

R. Chandrasekaran · S. Selladurai

## Preparation and characterization of a new polymer electrolyte (PEO:NaClO<sub>3</sub>) for battery application

Received: 17 January 2000 / Accepted: 23 June 2000 / Published online: 12 April 2001  
© Springer-Verlag 2001

**Abstract** A new sodium-ion conducting thin-film polymer electrolyte based on the poly(ethylene oxide) (PEO) system has been prepared by a solution-casting method. Characterization by XRD, IR, and AC conductivity and Wagner's polarization were carried out on these thin-film electrolytes. From the transference number experiment it was found that the charge transport in these electrolytes is mainly due to ions. Conductivity studies show that the conductivity value of the PEO:NaClO<sub>3</sub> complex increases with the increase of salt concentration. An increase in the conductivity and a change in the cell parameters for the electrolyte system were found by the addition of the low molecular weight dimethylformamide or propylene carbonate as plasticizers. The cell parameters of these electrolyte systems were measured from a discharge study of the cell with the application of a load of 100 kΩ at room temperature in the common cell configuration Na|electrolyte|MnO<sub>2</sub>. The open circuit voltage ranges from 2.02 V to 2.46 V and the short circuit current ranges from 570 μA to 1030 μA.

**Keywords** Polymer electrolyte · Transport number · Poly(ethylene oxide) · Manganese dioxide · Conductivity

### Introduction

Polymer-salt complexes among various ion conducting materials are of current interest owing to their possible applications in thin-film formation, interfacial contacts, desirable sizes, etc., as solid electrolytes in advanced high-energy electrochemical devices, e.g. batteries, fuel

cells, electrochemical devices or photo-electrochemical solar cells [1, 2, 3, 4, 5]. Poly(ethylene oxide) (PEO) in particular is an exceptional polymer which dissolves a wide variety of salts to form polymeric electrolytes and the chemical stability of the ether functional group strengthens the superiority of PEO as a host for a solid polymer electrolyte [6, 7]. Temperature-dependent conductivity studies, surface analyses, glass transition temperatures, structural changes, cell studies, etc., of many sodium-ion conducting polymer electrolytes based on PEO, poly(propylene oxide) (PPO) and poly(bismethoxyethoxyethoxyphosphazene) (MEEP) complexed with NaClO<sub>4</sub>, NaSCN, NaCF<sub>3</sub>SO<sub>3</sub>, NaPF<sub>6</sub>, NaI, NaYF<sub>4</sub> or NaNO<sub>3</sub> have been reported [8, 9, 10, 11, 12, 13, 14, 15]. In order to obtain moderate properties for polymer electrolytes like increased conductivity, changed amorphous phases, increased ionic mobility, decreased viscosity or a cell's stable discharge time, a new trend is the addition of plasticizers. Most plasticizers are low molecular weight organic solvents: propylene carbonate (PC), diethyl carbonate (DEC), ethylene carbonate (EC) and dimethyl carbonate (DMC) have all been studied [16, 17, 18, 19, 20, 21, 22, 23]. An enhanced conductivity value was obtained using low molecular weight poly(ethylene glycol) (PEG) [24, 25, 26]. Keeping this in view, the present paper reports conductivity studies, transference number experiment, spectral analysis and cell performance using thin-film polymer electrolytes based on PEO and NaClO<sub>3</sub> with the addition of the plasticizers PEG, PC and dimethylformamide (DMF).

### Experimental

The materials PEO (Aldrich, MW = 6 × 10<sup>6</sup>), PEG (Aldrich, MW = 4000) and NaClO<sub>3</sub> were dried well. Polymer thin films of thickness ~100–140 μm were prepared by the solvent cast technique [27]. Thin films of PEO:NaClO<sub>3</sub> were prepared in a molar ratio of 90:10, 80:20 and 70:30 by the solution cast technique using methanol (water free) as solvent. The required amount of PEO was added to the NaClO<sub>3</sub> solution, which was prepared using highly pure methanol as solvent. The solution of the polymer and salt was

R. Chandrasekaran · S. Selladurai (✉)  
Solid State Ionics Laboratory, Department of Physics,  
MIT campus, Anna University, Chromepet,  
Chennai-600 044, Tamil Nadu State, India  
E-mail: sselladurai@mitindia.edu  
Tel.: +91-44-2237276  
Fax: +91-44-2232403

stirred for 12 h for making the perfect complexation. The stirred solution was cast on to polypropylene dishes and the solvent was removed by slow evaporation at 40 °C. The final product was vacuum dried thoroughly at  $10^{-3}$  Torr to remove residual solvent. The above procedure was followed for PEG:PEO:NaClO<sub>3</sub>, PEG:PEO:NaClO<sub>3</sub>+PC (10% weight basis) and PEG:PEO:NaClO<sub>3</sub>+DMF (10% weight basis), but only PEO:NaClO<sub>3</sub> (90:10) was used for PEG, PC and DMF studies.

The polymer-salt complexation was confirmed by using both X-ray diffraction (XRD) and IR techniques for PEO-based electrolytes. The XRD investigations were performed using a Seifert diffractometer ( $2\theta$  up to 60°). The result is given in a chart form which gives a record of the counts per second, i.e., proportional to the diffracted beam intensity, versus the diffraction angle  $2\theta$ . The IR spectra of the films were recorded using a Hitachi 270-50 FTIR spectrophotometer over the range 450–4000 cm<sup>-1</sup>. A Chen-Hwa (model 1061) LCZ bridge was used for measuring conductivity values in AC methods by applying a frequency from 0.04 kHz to 200 kHz in the range 308–378 K. Here, both impedance and phase angle were measured as a function of frequency and temperature for each composition. The data were analyzed in two standard ways, i.e., Arrhenius plots of  $\log \sigma T$  vs.  $1000/T$ , where linear regions are identified, and complex impedance plots of  $Z \cos \theta$  vs.  $Z \sin \theta$ , where arcs of circles are fitted to give the bulk resistance ( $R_{dc}$ ) of the corresponding electrolyte.

The electrical conductivity is subsequently obtained from the relation:

$$\sigma = \frac{t}{R_{dc}A} \quad (1)$$

where  $t$  is the thickness of the pellets and  $A$  is the area of the cross section of the cylindrical pellets. In the transference number experiment, Wagner's polarization technique [28] was used to confirm the conducting species of the electrolyte. In this experiment, thin films were polarized in the general configuration Na|polymer electrolyte (thin film)|C under a DC bias (step potential of 1.5 V). The transference numbers ( $t_{ion}$  and  $t_{elec}$ ) were calculated from the polarization current vs. time plot using the equations:

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

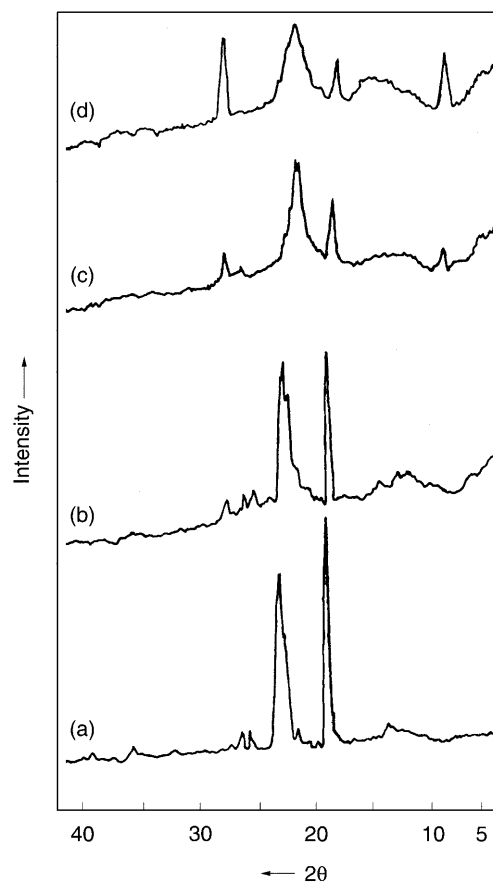
$$t_{elec} = I_f/I_i \quad (3)$$

Here  $I_i$  is the initial current and  $I_f$  is the final residual current.

Finally, Using these polymer electrolytes, the electrochemical cells were fabricated in the configuration Na|electrolyte|MnO<sub>2</sub> for all electrolytes at room temperature. In vacuum conditions, the sodium anode material (negative electrode) was taken in the form of a thin slice of thickness around 1 mm. This sodium metal slice was placed on the copper plate, the electrolyte was placed on the sodium metal and the cathode material was placed on the electrolyte. Another copper plate was placed on the top of the cathode. Those copper plates were used as current collectors. Finally, the cell was sealed under vacuum. The cell's cathode material (MnO<sub>2</sub>) was used in the form of pellets of thickness around 1.1 mm. In the presence of a load, the cells are discharged at room temperature.

## Results and discussion

The complexation of the salt NaClO<sub>3</sub> with pure PEO was confirmed by XRD and IR spectral studies. The XRD patterns of pure PEO, PEO:NaClO<sub>3</sub> (90:10), PEO:NaClO<sub>3</sub> (80:20), PEO:NaClO<sub>3</sub> (70:30) and NaClO<sub>3</sub> are given in Fig. 1. A comparison of the PEO:NaClO<sub>3</sub> pattern with the pure PEO pattern shows that the peak in PEO:NaClO<sub>3</sub> between 18.5 and 19° ( $2\theta$ ) is found to be less intense than the peak present in the pure PEO

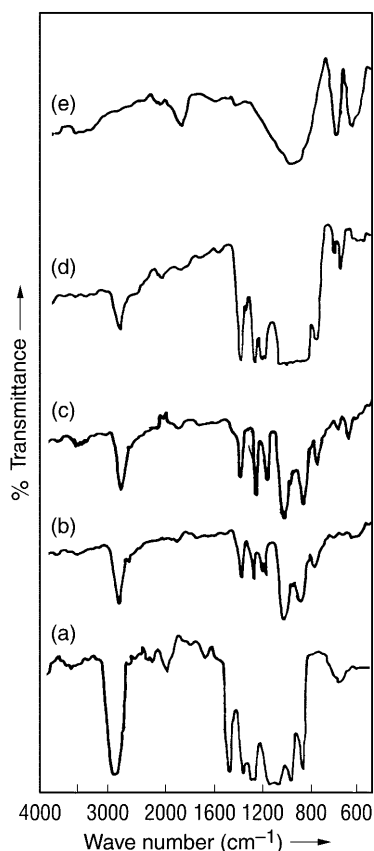


**Fig. 1** XRD spectra of (a) pure PEO, (b) PEO:NaClO<sub>3</sub> (90:10), (c) PEO:NaClO<sub>3</sub> (80:20) and (d) PEO:NaClO<sub>3</sub> (70:30)

pattern. The peak intensity at  $2\theta = 23\text{--}25.7^\circ$  in the PEO:NaClO<sub>3</sub> pattern is also less compared with the pure PEO pattern. That above changes in the PEO:NaClO<sub>3</sub> XRD pattern show a decrease in the degree of crystallinity of the polymer with the addition of the salt. Generally, the XRD studies show that the degree of amorphousness of the polymer increases as the addition of salt increases [29, 30]. The changes in the XRD pattern of these films clearly confirm the coordination of PEO with the addition of the NaClO<sub>3</sub> salt [31].

The IR spectra of pure PEO and PEO complexed with NaClO<sub>3</sub> at different compositions are shown in Fig. 2. The following changes are observed in the IR spectra of PEO:NaClO<sub>3</sub> compared with the IR spectra of PEO:

1. In pure PEO, the intensity of the aliphatic C-H stretching vibrational band around 2950 cm<sup>-1</sup> is found to be decrease with the addition of NaClO<sub>3</sub>.
2. The changes in the 1100 cm<sup>-1</sup> region of PEO are due to the C-O-C stretching vibrations in the complexed PEO [32, 33, 34].
3. The width of the C-O stretching band changes around 1200–1300 cm<sup>-1</sup> in PEO:NaClO<sub>3</sub> when compared with the PEO pattern.
4. The peak changes in PEO on either side of 1400 cm<sup>-1</sup> are due to the CH<sub>2</sub> bend in the complex.



**Fig. 2** IR spectra of (a) pure PEO, (b) PEO:NaClO<sub>3</sub> (90:10), (c) PEO:NaClO<sub>3</sub> (80:20) and (d) PEO:NaClO<sub>3</sub> (70:30) and NaClO<sub>3</sub>

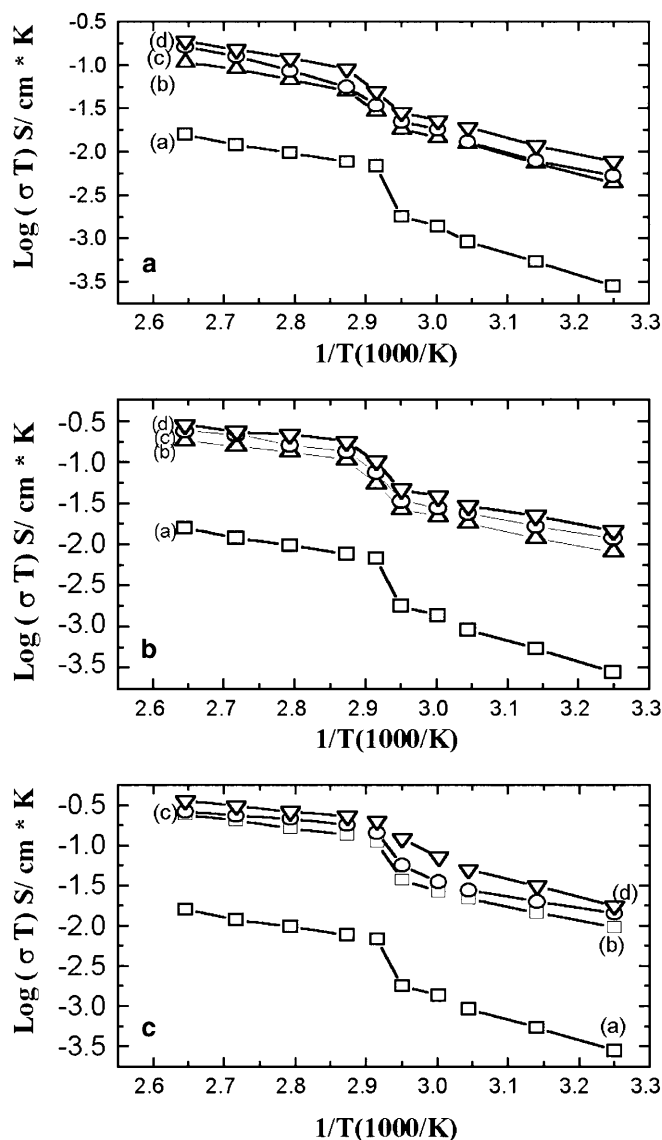
From the above observations, it is confirmed that the changes found in the XRD and IR spectra are due to the complexation of NaClO<sub>3</sub> with PEO.

From the AC conductivity measurements, conductivity values were calculated for all samples at different temperatures. Selected conductivity values for all systems are given in Table 1. The conductivity values of pure PEO, PEG, PEG:PEO (1:1) and NaClO<sub>3</sub> are  $0.98 \times 10^{-9}$ ,  $7.26 \times 10^{-7}$ ,  $5.12 \times 10^{-7}$  and  $1.8 \times 10^{-4}$  S/cm, respectively, at room temperature (35 °C). The conductivity value slowly increases with an increase of temperature for all four systems. Usually for PEO:salt complexes the conductivity values are in the range of  $10^{-3}$ – $10^{-4}$  S/cm at 80–100 °C, falling to  $10^{-6}$ – $10^{-8}$  S/cm at room temperature. The ionic transport in the PEO:MX complexes may be interpreted on the basis of a hopping mechanism between polymer chains [1, 35]. From the conductivity measurements the following results were obtained. At room temperature, the conductivity value of PEO increases sharply in the PEO:NaClO<sub>3</sub>, PEG:PEO:NaClO<sub>3</sub> and PEG:PEO:NaClO<sub>3</sub>+PC/DMF (10% weight basis) systems. The magnitude of the change is of the order of  $10^4$ – $10^2$  times when compared with pure PEO. The conductivity value of the PEO:NaClO<sub>3</sub> system increased by a  $10^2$  order of magnitude by the addition of PEG, which may be due to the reduced viscosity of the PEO:salt complexes. The conductivity value of the PEG:PEO:NaClO<sub>3</sub>+PC system when compared with PEG:PEO:NaClO<sub>3</sub> is higher, but compared with the PEG:PEO:NaClO<sub>3</sub>+DMF system it has a lower value. From the four systems of electrolytes, the PEG:PEO:NaClO<sub>3</sub>+DMF systems have the higher conductivity values. This may be due to the dimethylamido group, which better aids the association with the parent polymer. The increases in conductivity values for the PC- and DMF-containing electrolytes are small because their percentage in PEG:PEO:NaClO<sub>3</sub> is small [23].

Typical plots of  $\log(\sigma T)$  versus inverse temperature ( $10^3/T$ ) for PEO- and PEG:PEO-based systems are given

**Table 1** Selected conductivity values for PEO-based electrolyte systems

Temp. (°C)	Conductivity (S/cm)		
35	$9.06 \times 10^{-7}$	$1.42 \times 10^{-6}$	$3.40 \times 10^{-6}$
65	$5.80 \times 10^{-6}$	$7.62 \times 10^{-6}$	$1.02 \times 10^{-5}$
75	$2.20 \times 10^{-5}$	$5.01 \times 10^{-5}$	$7.02 \times 10^{-5}$
105	$4.19 \times 10^{-5}$	$1.30 \times 10^{-4}$	$2.12 \times 10^{-4}$
	PEG:PEO:NaClO <sub>3</sub> (30:60:10)	PEG:PEO:NaClO <sub>3</sub> (45:45:10)	PEG:PEO:NaClO <sub>3</sub> (60:30:10)
35	$1.65 \times 10^{-5}$	$2.65 \times 10^{-5}$	$3.07 \times 10^{-5}$
65	$5.35 \times 10^{-5}$	$7.90 \times 10^{-5}$	$1.08 \times 10^{-4}$
75	$1.45 \times 10^{-4}$	$3.05 \times 10^{-4}$	$3.80 \times 10^{-4}$
105	$2.85 \times 10^{-4}$	$4.85 \times 10^{-4}$	$6.40 \times 10^{-4}$
	PEG:PEO:NaClO <sub>3</sub> (30:60:10)+PC	PEG:PEO:NaClO <sub>3</sub> (45:45:10)+PC	PEG:PEO:NaClO <sub>3</sub> (60:30:10)+PC
35	$1.78 \times 10^{-5}$	$3.90 \times 10^{-5}$	$4.65 \times 10^{-5}$
65	$6.60 \times 10^{-5}$	$9.60 \times 10^{-5}$	$1.04 \times 10^{-4}$
75	$1.60 \times 10^{-4}$	$3.87 \times 10^{-4}$	$4.22 \times 10^{-4}$
105	$4.28 \times 10^{-4}$	$6.30 \times 10^{-4}$	$6.94 \times 10^{-4}$
	PEG:PEO:NaClO <sub>3</sub> (30:60:10)+DMF	PEG:PEO:NaClO <sub>3</sub> (45:45:10)+DMF	PEG:PEO:NaClO <sub>3</sub> (60:30:10)+DMF
35	$2.50 \times 10^{-5}$	$4.80 \times 10^{-5}$	$5.67 \times 10^{-5}$
65	$8.40 \times 10^{-5}$	$2.02 \times 10^{-4}$	$2.89 \times 10^{-4}$
75	$2.61 \times 10^{-4}$	$5.10 \times 10^{-4}$	$6.60 \times 10^{-4}$
105	$5.05 \times 10^{-4}$	$7.54 \times 10^{-4}$	$9.47 \times 10^{-4}$



**Fig. 3** a Conductivity vs. inverse temperature plot for (a) PEO:NaClO<sub>3</sub> (90:10), (b) PEG:PEO:NaClO<sub>3</sub> (30:60:10), (c) PEG:PEO:NaClO<sub>3</sub> (30:60:10)+10% PC and (d) PEG:PEO:NaClO<sub>3</sub> (30:60:10)+10% DMF. **b** Conductivity vs. inverse temperature plot for (a) PEO:NaClO<sub>3</sub> (90:10), (b) PEG:PEO:NaClO<sub>3</sub> (45:45:10), (c) PEG:PEO:NaClO<sub>3</sub> (45:45:10)+10% PC and (d) PEG:PEO:NaClO<sub>3</sub> (45:45:10)+10% DMF. **c** Conductivity vs. inverse temperature plot for (a) PEO:NaClO<sub>3</sub> (90:10), (b) PEG:PEO:NaClO<sub>3</sub> (60:30:10), (c) PEG:PEO:NaClO<sub>3</sub> (60:30:10)+10% PC and (d) PEG:PEO:NaClO<sub>3</sub> (60:30:10)+10% DMF

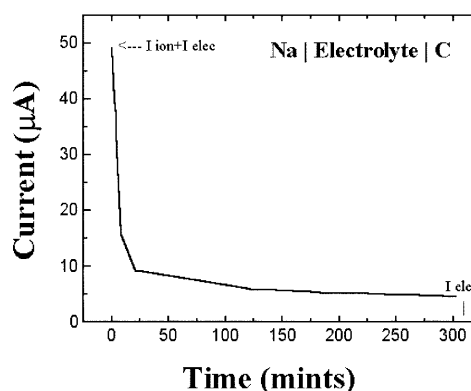
in Fig. 3a–c. The linear variation seen before and after the melting region shows an Arrhenius type of thermally activated process. The measured  $E_a$  values are given in Table 2. Decreasing  $E_a$  values show that the plasticizers reduce the crystal nature of the polymer salt complexes [18, 19, 20, 21]. In general, at higher temperature the conductivity value increases because the internal modes are activated, i.e., the semi-crystalline nature of the electrolytes becomes amorphous. This is particularly seen at the melting stage of the polymer.

**Table 2** Activation energies (eV) for PEO-based systems

Electrolyte system	Region I	Region II
PEO:NaClO <sub>3</sub> (90:10)	0.539	0.260
PEO:NaClO <sub>3</sub> (80:20)	0.527	0.444
PEO:NaClO <sub>3</sub> (70:30)	0.383	0.438
PEG:PEO:NaClO <sub>3</sub> (30:60:10)	0.391	0.287
PEG:PEO:NaClO <sub>3</sub> (45:45:10)	0.361	0.215
PEG:PEO:NaClO <sub>3</sub> (60:30:10)	0.417	0.215
PEG:PEO:NaClO <sub>3</sub> (30:60:10)+PC	0.432	0.340
PEG:PEO:NaClO <sub>3</sub> (45:45:10)+PC	0.300	0.274
PEG:PEO:NaClO <sub>3</sub> (60:30:10)+PC	0.360	0.250
PEG:PEO:NaClO <sub>3</sub> (30:60:10)+DMF	0.403	0.257
PEG:PEO:NaClO <sub>3</sub> (45:45:10)+DMF	0.339	0.197
PEG:PEO:NaClO <sub>3</sub> (60:30:10)+DMF	0.428	0.187

**Table 3** Transference numbers for the PEO:NaClO<sub>3</sub> electrolyte system

System	$t_{ion}$	$t_{elec}$
PEO:NaClO <sub>3</sub> (90:10)	0.940	0.060
PEO:NaClO <sub>3</sub> (80:20)	0.935	0.065
PEO:NaClO <sub>3</sub> (70:30)	0.936	0.064



**Fig. 4** Polarization current vs. time plot for the PEO:NaClO<sub>3</sub> (90:10) system

The ionic transference number was measured using Wagner's polarization technique. In this technique, the thin film was polarized in the configuration Na|PEO:NaClO<sub>3</sub>|C. After polarization of the cell with a constant DC voltage of 1.5 V, the current was recorded as a function of time; a typical resulting curve for PEO:NaClO<sub>3</sub> (90:10) is shown in Fig. 4. The ionic transference number,  $t_{ion}$ , was found to be 0.94. The charge transport in this electrolyte is predominantly due to an ionic process and the electronic contributions are very small. The above method was applied to all systems but there is no significant changes in transference

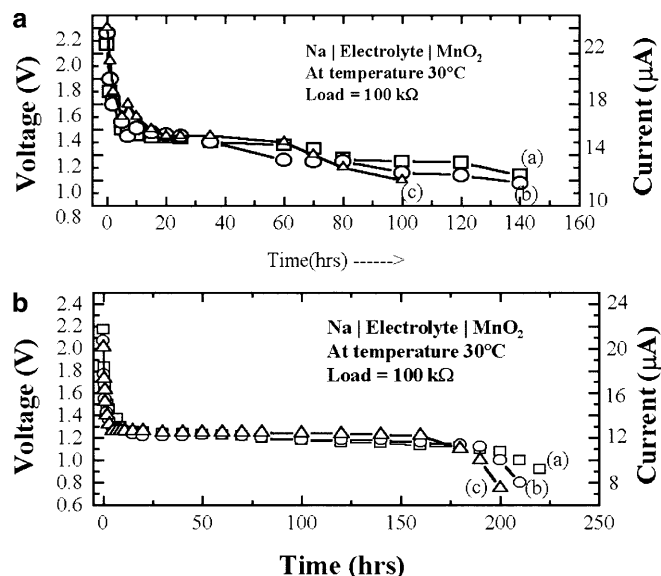
number values. The  $t_{ion}$  and  $t_{elec}$  numbers for PEO:NaClO<sub>3</sub> are given in Table 3.

From the cell studies, the following results are obtained. The possible chemical reactions are:

At the anode:  $Na \rightarrow Na^+ + e^-$

At the cathode:  $Na^+ + MnO_2 + e^- \rightarrow Na_{1+x}MnO_2$

Selected discharge curves are shown in Fig. 5. Fig. 5a and b shows the discharge characteristics of PEO:NaClO<sub>3</sub> and PEG:PEO:NaClO<sub>3</sub> based cells at room temperature. The sharp decrease in the discharge curve is due to layer formation at the cathode surface and intercalation of sodium ions into the MnO<sub>2</sub> matrix occurring at the time of discharge [36, 37, 38, 39, 40, 41, 42]. In the case of a higher salt content polymer electrolyte, i.e. a 7:3 ratio, the cell discharge time decreases due to the rapid formation of a layer at the site of the electrode and chain mobility is restricted by the higher salt concentration [43]; an ion-pairing effect also takes place [44]. The maximum open circuit voltage (OCV) was found in the PEO:NaClO<sub>3</sub> (90:10) based cell. The maximum short circuit current (SCC) value was observed for the DMF-added electrolyte. The addition of PEG gives a better cell performance when compared with the other electrolytes. However, a higher concentration of PEG shows very small changes in the cell parameters. Except for the OCV value, the discharge time, energy density and SCC value are all higher in the case of PEG:PEO-based electrolytes when compared with the PEO-based electrolyte. The electrolytes with added PC or DMF do not



**Fig. 5** a Cell discharge characteristic curves for (a) PEO:NaClO<sub>3</sub> (90:10), (b) PEO:NaClO<sub>3</sub> (80:20) and (c) PEO:NaClO<sub>3</sub> (70:30). b Cell discharge characteristic curves for (a) PEG:PEO:NaClO<sub>3</sub> (30:60:10), (b) PEG:PEO:NaClO<sub>3</sub> (45:45:10) and (c) PEG:PEO:NaClO<sub>3</sub> (60:30:10)

give further changes in their cell parameters, which closely resemble the properties of the PEO:PEG electrolytes. The various parameters evaluated are summarized in Tables 4, 5, 6, 7.

The present study has demonstrated that plasticized polymer electrolytes show better performances through

**Table 4** Various cell parameters for the three electrolyte systems with the cell configuration Na|electrolyte|MnO<sub>2</sub>

Cell parameters at 30 °C	PEO:NaClO <sub>3</sub> (90:10)	PEO:NaClO <sub>3</sub> (80:20)	PEO:NaClO <sub>3</sub> (70:30)
Area of the cell (cm <sup>2</sup> )	0.95	0.95	0.95
Wt. of the cell (g)	0.73	0.92	0.77
OCV (V)	2.46	2.32	2.29
SCC (µA)	570	688	900
Current density (µA/cm <sup>2</sup> )	600	724	947
Discharge time (h) <sup>a</sup>	142	132	92
Discharge capacity (µA/h)	4.01	5.21	9.78
Power density (W/kg)	1.92	1.73	2.68
Energy density (Wh/kg)	272	229	246

<sup>a</sup>Cut-off voltage for all cells is around 1.0 V

**Table 5** Various cell parameters for the PEG:PEO:NaClO<sub>3</sub> electrolyte systems with the cell configuration Na|electrolyte|MnO<sub>2</sub>

Cell parameters at 30 °C	PEG:PEO:NaClO <sub>3</sub> (30:60:10)	PEG:PEO:NaClO <sub>3</sub> (45:45:10)	PEG:PEO:NaClO <sub>3</sub> (60:30:10)
Area of the cell (cm <sup>2</sup> )	0.95	0.95	0.95
Wt. of the cell (g)	0.96	0.93	0.955
OCV (V)	2.37	2.32	2.29
SCC (µA)	746	766	787
Current density (µA/cm <sup>2</sup> )	785	806	828
Discharge time (h) <sup>a</sup>	212	192	181
Discharge capacity (µA/h)	3.52	3.99	4.35
Power density (W/kg)	1.84	1.91	1.88
Energy density (Wh/kg)	390.4	366.8	341.6

<sup>a</sup>Cut-off voltage for all cells is around 1.0 V

**Table 6** Various cell parameters for PEG:PEO:NaClO<sub>3</sub> + 10% PC electrolyte systems with the cell configuration Na|electrolyte|MnO<sub>2</sub>

Cell parameters at 30 °C	PEG:PEO:NaClO <sub>3</sub> (30:60:10)	PEG:PEO:NaClO <sub>3</sub> (45:45:10)	PEG:PEO:NaClO <sub>3</sub> (60:30:10)
Area of the cell (cm <sup>2</sup> )	0.95	0.95	0.95
Wt. of the cell (g)	0.962	0.935	0.95
OCV (V)	2.28	2.2	2.11
SCC (μA)	820	846	896
Current density (μA/cm <sup>2</sup> )	863	891	937
Discharge time (h) <sup>a</sup>	188	179	175
Discharge capacity (μA/h)	4.36	4.73	5.09
Power density (W/kg)	1.94	1.99	1.98
Energy density (Wh/kg)	365.4	356	346

<sup>a</sup>Cut-off voltage for all cells is around 1.0 V

**Table 7** Various cell parameters for PEG:PEO:NaClO<sub>3</sub> + 10% DMF electrolyte systems with the cell configuration Na|electrolyte|MnO<sub>2</sub>

Cell parameters at 30 °C	PEG:PEO:NaClO <sub>3</sub> (30:60:10)	PEG:PEO:NaClO <sub>3</sub> (45:45:10)	PEG:PEO:NaClO <sub>3</sub> (60:30:10)
Area of the cell (cm <sup>2</sup> )	0.95	0.95	0.95
Wt. of the cell (g)	0.98	0.97	0.96
OCV (V)	2.22	2.13	2.02
SCC (μA)	873	930	1030
Current density (μA/cm <sup>2</sup> )	919	979	1084
Discharge time (h) <sup>a</sup>	172	152	120
Discharge capacity (μA/h)	5.08	6.12	8.58
Power density (W/kg)	1.98	2.04	2.14
Energy density (Wh/kg)	340	310	257

<sup>a</sup>Cut-off voltage for all cells is around 1.0V

the energy density and high discharge time during the cell discharge when compared with PEO-based electrolytes. Some of the earlier results of PEO:Na-based polymer electrolytes are given in Table 8. From that table, the energy density of PEG-based polymer electrolytes is higher than other pure PEO-based systems and the discharge time is nearly two times higher in the presence of the same load applied (100 kΩ at room temperature). In the present study, the salt concentration is kept low (only 10% of the total weight of the polymer-salt complex) while the earlier reported cells operated with higher salt concentration electrolytes.

## Conclusions

From the conductivity results, the following observations can be made:

1. Plasticizers (PEG, PC and DMF) activate the polymer chain relaxations which are responsible for ion hopping in the polymer matrix.
2. Plasticizers are mainly used to enhance the conductivity value of the corresponding electrolytes, but their contributions to their respective electrolytes are different.
3. The plasticizing effect of a low molecular weight polymer with a higher molecular weight polymer is a limited one.
4. The addition of the solvents PC or DMF to the polymer electrolytes is used to increase the amorphousness in order to increase the conductivity value of the corresponding host polymer via chain relaxation.
5. From the discharge characteristic studies it was found that the stability of the electrolyte is higher for the case of lower salt concentrations, i.e., for 90:10 when compared to the other higher salt concentrations (80:20 and 70:30). The increased salt concentration decreases the stability of the electrolyte, i.e. the high salt concentration reduces the chain flexibility. We can achieve higher conductivity values as well as a short circuit current using more plasticizers in the corresponding battery systems.

**Table 8** Comparison of present cell parameters with those of other cells reported previously

Battery configuration	OCV (V)	SCC (μA)	Discharge time (h)	Energy density (Wh/kg)	Ref
Na PEO + glass (60:40) (15Na <sub>2</sub> O-15NaF-70B <sub>2</sub> O <sub>3</sub> ) I <sub>2</sub> + C + electrolyte	2.45	815	98	359	[45]
Na PEO:NaYF <sub>4</sub> (8:2) I <sub>2</sub> + C + electrolyte	2.45	560	96	165	[14]
Na PEO:NaNO <sub>3</sub> (7:3) I <sub>2</sub> + C + electrolyte	2.61	1350	62	240	[15]
Na PEG:PEO:NaClO <sub>3</sub> (30:60:10) MnO <sub>2</sub>	2.37	746	212	390	Present work

**Acknowledgements** The authors thank Prof. U.V. Subba Rao and The Head, Department of Physics, Osmania University, Hyderabad, for their encouragement. The authors thank Prof. K.V. Reddy, CIL, Hyderabad, for his help in recording the XRD spectra. The authors also thank Prof. M. Palinisamy, Department of Chemistry, Anna University, for his suggestions and Dr. K. Subramaniam for recording the IR spectra.

## References

- Aramand MB, Chabangno JM, Duclot MJ (1979) In: Vashista P, Mundy JN, Shenoy GF (eds) Fast ion transport in solids. Elsevier North-Holland, Amsterdam, p 131
- Steele BCH, Lagos GE, Spurdens PC, Forsyth C, Foord AD (1983) *Solid State Ionics* 9/10:391
- Hooper A, North JM (1983) *Solid State Ionics* 9/10:1161
- Wantanabe M, Nagano S, Sanui K, Ogata N (1986) *Polym J* 18:809
- Ballard DGH, Cheshire P, Mann TS, Przeworski JE (1990) *Macromolecules* 23:1256
- Vincent CA (1987) *Prog Solid State Chem* 17:145
- Armand MB (1987) In: MacCallum JR, Vincent CA (eds) *Polymer electrolyte reviews*. Elsevier, London, p 1
- Fautenx D, Robitaille C, Lupien MD (1987) *J Electrochem Soc* 134:2761
- Greenbaum SG, Pak YS, Wintersgill MC, Fontanella JJ, Schultz JW (1988) *J Electrochem Soc* 135:235
- Greenbaum SG, Adamic KJ, Pak YS, Wintersgill MC, Fontanella JJ (1988) *Solid State Ionics* 28–30:1042
- Hashmi SA, Chandra A, Chandra S (1992) In: Chowdari BVR (ed) *Solid state ionics – materials and applications*. World Scientific, Singapore, p 567
- Skaarup S, West K, Zachau-Christian B, Jacobse T (1998) In: Chowdari BVR, Radhakrishna S (eds) *Solid state ionic devices*. World Scientific, Singapore, p 75
- Munishi MZA, Gilmour A, Smryl WH, Owens BB (1989) *J Electrochem Soc* 136:1847
- Sreepathi Rao S, Jaibal Reedy M, Laxmi Narsaiah E, Subba Rao UV (1995) *Mater Sci Eng B33*:173
- Sreekanth T, Jaipal Reddy M, Ramalingaiah S, Subba Rao UV (1999) *J Power Sources* 79:105
- Sheldon MH, Glasse MD, Latham RJ, Linford RG (1989) *Solid State Ionics* 34:135
- Walker CW Jr, Salomon M (1993) *J Electrochem Soc* 140:3409
- Yang XQ, Lee HS, Hanson L, McBreen J, Okamoto Y (1995) *J Power Sources* 54:198
- Lee HS, Yang XQ, Xu LS, McBreen J, Skotheim TA, Okamoto Y (1995) *J Electrochem Soc* 141:886
- Kovac M, Gaberscek M, Grdadolnik J (1998) *Electrochim Acta* 44:863
- Tobishima S, Hayashi K, Nemoto, Yamaki J (1998) *Electrochim Acta* 43:925
- Hayashi K, Nemoto Y, Tobishima S, Yamaki J (1999) *Electrochim Acta* 44:2337
- Michael MS, Jacob MME, Prabaharan SRS, Radhakrishna S (1997) *Solid State Ionics* 98:167
- Hardy LC, Shrivier DF (1984) *Macromolecules* 17:977
- Kelly IE, Owen JE, Steele BCH (1985) *J Power Sources* 14:13
- Kelly IE, Owen JR, Steele BCH (1984) *J Electroanal Chem* 168:467
- Scrosati B (1988) In: Chowdari BVR, Radhakrishna S (eds) *Solid state ionic devices*. World Scientific, Singapore, p 133
- Wagner JB, Wagner C (1957) *J Chem Phys* 26:1597
- Maurya KK, Srivastava N, Hashmi SA, Chandra S (1992) *J Mater Sci* 27:6357
- Maurya KK, Hashmi SA, Chandra S (1992) *J Phys Soc Jpn* 61:1709
- Sreepathi Rao S, Satyanarayana Rao KV, Shareefuddin MD, Subba Rao UV (1994) *Solid State Ionics* 67:331
- Papke BL, Ratner MA, Shrivier DF (1981) *J Phys Chem Solids* 42:493
- Papke BL, Ratner MA, Shrivier DF (1982) *J Electrochem Soc* 129:1434
- Hashmi SA, Kummar A, Maurya KK, Chandra S (1990) *J Phys D* 23:1307
- Steele BCH, Weston SE (1990) *Solid State Ionics* 40/41:648
- Guyomard D, Tarascon JM (1992) *J Electrochem Soc* 139:937
- Ohzuku T, Iwakoshi Y, Sawai K (1993) *J Electrochem Soc* 140:2490
- Sawai K, Iwakoshi Y, Ohzuku T (1994) *Solid State Ionics* 69:273
- Chandrasekaran R, Selladurai S, Kalpana D, Manoravi P (1999) *Indian J Pure Appl Phys* 37:345
- Selladurai S, Chandrasekaran R (1999) In: Chowdari BVR (ed), *Solid state ionics*. World Scientific, Singapore, p 585
- Kozawa A (1980) In: Schumm B, Joseph HM, Kozawa K (eds) *Proceedings of MnO<sub>2</sub> symposium 2*, Tokyo, paper 22
- Do JS, Chang CP, Lee TT (1996) *Solid State Ionics* 89:291
- Weston JE, Steele BCH (1983) *Solid State Ionics* 2:347
- Dominquez L, Meyar WH (1988) *Solid State Ionics* 28–30:941
- Jaipal Reddy M, Sreekanth T, Subba Rao UV (1998) *J Power Sources* 76:30