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Short Communication

Characteristics of poly(ethylene oxide)–NaI polymer electrolyte and electrochemical cell performances

N.S. Mohamed, M.Z. Zakaria, A.M.M. Ali, A.K. Arof

Physics Division, Centre for Foundation Studies in Science, University of Malaya, Lembah Pantai, 50603 Kuala Lumpur, Malaysia

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Abstract

Poly(ethylene oxide) (PEO)–NaI complexes with different sodium:oxygen ratios are prepared by the solution-casting method. The complex with $Na^+/O = 0.022$ gives the highest conductivity, viz., 5.21×10^{-5} S cm^{-1}. X-ray diffraction studies studies show that the sample with the highest electrical conductivity exhibits the smallest coherent length. This complex is used as an electrolyte for the fabrication of (metal)/PEO–NaI/(metal oxide) electrochemical cells. The open-circuit voltage of the fabricated cell with the best performance is 407 mV. The short-circuit current is about 14 μA.

Keywords: Polymer electrolyte; Poly(ethylene oxide); Sodium iodide; Performance

1. Introduction

Studies have shown that poly(ethylene oxide) (PEO) can form highly crystalline complexes with several compounds including urea, thiourea and mercuric chloride [1] and complexes with disrupted crystalline order including PEO when associated with simple salts such as the thiocyanates of ammonium, sodium and potassium and with sodium iodide and potasium iodide [2]. Complexation involves an interaction of the cation with the lone pair electrons of the ether-oxygen atom. There are, however, not many data concerning the electrolytic potential of these materials in solid-state batteries. Polymer electrolytes formed by dissolving inorganic salts, e.g., NH_4ClO_4, NH_4I, $LiClO_4$, in PEO have shown potential applications as electrolyte materials in solid-state electrochemical cells [3,4]. A solid polymer battery has the advantage of being spill proof and does not corrode easily compared with conventional liquid batteries.

In this work, the polymer–salt complexed system of PEO with NaI containing different sodium:oxygen ionic ratios are prepared by the solution-cast technique. The complexes are studied using X-ray diffraction (XRD) and impedance spectroscopy. From impedance spectroscopy, the variation of conductivity (σ) with composition of the complex and with the reciprocal of temperature (T) are obtained. The variation of σ and electrical modulus with frequency (f) for pure PEO and the complex exhibiting the highest electrical conductivity are also analysed. Finally, the highest conducting film is used as an electrolyte for the fabrication of ($Zn + ZnSO_4 \cdot 7H_2O$)/PEO–NaI/metal oxide cells.

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2. Experimental

2.1. Material preparation

PEO–NaI compounds with different metal:oxygen (M/O) ratios in the range $0.000 \leq M/O \leq 0.029$ were prepared by the solution-casting method. 1 g of PEO (Aldrich with mol. wt. 10^5 g mol^{-1}) was dissolved in 100 ml of methanol and stirred using a magnetic stirrer until a clear solution was obtained. The dissolving process was carried out for several hours. The solution was then poured into Petri dishes and left to dry at room temperature. The preparation of NaI-doped PEO was prepared similarly but NaI was added to the solution in different weight ratios.

2.2. Sample characterization

2.2.1. X-ray diffraction (XRD)

The XRD studies were carried out using a Philips PW 1840 diffractometer. The wavelength of the X-radiation was 1.5406 Å and the diffraction pattern was recorded for 2θ values between 10° and 70°. The coherent or Scherrer length was calculated using the equation

$$L=\frac{0.9\lambda}{\Delta 2\theta_b \cos \theta_b} \quad (1)$$

where λ is the X-ray wavelength, $\Delta 2\theta_b$ the full width at half-maximum, and θ_b the angle of the peak.

2.2.2. Electrical properties studies

To study the electrical properties of the samples, impedance spectroscopy was performed using a Hioki 3520-01 LCR Hi-Tester that was interfaced to a computer. The sample was subjected to a pressure of 2 kPa and the study was carried out in the frequency range 40 Hz to 100 kHz. Computer software was used to calculate other admitance response quantities using the impedance data obtained. The electrical conductivity, σ, was calculated using the equation

$$\sigma=\frac{l}{R_B A} \quad (2)$$

where l is the thickness of the sample, R_B the bulk impedance, and A the electrode/electrolyte contact area.

2.2.3. Thermal conductivity and ion transport studies

Thermal conductivity was measured in the temperature range from room temperature to 60 °C using the technique described above. The sample was clamped in a conductivity mount and then put into a furnace. The temperature was set by a temperature controller and the readings were taken by the bridge from 40 Hz to 100 kHz.

2.3. Electrochemical cell fabrication

The highest conducting sample was used as an electrolyte for electrochemical cell fabrication. The cathode was a mixture of PbO_2 and MnO_2 and a mixture of Zn and $ZnSO_4 \cdot 7H_2O$ was used as the anode. The ratio of Zn to $ZnSO4 \cdot 7H_2O$ was 3:1 by weight. The anode and cathode composition were mixed with conducting carbon cement and smeared onto the electrolyte surfaces.

2.4. Electrochemical cell characterization

2.4.1. Open-circuit voltage

The open-circuit voltage (OCV) of the cell was measured by directly connecting the '+' terminal of a digital multimeter to the anode of the cell and the '−' terminal of the multimeter to the cathode of the cell.

2.4.2. Discharge characteristics

The cells were discharged by connecting each cell to an ammeter and a 100 kΩ resistor in series. A voltmeter was connected across the cell to monitor its voltage. The readings of the voltage and current were taken until the current drawn showed a drastic drop. The variation of voltage and current with time were then plotted.

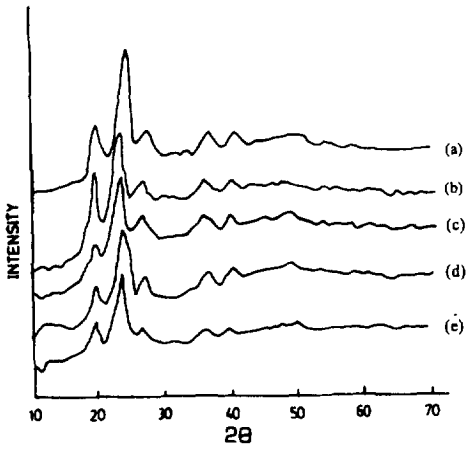

Fig. 1. XRD patterns for: (a) pure PEO; (b) film with M/O = 0.029; (c) film with M/O = 0.019; (d) film with M/O = 0.006, and (e) film with M/O = 0.022.

3. Results

Fig. 1 shows some of the XRD patterns of the PEO–NaI complexes. Broad peaks between $2\theta = 16°$ to 30° and related to the amorphous phase were observed for pure PEO and all other NaI-doped PEO complexes. Fig. 2(a) shows the Cole–Cole plot for the sample with M/O = 0.022 and Fig. 2(b) shows the plot of its imaginary admittance versus real admittance. The intercept on the real impedance axis in the complex impedance plot is approximately the same as the reciprocal of the intercept on the real admittance axis in the complex admittance plot. The variations of coherent length and electrical conductivity at room temperature with the composition (M/O ratio) of the complexes are presented in Fig. 3. Fig. 4 shows the variation of conductivity with frequency for pure PEO and for the sample with M/O = 0.022. It can be seen that the dopant increases the conductivity but reduces the dispersion of conductivity with frequency. The variations of the electric modulus, M_R, with frequency for pure PEO and for the sample with M/O = 0.022, are given in Fig. 5. At very low frequencies, M_R is very small in value and indicates the highly capacitive nature of the sample. The effect of the dopant also decreases the real part of the electrical modulus.

Table 1 lists some characteristics of the cells fabricated. From the equation $V = E - Ir$ (where E is the open-circuit voltage (OCV), V is the voltage of the cell when a current I is drawn out of the cell and r is the internal resistance), the short-circuit current (SCC) of the cell was calculated.

The cell with the highest energy density is the $(Zn + ZnSO_4 \cdot 7H_2O)$/PEO–NaI/$(PbO_2 + MnO_2)$ cell. The OCV is 407 mV. Figs. 6 and 7 present the voltage–time and current–time curves, respectively, of the cell discharged at a constant load of 100 kΩ. The internal resistance is ~30 kΩ and is the lowest compared with the other cells.

4. Discussion

The intensity of the peaks corresponding to pure PEO in the XRD analysis is observed to decrease with the increase

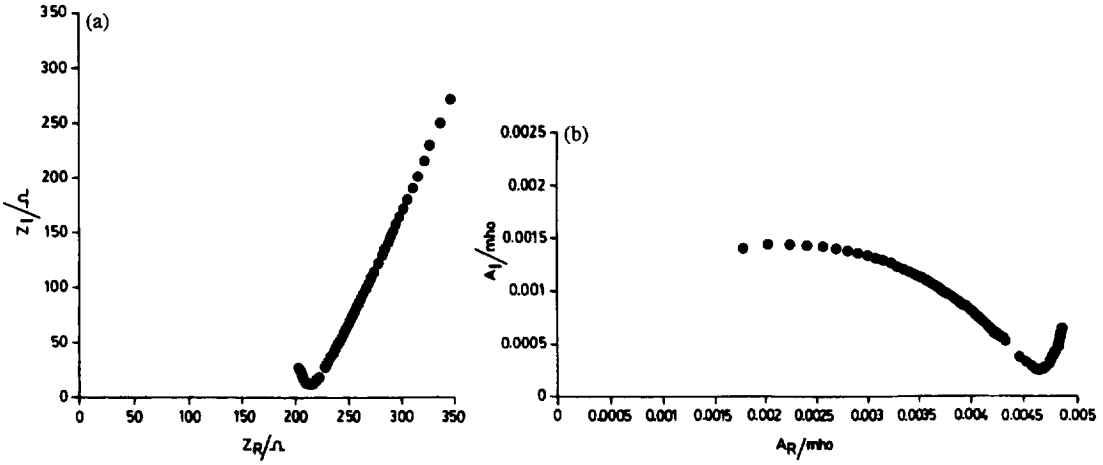

Fig. 2. (a) Complex impedance plot of the highest conducting film. (b) Complex admittance plot of the highest conducting film.

Table 1
Characteristics of $(Zn + ZnSO_4 \cdot 7H_2O)$/PEO-NaI/$(X)$ cells. Characteristics were taken when the cells were discharged under a load of 100 kΩ

X	r (Ω)	OCV (SCC)	Current density (μA cm^{-2})	Discharge capacity (mAh)	Energy density (J kg^{-1})
0.04 g PbO_2	41.3	370 mV (9 μA)	1.6	0.06	76.8
0.02 g PbO_2 + 0.02g MnO_2	46.9	312 mV (7 μA)	1.4	0.09	84.4
0.01 g PbO_2 + 0.03g MnO_2	48.7	330 mV (7 μA)	0.9	0.05	42.1
0.04 g MnO_2	48.7	309 mV (6 μA)	1.5	0.11	107.2
0.03 g PbO_2 + 0.01g MnO_2	30	407 mV (14 μA)	2.1	0.10	135.7

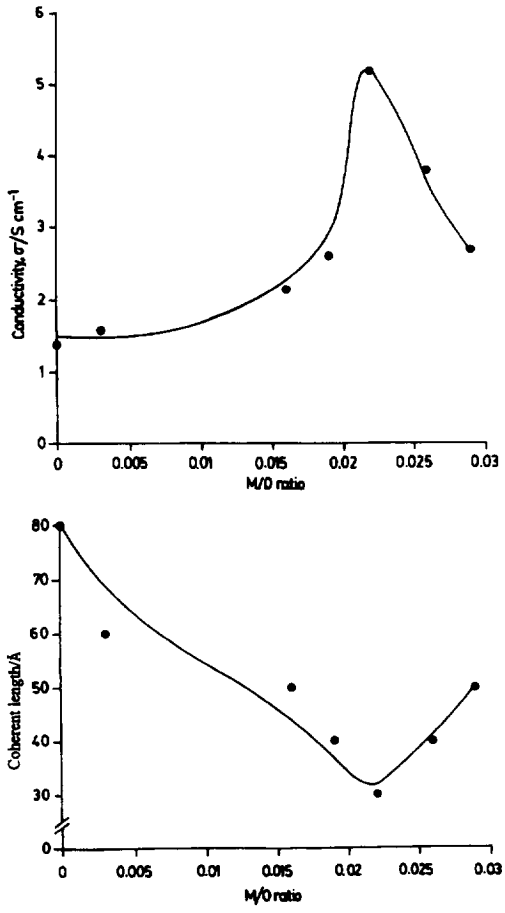

Fig. 3. Variations of coherent length and conductivity vs. M/O ratio.

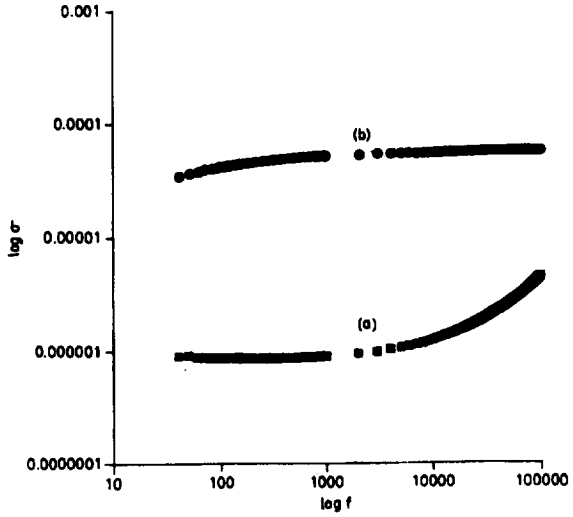

Fig. 4. σ vs. f for (a) pure PEO, and (b) film with M/O = 0.022.

in salt concentration. This indicates the partial conversion of the crystalline phase in the PEO to an amorphous phase upon complexation of the PEO with NaI. Uncomplexed PEO seems to be present in all samples. No sharp peaks corresponding to the complexation of PEO with NaI was observed in these patterns. This infers that complexation occurs only in the amorphous region of PEO. Calculation of coherent length based on a particular peak present in the diffractograms of all the samples showed that the sample with M/O = 0.022 has the shortest coherent length and the undoped sample exhibits the longest coherent length. This implies that the sample with

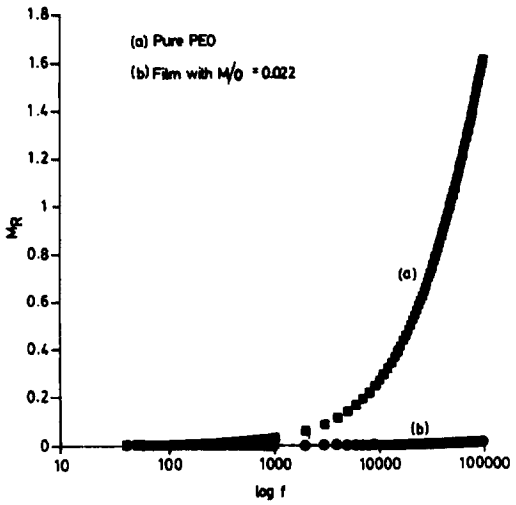

Fig. 5. M_R vs. f for (a) pure PEO, and (b) film with M/O = 0.022.

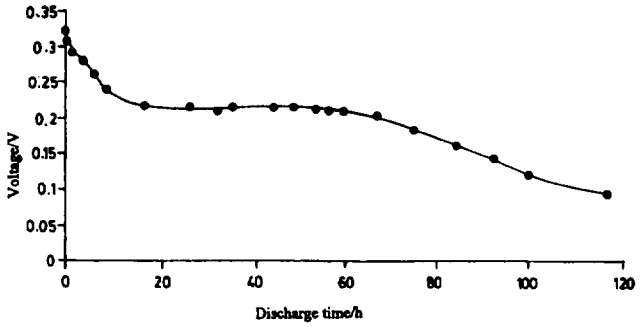

Fig. 6. Voltage vs. time for $(Zn + ZnSO_4 \cdot 7H_2O)/PEO–NaI/(PbO_2 + MnO_2)$ cell.

M/O = 0.022 has the lowest degree of crystallinity. Therefore, the sample with M/O = 0.022 gives the highest conductivity value of 5.21×10^{-5} S cm^{-1} since complexation has caused a maximum amount of conversion of the crystalline phase into the amorphous phase through which conductivity occurs in PEO [5].

The increase in conductivity with frequency implies the decrease in the dielectric constant with frequency [6] and infers that the resistance to charge flow in such materials is reduced as the frequency increases. As a result, the electrical conductivity increases with frequency. The characteristics of the electrochemical cells are quite comparable with those of other cells using PEO as the host electrolyte [3,4].

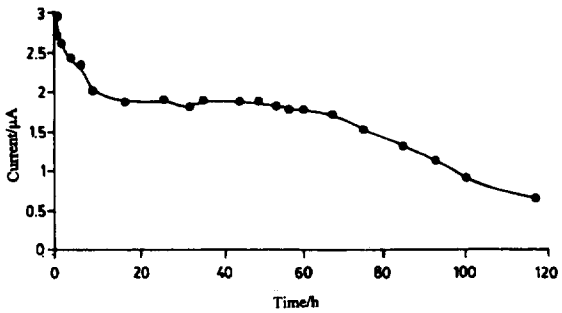

Fig. 7. Current vs. time for $(Zn + ZnSO_4 \cdot 7H_2O)/PEO–NaI/(PbO_2 + MnO_2)$ cell.

5. Conclusions

It has been shown that the PEO–NaI complex can be used as an electrolyte in solid-state polymer electrochemical cells. Theoretically, it should be able to run a 1 μA consuming device for about 100 h.

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