%) is found to be 0.64 eV, while that of the plasticized polymer electrolyte with compositions x = 30 and 50 wt% to be ~0.50 eV.

Figure 7 shows frequency (angular) dependence of ac conductivity of the membranes of (100-x) PE + x

polysorbate 80 polymer electrolyte for the compositions x = 0–50 wt% in the frequency range 10^2–10^6 Hz. The plasticized compositions (x = 10–50 wt%) show better ac conductivity than the unplasticized one (x = 0 wt%). The plots typically show a plateau in the high-frequency range followed by dispersion in low-frequency range for all the compositions of the electrolyte. The conductivity pattern follows the well-known Jonscher's universal power law [19], $\sigma(\omega) = \sigma_0 + A\omega^\eta$, where σ_0 is the dc conductivity, A is the pre-exponential factor, ω is the angular frequency, and η is the fractional exponent related to the ratio of backward hopping to the site relaxation time of the ions, which lies between 0 and 1 [20]. The solid lines in the plot represent non-linear least square fitting for the universal power law. The fitting parameters are shown in Table 1. In the lower frequency region, a difference in the experimental and the fitted curve is observed. This difference is due to electrode polarization. In this region, more charge carriers settle at the electrode–electrolyte interface which results into decrease in the number of free charge carriers in the bulk of the electrolyte resulting into drop in the conductivity. This difference is more prominent in the case of the unplasticized PE as compared to the plasticized PE. This may be due to better electrode–electrolyte interface in the case of plasticized PE. The plateau region of the plot provides dc conductivity (σ_0) of the polymer electrolyte membranes, which has been found to be increasing (Table 1) with the increasing concentration of polysorbate 80 from x = 0 to 50 wt%. The value of η is found to be less than 1 for all the compositions which shows slower backward hopping than the site relaxation of ions. This indicates dominance of translational motion of ions in the unplasticized as well as in the plasticized PE membranes [21, 22]. Also, the value
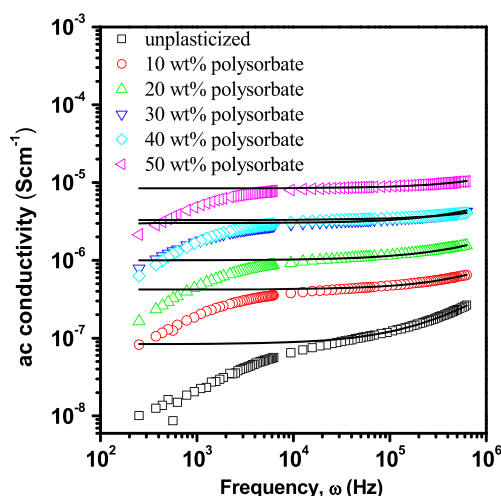
Table 1 Jonscher's power law fitting parameters for unplasticized and plasticized polymer electrolyte system [(100-x) PE + x polysorbate 80]

x (wt%)	σ_0 (S/cm)	A	η
0	8.4×10^{-8}	2.1×10^{-12}	0.85
10	4.2×10^{-7}	2.7×10^{-12}	0.85
20	1.0×10^{-6}	2.5×10^{-11}	0.75
30	3.0×10^{-6}	2.4×10^{-11}	0.81
40	3.3×10^{-6}	1.8×10^{-11}	0.80
50	8.4×10^{-6}	2.4×10^{-11}	0.80

of η is found to be lower for plasticized than unplasticized PE, which may be attributed to the higher order ion hopping or faster translational motion of ions through the extra hopping sites provided by polysorbate 80.

Electrochemical stability window (ESW) measurement and confirmation of protonic transport

The electrochemical stability window or the working voltage range of an electrolyte is an important parameter as it defines the stable voltage range in which the electrolyte is neither oxidized nor reduced. In order to study the effect of the plasticizer on the ESW of (100-x) PE + x polysorbate 80 polymer electrolyte, a comparative cyclic voltammograms of the unplasticized (x = 0 wt%) and the plasticized (x = 50 wt%) electrolyte membranes have been obtained (Fig. 8). The ESW has been observed to be in the range −2.3 to 2.3 V for the unplasticized and in the range −2.2 to 2.2 V for the plasticized polymer electrolyte membranes. This indicates that plasticization of PE with polysorbate 80 reduces its electrochemical stability.

In order to confirm protonic conduction in (100-x) PE + x polysorbate 80 polymer electrolyte membranes, cyclic voltammetry (CV) technique has been used. The
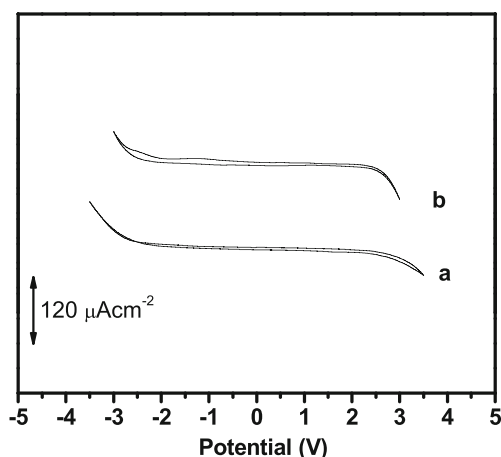

Fig. 7 Frequency dependence of ac conductivity of different compositions of (100-x) PE + x polysorbate 80 polymer electrolyte membranes. The *solid lines* represent the Jonscher's power law fitting for the experimental data

Fig. 8 Cyclic voltammogram of (100-x) PE + x polysorbate 80 polymer electrolyte membranes with compositions x = 0 wt% (**a**) and x = 50 wt% (**b**)
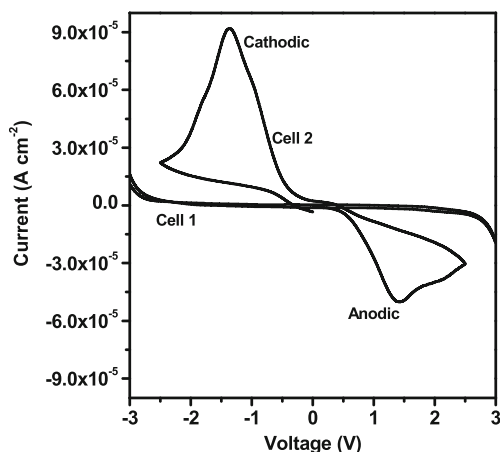
Fig. 9 Cyclic voltammogram for cell-1: SS|50 wt% PE + 50 wt% polysorbate 80|SS (**a**) and cell-2: Zn + ZnSO$_4$·7H$_2$O|50 wt% PE + 50 wt% polysorbate 80|Zn + ZnSO$_4$·7H$_2$O (**b**)

details of this technique have been reported elsewhere by us [23, 24]. The CV was carried out on the following two symmetric cells using the polymer electrolyte membrane with 50 wt% polysorbate 80:

Cell-1: SS|50 wt% PE + 50 wt% polysorbate 80|SS
Cell-2: Zn + ZnSO$_4$·7H$_2$O|50 wt% PE + 50 wt% polysorbate 80|Zn + ZnSO$_4$·7H$_2$O

In cell-1, SS is used as an ion-blocking electrode, while in cell-2, Zn + ZnSO$_4$·7H$_2$O is used as a reversible electrode which acts as H$^+$ source as per the reaction given below:

$$\eta Zn + ZnSO_4 \cdot 7H_2O \rightleftarrows Zn_{\eta+1}SO_4 \cdot (7-2\eta)H_2O \cdot 2\eta OH + 2\eta H^+ + 2\eta e^-$$
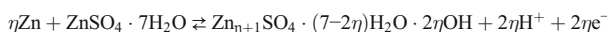
Figure 9 shows the comparative CV plots of cell-1 and cell-2 taken at scan rate of 10 mV/s. The voltammograms show two distinct cathodic and anodic current peaks for cell-2 separated by ∼2.5 V. The above shifting of the positions of the cathodic and anodic peak is the effect of two electrode geometry with no reference electrode. However, no such feature is observed for cell-1. The presence of the peaks in voltammogram of cell-2 suggests the occurrence of the cathodic deposition and anodic oxidation of protons at the electrode–electrolyte interface. This is indicative of protonic conduction in the prepared polymer electrolyte membranes.

Conclusion

The free standing membranes of (100-x) PE + x polysorbate 80 polymer electrolyte have been prepared by solution cast technique in the compositional range x = 0–50 wt%. The plasticization by polysorbate 80 results into significant decrease in the crystallinity of the polymer electrolyte membranes. The electrical conductivity of the polymer electrolyte increases continuously

with the concentration of the polysorbate 80. The maximum RT ionic conductivity is found to be ∼10^{-5} S/cm for the composition 50 wt% PE + 50 wt% polysorbate 80 of the electrolyte membrane, which is ∼2 orders higher than that of the unplasticized membrane. Polysorbate 80 is understood to provide extra free ether oxygen sites for the ion hopping in the electrolyte membranes. The ac conductivity of the electrolyte membranes follows Jonscher's universal power law. The ion transport occurs through translational motion in the electrolyte membranes. The electrolyte membranes are found to show protonic conduction.

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