

Study of dc conductivity and battery application of polyethylene oxide/polyaniline and its composites

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Abstract

The polymer electrolyte based on polyethylene oxide (PEO) complexed with conducting polyaniline (PANI) and salts of AgNO_3 and NaNO_3 has been prepared in different weight percentage ratios. The complexation is confirmed by infra-red and X-ray diffraction studies. Conductivity (dc) measurements are carried out using a two-probe technique in the temperature range 30–80 °C. Electrochemical cell parameters for battery application at room temperature are also been determined. The electric conductivities are $1.5 \times 10^{-5} \text{ S cm}^{-1}$ at 30 °C and $5.5 \times 10^{-2} \text{ S cm}^{-1}$ at 80 °C for a PEO:PANI (50:50) composite. The conductivity increases with increasing weight percentage of polyaniline in polyethylene oxide, which may be due to a strong hopping mechanism between the ether group of polyethylene oxide and conducting polyaniline. Samples are fabricated for battery application in configurations of Na:(PEO + PANI):(I₂ + C + sample) and their experimental data are measured using the Wagner polarization technique.

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1. Introduction

Polymer electrolytes based on polyethylene oxide (PEO)-salt complexes are of great interest due to their theoretical as well as practical importance for the development of solid-state batteries, fuel cell, smart windows, sensors, and electrochromic display devices [1–4]. The main advantage of polymer electrolytes are their favourable mechanical properties, ease of combination with salts or some polymers and an ability to form proper electrode–electrolyte contacts. The interest in these electrolytes arose following the studies of materials based on alkali metal salts complexed with polyethylene oxide that were conducted by Wright and co-workers [5,6] and Armand and co-workers [7,8] in the 1970s. Polyethylene oxide (PEO), in particular, is an exceptional polymer which dissolves with concentrations of a wide vari-

ety of salts to form polymeric electrolytes [9]. Complexes of PEO with LiBF_4 , LiPF_4 and $\text{Li}(\text{C}_6\text{H}_5)$ [10], LiSCN [11], LiSO_3CF_3 , and LiClO_4 [12], NaSCN [13], NaPF_6 [14], NaXF_4 and KYF_4 [15], and $\text{PEO} + \text{NH}_4 + \text{Al}_2\text{O}_3$ [16] have been examined. Recently, a new class of polyethylene oxide/polyaniline (PANI) composites have been reported by Sixou et al. [17], Norris et al. [18] and Wang et al. [19]. From technological point of view, these materials are very interesting because the combining of conducting PANI with insulating polymers is easy to perform [20]. In these materials, the threshold for the onset of the electrically conductivity can be reduced to very low volume fractions of PANI and the increase in conductivity above the threshold is very smooth. Therefore, conducting polyblends can be obtained with controlled levels of electrical conductivity, while retaining the mechanical properties of the polymer matrix [21–24].

In polyblends, PANI associated with an ionic matrix is of particular interest. First, the kinetics of the doping/undoping process for a massive electrode are strongly improved by

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the greater proximity of the required ions of the polyaniline chains, as compared with that case of a pure PANI electrode [25]. This property is very attractive for applications that use the electrochemical properties of an electrically conducting polymer (ECP), such as energy-storage devices.

This study explores the conductivity and the electrochemical parameters of (PEO + PANI), (PEO + PANI + AgNO₃) and (PEO + PANI + NaNO₃) composites. The samples are characterized by means of X-ray diffraction (XRD) and infra-red spectroscopy. The composition-dependent and temperature-dependent conductivities, as well as the electrochemical cell parameters, are reported.

2. Experimental

2.1. Synthesis of polyaniline

Ammonium peroxy sulfate (0.1 mol aqueous solution in protonic acid) is added drop-wise to a stirred solution of 0.1 mol aniline dissolved in 1 mol of aqueous solution of hydrochloric acid that was pre-cooled to 3–5 °C. The ammonium peroxy sulfate solution is added very slowly to prevent warming of the solution. After completion of the addition, stirring is continued for 2 h by using a mechanical stirrer to ensure completion of reaction. The time of initial colouration on mixing of the reactants depends on the temperature and the type of protonic acid. During the polymerization reaction, hydrochloric acid was used as a protonic acid and a temperature of 0–2 °C was maintained by using a freezing mixture. The sequence of colouration was:

light blue → blue green → coppery tinny
→ green precipitate

2.2. Preparation of polyethylene oxide/polyaniline composites

Pure PEO ($M_w = 5 \times 10^6$) white powder was procured from Shanghai Research Institute, Shanghai, China. To prepare mixtures of PEO and PANI with different weight ratio percentages of 60:40, 70:30, 80:20 and 90:10, powder was ground in a crucible to give homogeneous mixing. The powder was put in hydraulic press under a load 5 t to make a pellet. The pellets were kept in an oven at about 40–45 °C for 24 h to avoid moisture and porosity in the sample. The pellets so obtained have a thickness of 2 mm and a diameter of 10 mm.

2.3. Preparation of polyethylene oxide/polyaniline and its complexes

Composites of PEO + PANI + AgNO₃ with weight ratio percentages of 60:30:10, 60:20:20 and 60:10:30 were ground in a crucible for homogeneous mixing. Each powder was pressed at 5 t to produce a pellet. The pellets were kept in an oven at about to 40–45 °C 24 h to avoid moisture and

porosity in the sample. The pellets have a thickness of 2 mm and a diameter 10 mm.

A similar procedure was carried out for PEO + PANI + NaNO₃ composites with weight ratio percentages of 60:30:10, 60:20:20 and 60:10:30.

2.4. Characterization and measurement techniques

The characterization of polyethylene oxide, polyaniline and the composites was done at room temperature using X-ray powder diffractometry (XRD). The diffraction patterns were obtained over the 2θ range of 5°–75° at a scanning rate of 3° per minute infra-red spectra were also recorded.

dc electrical conductivity measurements were performed using the standard two-probe dc method [26] by measuring the current with a Keithly Electrometer (model 604). The measurements were conducted on pellets coated with silver paste on either side for good electrical contact. The sample was placed between two electrodes in the conductivity cell and measurements were carried out in the temperature range of 30–80 °C.

Using the polymer electrolyte samples, solid-state electrochemical cells were fabricated with the configuration of anode/polymer electrolyte/cathode. The anode materials were sodium and silver metals. For cathode, iodine (I₂) + carbon (C) + electrolyte was used in the form of a thin pellet. The open-circuit voltage (OCV), short-circuit current (SCC) and other cell parameters were evaluated from discharge curves at room temperature under a constant load of 10 kΩ.

3. Results and discussion

3.1. X-ray diffraction

The XRD pattern for pure polyethylene oxide is shown in Fig. 1 (curve (a)). Sharp peaks are observed at $2\theta = 19^\circ$ and

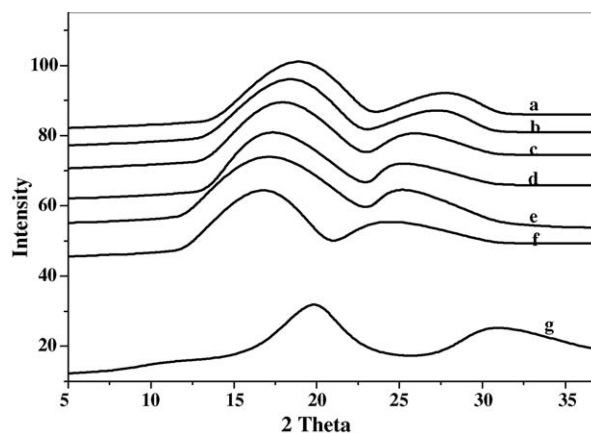


Fig. 1. X-ray diffraction pattern of (a) pure PEO, (b) PEO:PANI (50:50), (c) PEO:PAM (60:40), (d) PEO:PANI (70:30), (e) PEO:PANI (80:20), (f) PEO:PANI (90:10) and (g) pure PANI.

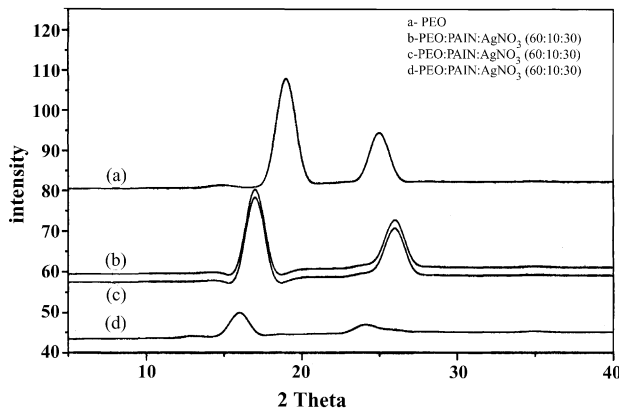


Fig. 2. X-ray diffraction pattern of PEO:PANI:AgNO₃ composites.

25°, which confirms the crystallinity of the pure polyethylene oxide. The XRD data of PEO:PANI of various composition are presented in Fig. 1 (curves (b) to (f)). As the composition PANI increases, there is a decrease in the intensity of the peaks, which indicates an increase in the amorphous nature of the composites.

The relative intensity of certain diffraction patterns peaks changes significantly with the weight percentage of polyaniline. When the composites are compared with pure polyethylene oxide at $2\theta = 19^\circ$ and 25° , the crystallinity is found to decrease with addition of the polyaniline due to H-bonding interaction between the amorphous PEO and the dopant of polyaniline [27]. This nature is a clear indication of the reduction in the crystalline phase in the polymer complex at room temperature. Also, the background noise increases, which indicates an increase in the amorphous phase in the polymer complex [17].

The diffraction pattern of the pure polyaniline is shown in Fig. 1 (curve (g)). No sharp peaks are observed and the pattern clearly indicates a completely amorphous nature. These results clearly demonstrate the dominant presence of an amorphous phase in the materials. Due to this amorphous nature, the mobility of ions in the material is high.

The diffraction pattern of complexed PEO + PANI + AgNO₃ (60:10:30, 60:20:20, 60:30:10) are presented in Fig. 2. Distinct peaks are observed at $2\theta = 15^\circ$ and 19.25° , which indicates the amorphous phase of the polymer. This represents a change in crystalline phase to amorphous phase due to H-bonding interaction between the amorphous PEO/PANI and its composites of AgNO₃.

The diffraction patterns of complexed PEO + PANI + NaNO₃ (60:10:30, 60:20:20, 60:30:10) are shown in Fig. 3. Maximum peaks are observed at $2\theta = 19.32^\circ$ and 23.55° for all the composites. The relative intensity of certain diffraction peaks changes significantly with addition of polyaniline and NaNO₃ in the composite. It is observed there is change from crystalline to amorphous phase due to H-bonding interaction between the amorphous PEO/PANI and its composites of NaNO₃.

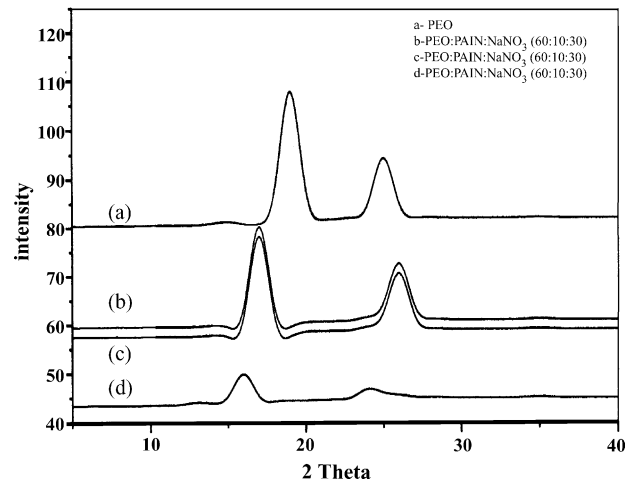


Fig. 3. X-ray diffraction pattern of PEO:PANI:NaNO₃ composites.

3.2. Infra-red spectra

The infra-red spectra of pure polyethylene oxide is shown in Fig. 4 (curve (a)). Spectral peaks at 2885.58, 2732.63, 2688.92, 1716.54, 1618.21, 1465.23, 1355.99, 1099.24, 926 and 824 cm^{-1} appear in the symmetrical and asymmetrical rocking of CH₂ and COC stretching regions. The C–O–C stretching bands occur at 1153.87 cm^{-1} , where the peak is so broad that any change in shift cannot be discerned. The peak at 1099.24 cm^{-1} is assigned to a combination of the symmetric and asymmetric stretching modes of C–O–C.

The infra-red spectra for PEO:PANI (90:10, 80:20, 70:30, 60:40, 50:50) composites are also shown in Fig. 4 (curves (b)–(f)). There are significant changes in both the intensities and the frequencies in the various PEO:PANI composites. These are more pronounced between 842 and 1600 cm^{-1} . The bands also show doublets and triplets. This may indicate that there is significant interaction between the oxygen of the ether groups of polyethylene oxide and the nitrogen in the aniline

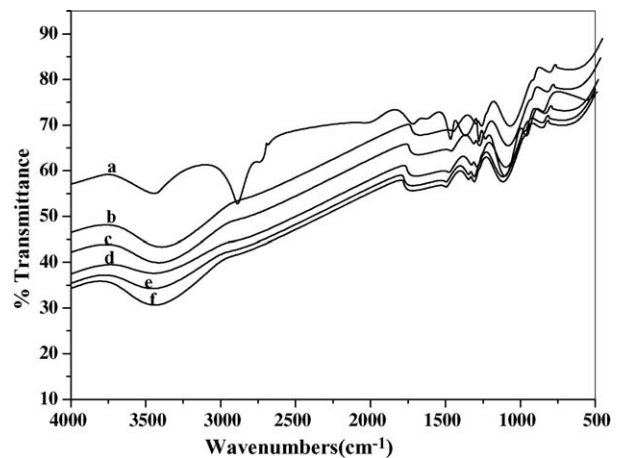


Fig. 4. Infra-red spectra of (a) pure PEO, (b) PEO:PANI (90:10), (c) PEO:PANI (80:20), (d) PEO:PANI (70:30), (e) PEO:PANI (60:40) and (f) PEO:PANI (50:50) composites.

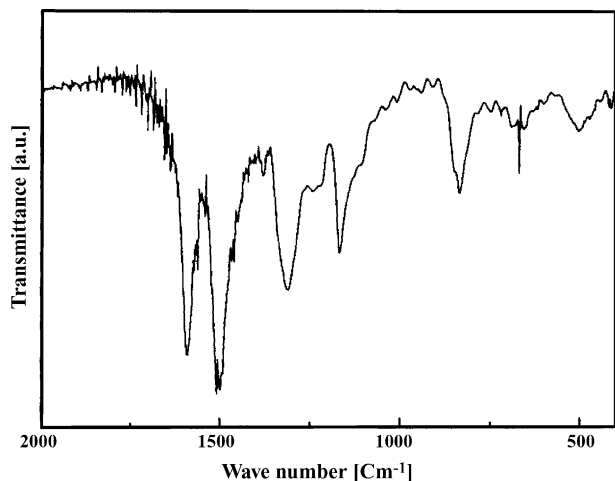


Fig. 5. Infra-red spectra of pure polyaniline.

of polyaniline. These may also be some hydrogen bonding, which is probable in polyethylene oxide/polyaniline composites. Also, the intensity of the band at 2885 cm^{-1} , which is due to methyl (CH_2) group stretching, is very significantly reduced in PEO:PANI composites with a doublet. This may be taken as further evidence of the interaction between the ether group of polyethylene oxide and the aniline group of polyaniline.

The infra-red spectra of pure polyaniline are shown in Fig. 5. The principle characteristic peaks of quinoid-benzenoid N moieties for C–N stretching, C–H aromatic in-plane and out-plane bending vibration of polyaniline are reported to occur at about 1600 , 1500 , 1350 , 1130 and 820 cm^{-1} [28].

The infra-red spectra for PEO:PANI:AgNO₃ (60:30:10, 60:20:20, 60:10:30) composites are given in Fig. 6. The intensity of the band around 2900 cm^{-1} is significantly reduced with a doublet. This band is assigned to CH_2 stretching in the polyethylene oxide. Rest of the absorptions between 820 and 1600 cm^{-1} are due to C–N stretching, C–H aromatic in-plane and out-plane vibration of polyaniline, CH_2 asymmetrical and symmetrical vibrations, along with C–O–C stretching regions, in the polyethylene oxide. These show significant shifts along with significant changes in intensity. This indicates further enhancement of the ionic character in the composites.

The broadness in the bands of C–N stretching and CH_2 aromatic of polyaniline as well as C–O–C of polyethylene oxide may probably indicate complexation with the Ag. As Ag is a large ion there is a probability of $d\pi$ – $p\pi$ bonding with the composite, which would enhance the ionic character of the composite.

The infra-red spectra for PEO:PANI:NaNO₃ (60:10:30, 60:20:20) composites are shown in Fig. 7. In these spectra, similar changes are observed with the appearance of a new absorption, which is broad at 1612 cm^{-1} , and another absorption at 2366 cm^{-1} . The appearance of the 1612 cm^{-1} band corresponds to C–N stretching, C–H aromatic in-plane

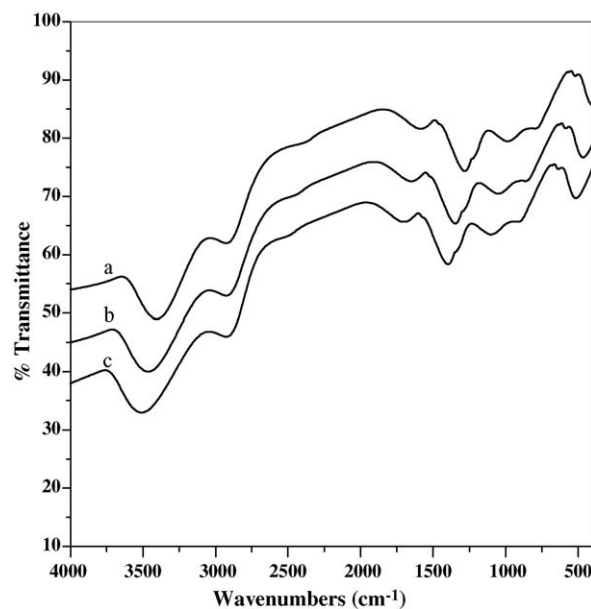


Fig. 6. Infra-red spectra of (a) PEO:PANI:AgNO₃ (60:30:10), (b) PEO:PANI:AgNO₃ (60:20:20) and PEO:PANI:AgNO₃ (60:10:30) composites.

and out-plane of polyaniline, that is broadened and may be attributed as a shift of the 1559 cm^{-1} absorption in pure polyaniline. This shift towards the higher frequency side is a clear indication of the enhancement of the ionic character of PEO:PANI:NaNO₃ composites.

3.3. dc Conductivity

The dc conductivity (σ_{dc}) versus $10^3/T$ plot for pure polyethylene oxide in the temperature range 30 – 80°C , is shown in Fig. 8. This plot indicates an increase in conductivity with temperature that may be due to a hopping mechanism between coordinating sides, local structural relaxations and segmental motions of the polymer. This plot follows Arrhenius behaviour, with two regions (I&II) with activation ener-

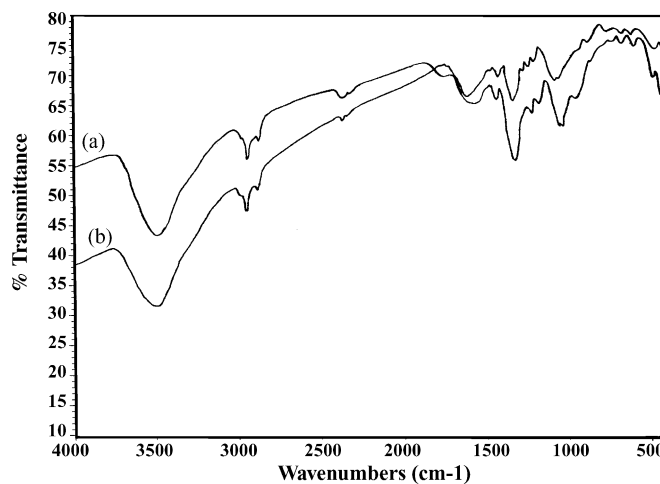


Fig. 7. Infra-red spectra for PEO:PANI:NaNO₃ (60:10:30) and PEO:PANI:NaNO₃ (60:20:20) composites.

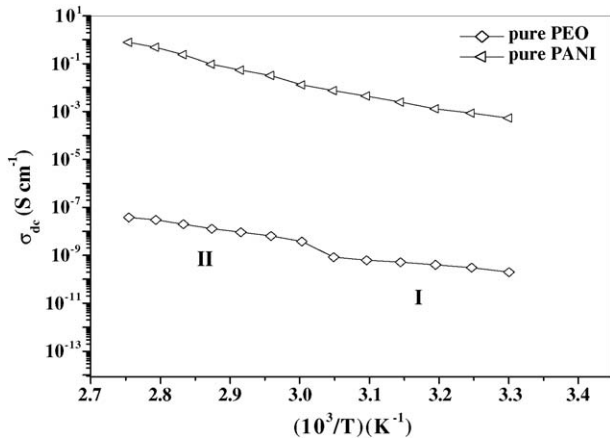


Fig. 8. Temperature dependence of dc conductivity of pure polyethylene oxide and polyaniline.

gies above and below the melting region, (60–65 °C) of the polymer. In region I, the conductivity increases slowly, while in region II it increases at a higher rate. The latter may be due to a change in phase from a semi-crystalline to an amorphous state at the melting point. Further, the amorphous region progressively increases in region II as a result of which polymer chain acquires faster internal modes for which bond rotations produce segmental motion. This favours hopping of ions within and between chains and therefore the conductivity becomes high [29]. Similar results have also been reported for electrolytes based on polyethylene oxide [30,31]. The conductivity values at room temperature for this class of polymer are given in Table 1.

A plot of σ_{dc} versus $10^3/T$ for pure polyaniline in the temperature range 30–80 °C is presented in Fig. 8. The conductivity is 5.3×10^{-4} and 0.77 S cm^{-1} at 80 °C. The increase conductivity with increasing temperature indicates a complete amorphous phase and is similar to that observed in lightly doped polypyrrole films. It was proposed that a variable range hopping conduction model can be applied for such case wherein the conductivity consists of two components,

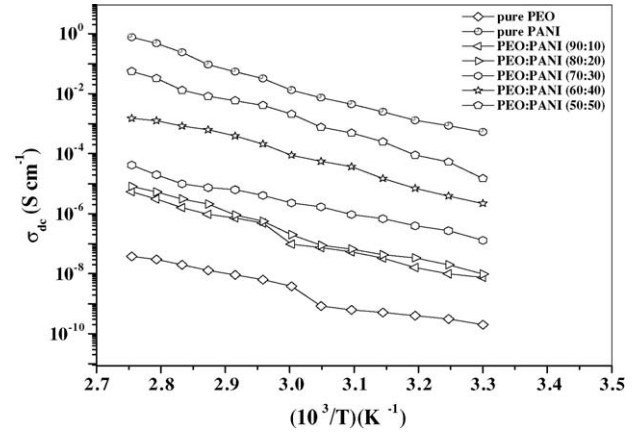


Fig. 9. Temperature dependence of dc conductivity for PEO:PANI composites.

namely, σ_B and σ_H .

$$\sigma = \sigma_B + \sigma_H \quad (1)$$

where σ_B and σ_H are the inter-chain and intra-chain conductivities, respectively. The conductivity values at room temperature for this class of composites are shown in Table 1.

The linear variation of the conductivity versus temperature plots of all the composites suggests an Arrhenius-type, thermally activated process. The calculated activation energies (E_a) for these are shown in Table 1.

The conductivity may be expressed as

$$\sigma = \sigma_0 \exp(-E_a/KT) \quad (2)$$

where σ_0 is the pre-exponential factor and E_a is the activation energy.

Plots of σ_{dc} versus $10^3/T$ for PEO + PANI (90:10, 80:20, 70:30, 60:40, 50:50) composites in the temperature range 30–80 °C. It is observed that the conductivity increases with temperature, as well as with the weight ratio of polyaniline (Fig. 9). This could be due to the fact that the conductivity domain increases in number and size with increase in the weight ratio of polyaniline. This may facilitate the ease of ori-

Table 1
Calculated data for polyethylene oxide/polyaniline and its composites

Polymer electrolyte	Conductivity (S cm^{-1}) at 30 °C	Activation energy (eV)	Initial current (μA)	Final current (μA)	t_{ion}	t_{ele}
Pure PEO	10^{-10}	0.37	–	–	–	–
Pure PANI	5.3×10^{-4}	–	–	–	–	–
PEO:PANI (90:10)	7.5×10^{-10}	0.44	208	2	0.99	0.009
PEO:PANI (80:20)	9.8×10^{-9}	0.45	333	114	0.65	0.342
PEO:PANI (70:30)	1.3×10^{-7}	0.34	481	268	0.44	0.557
PEO:PANI (60:40)	2.2×10^{-6}	0.41	648	446	0.31	0.688
PEO:PANI (50:50)	1.5×10^{-5}	0.51	912	728	0.20	0.798
PEO:PANI:AgNO ₃ (60:30:10)	4.3×10^{-5}	0.47	265	78	0.70	0.294
PEO:PANI:AgNO ₃ (60:20:20)	7.1×10^{-6}	0.46	234	38	0.83	0.162
PEO:PANI:AgNO ₃ (60:10:30)	3.3×10^{-7}	0.35	215	15	0.93	0.069
PEO:PANI:NaNO ₃ (60:30:10)	8.1×10^{-6}	0.42	240.88	40.88	0.83	0.169
PEO:PANI:NaNO ₃ (60:20:20)	9.9×10^{-7}	0.43	225.72	25.72	0.88	0.113
PEO:PANI:NaNO ₃ (60:0:30)	1.7×10^{-9}	0.37	214.13	14.13	0.93	0.065

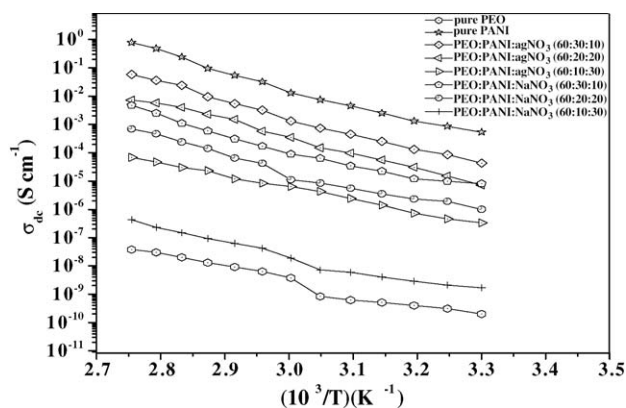


Fig. 10. Temperature dependence of dc conductivity for PEO:PANI:X (AgNO_3 , NaNO_3) composites.

entation of domains, which in turn produces paths through which ions move and leads to high conductivity. The conductivity values at room temperature and 80°C for this class of composites are shown in Table 1.

The dc conductivity measurements as a function of temperature for the composites PEO + PANI + AgNO_3 and PEO + PANI + NaNO_3 are shown in Fig. 10. The conductivity of PEO + PANI + AgNO_3 (60:30:10) at 80°C is 0.058 S cm^{-1} , and for PEO + PANI + NaNO_3 (60:30:10) is 0.0047 S cm^{-1} . This implies that the addition of AgNO_3 to the PEO + PANI composite is advantageous over that of adding NaNO_3 . This is also found to be true at room temperature. As the concentration of AgNO_3 is increased further, however, the conductivity of PEO + PANI + AgNO_3 decreases. In the composite PEO + PANI + NaNO_3 also, the conductivity is observed to decrease with increase in the concentration of NaNO_3 . In both the composites, the simultaneous decrease in conductivity with increase in concentrations of AgNO_3 or NaNO_3 (as the case may be) is perhaps due to a decrease in the concentration of polyaniline. The calculated activation energies (E_C) for these composites PEO + PANI + AgNO_3 and PEO + PANI + NaNO_3 are given in Table 1.

3.4. Electrochemical cell parameters

Electrochemical cells have been fabricated based on PEO:PANI and PEO:PANI:X ($X = \text{AgNO}_3$, NaNO_3) polymer electrolytes and their discharge curves determined under a constant load. There is an initial rapid decrease in polarization current as a function of time (Figs. 11 and 12) that may be due to the formation of a thin layer of sodium salt at the electrode|electrode interface. This suggests that the charge transport in PEO:PANI composite is predominantly ionic. This indicates that the PEO:PANI composites have an electrochemical stability and are thus suitable for application in solid-state batteries. As the PANI content increases in PEO, there is an increase in the polarization current and in the voltage stability. With addition of AgNO_3 and NaNO_3

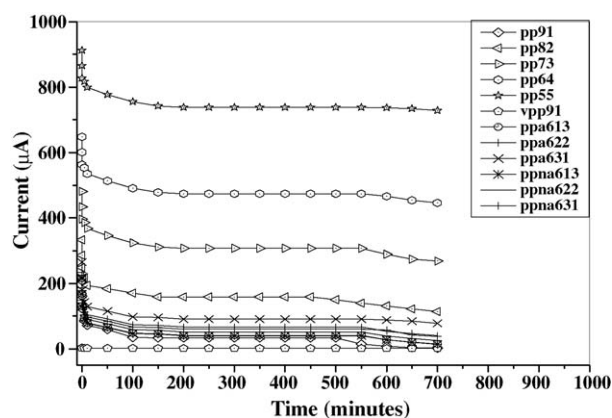


Fig. 11. Current vs. time for PEO:PANI composites.

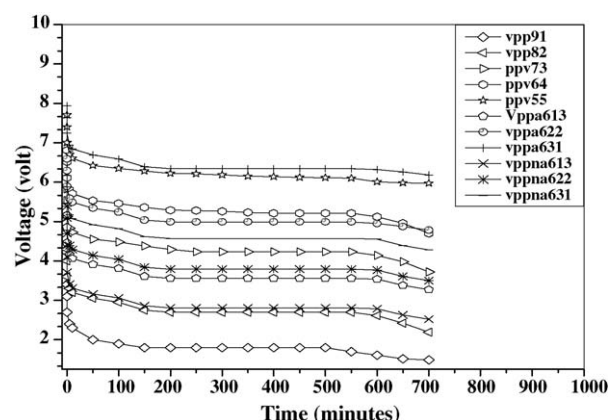


Fig. 12. Voltage vs. time for PEO:PANI:X ($X = \text{AgNO}_3$, NaNO_3) composites.

content, however, there is no considerable effects in the stability. The cell parameters results in an open-circuit voltage (OCV) of 6.13 V and a short-circuit current (SCC) of $912\text{ }\mu\text{A}$ for PEO:PANI (50:50) composite. The parameters obtained for other cells are listed in Table 1. These data demonstrate the potential application of these electrolytes in solid-state batteries. This may be confirmed by characterization and conductivity studies. The transference numbers calculated for the polymer electrolytes are also included in Table 1.

The above results suggest that the charge transport in these composites is predominantly due to ions. Sreepathi et al. [17] have reported the cell parameters for PEO + NaYF_4 and PEO + KYF_4 polymer electrolytes, Srekanth et al. [27] for PEO + NaNO_3 , Sun et al. [31] for PEO + 1.4 BaTiO_3 , and Kim et al. for PEO with ethylene carbonate and poly(ethyl glycol dimethyl ether). The findings from the present study of PEO/PANI composites agree well with those of earlier work.

4. Conclusions

The electric conductivity and electrochemical cell parameters are obtained for PEO:PANI and PEO:PANI:X

($X = \text{AgNO}_3, \text{NaNO}_3$) composites with different weight ratios. The complexation is confirmed by XRD and infra-red spectra studies. The phase change is observed in the X-ray diffraction pattern with increase of PANI in PEO. From infra-red spectra, it is seen that there are significant changes in the intensities as well as the frequencies in the various PEO:PANI and PEO:PANI:X ($X = \text{AgNO}_3, \text{NaNO}_3$) composites. The temperature dependence of the conductivity increases with increase in the PANI content in PEO due to a strong hopping mechanism between conducting PANI and PEO. The open-circuit voltage (OCV) is 6.13 V and short-circuit current (SCC) is 912 μA for a cell with a PEO:PANI (50:50) composite. Thus, PEO:PANI and PEO:PAM:X ($X = \text{AgNO}_3, \text{NaNO}_3$) composites are possible candidates for solid-state batteries.

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