

## Conductivity study of polyethylene oxide (PEO) complexed with sodium bicarbonate

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**Abstract** Ion conducting thin film polymer electrolytes based on polyethylene oxide (PEO) complexed with  $\text{NaHCO}_3$  salt has been prepared using solution-cast technique. The complexation of  $\text{NaHCO}_3$  salt with PEO is confirmed by XRD and IR studies. DC conductivity in the temperature range 303–368 K has been evaluated. The conductivity is found to increase in the PEO complex with the  $\text{NaHCO}_3$  salt and also with an increase in temperature. Using this polymer electrolyte, an electrochemical cell with the configuration  $\text{Na}/(\text{PEO} + \text{NaHCO}_3)/(\text{I}_2 + \text{C} + \text{electrolyte})$  has been fabricated and its discharge characteristics studied. Open Circuit Voltage (OCV) and Short Circuit Current (SCC) are found to be 2.69 V and 1.28 mA, respectively. Other parameters associated with the cell are evaluated and presented in this paper.

### Introduction

Ion conducting polymer electrolytes have recently become an area of wide spread interest in solid-state ionics because of their potential application in solid electrochemical devices such as energy conversion systems batteries/fuel cells, electro chromic display devices/smart windows,

photo electro chemical solar cells, etc. [1–6]. Advantages of polymer electrolytes are ease of fabrication into films of desirable sizes and good electrode–electrolyte contacts in different electrochemical devices. Interest began in this field after the studies of materials based on alkali metal salts complexed with polyethylene oxide (PEO) reported by Wright and coworkers [7, 8]. PEO is an exceptional polymer having ability to solvate ionic salts and forms solid polymer electrolyte [9]. Polymer electrolytes consisting of PEO and alkali metal salts were reported for the purpose of application to several kinds of electrochemical cells [10, 11].

In the past three decades, many polymeric electrolytes, based on various salts dissolved in polyethers, particularly PEO, have been widely investigated because of their potential application in high performance batteries. Such electrolytes have been mainly based on alkali metal salt systems, with particular attention given to lithium. The studies on sodium ion conducting polymers are scanty. Less effort has been made on solid polymer electrolytes based on sodium complex systems. Apart from the scientific interest, the use of sodium has several advantages over lithium. Sodium is much more abundant and lower in price than lithium. The softness of this metal makes it easier to achieve and maintain contact to other components in the electrochemical devices.

In the present investigation, the authors prepared solid polymer electrolytes by complexing poly(ethylene oxide) (PEO) with sodium bicarbonate ( $\text{NaHCO}_3$ ). Various properties such as XRD, IR studies and dc electrical conductivity measurements in the temperature range 303–368 K have been carried out to characterize this polymer electrolyte system and the results obtained are presented in this paper. Based on this polymer system a new polymer battery with the configuration  $\text{Na}/(\text{PEO} + \text{NaHCO}_3)/$

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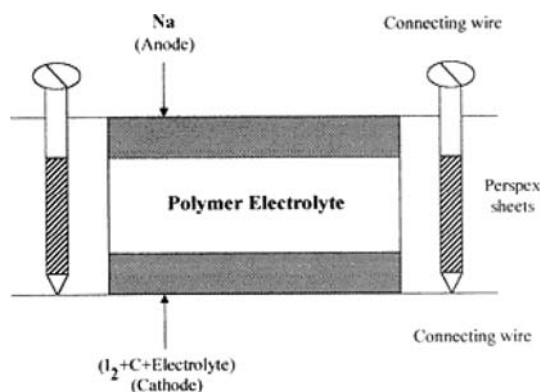
(I<sub>2</sub> + C + electrolyte) has been fabricated and its discharge characteristics studied.

## Experimental

Films (thickness  $\approx$  100–150  $\mu\text{m}$ ) of pure PEO (Aldrich MW  $\sim 6 \times 10^5$ ) and PEO complexed with NaHCO<sub>3</sub> salt were prepared in the weight ratios (90:10), (80:20) and (70:30). EO/Na<sup>+</sup>, monomer to cation ratio is (4.7:1), (2.1:1), and (1.2:1). The films were prepared by the solution cast method with methanol (water free) as solvent. Mixtures of PEO and NaHCO<sub>3</sub> were stirred for about 10–12 h. The stirred homogeneous solutions were cast onto polypropylene dishes and evaporated slowly at room temperature. The final product was vacuum dried thoroughly at  $10^{-3}$  Torr.

The XRD studies of these samples were carried out with the help of PHILIPS PW 3710 X-RAY diffractometer in the range  $10^\circ$ – $70^\circ$ . The infrared (IR) Spectra of these samples have been recorded with the help of JASCO FT-IR-5300 Spectrophotometer in the range 400–4,000  $\text{cm}^{-1}$  with resolution of 2  $\text{cm}^{-1}$ .

The dc conductivity measurements of these samples have been made using in house made conductivity setup in the temperature range 303–368 K. The solid-state electrochemical cell has been fabricated with the configuration anode (Na)/(PEO + NaHCO<sub>3</sub>)/cathode (I<sub>2</sub> + C + electrolyte). The construction of the electrochemical cell is shown in Fig. 1 [12]. The discharge characteristics of these cells were monitored under the constant load of 100 k $\Omega$ . Sodium metal is used as anode; and iodine (I<sub>2</sub>), graphite (C), and electrolyte materials are used in the weight ratio of 5:5:1, respectively as cathode. The cathode is made in the form of a thin pellet after proper mixing the constituents. In the cathode material iodine is an active cathodic material, graphite to assure adequate electronic conductivity and electrolyte to favour electrode/electrolyte interfacial contact.

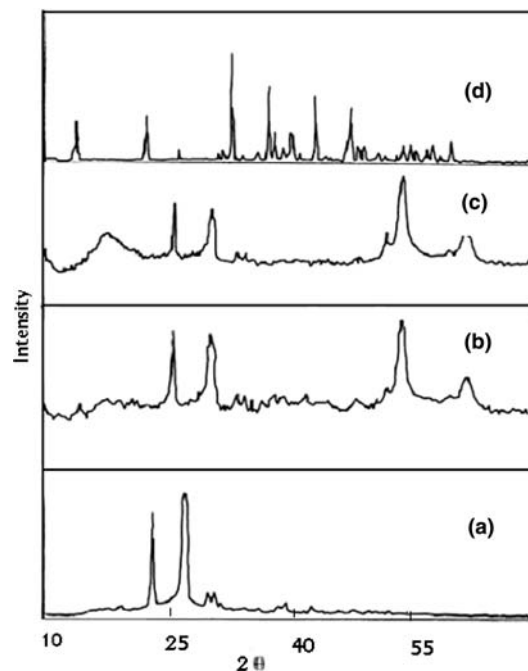


**Fig. 1** Fabrication diagram of an electrochemical cell

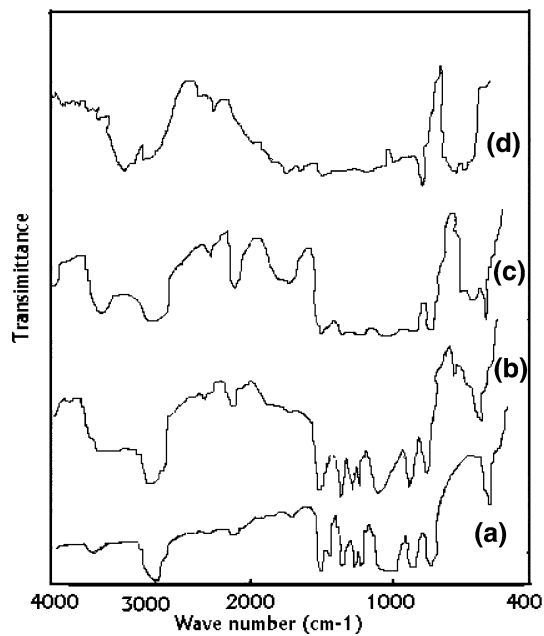
## Results and discussion

The X-Ray diffraction (XRD) spectra of pure PEO, PEO complexed with NaHCO<sub>3</sub> and pure NaHCO<sub>3</sub> are shown in Fig. 2. A comparison of X-Ray diffraction spectra shows that the few differences in diffraction patterns are identified between the complexed PEO films and that of pure PEO. The diffraction peaks between  $2\theta = 15^\circ$ – $30^\circ$ , clearly apparent in pure PEO [13–17] were found to be less prominent and shifted to higher angle in NaHCO<sub>3</sub> complexed PEO films. Accompanying the decrease in intensity with the gradual broadening of the diffraction peaks by increasing of NaHCO<sub>3</sub> salt concentration to PEO is apparent. The results affirm both the decrease of degree of crystallinity and the lamellae size with increasing of NaHCO<sub>3</sub> salt. However, the additional/new diffraction peaks corresponding to the formation of a stable Na:PEO crystalline complex is apparent between  $2\theta = 50^\circ$  and  $62^\circ$ . The X-ray diffraction results evidence of decrease in PEO crystallinity with increasing concentration of NaHCO<sub>3</sub> ionic salt and also found Na ion–PEO crystalline stable complex.

IR spectra of pure PEO and PEO complexed with NaHCO<sub>3</sub> are shown in Fig. 3. The intensity of the aliphatic C–H stretching vibration band observed around 2,950  $\text{cm}^{-1}$  in PEO is found to increase with increasing the concentration of NaHCO<sub>3</sub> salt in the PEO. This spectral change is different from the earlier reported results on various ionic



**Fig. 2** XRD spectra of (a) Pure PEO (b) PEO + NaHCO<sub>3</sub> (90:10) (c) PEO + NaHCO<sub>3</sub> (70:30) and (d) Pure NaHCO<sub>3</sub>

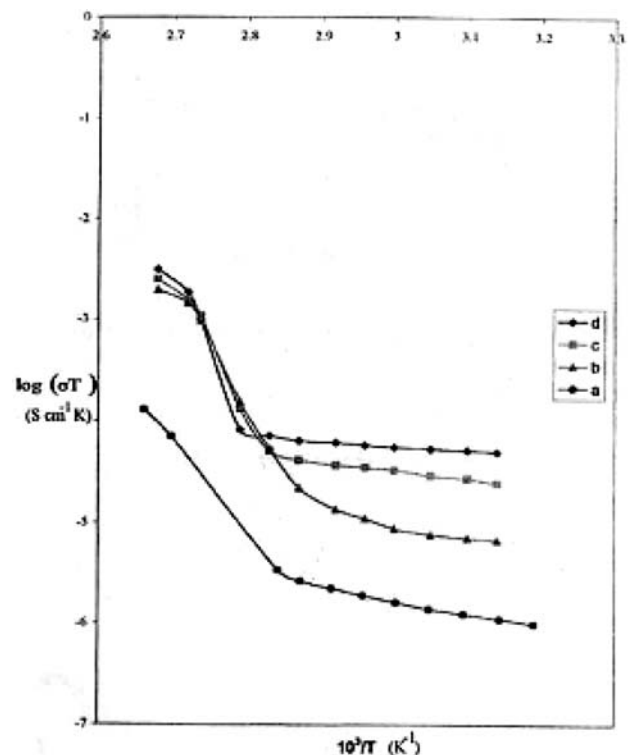


**Fig. 3** IR spectra of (a) Pure PEO (b) PEO + NaHCO<sub>3</sub> (90:10) (c) PEO + NaHCO<sub>3</sub> (70:30) and (d) NaHCO<sub>3</sub>

salt complexes to PEO [17–19]. The increase in intensity of aliphatic C–H stretching vibration band in complexed NaHCO<sub>3</sub> with PEO maybe due to the physical interaction through hydrogen of (HCO<sub>3</sub>)<sup>−</sup> with the PEO chain. The width of the C–O stretching band observed around 1,100 cm<sup>−1</sup> in PEO showed a decrease, with an increase of NaHCO<sub>3</sub> salt. New peaks around 2,895.41, 1,963.71 and 530.47 cm<sup>−1</sup> have been observed in the complexed PEO. If the cations of NaHCO<sub>3</sub> get coordinated with the oxygen of PEO, the spectral changes are expected to be in the C–O stretching and deformation ranges. The decrease in the width of 1,100 cm<sup>−1</sup> band which is assigned to C–O symmetrical and asymmetrical stretching [18–20] suggested the coordination/complexation of the salt with PEO. The complexations of PEO with alkali metal salts have been studied by using vibration spectroscopic studies [15–20]. The appearance of new peaks along with changes in existing peaks in the IR spectra directly indicates the complexation of PEO with NaHCO<sub>3</sub>. Thus, the results of XRD and IR data clearly indicate the complexation of NaHCO<sub>3</sub> salt with PEO.

Figure 4 shows the variation of conductivity as a function of temperature for pure PEO and different compositions of (PEO + NaHCO<sub>3</sub>) polymer electrolyte in the temperature range 303–368 K. From Fig. 4 the following have been drawn

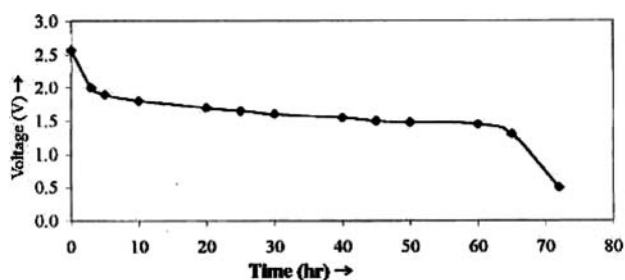
- (a) In the temperature range of study, the conductivity is found to increase with the temperature in pure PEO and in PEO complexed with NaHCO<sub>3</sub> salt films.



**Fig. 4** The temperature dependence of dc conductivity of (a) Pure PEO (b) PEO + NaHCO<sub>3</sub> (90:10) (c) PEO + NaHCO<sub>3</sub> (80:20) and (d) PEO + NaHCO<sub>3</sub> (70:30)

- (b) The conductivity versus temperature plots indicates two regions (region-I & region-II). In region-I, the conductivity slowly increases with temperature up to melting temperature ( $T_m \sim 65^\circ\text{C}$ ). At  $T_m$  there is a sudden increase in conductivity. In the region-II, above  $T_m$  the conductivity again rapidly increases with temperature. Similar behaviour has been observed in all the composition of (PEO + NaHCO<sub>3</sub>) polymer electrolyte systems. The temperature, which corresponds to the sudden increase in conductivity indicate that there is a change of phase from semicrystalline to amorphous. The existence of two regions in the conductivity versus temperature plots has been observed in a number of PEO based polymer electrolytes [15, 17–19, 21]. The calculated activation energies ( $E_a$ ) in two regions (I and II) for pure PEO and PEO complexed with NaHCO<sub>3</sub> salt are given in Table 1.

Using the new polymer electrolyte system (PEO + NaHCO<sub>3</sub>), an electrochemical cell with the configuration Na/(PEO + NaHCO<sub>3</sub>)/(I<sub>2</sub> + C + electrolyte) has been prepared and studied its discharge characteristics is shown in Fig. 5. From the figure it is observed that the initial sharp decrease in the voltage in these cells may be due to polarization effect or formation of a thin-layer of



**Fig. 5** Discharge characteristics of Na/(PEO + NaHCO<sub>3</sub>) (70:30)/ (I<sub>2</sub> + C + electrolyte) electrochemical cell for a constant load of 100 kΩ

**Table 1** Activation energies calculated for (PEO + NaHCO<sub>3</sub>) polymer electrolyte system

Polymer electrolyte system	Activation energies (eV)	
	Region-I (eV)	Region-II (eV)
Pure PEO	0.34	0.59
(PEO + NaHCO <sub>3</sub> ) (90:10)	0.32	0.48
(PEO + NaHCO <sub>3</sub> ) (80:20)	0.25	0.33
(PEO + NaHCO <sub>3</sub> ) (70:30)	0.19	0.28

sodium salt at the electrode–electrolyte interface. The Open Circuit Voltage (OCV) and the Short Circuit Current (SCC) are 2.69 V and 1.28 mA, respectively. The various other parameters of the cell evaluated are presented below:

Cell weight = 1.46 g

Effective area of the cell = 1.34 cm<sup>2</sup>

Thickness of the cell = 150 μm

Power density = 2.31 W kg<sup>-1</sup>

Energy density = 183 W h kg<sup>-1</sup>

Plateau region = 65 h

On the basis of present study, a solid state battery with (PEO + NaHCO<sub>3</sub>) as an electrolyte is promising one. The cell parameters obtained is comparable with the earlier reported sodium based polymer electrolyte systems [12, 13, 22]. Further work is in progress to achieve higher cell parameters.

## Conclusions

The complexation of NaHCO<sub>3</sub> salt with PEO is confirmed by XRD and IR studies. The conductivity is found to increase in the PEO complexed with the NaHCO<sub>3</sub> salt and also with an increase in temperature. An electrochemical

cell with the configuration Na/(PEO + NaHCO<sub>3</sub>)/ (I<sub>2</sub> + C + electrolyte) has been fabricated and its discharge characteristics studied. Open Circuit Voltage (OCV) and Short Circuit Current (SCC) are 2.69 V and 1.28 mA, respectively. The cell parameters obtained on this polymer electrolyte system is comparable with the earlier reported sodium based polymer electrolyte systems.

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