



Polyethylene oxide (PEO)–ammonium sulfate $((\text{NH}_4)_2\text{SO}_4)$ complexes and electrochemical cell performance

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Abstract

The PEO– $(\text{NH}_4)_2\text{SO}_4$ systems with different NH_4^+/EO ratio have been prepared by the solution-cast technique and investigated by X-ray diffraction, infrared spectroscopy and impedance spectroscopy. The highest conductivity ($2.7 \times 10^{-6} \text{ S cm}^{-1}$) is obtained from the film with a NH_4^+/EO ratio of 0.050. Some electrochemical cells are then fabricated using the film with the highest electrical conductivity as the electrolyte. Different metal oxides and their combination are used as the cathode active materials. The highest open-circuit voltage (OCV) of 1.059 V is provided by the cell with configuration $(\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O})/\text{PEO}-(\text{NH}_4)_2\text{SO}_4/(0.02 \text{ g PbO}_2 + 0.02 \text{ g MnO}_2)$. The short-circuit current of this cell is $97 \mu\text{A}$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Electrochemical cell; Polymer; Electrolyte; Polyethylene oxide; Ammonium sulfate; Solid-state

1. Introduction

Polymer electrolytes have occupied an important position in solid-state ionics. This is due to their unique properties which includes the ease of preparation in a thin film form; an ability to accommodate a wide range of doping compositions which enables the control of properties; good electrode–electrolyte contact due to their flexibility; and relatively high ionic conductivity. The discovery of PEO–alkali metal salt complexes by Wright [1] and Fenton et al. [2] has led to the rapid development in polymer electrolytes and electrochemical devices. Polymer electrolyte-based electrochemical cells are actively being developed because of their advantages over conventional systems containing liquid electrolytes. The major technical problem in the development of room-temperature polymer electrolyte cells has been, however, the identification of a suitable electrolyte [3]. Many studies have been devoted to polyethylene oxide (PEO)-based electrolytes using alkali salts. Other salts include ammonium salt and examples of such complexes are PEO– NH_4SCN and PEO– $\text{NH}_4\text{SO}_3\text{CF}_3$ [4], PEO and polyacrylic (PAA): NH_4HSO_4

[5], PEO: NH_4ClO_4 [6,7] and PEO: NH_4I [8]. All these complexes are reported to be proton conductors. Nevertheless, there are few data on the performance of such proton conductors in solid-state electrochemical cells or batteries.

In this study, the PEO– $(\text{NH}_4)_2\text{SO}_4$ system is prepared and investigated. Although, such complexes have already been shown to be proton conductors [9], their performance as an electrolyte in polymer-based electrochemical cells has not been studied. Hence, the highest conducting film is used as an electrolyte to fabricate solid polymer electrochemical cells. It is hoped that the additional protons that can be obtained from the salt will improve the electrical conductivity of the polymer and the cell performance.

2. Experimental

2.1. Material preparation

PEO– $(\text{NH}_4)_2\text{SO}_4$ systems having different ammonium to oxygen ratios in the range $0.000 \leq \text{NH}_4^+/\text{O} \leq 0.084$ were prepared by the solution-cast technique. A total of 1 g PEO (Aldrich of molecular weight 10^5 g mole^{-1}) and $(\text{NH}_4)_2\text{SO}_4$ (in suitable proportions) were dissolved in methanol and stirred with a magnetic stirrer to obtain a uniform solution. The solutions were then poured into petri dishes and allowed to evaporate slowly to form films. All

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samples were prepared at room temperature and the films were stored under dry conditions.

2.2. Material characterization

2.2.1. X-ray diffraction (XRD)

Literature [6,8–10] has shown that the two distinct peaks of PEO are situated at $2\theta \approx 20^\circ$ and 24° . For complexation to take place, these peaks must show some shifts in position. Literature [6,8,9,11] has also shown that a reduction in intensity of the two peaks can also occur; this implies that the salt has disrupted the crystalline nature of the PEO and increased the amorphous region. To check for complexation, XRD studies were carried out using a Philips PW 1840 diffractometer. The diffraction patterns were recorded for 2θ -values between 10° and 50° at a scan rate of 2° per min. The wavelength of the x-radiation was 1.54060 \AA . For comparison, the X-ray diffraction pattern of $(\text{NH}_4)_2\text{SO}_4$ was also taken under identical conditions.

2.2.2. Infrared (IR) spectroscopy

Complexation can be reconfirmed by IR studies. Spectral changes are expected to occur in the C–O–C stretching and deformation regions between 800 to 1500 cm^{-1} where the NH_4^+ ion is expected to bond with the ether oxygen of the PEO. Shifts in the spectrum of PEO + salt can also indicate complexation [12]. The infrared spectra were recorded in the range 400 to 4000 cm^{-1} using a Perkin Elmer FTIR Model 2000 spectrophotometer.

2.2.3. Impedance spectroscopy

In order to test the hypothesis that $(\text{NH}_4)_2\text{SO}_4$ will give more protons compared to other ammonium salts and, therefore, will increase the electrical conductivity of the material, impedance spectroscopy was carried out. Impedance spectroscopy was performed using a Hioki 3520-01 LCR Hi-Tester that was interfaced to a microcomputer. The study was carried out in the frequency range of 40 to 100 kHz . The impedance plots were drawn and the conductivity was calculated using the expression:

$$\sigma = \frac{l}{R_b A} \quad (1)$$

In this expression, l is the thickness of the film, R_b is the bulk impedance, and A is the area of the cross-section of the film. The value of R_b was confirmed from the complex admittance plots.

The conductivity–temperature behaviour was investigated for temperatures below the melting temperature of PEO ($\sim 65^\circ\text{C}$). The sample was placed in a conductivity mount and then placed in a heating chamber. The temperature was set using a temperature controller and then stabilized for examination with the impedance analyzer.

2.3. Electrochemical cells fabrication

It has been shown that $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is a proton conductor [13]. It has also been shown in the same work that an electrochemical cell could be fabricated using $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ as the electrolyte and Zn powder as the anode. The anode mixture also contained the electrolyte, as is normally practiced in the fabrication of silver batteries. Thus, the anode is an ionic conductor (in this case the ions are protons). Since it is claimed that $\text{PEO}-(\text{NH}_4)_2\text{SO}_4$ is also a proton conductor [9], a cell was fabricated with the configuration $(\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O})/\text{PEO}-(\text{NH}_4)_2\text{SO}_4/\text{metal oxide}$; the $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is used to make the anode an ionic conductor. Using the standard reduction potentials for the possible reactions (see Table 1) that may take place in the cell, the open-circuit voltage is expected to be 1.262 V .

For a $(\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O})/\text{PEO}-(\text{NH}_4)_2\text{SO}_4/\text{PbO}_2$ cell, the reduction potential for the reaction $\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$ is 1.455 and the total theoretical OCV is therefore estimated to be 1.492 V .

The cells were fabricated using the film with the highest conductivity. A mixture of Zn and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in the weight ratio of $3:1$ was used as the anode. Different cathode compositions, i.e., PbO_2 , $\text{PbO}_2 + \text{MnO}_2$, MnO_2 , $\text{MnO}_2 + \text{V}_2\text{O}_3$, V_2O_3 , $\text{V}_2\text{O}_3 + \text{PbO}_2$, and $\text{V}_2\text{O}_3 + \text{PbO}_2 + \text{MnO}_2$, were used to find the most suitable cathode material for such a cell configuration. It is expected that a combination of oxides may improve the performance of the cell.

2.4. Characterization of electrochemical cells

2.4.1. Open-circuit voltage (OCV)

The OCV of the cell was measured by connecting the cell to a $4 \frac{1}{2}$ -digit multimeter.

2.4.2. Discharge characteristics

The cells were discharged under a load of $100 \text{ k}\Omega$. The discharge characteristics of the cells were recorded using a

Table 1

Possible anode and cathode reactions for $(\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O})/\text{PEO}-(\text{NH}_4)_2\text{SO}_4/\text{MnO}_2$ cell

Possible anode reactions	Possible cathode reaction	E° (V)
$\text{Zn} = \text{Zn}^{2+} + 2\text{e}^-$		0.7618
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + 2\text{e}^- = \text{Zn}(\text{Hg}) + \text{SO}_4^{2-}$		–0.7993
	$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- = \text{Mn}^{2+} + \text{H}_2\text{O}$	1.224
Open-circuit voltage (OCV)		1.2615

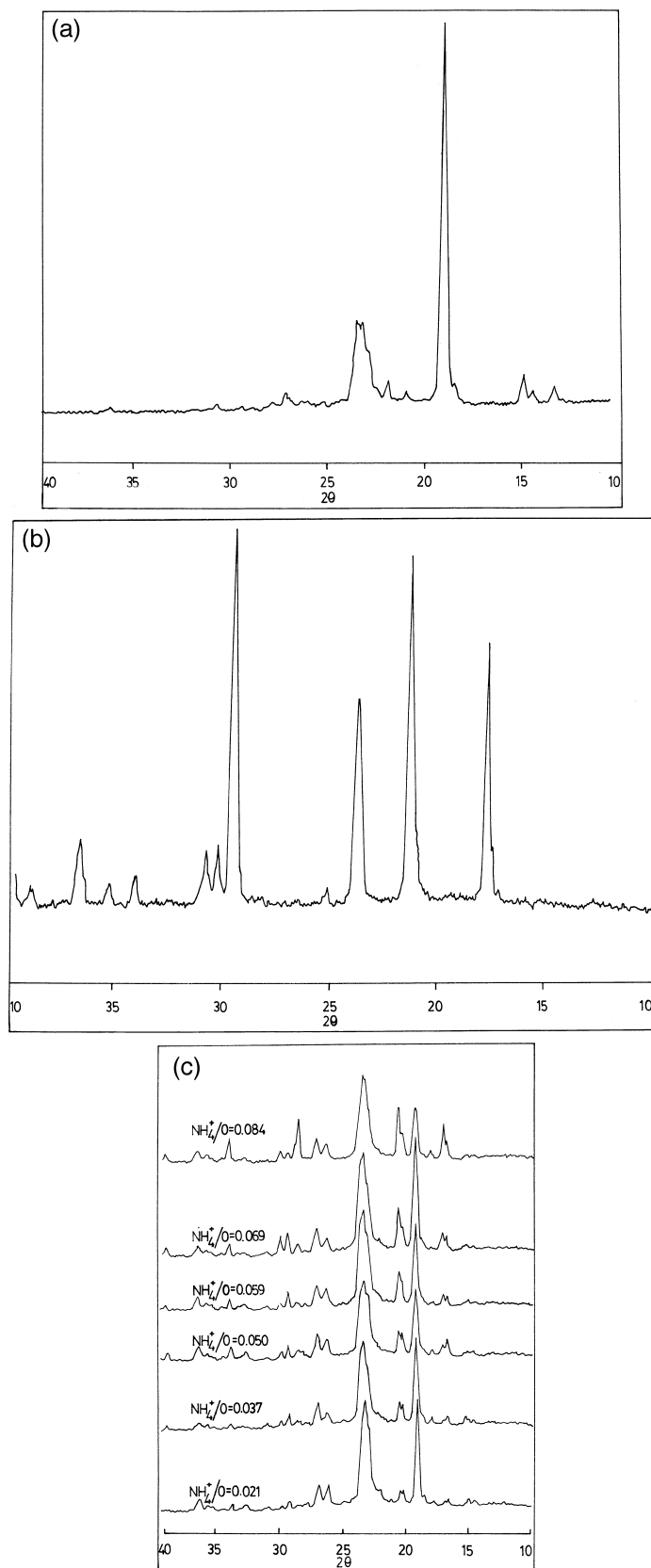


Fig. 1. XRD patterns for: (a) pure PEO; (b) $(\text{NH}_4)_2\text{SO}_4$; (c) PEO- $(\text{NH}_4)_2\text{SO}_4$ complexes.

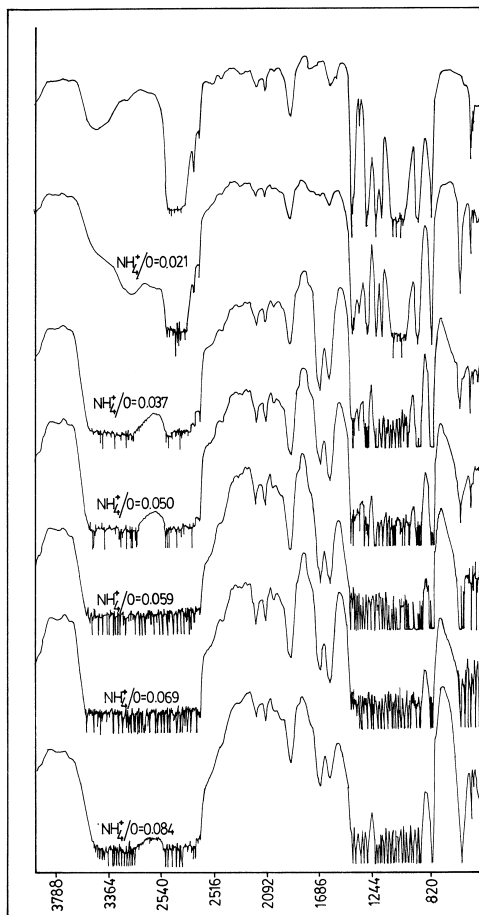


Fig. 2. IR spectra for pure PEO and its complexes.

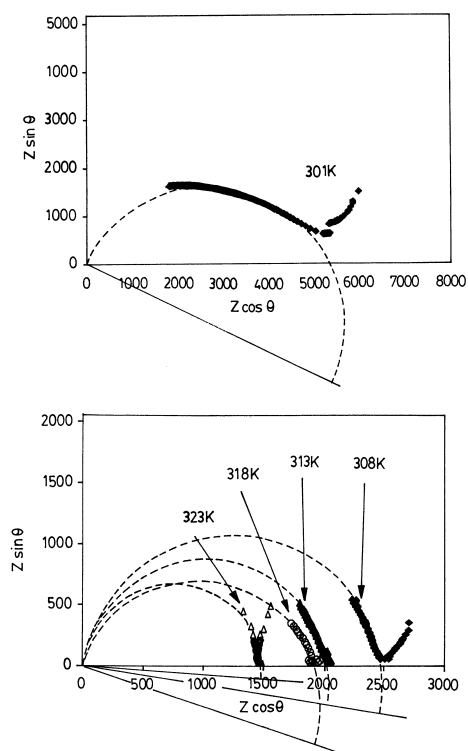


Fig. 3. Impedance plots of film with a NH_4^+/O ratio of 0.059.

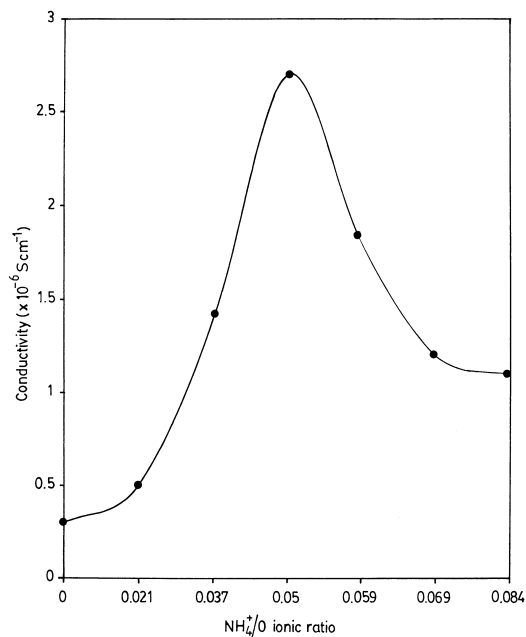


Fig. 4. Variation of conductivity with NH_4^+/O ratio.

data logger Pico ADC-10 instrument which was interfaced to a computer. Data collection was terminated when the cell voltage dropped below 50 mV.

3. Results

The XRD patterns of all the $\text{PEO}-(\text{NH}_4)_2\text{SO}_4$ phases together with that of $(\text{NH}_4)_2\text{SO}_4$ are shown in Fig. 1. For pure PEO, the main peaks are observed at $2\theta = 19.3^\circ$ and

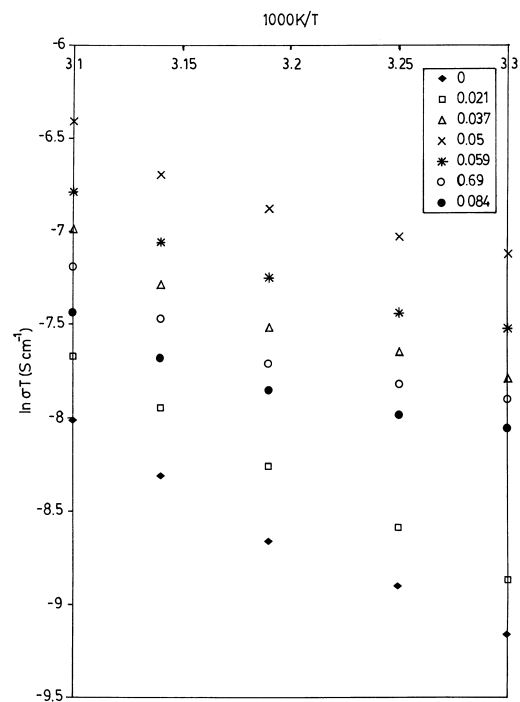


Fig. 5. $\ln \sigma T$ vs. $1000/T$ for $\text{PEO}-(\text{NH}_4)_2\text{SO}_4$ complexes.

Table 2
 r^2 values for $\ln \sigma T$ with $1000/T$ plots and the activation energy values of the complexes

NH_4^+/EO ratio	r^2	Activation energy (eV)
0.000	0.980	0.48
0.021	0.998	0.51
0.037	0.941	0.32
0.050	0.932	0.29
0.059	0.950	0.31
0.069	0.909	0.29
0.084	0.928	0.26

23.7°, and for pure ammonium salt, the main peaks are at $2\theta = 17.7^\circ, 21.3^\circ, 23.8^\circ, 29.3^\circ, 30.0^\circ, 31.0^\circ, 34.0^\circ, 35.0^\circ$ and 36.5° . For $\text{PEO}-(\text{NH}_4)_2\text{SO}_4$ complexes, peaks are observed at $2\theta = 16.5^\circ, 20-21^\circ, 26-27^\circ, 28.5^\circ$ and 29° . The IR spectra of pure PEO and $\text{PEO}-(\text{NH}_4)_2\text{SO}_4$ phases are presented in Fig. 2. The impedance plots of the $\text{PEO}-(\text{NH}_4)_2\text{SO}_4$ film with a NH_4^+/EO ratio of 0.059 and taken at various temperatures are given in Fig. 3. The variation of the electrical conductivity, σ , at room temperature and with different NH_4^+/EO ratios is shown in Fig. 4. The variation of $\ln \sigma T$ with $1000/T$ for the complexes is given in Fig. 5 and their respective linear regression coefficients, r^2 , are listed in Table 2.

The film with the highest electrical conductivity (i.e., a film with $\text{NH}_4^+/\text{EO} = 0.050$) was used for cell fabrication. Eight cells with the configuration $(\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O})/\text{PEO}-(\text{NH}_4)_2\text{SO}_4/(\text{metal oxide or oxides})$ were fabricated. Table 3 lists some characteristics of the cells. The discharge plots (voltage–time, current–time) are presented in Fig. 6.

4. Discussion

The XRD spectra for $\text{PEO}-(\text{NH}_4)_2\text{SO}_4$ phases show a decrease in the PEO peak at $2\theta = 20^\circ$. This indicates that

the degree of crystallinity decreases after the addition of salt to the PEO. The presence of peaks at $2\theta = 16.5^\circ, 20-21^\circ, 26-27^\circ, 28.5^\circ$ and 29° in all $\text{PEO}-(\text{NH}_4)_2\text{SO}_4$ samples suggests the presence of a new PEO –salt crystalline phase.

Analysis of the IR spectra of the $\text{PEO}-(\text{NH}_4)_2\text{SO}_4$ complexes shows that as the amount of salt is increased, the band between $3000-3600 \text{ cm}^{-1}$ of pure PEO is broadened and finally merges with the band between $2600-2800 \text{ cm}^{-1}$. The distinctive peaks between $800-1400 \text{ cm}^{-1}$ in the spectrum of pure PEO also broaden as the amount of salt increases. The $-\text{C}-\text{O}-\text{C}-$ stretching and deformation lies in this region, and from the broadening of the peaks, it can be inferred that the salt has solvated to form a complex with PEO. Apart from these observations, peaks are also present at $\approx 616 \text{ cm}^{-1}$ (attributable to SO_4^{2-} ion vibration) and at 1653 and 3238 cm^{-1} (attributable to NH_4^+ ion vibration) [14,15]. Thus, as the amorphous region in the PEO –salt complexes increases, $(\text{NH}_4)_2\text{SO}_4$ is dissociated to NH_4^+ and SO_4^{2-} ions. According to Linford [16], these ions exist in the amorphous region with comparable mobilities and contribute to the electrical conductivity.

The conductivity of the complexes increases with the content of the doping salt and reaches a maximum value of $2.7 \times 10^{-6} \text{ S cm}^{-1}$ for a film with a NH_4^+/EO ratio of 0.050. The increase in the conductivity is attributed to the increase in the number of free mobile ions. The electrical conductivity decreases upon further addition of salt as a result of the formation of neutral ion pairs [12]. The electrical conductivity for the $\text{PEO}-(\text{NH}_4)_2\text{SO}_4$ system with a NH_4^+/EO ratio equal to 0.0416 approaches $10^{-6} \text{ S cm}^{-1}$ [9]. This value is comparable to that found in the present investigation, $2.7 \times 10^{-6} \text{ S cm}^{-1}$ at an NH_4^+/EO ratio of 0.050. Prusinowska et al. [17] obtained an ambient temperature conductivity (290 K) which varied from 3 nS cm^{-1} for $(\text{PEO})_{40}\text{NH}_4\text{SCN}$ to 700 nS cm^{-1} for $(\text{PEO})_{30}\text{NH}_4\text{SCN}$ and $(\text{PEO})_{20}\text{NH}_4\text{SCN}$ electrolytes. Stainer et al. [4] reported an electrical conductivity of between 2 and 6 $\mu\text{S cm}^{-1}$ (ambient temperature) for

Table 3
 Characteristics of $(\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O})/\text{PEO}-(\text{NH}_4)_2\text{SO}_4/(\text{C})$ cells

C ^a	Internal resistance (k Ω)	OCV (mV)	SCC ^b (μA)	Plateau time (h) ($\mu\text{A cm}^{-2}$)	Current density ($\mu\text{A h}$)	Discharge capacity (J kg^{-1})	Specific energy
0.04 g PbO_2	8.9	745	83.7	40	0.454	44.0	84.96
0.02 g PbO_2 + 0.02 g MnO_2	10.9	1059	97.1	30	1.072	78.0	428.5
0.01 g PbO_2 + 0.03 g MnO_2	11.2	599	53.5	37	0.412	37.0	67.27
0.04 MnO_2	10.8	647	59.9	30	0.825	60.0	251.64
0.03 g MnO_2 + 0.01 g V_2O_3	12.9	428	33.2	15	0.495	18.0	47.20
0.04 g V_2O_3	24.8	547	22.1	6	0.392	5.7	13.24
0.02 g V_2O_3 + 0.02 g PbO_2	27.4	467	17.0	7	0.379	6.4	149.2
0.01 g V_2O_3 + 0.01 g PbO_2 + 0.01 g MnO_2	9.8	463	47.2	40	0.412	40.0	85.68

^aC: Cathode active materials.

^bSCC: short circuit current.

PEO–NH₄SCN systems with polymer to salt ratios of 8:1, 5:1, 4:1, and 3:1. They have also reported electrical conductivity in the range 17 to 45 $\mu\text{S cm}^{-1}$ for PEO–NH₄SO₃CF₃ systems. A higher electrical conductivity has been obtained for the NH₄ClO₄ system [6,7]. These results are quite comparable to ours and seem to disprove the hypothesis that the additional protons in (NH₄)₂SO₄ compared with other salts can enhance the electrical conductivity.

The information given in Fig. 5 and Table 2 suggest that the electrolytes obey Arrhenius behaviour in the temperature range studied and that the conductivity occurs by a thermally activated transport process [18]. The sample with the highest conductivity at room temperature does not necessarily have the smallest activation energy. This observation is in reasonable agreement with the findings of other authors [6,8,19] and must be due to the polycrystalline nature of the materials.

For cells with PbO₂ and MnO₂ cathode active materials, the measured OCV is 745 and 647 mV, respectively. Assuming that the cell reactions considered in Table 1

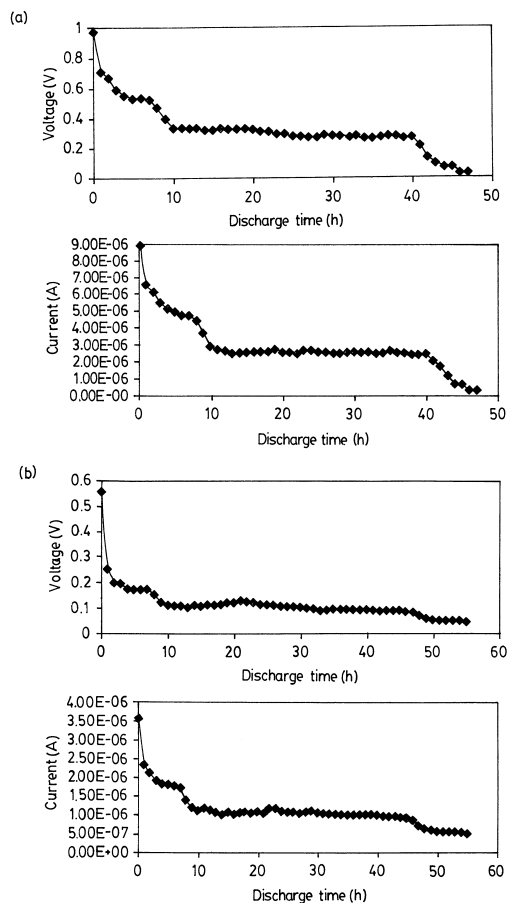


Fig. 6. Discharge characteristics of: (a) (Zn + ZnSO₄·7H₂O)/PEO–(NH₄)₂SO₄/(0.02 g PbO₂ + 0.02 g MnO₂) cell; (b) (Zn + ZnSO₄·7H₂O)/PEO–(NH₄)₂SO₄/(0.01 g PbO₂ + 0.03 g MnO₂) cell; (c) (Zn + ZnSO₄·7H₂O)/PEO–(NH₄)₂SO₄/(0.04 g MnO₂) cell; (d) (Zn + ZnSO₄·7H₂O)/PEO–(NH₄)₂SO₄/(0.03 g MnO₂ + 0.01 g V₂O₅) cell.

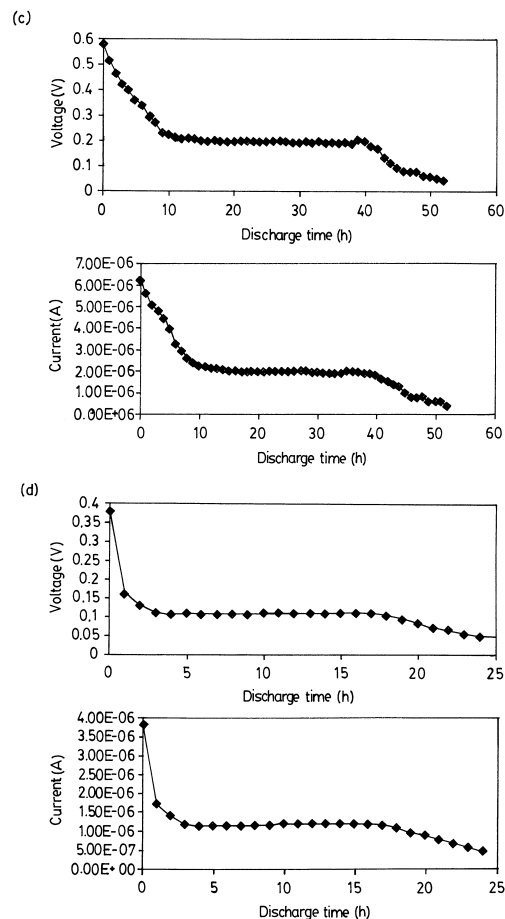


Fig. 6. (continued).

occur, from the emf method [20], the corresponding protonic transference number is estimated to be 0.50 and 0.51. Given the limitation of the emf method, these values are comparable with the protonic transference number of 0.61 obtained by Maurya et al. [9]. This again infers that the use of (NH₄)₂SO₄ does not increase the number of available protons to enhance ionic conductivity in the system. The combination of oxides does not seem to necessarily improve cell performance and the best oxide seems to be PbO₂ followed by MnO₂ and then V₂O₅.

5. Conclusions

PEO–(NH₄)₂SO₄ complexes have been shown to have ionic conductivity. The highest electrical conductivity at room temperature is $2.7 \times 10^{-6} \text{ S cm}^{-1}$ for a film with a NH₄⁺/EO of 0.050. The characteristics of cells fabricated from this film show that (PEO–NH₄)₂SO₄ can be used as an electrolyte in solid-state cells with a mixture of conducting species. PbO₂ and MnO₂ are good cathode materials, but a mixture of oxides does not necessarily improve cell performance.

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