

Ion-conducting polymer electrolyte based on poly (ethylene oxide) complexed with NaNO_3 salt-application as an electrochemical cell

T. Sreekanth, M. Jaipal Reddy, S. Ramalingaiah, U.V. Subba Rao *

Department of Physics, Osmania University, Hyderabad, 500007, India

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Abstract

Solid polymer electrolyte films based on poly (ethylene oxide) (PEO) complexed with sodium nitrate (NaNO_3) have been prepared by a solution-cast technique. The complexation of NaNO_3 salt with PEO has been confirmed by X-ray diffraction, infrared (IR) and optical microscopic studies. Measurements of the dc conductivity in the temperature range 303 to 373 K and the transference numbers have been carried out to investigate the charge transport in this polymer electrolyte system. Transport number data show that the charge transport in this polymer electrolyte system is predominantly due to ions. Using the polymer electrolyte, solid-state electrochemical cells have been fabricated. The various cell parameters are evaluated and reported. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Poly (ethylene oxide); Polymer electrolyte; Ionic conductivity; Transport numbers; Discharge characteristics; Solid-state cell

1. Introduction

Polymer electrolytes have been a subject of great interest in recent years due to theoretical interest as well as practical importance for the development of solid-state batteries and fuel cells, as well as sensors and electrochromic display devices [1–4]. The main advantages of polymeric electrolytes are favourable mechanical properties, ease of fabrication of thin films of desirable sizes, and an ability to form effective electrode–electrolyte contacts. Poly (ethylene oxide) (PEO), in particular, is an exceptional polymer; it dissolves high concentrations of a wide variety of salts to form polymeric electrolytes [5]. The complexes of PEO with a number of alkali salts such as LiBF_4 , LiPF_6 and $\text{Li}(\text{C}_6\text{H}_5)$ [6], LiSCN [7], LiSO_3CF_3 and LiClO_4 [8], NaSCN [9], NaPF_6 [10], NaYF_4 and KYF_4 [11] have been reported. Sodium-ion conducting polymer electrolytes have been investigated [12–14] based on PEO, poly (propylene oxide) (PPO) or polybismethoxy ethoxy phosphazene (MEEP) complexed with NaI , NaClO_4 , NaSCN or NaCF_3SO_3 . Some silver-ion conducting polymer complexes with PEO have also been examined [15–

17]. Other studies have been conducted [18–21] on PEO-based electrolytes using divalent cationic salts as dopants. The effect of the addition of $\beta\text{-Al}_2\text{O}_3$ has been investigated in $\text{PEO} + \text{LiClO}_4$ [22] and $\text{PEO} + \text{NaSCN}$ [23] systems. Amita Chandra et al. [24] studied a composite polymer electrolyte ($\text{PEO} + \text{NH}_4\text{I} + \text{Al}_2\text{O}_3$) which showed improved film stability.

The present work is concerned with solid-state electrochemical cells which are based on ($\text{PEO} + \text{NaNO}_3$) electrolyte films. Several experimental techniques such as X-ray diffraction, infrared (IR), optical microscopy, composition-dependent conductivity, temperature-dependent conductivity and transference number measurements are employed to characterize this polymer electrolyte system. Various cell parameters are reported.

2. Experimental

Films (thickness about 100 to 150 μm) of pure PEO (Aldrich, molecular weight = 6×10^5) and various compositions of complexed films of PEO with NaNO_3 salt were prepared with weight ratios of (90:10), (80:10) and (70:30) by a solution-cast technique using methanol (water-free) as solvent. The solutions were stirred for 10 to 12 h, cast on to polypropylene dishes and then evaporated slowly at room temperature. The final products were vacuum-dried

* Corresponding author. Tel.: +91-7018951 ext. 242; Fax: +91-040-701-9020

thoroughly at 10^{-3} Torr. The X-ray diffraction studies of these films were performed by means of a SEIFERT X-ray diffractometer in the range 5 to 50° . IR spectra of these films were obtained with a Perkin Elmer FTIR spectrophotometer [Model 1605] in the range 450 to 4500 cm^{-1} .

The dc conductivity was measured by means of an in-house conductivity set-up [11] in the temperature range 303 to 373 K . Ionic and electronic transport numbers (t_{ion} , t_{ele}) were evaluated using Wagner's polarization technique [25]. In this technique, freshly prepared films of (PEO + NaNO_3) were polarized in the configuration Ag/polymer electrolyte/C under a dc bias (step potential of 1.5 V). The resulting current was monitored, as a function of time, on a Keithly electrometer [Model 614].

Solid-state electrochemical cells were fabricated in the configuration $\text{Na}/(\text{PEO} + \text{NaNO}_3)/(\text{I}_2 + \text{C} + \text{electrolyte})$. Full details of the method of cell fabrication have been reported elsewhere [26]. The discharge characteristics of the cells were monitored under a constant load of $100\text{ k}\Omega$.

3. Results and discussion

The complexation of pure PEO with various salts has been studied extensively by means of X-ray diffraction, optical microscopy and vibrational spectroscopy [16,27–33]. X-ray diffraction (XRD) patterns for pure PEO, NaNO_3 salt and PEO complexed with NaNO_3 salt are given in Fig. 1. Comparison of the XRD patterns of complexed PEO films with those of pure PEO and NaNO_3 reveals the following differences.

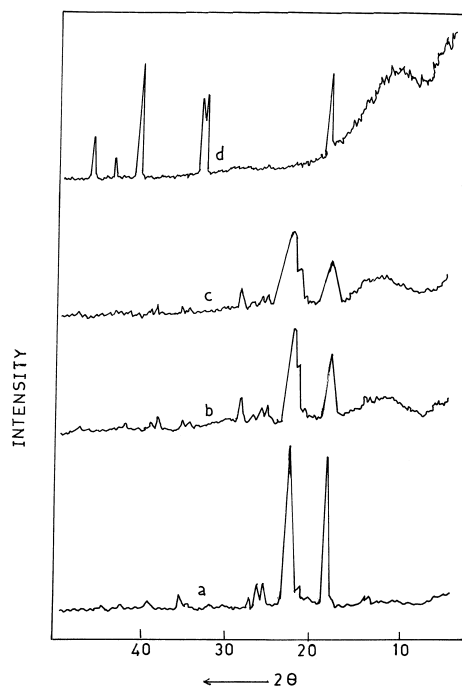


Fig. 1. XRD patterns of: (a) pure PEO; (b) (PEO + NaNO_3) (80:20); (c) (PEO + NaNO_3) (70:30); (d) NaNO_3 .

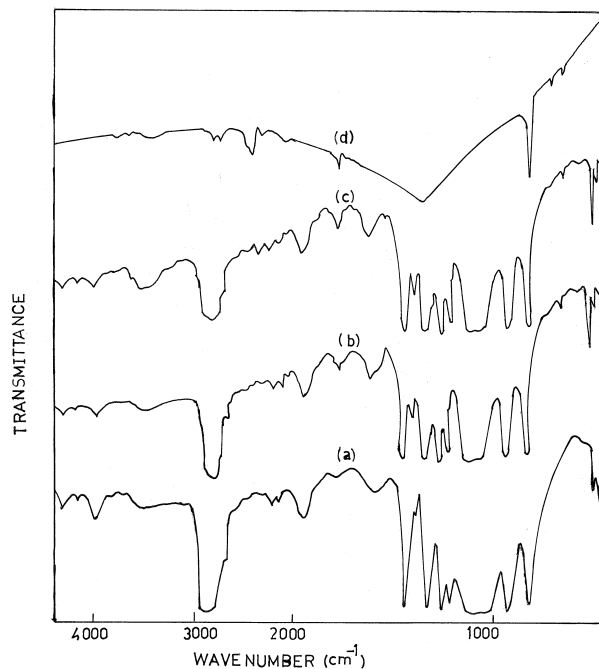


Fig. 2. IR spectra of: (a) pure PEO; (b) (PEO + NaNO_3) (80:20); (c) (PEO + NaNO_3) (70:30); (d) NaNO_3 .

(i) The diffraction peaks observed between $2\theta = 10^\circ$ and 30° are less intense in complexed PEO films compared with those in pure PEO films. This indicates that the addition of NaNO_3 salt causes a decrease in the degree of crystallinity of the polymer PEO.

(ii) Peaks corresponding to the polymer PEO are also present in the complexed PEO films. This shows the simultaneous presence of both crystalline complexed and uncomplexed PEO.

(iii) No peaks corresponding to NaNO_3 are observed in complexed PEO. This indicates the absence of excess salt (uncomplexed) in the complexed polymer films.

(iv) The peaks exhibit a decrease in intensity with broadening at higher concentrations of NaNO_3 salt in the polymer. This indicates a decrease in the crystalline phase and the dominant presence of the amorphous phase.

The IR spectra of pure PEO, NaNO_3 and PEO complexed with NaNO_3 are shown in Fig. 2. The following differences in the spectral features are observed on comparing the spectra of complexed PEO with those of pure PEO and NaNO_3 .

(i) The intensity of the aliphatic C–H stretching vibrational band observed around 2900 cm^{-1} in PEO decreases with increasing concentration of NaNO_3 salt in the polymer.

(ii) The width of the C–O stretching band observed around 1100 cm^{-1} in PEO also decreases with increase of NaNO_3 in the polymer.

(iii) New peaks around 2366.9 , 1788.2 and 1412.2 cm^{-1} are present in the IR pattern for complexed PEO.

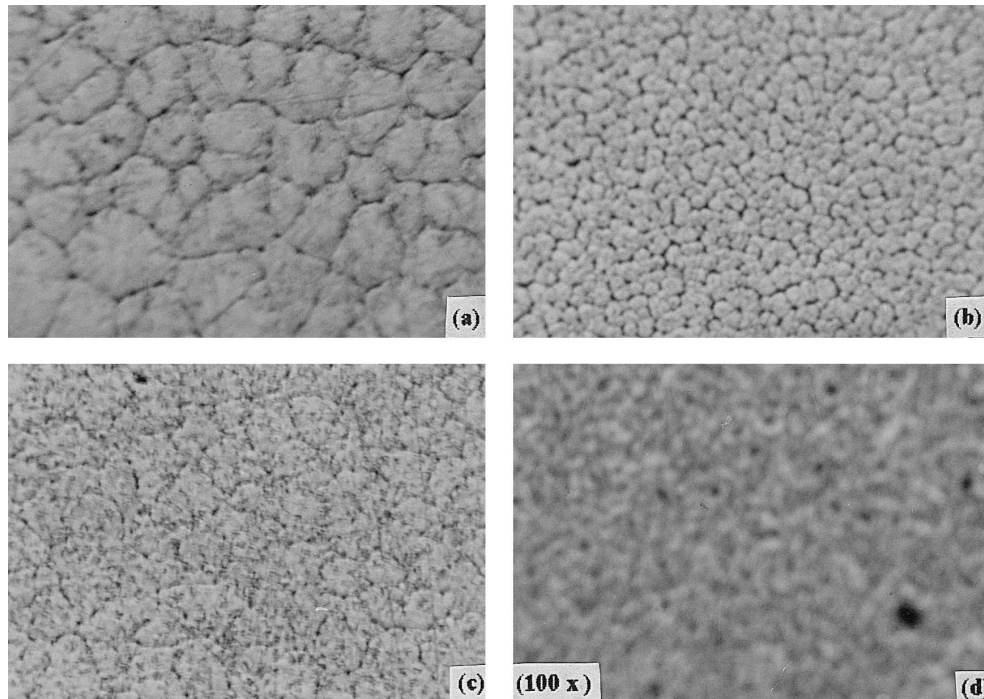


Fig. 3. Optical micrographs ($\times 100$) of: (a) pure PEO; (b) (PEO + NaNO_3) (90:10); (c) (PEO + NaNO_3) (80:20); (d) (PEO + NaNO_3) (70:30).

The appearance of new peaks along with changes in existing peaks (and/or their disappearance) in the IR spectra directly indicate the complexation of PEO with NaNO_3 . If the cations of NaNO_3 become coordinated with the ether oxygen of PEO, the spectral changes are expected to be in the COC stretching and deformation ranges. The decrease in the width of the 1100 cm^{-1} band, which is assigned to COC symmetrical and asymmetrical stretching

[27,28,32], suggests the coordination/complexation of the salt with PEO.

Optical micrographs of different compositions of (PEO + NaNO_3) are shown in Fig. 3. Large spherulites of different size are observed in samples with a low concentration of the salt in the polymer PEO. Some amorphous

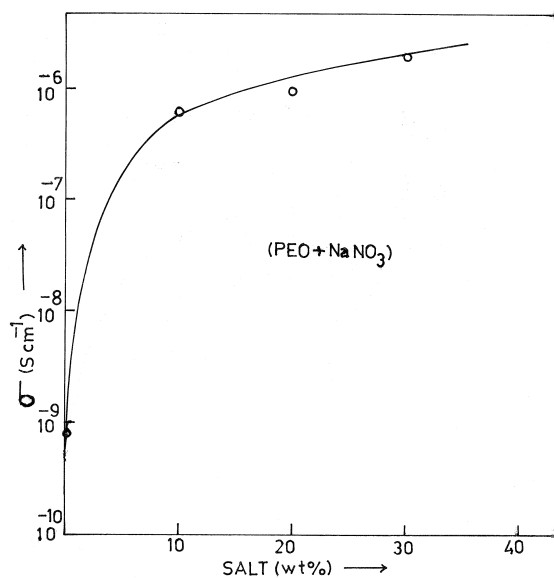


Fig. 4. Composition-dependent conductivity of (PEO + NaNO_3) polymer electrolyte system at room temperature.

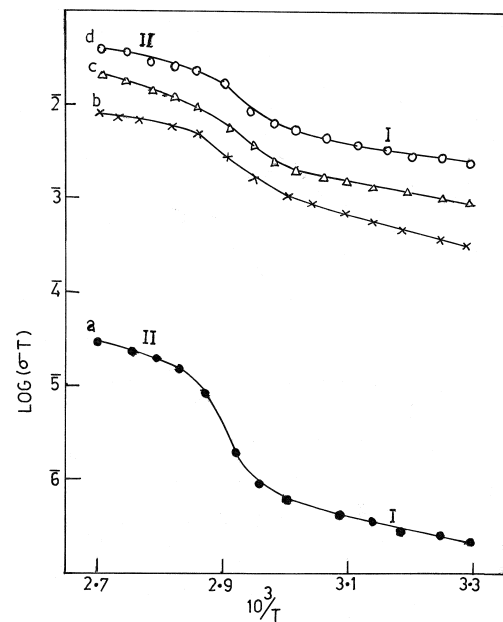


Fig. 5. Temperature-dependent conductivity of: (a) pure PEO; (b) (PEO + NaNO_3) (90:10); (c) (PEO + NaNO_3) (80:20); (d) (PEO + NaNO_3) (70:30).

Table 1
Conductivity and transport number data of (PEO + NaNO₃) electrolyte

Polymer electrolyte (wt.%)	Conductivity at RT (303 K) S cm ⁻¹	Activation energies		Transport numbers	
		Region-I (eV)	Region-II (eV)	<i>t</i> _{ion}	<i>t</i> _{ele}
PEO	8.35×10^{-10}	0.32	0.35	–	–
(PEO + NaNO ₃)(90:10)	7.89×10^{-7}	0.36	0.28	0.90	0.10
(PEO + NaNO ₃)(80:20)	9.75×10^{-7}	0.25	0.31	0.92	0.08
(PEO + NaNO ₃)(70:30)	2.83×10^{-6}	0.18	0.25	0.94	0.06

regions are also present between the spherulites. These amorphous regions are also increasing and consequently the spherulitic regions become smaller with increasing concentration of NaNO₃ in PEO. This suggests the simultaneous presence of both crystalline uncomplexed and complexed PEO. For a higher composition of NaNO₃ salt with the polymer (70:30), the spherulites disappear. This clearly demonstrates a rapid decrease in the degree of crystallinity of the polymer with the addition of salt.

Thus, the XRD, IR and optical micrographic data for the films confirm the complexation between the NaNO₃ salt and the PEO polymer

The variation of dc conductivity, σ , as a function of the concentration of NaNO₃ salt in PEO at room temperature (RT) is given in Fig. 4 and Table 1. The data reveal that, the conductivity of pure PEO is $\sim 10^{-10}$ S cm⁻¹ at RT and its value increases sharply to $\sim 10^{-7}$ S cm⁻¹ with 10 wt.% NaNO₃ salt. The increase in conductivity becomes slower on further addition of salt to the polymer.

In general, it is believed that the conductivity increases as the degree of crystallinity decreases or, in other words, as the flexibility of the polymeric backbone increases. The observed continuous increase in conductivity of the (PEO + NaNO₃) system with increasing salt concentration is attributed to a decrease in the degree of crystallinity, as confirmed by XRD and optical micrographic analysis.

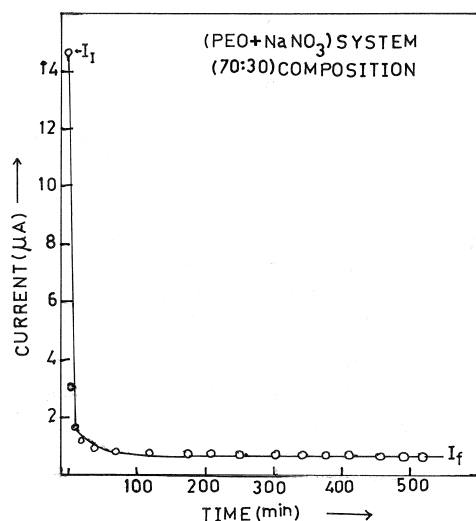


Fig. 6. Polarization current vs. time plot of (PEO + NaNO₃) (70:30) electrolyte film.

In Fig. 5, the variation in conductivity is presented as a function of temperature for different compositions of (PEO + NaNO₃) polymer electrolyte system along with pure PEO in the temperature range 303 to 373 K. From the following features are observed.

(i) The conductivity is found to increase with temperature in pure PEO and also in all the compositions of the (PEO + NaNO₃) polymer electrolyte system.

(ii) The conductivity vs. temperature plots follow Arrhenius behaviour throughout, but with two regions (region I and region II) with two activation energies above and below melting point (T_m) of the polymer. In region I (i.e., below T_m), the conductivity slowly increases with temperature up to 66°C. At 66°C, there is a sudden increase in conductivity. In the region II (i.e., above T_m), the conductivity again increases with temperature. Similar behaviour has been observed for all compositions of the (PEO + NaNO₃) polymer electrolyte system.

At the melting point of the polymer, there is a change from a semicrystalline to an amorphous phase. Due to this phase change, the conductivity shows a sudden increase at the melting point. The increase in conductivity with temperature is interpreted as a hopping mechanism between coordinating sites, local structural relaxations and segmental motions of polymer. As the amorphous region progressively increases (region II), however, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This, in turn, favours hopping inter-chain and intra-chain ion movements and the conductivity of the polymer electrolyte thus becomes high. The existence of two regions in the conductivity vs. tempera-

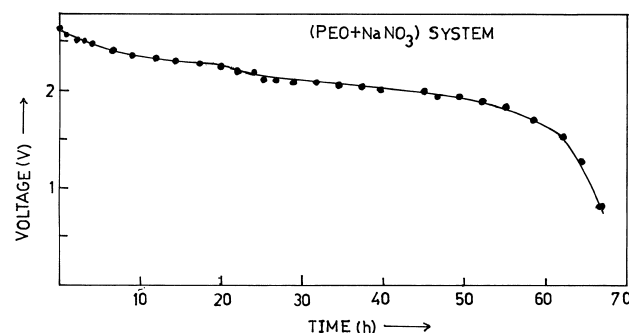


Fig. 7. Discharge characteristic plot of (PEO + NaNO₃) electrochemical cell.

Table 2
Cell parameters of (PEO + NaNO₃) solid polymer electrochemical cell

Cell parameters	Na/(PEO + NaNO ₃)(70:30)/ (I ₂ + C + electrolyte)
OCV	2.61 V
SCC	1350 μA
Effective area of the cell	1.34 cm ²
Cell weight	0.91 g
Load	100 kΩ
Time for plateau region	62 h
Specific power	48.5 mW kg ⁻¹
Specific energy	3007 mW h kg ⁻¹

ture plots has been observed in a number of PEO based polymer electrolytes [11,29,31,33].

The linear variation of the conductivity vs. a temperature plots below and above T_m suggests an Arrhenius-type, thermally activated process. The conductivity can be expressed as:

$$(\sigma T) = (\sigma T)_0 \exp(-E_a/kT) \quad (1)$$

where: $(\sigma T)_0$ is a pre-exponential factor; E_a is the activation energy; k is the Boltzmann constant. The calculated activation energies (E_a) for pure PEO and the (PEO + NaNO₃) polymer electrolyte system are given in Table 1.

The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) transfer were evaluated for the (PEO + NaNO₃) electrolyte system using Wagner's polarization method. In this technique, the dc current is monitored as function of time on application of a fixed dc voltage across the Ag/electrolyte/C cell. After polarization of the cell with 1.5 V dc, the current versus time plot is obtained, which is shown in Fig. 6 for the (PEO + NaNO₃) (70:30) electrolyte. The transference numbers (t_{ion} and t_{ele}) were calculated from the polarization current versus time plot using the equations:

$$t_{ion} = (I_1 - I_f)/I_1 \quad (2)$$

$$t_{ele} = I_f/I_1 \quad (3)$$

where I_1 is the initial current and I_f is the final residual current. The calculated transference number data are given in Table 1. For all compositions of the (PEO + NaNO₃) electrolyte system, the values of ionic transference numbers t_{ion} are in the range 0.90 to 0.94. This suggests that

the charge transport in these polymer electrolyte films is predominantly due to ions, only a negligible contribution comes from the electrons.

Using (PEO + NaNO₃) polymer electrolyte films, solid-state electrochemical cells were fabricated in the configuration Na/(PEO + NaNO₃)/(I₂ + C + electrolyte).

The discharge characteristics of the cell Na/(PEO + NaNO₃)/(I₂ + C + electrolyte) at ambient temperature for a constant load of 100 kΩ are given in Fig. 7. The initial sharp decrease in voltage may be due to polarization and/or the formation of a thin layer of sodium salt at the electrode–electrolyte interface. The open-circuit voltage (OCV), short-circuit current (SCC) and other cell parameters are listed in Table 2.

The values of cell parameters reported elsewhere [10,11,17,33] for other cells along with the data for the present polymer electrolyte cells are composed in Table 3. It is clear that the cell parameters of the present electrolyte system are comparable with those disclosed for other PEO-based cells. This supports the practical application of the present electrolytes in solid-state batteries.

4. Conclusions

The ionic transport number data in the (PEO + NaNO₃) polymeric electrolyte films indicate that the conduction is predominantly due to ions. Using those films, electrochemical cells have been fabricated for which OCV and SCC are 2.61 V and 1.35 mA, respectively. The cell parameters are comparable with those reported by earlier workers for various other cells. Thus, (PEO + NaNO₃) electrolytes are possible candidates for solid-state batteries.

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Table 3
Comparison of present cell parameters with those of other cells reported elsewhere

Solid-state electrochemical cell configuration	OCV (V)	SCC (μA)	Plateau region time (h)	Reference
Ag/(PEO + AgNO ₃)/I ₂ + C + electrolyte	0.61	4.4	48	[17]
Na/(PEO + NaYF ₄)/I ₂ + C + electrolyte	2.45	560	96	[11]
K/(PEO + KYF ₄)/I ₂ + C + electrolyte	2.4	240	51	[11]
Na–Hg/(PEO + NaPF ₆)/V ₂ O ₅ + C + electrolyte	2.26	–	–	[10]
Na/(PEO + glass)/I ₂ + C + electrolyte	2.45	815	98	[33]
Na/(PEO + NaNO ₃)/I ₂ + C + electrolyte	2.61	1350	62	present

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