

# Preparation of a Microporous Gel Polymer Electrolyte with a Novel Preferential Polymer Dissolution Process for Li-Ion Batteries

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**ABSTRACT:** A special type of polyacrylonitrile (PAN)-based microporous polymer electrolyte was prepared by the dissolution of poly(vinyl chloride) (PVC) with a novel preferential polymer dissolution process from cast polymer films containing various amounts of PAN and PVC. PVC, dissolved from a 50 : 50 (w/w) PAN/PVC blended polymer film, had a high ionic conductivity of  $5.01 \times 10^{-3}$  S/cm at the ambient temperature when soaked in a 1M solution of LiClO<sub>4</sub> in ethylene carbonate and diethyl carbonate. The amorphosity, surface morphology, and thermal stability of the microporous gel polymer electrolyte were characterized

by X-ray diffraction, scanning electron microscopy, and differential scanning calorimetry studies. Chronoamperometry and linear-sweep voltammetry studies were performed to determine the lithium transference number and stability of the microporous polymer electrolyte membrane, respectively. Finally, a Li-ion polymer cell was assembled with the prepared microporous gel polymer electrolyte, and its compatibility with electrode materials was studied by cyclic voltammetry. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1891–1896, 2005

**Key words:** gels; poly(vinyl chloride); gel

## INTRODUCTION

Polymer electrolytes have been extensively studied in recent years to develop advanced electrochemical storage systems.<sup>1,2</sup> Recently, there has been special interest in improving the ionic conductivity of polymer electrolytes at the ambient temperature because of their unique applications in high-power rechargeable lithium batteries. Among the various types of polymer electrolytes, the gel polymer electrolyte has better ionic conductivity and also maintains good mechanical properties even at room temperature because of the encapsulation of a higher amount of the organic electrolyte in the polymer host. The gel polymer electrolyte is usually prepared by the casting of a mixture of the electrolyte solution and a polymer matrix in a low-boiling-point solvent. This casting process requires a moisture-free environment because of the higher water sensitivity of Li salts. The mechanical properties of cast gel polymer electrolytes are often very poor, and hence the film has to be hardened by either chemical or physical curing. To overcome these difficulties, an activation process has been developed in which a solid polymer film is soaked in the electrolyte solution. In comparison to the solution-casting

process, the activation process requires critical moisture control only during the last activation step. To achieve high ionic conductivity with the activation method, materials with either less entangled polymer chains or high interconnected porosity are required to encapsulate as much electrolyte solution to the polymer host as possible.<sup>3</sup>

Recently, Min et al.<sup>4</sup> prepared a polyacrylonitrile (PAN)-based microporous polymer membrane by immersing a cast film in a pool of excess of deionized water for 6 h to induce phase inversion. The resultant membrane was washed with running water and immersed in a pool of deionized water for 24 h. The membrane was then vacuum-dried at 80°C for 24 h. However, in the polymer membrane, pores were not formed uniformly, and low ionic conductivity ( $2.8 \times 10^{-3}$  S/cm) was exhibited. This process of preparation of polymer membrane is very tedious, and to overcome these drawbacks, in this article a novel preferential polymer extraction process is introduced for the first time to prepare a PAN-based microporous polymer membrane. The resultant polymer membrane was soaked in an electrolyte solution to obtain the microporous gel polymer electrolyte, and then its physical and electrochemical characteristics were also studied.

## EXPERIMENTAL

### Materials

PAN with an average molecular weight greater than 1,00,000 (Aldrich, St. Louis, MO), poly(vinyl chloride)

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(PVC) with an average molecular weight of 99,000 (Aldrich), dimethylformamide (DMF; analar-grade) and tetrahydrofuran (THF; analar-grade; E-Merk, Darmstadt, Germany), and  $\text{LiClO}_4$  (analar-grade) were dried in a vacuum oven at  $100^\circ\text{C}$  under  $10^{-3}$  Torr of pressure for 48 h. Ethylene carbonate (EC; analar-grade) and diethyl carbonate (DEC; analar-grade; Across Organic, Belgium) were used without further purification.

### Preparation of the blended polymer films

Different compositions of PAN and PVC blended polymer films were prepared by the dissolution of a PAN/PVC mixture in the required amounts of DMF. The solution was stirred well and heated continuously at  $60^\circ\text{C}$  for several hours until the mixture became a uniform, homogeneous, and viscous solution. This viscous solution was poured onto a glass plate to form a thin film of the required thickness with a doctor's blade. Finally, the film was dried at  $80^\circ\text{C}$  in a vacuum oven under  $10^{-3}$  Torr of pressure for 5 h to remove any further traces of DMF. The thickness of the formed films was 150–200  $\mu\text{m}$ .

### Preparation of the microporous gel polymer electrolyte

The prepared cast polymer films were immersed in THF to dissolve PVC to get microporous polymer films. Finally, the microporous polymer membranes were activated via soaking in a 1M  $\text{LiClO}_4$  electrolyte solution of EC and DEC [1 : 1 v/v ratio] to get the microporous gel polymer electrolyte.

### Physical characterization

#### X-ray diffraction (XRD) analysis

The XRD patterns were recorded with a JEOL JDX-8030 diffractometer (Tokyo, Japan) with nickel-filtered  $\text{Cu K}\alpha$  radiation at a scanning rate of  $10^\circ/\text{min}$  to examine the nature of the crystallinity with respect to EC, DEC, and  $\text{LiClO}_4$  in the polymer network.

#### Scanning electron microscopy (SEM) analysis

SEM patterns were photographed with a JOEL JSM-35CF scanning electron microscope to examine the surface morphology of the PAN-based polymer film as well as the PAN-based microporous polymer membrane.

#### Thermal analysis

The thermal properties were recorded with a DuPont DSC 2010 analyzer (Gilroy, CA) under an argon atmo-

sphere at a scanning rate of  $10^\circ\text{C}/\text{min}$  to determine the glass-transition temperature ( $T_g$ ) and the thermal stability of the microporous polymer electrolyte membrane.

### Electrochemical characterization

#### Impedance analysis

The alternate current (ac)-impedance measurements were made with an EG & G electrochemical impedance analyzer (TX) in the frequency range of 10 Hz to 100 KHz by the placement of the microporous gel polymer electrolyte between two stainless steel (SS) disc electrodes of a specially designed cell for conductivity measurements.

#### Electrochemical stability studies

The electrochemical stability of the microporous gel polymer electrolyte was studied by linear-sweep voltammetry. A cell arrangement containing SS as the working electrode and lithium as the counter and reference electrodes and the microporous gel polymer electrolyte kept between the electrodes was used for linear-sweep voltammetry studies. The scanning rate of the study was 1 mV/s. The cell was assembled in a dry box under an argon atmosphere.

#### Determination of the lithium transference number

The lithium transference number of the microporous gel polymer electrolyte was determined by chronoamperometry studies. Chronoamperometry studies were conducted by the placement of the microporous gel polymer electrolyte between two symmetrical lithium metal electrodes, and the experiments were carried out as described previously.<sup>5</sup>

#### Cyclic voltammetry studies

Cyclic voltammetry experiments were carried out with an EG & G electrochemical analyzer on carbon/microporous polymer electrolyte membrane/ $\text{LiSr}_{0.25}\text{Mn}_{1.75}\text{O}_4$  cells in the potential range of 3.0–4.8 V versus  $\text{Li}^+$  at a scanning rate of 1 mV/s.

## RESULTS AND DISCUSSION

### XRD studies

Figure 1 shows the XRD patterns of both the PAN-based gel polymer electrolyte and the microporous gel polymer electrolyte with a high-ionic-conductivity composition. The diffraction patterns reveal clearly that the addition of EC and DEC reduces the crystallinity considerably, as shown in Figure 1(a,b). The plasticizer may induce significant disorder in the orig-

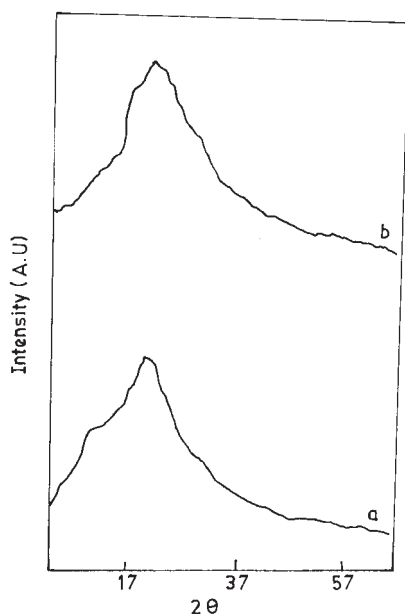
inal polymer structure. This may create an interaction between the polymer and the plasticizer that results in a gel polymer electrolyte with lower crystallinity, as shown in Figure 1(a) by the broad diffraction peak centered at  $2\theta = 20.07^\circ$ . For the microporous gel polymer electrolyte, the degree of crystallinity is much lower than that for the gel polymer electrolyte, which is shown in Figure 1(b). This is manifested in the broad diffraction peak centered at  $2\theta = 21.62^\circ$ . Hence, the uptake of the electrolyte solution by the microporous polymer membrane is somewhat higher than that of the solid polymer film.

### SEM studies

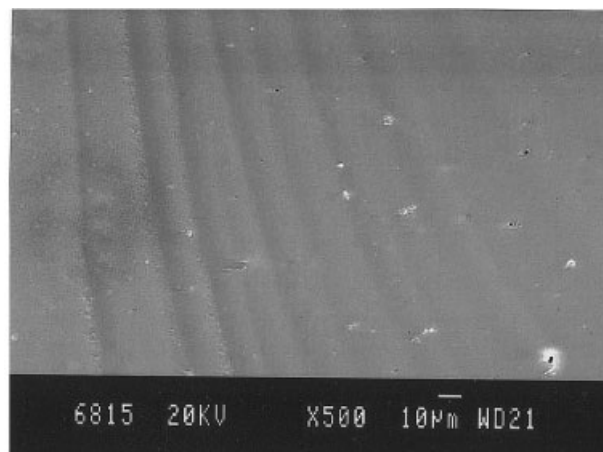
SEM micrographs of the PAN-based polymer film and microporous polymer membrane are shown in Figure 2(a,b). Figure 2(a) shows that the PAN-based solid polymer film has no pores or voids. However, for the microporous polymer membrane, large voids and cavities of almost uniform size can be observed in Figure 2(b). Hence, the uptake of the electrolyte solution by the microporous polymer membrane is higher than that of the conventional polymer film.

### Thermal studies

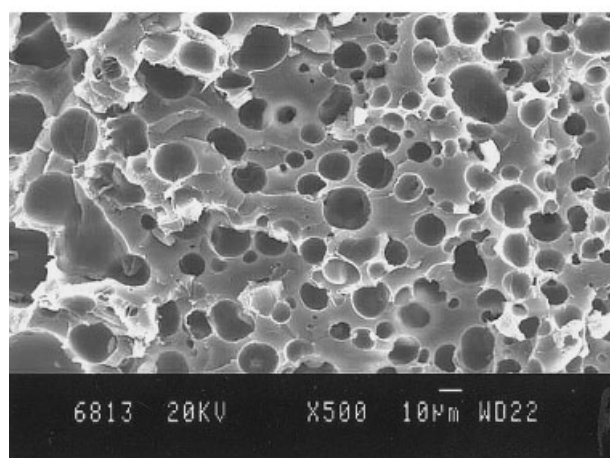
Figure 3(a,b) shows the differential scanning calorimetry (DSC) curves for both the PAN-based gel polymer electrolyte and the microporous gel polymer electrolyte. In the gel polymer electrolyte, the  $T_g$  peak can be observed at  $126.34^\circ\text{C}$ , followed by one endothermic peak and two exothermic peaks at  $152.17$ ,  $253.06$ , and



**Figure 1** XRD patterns for (a) the PAN-based gel polymer electrolyte and (b) the microporous gel polymer electrolyte.



(a)

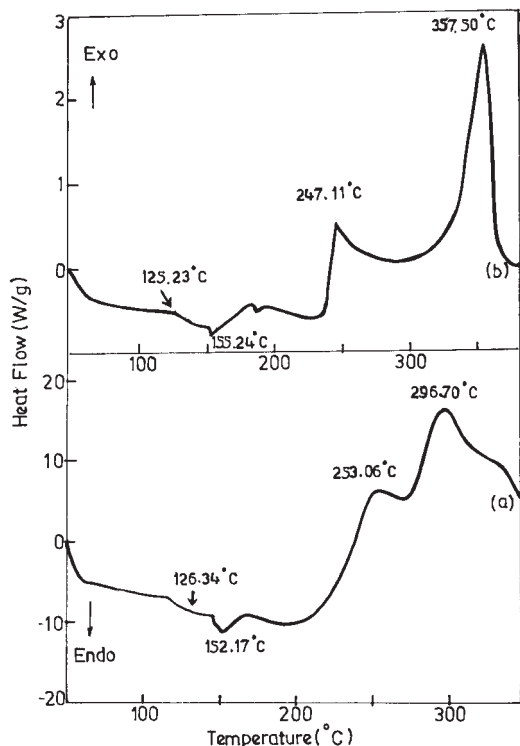


(b)

**Figure 2** SEM photograph views of (a) the PAN-based polymer film and (b) the microporous polymer membrane.

$296.70^\circ\text{C}$ , respectively. The endothermic peak at  $253^\circ\text{C}$  with no appreciable weight loss indicates the predecomposition of the polymer. The second exothermic peak at  $296.70^\circ\text{C}$  indicates the decomposition of the gel polymer electrolyte, and its corresponding weight loss is 14.2%. From this result, it can be concluded that the gel polymer electrolyte film is thermally stable up to  $253^\circ\text{C}$ .

However, in the case of the microporous gel polymer electrolyte [Fig. 3(b)], the  $T_g$  peak can be observed at  $125.23^\circ\text{C}$ , followed by one endothermic peak and two exothermic peaks at  $155.24$ ,  $247.11$ , and  $357.50^\circ\text{C}$ , respectively. The endothermic peak at  $155.24^\circ\text{C}$  indicates the melting of the microporous gel polymer electrolyte. The first exothermic peak at  $247.11^\circ\text{C}$  with no appreciable weight loss indicates the predecomposition of the polymer. The second exothermic peak at



**Figure 3** DSC curves for (a) the PAN-based gel polymer electrolyte and (b) the microporous gel polymer electrolyte.

357.50°C indicates the decomposition of the microporous gel polymer electrolyte, and its corresponding weight loss is 20.4%. From this, it can be concluded that the microporous gel polymer electrolyte is thermally stable up to 247.11°C.

The microporous gel polymer electrolyte has a lower  $T_g$  value than the gel polymer electrolyte with an increase in the absorbed electrolyte concentration, and this signifies that the flexibility of the polymer chain increases with an increase in the absorbed electrolyte concentration in the polymer system because of the effect of the decrease in the intramolecular and intermolecular coordination sites on the same and different polymer chains by the ions acting as transient crosslinks.<sup>6</sup>

### Conductivity studies

The ionic conductivity values of the PAN-based gel polymer electrolyte and microporous gel polymer electrolyte are given in Table I. The microporous gel polymer electrolyte obtained by the removal of PVC from a 50 : 50 (w/w) PAN/PVC blended polymer film has a higher ionic conductivity of  $5.01 \times 10^{-3}$  S/cm at room temperature than all other microporous gel polymer electrolytes besides the PAN-based conventional gel polymer electrolyte. This is due to the higher uptake of the electrolyte solution by the microporous gel polymer electrolyte (50 : 50) in comparison with all other microporous gel polymer electrolytes obtained from PAN/

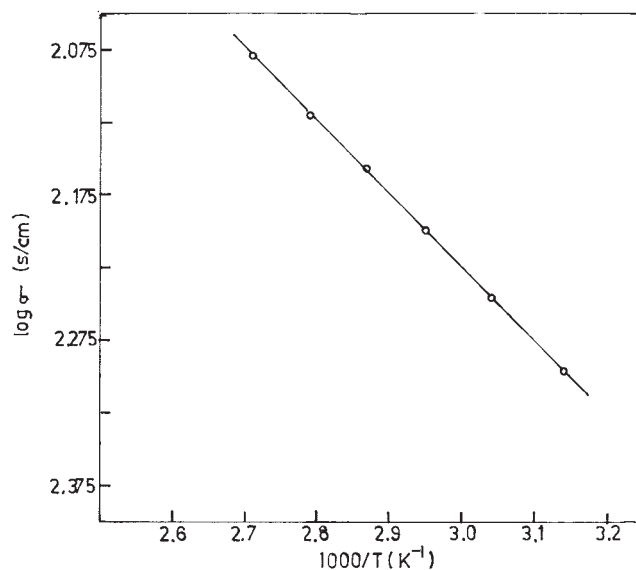
**TABLE I**  
Conductivity Data of the Gel and Microporous Gel Polymer Electrolyte at Room Temperature

No.	PAN (%)	PVC (%)	Conductivity (S/cm)
1	100	0	$3.92 \times 10^{-3}$
2	90	10	$4.20 \times 10^{-3}$
3	80	20	$4.38 \times 10^{-3}$
4	70	30	$4.79 \times 10^{-3}$
5	60	40	$4.93 \times 10^{-3}$
6	50	50	$5.01 \times 10^{-3}$

PVC blended polymer films of various percentages.<sup>7</sup> To examine the temperature dependence of the ionic conductivity of the polymer electrolyte, the conductivity measurements were performed at different temperatures in the range of 318–368 K for the microporous gel polymer electrolyte of higher ionic conductivity, as shown in Figure 4. It obeys the Arrhenius plot of conductivity and also seems to obey the Vogel Tamman Fulcher (VTF) relation. The completely amorphous nature of this polymer electrolyte facilitates the fast Li-ion motion in the polymer network and further provides a higher free volume with increasing temperature.<sup>8</sup> This leads to an inverse in the ionic mobility and also segmental mobility that will assist ion transport and virtually compensate the retarding effect of the ion clouds.

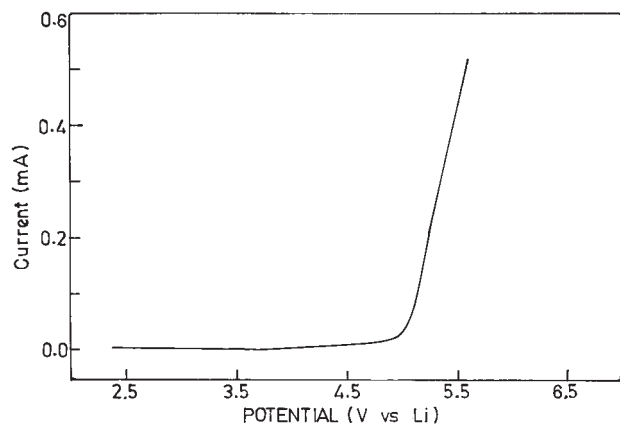
### Electrochemical stability

The electrochemical stability of the microporous gel polymer electrolyte was studied by linear-sweep voltammetry, and its corresponding voltammogram is



**Figure 4** Arrhenius plot for the microporous gel polymer electrolyte with a high-ionic-conductivity system.



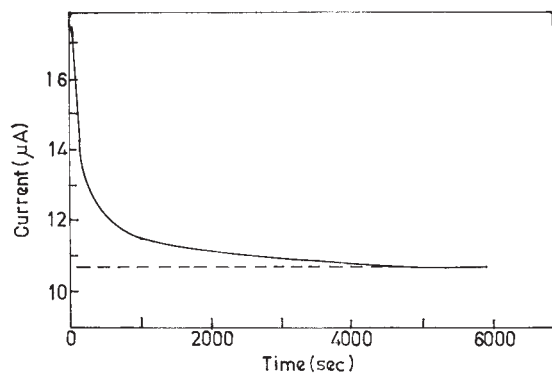


**Figure 5** Linear-sweep voltammogram of the cell prepared for the microporous gel polymer electrolyte.

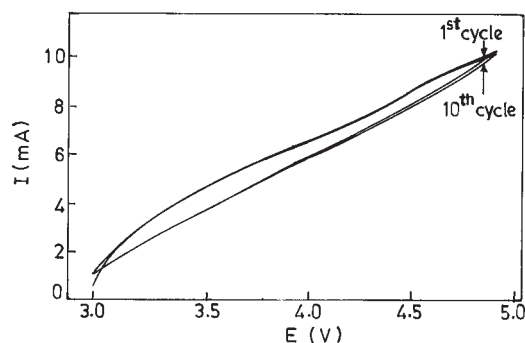
shown in Figure 5. It can be concluded from the voltammogram that the decomposition voltage of the microporous gel polymer electrolyte is around 5.0 V versus Li.

#### Lithium transference number

Figure 6 shows the depolarization curve of the microporous gel polymer electrolyte of high ionic conductivity. The current is  $17.40 \mu\text{A}$  initially and reaches a steady-state value of  $10.78 \mu\text{A}$  within about 1.27 h. This relaxation time is fast in comparison with that of the PAN-based gel polymer electrolyte,<sup>9</sup> which normally needs several hours to attain the steady state. Theoretically, this phenomenon implies that the ionic mobility of the microporous gel polymer electrolyte is more facile than that of conventional gel polymer electrolytes. In addition, there is no obvious difference in the impedance spectra of the test cell just before and after the direct-current (dc) polarization studies. In other words, the interfacial resistances caused by the formation of a new passive film and the bulk resistance did not change significantly during the dc polarization, which may be due to the unique



**Figure 6** Depolarization curve of the microporous gel polymer electrolyte.



**Figure 7** Cyclic voltammogram of the carbon/microporous gel polymer electrolyte/ $\text{LiSr}_{0.25}\text{Mn}_{1.75}\text{O}_4$  cell at a sweep rate of  $1 \text{ mV/s}$ .

stability of the passive film formation. Hence, the lithium transference number of the microporous gel polymer electrolyte is about 0.62.

In fact, the transference number obtained by this study is substantially higher than those in the literature.<sup>10–13</sup> Besides, the microstructure of the polymer membrane, which provides a more liquid pathway, is probably a positive factor leading to superior ionic transport as well.

#### Cyclic voltammetry studies

The cyclic voltammogram of the carbon/microporous gel polymer electrolyte/ $\text{LiSr}_{0.25}\text{Mn}_{1.75}\text{O}_4$  cell at room temperature is given in Figure 7. It can be concluded from the cyclic voltammogram that the microporous gel polymer electrolyte has very good reversibility and electrochemically stability up to 5 V.

#### CONCLUSIONS

1. It is possible to prepare a PAN-based microporous gel polymer electrolyte by a preferential polymer extraction process by the extraction of one of the polymers from a blended polymer film.
2. A maximum ionic conductivity of  $5.01 \times 10^{-3} \text{ S/cm}$  can be observed when the microporous gel polymer electrolyte is prepared by the removal of PVC from a 50 : 50 (w/w) PAN/PVC blended polymer film.
3. The microporous gel polymer electrolyte has high thermal stability up to  $247.11^\circ\text{C}$ , even when a large amount of a liquid electrolyte is impregnated into it.
4. The dependence of the ionic conductivity on the temperature is linear on a logarithmic scale. It obeys an Arrhenius plot of conductivity and also obeys the VTF relation.
5. The lithium transference number of the microporous gel polymer electrolyte is 0.62. This im-

plies that the ionic mobility of the microporous gel polymer electrolyte is more facile than that of the conventional gel polymer electrolyte. For this reason, the microporous gel polymer electrolyte can be used as a polymer electrolyte for Li-ion battery applications.

6. The linear-sweep and cyclic voltammogram studies have revealed that the microporous gel polymer electrolyte has very good electrochemical stability up to 5 V and very good reversibility.

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