

Characterisation of plasticised PVDF–HFP polymer electrolytes

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This study focuses on the preparation and characterisation of sodium ion conducting polymer electrolytes. Poly(vinylidene fluoride-co-hexafluoropropylene) has been used as the host matrix and hydrated sodium sulphide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) salt as the source of charge carriers in the polymer electrolyte system. To the highest conducting polymer–salt electrolyte, different concentrations of equal weight of propylene carbonate and diethyl carbonate mixture have been added, and the electrolytes have been characterised by X-ray diffraction, Fourier transform infrared spectrometry, scanning electron microscopy and electrochemical impedance spectroscopy. The room temperature ionic conductivity of $1.34 \times 10^{-4} \text{ S cm}^{-1}$ for the unplasticised electrolyte with a composition of 65 wt-% poly(vinylidene fluoride-co-hexafluoropropylene)–35 wt-% Na_2S increased to $3.49 \times 10^{-4} \text{ S cm}^{-1}$ when 30 wt-% propylene carbonate/diethyl carbonate (w/w=1) plasticisers were added.

Keywords: Polymer electrolytes, PVDF–HFP, Ionic conductivity

Introduction

A polymer electrolyte is an ionic conductor containing inorganic salt dissolved in polymer host matrix. The optimum value of the ionic conductivity of a polymer electrolyte is important for its application in electrochemical devices. Many polymer electrolytes have been investigated, and the various polymers used include polyethylene oxide,^{1,2} polyacrylonitrile,^{3,4} poly(methyl methacrylate)^{5,6} and poly(vinylidene fluoride) (PVDF).^{7,8} The addition of plasticiser to the polymer–salt system is one of the approaches to enhancing the ionic conductivity of the polymer electrolyte. In this study, PVDF–hexafluoropropylene (PVDF–HFP), which consists of crystalline vinylidene fluoride and amorphous HFP units, is used as the polymer host in a plasticised polymer electrolyte system. The vinylidene fluoride units provide mechanical stability, and the HFP units provide plasticity properties. With a high dielectric constant value of $\epsilon=8.4$, PVDF–HFP could solvate more salt, contributing towards the electrical conductivity of the polymer electrolyte.⁹ The effect of different amounts of hydrated sodium sulphide, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ salt and different amounts of equal weight ratio of propylene carbonate (PC)/diethyl carbonate (DEC) plasticiser on the polymer host has been investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectrometry (FTIR) and electrochemical impedance spectroscopy (EIS).

Experimental

Materials

Poly(vinylidene fluoride–hexafluoropropylene) of molecular weight 400 000 obtained from Aldrich company was used as received. Hydrated sodium sulphide ($\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$) purchased from Ajax Finechem Chemical was used as the source of the conducting ions. The water content of the salt corresponds approximately to sodium sulphide nonahydrate ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) after the composition was confirmed by XRD.¹⁰ Tetrahydrofuran (THF) from Sigma Aldrich was directly used as solvent without further purification. The PC and DEC from Merck were used as plasticisers without further treatment.

Sample preparation

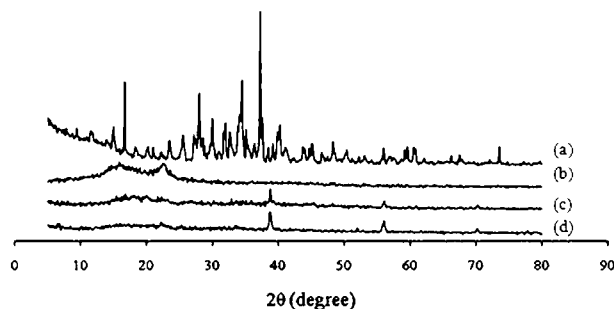
A fixed amount of PVDF–HFP was added to THF and stirred continuously for ~ 2 h at 40°C until the polymer is fully dissolved. Different amounts of $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ salt from 0 to 45 wt-% were added into the polymer solution and vigorously stirred until the solution becomes homogeneous. The polymer–salt solution was then cast onto separate clean glass plates to allow the solvent to evaporate slowly until the polymer–salt films are formed. The mixture of PC and DEC at weight ratio of 1 : 1 respectively was used as plasticiser to prepare the plasticised polymer–salt electrolytes. This mixture ratio of PC/DEC was chosen to compromise for a high dielectric constant and low viscosity plasticiser to enhance the ionic conductivity value.¹¹ Different amounts of the plasticiser from 10 to 40 wt-% were added to the highest conducting sample of polymer–salt electrolyte solution before casting onto separate clean glass plates to produce the best conducting plasticised polymer–salt films. The polymer–salt and plasticised

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1 X-ray diffraction pattern of *a* $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, *b* salt free PVDF–HFP, *c* PVDF–HFP/ Na_2S at 65:35 wt-% ratio and *d* (65:35 wt-%PVDF–HFP/ Na_2S)/(PC/DEC) at 70:30 wt-% ratio

polymer–salt films were characterised using XRD, FTIR, SEM and EIS.

Sample characterisations

X-ray diffraction

A Siemens D5000 X-ray diffractometer with operating voltage and current of 40 kV and 40 mA respectively was used to identify the crystallinity and amorphousness of the samples. X-rays of 1.5406 Å wavelengths were generated by Cu K_α source, and the 2θ angle was varied from 5 to 80°. The salt was also X-rayed, and the diffractogram was compared with Joint Committee on Powder Diffraction Standards data no. 00-003-0745 (D).

Fourier transform infrared spectrometry

The FTIR spectra were collected using an FTIR spectrophotometer (Thermo Scientific/Nicolet iS10) over the range of 650–4000 cm^{-1} . The spectrophotometer resolution was 1 cm^{-1} .

Scanning electron microscopy

To examine the morphology of the samples, a Leica 440 SEM at $\times 5000$ magnification was used.

Electrochemical impedance spectroscopy

The EIS technique was used to determine the highest conducting composition. The impedance of the samples

was measured using a Hioki 3531-01 LCR HiTester interfaced to a computer with frequency ranging from 50 Hz to 1 MHz at room temperature. Each sample was sandwiched between two stainless steel electrodes of diameter 2.0 cm before performing the measurement. To the composition giving the highest conductivity, equal amounts by weight of PC and DEC were added to enhance the conductivity. The conductivity was calculated using the equation

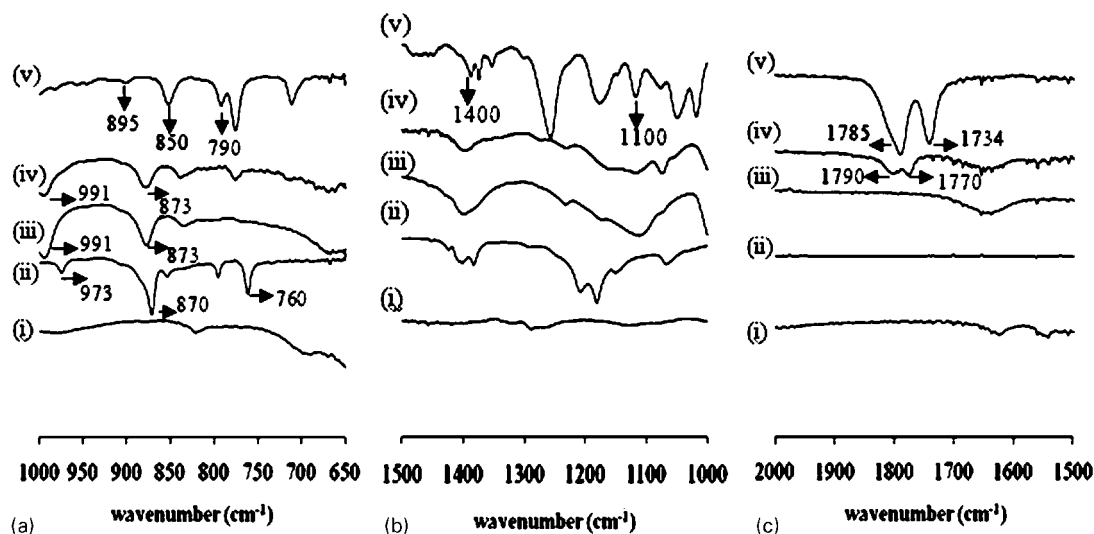
$$\sigma = \frac{l}{R_B A}$$

where R_B is the bulk resistance taken at the intersection of the plot with the real impedance axis, l is the film thickness and A is the surface area of the stainless steel electrode of diameter 2.0 cm.

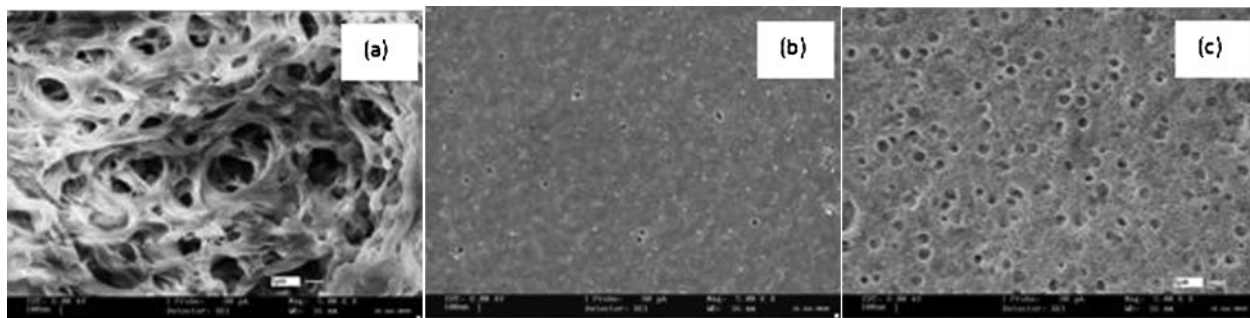
Results and discussion

X-ray diffraction

Figure 1 shows the XRD patterns of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, PVDF–HFP polymer and their complexes with salt and salt/plasticiser respectively. Generally, it is reported that the characteristic diffraction peaks (2θ) of semi-crystalline PVDF–HFP appear in the range between 15 and 40° at $2\theta=18.2$, 19.8, 26.6 and 38.6°, which are assigned as the (100), (020), (110) and (021) planes of crystalline PVDF.¹² However, the diffractogram of the salt free PVDF–HFP membrane in Fig. 1*b* shows only two peaks seen within this range, i.e. a broad peak centred at $2\theta=17^\circ$ and a second peak at $2\theta=22.4^\circ$. Upon addition of hydrated sodium sulphide salt and PC/DEC plasticiser as in Fig. 1*c* and *d* respectively, the two peaks merge with decreased height. This indicates that the sample has become more amorphous and that should enhance ion migration in the electrolyte.¹³ However, for the polymer–salt and plasticised samples in Fig. 1*c* and *d* respectively, three additional peaks are also observed at $2\theta=38.7$, 56.1 and 70°, which are attributed to the salt. This indicates that the polymer is unable to accommodate all the salt added during film formation. The excess salt recrystallised on the surface of the film. Upon comparing with Joint Committee on Powder Diffraction



2 Fourier transform infrared spectrometry spectra of (i) $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, (ii) P(VDF–HFP), (iii) P(VDF–HFP)/ $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, (iv) P(VDF–HFP)/ $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ /(PC/DEC) and (v) (PC/DEC) at different wavenumber, *a* 650–1000 cm^{-1} , *b* 1000–1500 cm^{-1} and *c* 1500–2000 cm^{-1}



3 Image (SEM) of *a* salt free PVDF–HFP, *b* PVDF–HFP/Na₂S at 65:35 wt-% ratio and *c* (65:35 wt-%PVDF–HFP/Na₂S)/(PC/DEC) at 70:30 wt-% ratio

Standards data no. 00-003-0745 (D), it may be deduced from Fig. 1a that the salt is Na₂S.9H₂O.

Fourier transform infrared spectrometry

In order to check the interaction among PVDF–HFP, Na₂S.9H₂O and PC/DEC plasticiser, the FTIR spectra of the samples were investigated. The FTIR results of Na₂S.9H₂O, PVDF–HFP, PVDF–HFP/Na₂S.9H₂O, PVDF–HFP/Na₂S.9H₂O/PC/DEC and PC/DEC respectively are shown in Fig. 2. Upon addition of hydrated sulphide salt and plasticiser to PVDF–HFP, as shown in Fig. 2*a–c*, (iii) and (iv), some peaks shifted and disappeared, and new peaks are observed if compared to pure PVDF–HFP spectra in Fig. 2*a–c*, (ii). For the pure PVDF–HFP spectra in Fig. 2*a* and *b*, (ii), vibrational bands at 760, 870 and 973 cm⁻¹ can be assigned to the α phase crystals of PVDF–HFP, and the 1060 and 1180 cm⁻¹ bands found are assigned to the CF₂ and CF stretching of the vinyl group respectively.^{14,15} The 760 cm⁻¹ band disappears, and 870 and 973 cm⁻¹ shifted to 873 and 991 cm⁻¹ respectively upon addition of salt and plasticiser. Figure 2*a–c*, (v), shows the FTIR spectra for PC/DEC plasticisers. Figure 2*a*, (v), shows that the vibrational bands found at 790, 850 and 895 cm⁻¹ were due to DEC, which represent (–OCOO–) out of plane deformation, CH₂ rocking and CH₂ out of plane skeleton deformation respectively.¹⁴ Figure 2*b*, (v), shows peaks between 1100 and 1400 cm⁻¹, which are assigned to the C–O stretching vibration of PC.¹⁵ For the plasticised polymer electrolytes shown in Fig. 2*a* and *b*, (iv), the peaks observed at 790, 850 and 895 cm⁻¹ and C–O stretching vibration of PC that occurred at 1100–1400 cm⁻¹ completely disappeared.

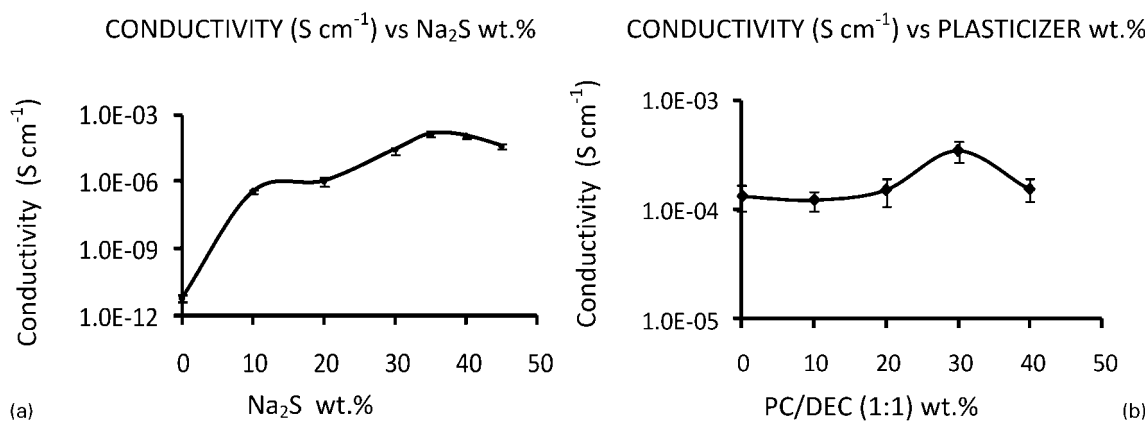
However, the peaks observed at 1734 and 1785 cm⁻¹ diminished and shifted to 1770 and 1790 cm⁻¹, which are assigned to the C=O stretching vibration of DEC.¹⁶ These observations show that polymer–salt plasticiser complexation has occurred.

Scanning electron microscopy

Figure 3 shows the morphology (SEM) of the prepared films for pure polymer (Fig. 3*a*), highest conducting polymer–salt (Fig. 3*b*) and plasticised polymer electrolytes (Fig. 3*c*) respectively. From the results, it can be seen that the addition of salt and plasticiser has changed the structure and size of the pores of pure PVDF–HFP. Figure 3*b* shows that the pore size decreased upon addition of salt in the polymer matrix after the removal of THF, and Fig. 3*c* shows that the size of the pores increases after the addition of plasticiser. In comparison to the polymer–salt system in Fig. 3*b*, the pore size is bigger due to the evaporation of THF and also the removal of PC/DEC after casting. This result suggests that the change in pore size is due to the solvent and plasticiser removal.

Electrochemical impedance spectroscopy

The ionic conductivity of the polymer electrolytes depends on the concentration of conducting species and their mobility.¹⁷ Conductivity variations with salt and plasticiser concentrations at room temperature are illustrated in Fig. 4*a* and *b* respectively. Figure 4*a* shows that in the PVDF–HFP/Na₂S electrolyte, the ionic conductivity initially increases with the salt content until 35 wt-%Na₂S. This is due to the increase in charge carriers or mobile ions when the salt content is



4 Ionic conductivity of *a* PVDF–HFP with various amounts of Na₂S salt and *b* (65 wt-%PVDF–HFP)–(35 wt-% Na₂S) with various amounts of PC/DEC

increased. The maximum value in the conductivity of $1.34 \times 10^{-4} \text{ S cm}^{-1}$ is observed at 35 wt-% salt content. The conductivity gradually decreases thereafter. At high salt concentration, the distance between dissociated ions may become too close to each other; thus, they are able to recombine into neutral ion pairs, which do not contribute to conductivity.¹⁸ Hence, the number density of mobile ions decreases, leading to a drop in conductivity. The mobility of the ions can also decrease at high salt concentrations since the increase in salt concentration will increase the viscosity of the solution before film formation. The addition of up to 30 wt-% PC/DEC plasticiser increased the conductivity threefold to a value of $3.49 \times 10^{-4} \text{ S cm}^{-1}$, as shown in Fig. 4b. The plasticisers were used to promote ion transfer and ion dissociation with respect to dielectric constant and viscosity.¹⁹ The increased ionic conductivity with the concentration of the plasticiser may be due to the lowered viscosity, which can facilitate ionic dissociation and able to dissociate more salt into ions.²⁰ However, the conductivity tends to reduce with further addition of plasticiser after 30 wt-%. The decrease in conductivity for a system that contains a high salt or plasticiser content could be due to the association of ions or a decrease in the mobility of ions.²¹

Conclusions

These studies have shown that a plasticised polymer electrolyte film can be formed from the mixture of PVDF–HFP, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, PC and DEC. The complexation and structure of the polymer–salt plasticiser have been confirmed by FTIR, XRD and SEM. The change in FTIR peaks of PVDF–HFP after the addition of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and PC/DEC mixture shows that the interaction between polymer–salt plasticiser has taken place in the reaction. The crystallinity of PVDF–HFP decreases upon the addition of hydrated sodium sulphide salt and PC/DEC plasticiser, as shown by the XRD result. From the SEM morphology, the porosity of the polymer–salt has been improved after the addition of plasticiser. The plasticised polymer electrolyte with the composition of 45.5 wt-%PVDF–HFP–24.5 wt-% Na_2S –30.0 wt-%PC/DEC (w/w=1) shows the maximum conductivity of $3.49 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature,

which is nearly three times higher than the conductivity of the polymer–salt system without the plasticiser ($1.34 \times 10^{-4} \text{ S cm}^{-1}$).

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