Ionic liquid entrapment by an electrospun polymer nanofiber matrix as a high conductivity polymer electrolyte


Through external doping, novel conductive polymer nanofibers were successfully fabricated using ionic liquids. In this study, a polymer blend of polyvinyl alcohol (PVA) and chitosan (CS) in a 4 : 1 weight ratio was fabricated in the form of nanofibers through electrospinning and used as a scaffold membrane to capture room-temperature ionic liquids (RTILs), such as 1-ethyl-3-methylimidazolium chloride (EMIMCl) and 1-butyl-3-methylimidazolium bromide (BMIMBr). Morphological analysis using scanning electron microscopy (SEM) showed that the scaffold structure of the electrospun membrane facilitated sufficient trapping of RTILs. This membrane demonstrated significantly increased conductivity from 6 × 10⁻⁶ S cm⁻¹ to 0.10 S cm⁻¹, interestingly surpassing the value of pure ionic liquids, where the polymer chain breathing model has been suggested as a hypothesis to explain this phenomena. The dominance of ions as charge carriers was explained using an ionic transference number measurement. The interaction between the polymer nanofiber matrix and an ionic liquid has been explained using Fourier-transform infrared spectroscopy (FTIR), where the ionic liquid was found to be physically dispersed in the polymer nanofiber matrix. These materials have also shown some thermoelectric (TE) activity, by demonstrating Seebeck coefficients up to 17.92 μV K⁻¹. The existence of freely movable ions in this type of membrane shows their applications as energy storage/conversion devices such as organic thermoelectrics (TEs), sensors, and dye-sensitised solar cells.

1. Introduction

The electrospinning technique is an efficient and popular technique to fabricate polymer nanofibrous materials with a high surface-to-volume ratio, controllable composition and high porosity for a wide range of applications. The electrospun polymer nanofibers have smaller pores and a higher surface area than regular fibers. This technique provides a small particle size distribution, which helps to achieve a better contact between the electrode and the electrolyte and decreases the ion diffusion distance. To date, electrospun polymer nanofibers have been successfully investigated in tissue engineering, filtration, nanocatalysis, biomedical applications, pharmaceutical applications, protective clothing, and environmental engineering. However, very few reports have been found that target their applications in energy storage/conversion and generation. Some studies have reported the increased conductivity of electrospun polymer nanofibers. For example, Chronakis et al. reported an electrical conductivity value of 1.2 × 10⁻⁵ S cm⁻¹ for a electrospun polypyrrole-poly(ethylene oxide) nanofibrous membrane, and a conductivity value of 7.7 × 10⁻⁵ S cm⁻¹ for electrospun hybrid nanofibers of amphiphilic salts was reported by Zhou et al., which showed a great promise to obtain enhanced conductivity in electrospun polymer nanofibers. The fabrication of the nanofibrous scaffold from a variety of natural and synthetic polymers, in particular biopolymers, have attracted considerable attention in sustainable energy production not only because their abundance in nature, but also due to their outstanding biocompatibility and biodegradability; resulting in their widespread use in electrospinning.

Chitosan (CS), the N-deacetylated derivative of chitin, has received attention due to its promising prospects in industrial applications. The molecular structure of CS is illustrated in Fig. 1. CS is a natural polymer; therefore, it has been a good replacement for the role of synthetic polymers in many polymer industries.
The free amino and hydroxyl groups on its backbone provide the opportunity to tune the properties of CS via organic reactions. It possesses excellent properties such as high charge carrier density, biodegradability, non-toxicity, film and fiber forming, cross-linking, and bonding ability with heavy metals. Therefore, it has been a leading candidate material in many areas of applications such as energy storage/conversion, biomedical applications, wastewater treatment and industrial applications.

Polyvinyl alcohol (PVA) is a naturally non-toxic and water-soluble synthetic polymer. Its biocompatibility, high fibre-forming ability, chemical and thermal stability, and other desirable properties make it ideal for industrial applications. In particular, PVA facilitates blending with various synthetic and biopolymers due to its highly hydrophilic nature. Importantly, the bio-inertness of PVA determines its extensive use in implantable medical devices.26–28 The free amino and hydroxyl groups on its backbone provide the opportunity to tune the properties of CS via organic reactions. It possesses excellent properties such as high charge carrier density, biodegradability, non-toxicity, film and fiber forming, cross-linking, and bonding ability with heavy metals. Therefore, it has been a leading candidate material in many areas of applications such as energy storage/conversion, biomedical applications, wastewater treatment and industrial applications.

Ionic liquids (ILs) are organic salts that offer substantial promise in chemical processing and related industries due to their unique physical and chemical properties. ILs are essentially found in the liquid state at room temperature and exhibit high ionic conductivity and extremely low volatility, which make them ideal for device applications.22–25 Fig. 1 presents the molecular structure of PVA.

In general, polymer membranes formed by the blending of polymers exhibit improved mechanical and physical properties compared with membranes fabricated from individual materials.21 In this study, a novel method was used, where a blend polymer solution of PVA and CS was fabricated in the form of nanofibers through electrospinning. The electrospun polymer membrane was found to act as a scaffold for trapping the room-temperature ionic liquids (RTILs) which are the conducting host molecules such as 1-ethyl-3-methylimidazolium chloride (EMIMCl) (Fig. 1c) and 1-butyl-3-methylimidazolium bromide (BMIMBr) (Fig. 1d), and thus successfully demonstrated significantly increased conductivity with promising Seebeck coefficients. Furthermore, charge transport was investigated through ionic transference number measurements. The participation of the PVA/CS/RTIL functional groups in the system was explained using Fourier-transform infrared (FTIR) spectroscopy, and the morphology was investigated using scanning electron microscopy (SEM).

2. Experimental

2.1. Materials and methods

2.1.1. Fabrication of PVA:CS blends. First, 7 wt% CS was dissolved in a 90% acetic acid solution in distilled water. On the other hand, 8 wt% PVA was dissolved in distilled water. Finally, PVA : CS at a weight ratio of 4 : 1 was prepared as a polymer blend solution by stirring for 2 h.26

2.1.2. Electrospinning parameters. The polymer blend solution was enclosed in a 10 mL plastic syringe. An electrically grounded aluminium (Al) plate wrapped with Al foil was used as the collector. Table 1 lists the parameters used to fabricate the PVA:CS nanofibers.

2.1.3. Preparation of ionic liquid solutions. Electrolyte solutions were prepared to improve the electrical conduction of the PVA:CS electrospun polymer membranes. Molar concentrations of 1 mol L−1 and 2 mol L−1 of the imidazolium substituted RTILs were prepared separately using distilled water as the solvent in every set. The solutions were stirred for 1 h at room temperature (25 °C) to ensure complete dissolution of the RTILs.

2.1.4. Preparation of the PVA:CS nanofiber-scaffolded ionic liquid membrane. The nanofiber-scaffolded thin polymer membrane of PVA:CS fabricated via electrospinning was immersed in the RTIL solutions individually for 24 h to ensure the adequate trapping of RTILs. After immersion, the polymer membranes adhered to glass substrates were stored with silica gel in a Petri dish for 5 days inside a dry cabinet under 40 °C/30% humidity conditions for drying.

2.2. Characterization

2.2.1. Morphological properties. The membrane thicknesses were measured using a KLA TencorP-6 stylus profiler, which is a contact-type measurement technique. The morphological analysis of the nanofiber-scaffolded thin polymer

Fig. 1 Molecular structures of (a) CS, (b) PVA, (c) EMIMCl, and (d) BMIMBr.
membrane of PVA:CS was conducted using an FEI scanning electron microscope (SEM) in a low-vacuum mode.

2.2.2. Electrical properties. The electrical properties of the nanofiber-scaffolded thin polymer membranes of PVA:CS immersed in the RTILs were investigated using the four-point probe technique. In the four-point probe method, separate pairs of current-carrying and voltage-sensing electrodes eliminate the impedance contribution of the wiring and contact resistances, yielding more accurate results for thin films. The following equation was used to calculate the conductivity:

\[
\sigma = \frac{1}{4.5324 \times R_s \times t} \text{ S cm}^{-1}
\]

where \(R_s\) = sheet resistance (measured by the four-point probe), \(t\) = thickness (measured by profilometer) and 4.5324 = correction factor.

2.2.3. Ionic transference number measurement. GAMRY four-point probe equipment was used to measure the ionic transference number of the samples. In this case, a DC polarization method was applied to observe the DC current as a function of time by applying a fixed DC voltage across the sample. The fixed DC voltage was supplied through the tungsten carbide probes of the four-point probe equipment. Table 2 lists the parameters used during the measurement. Similar parameters were applied to all the samples to identify the accurate ionic contribution under constant conditions.

2.2.4. Seebeck coefficient measurement. The Seebeck coefficient measurement was carried out using an Ozawa Science RZ2000i Instrument. Fig. 2 presents a schematic of the experimental layout. The measurements were carried out under a 5 \(\times\) 10^{-5} Torr vacuum. The sample was wound with a Pt wire and mounted horizontally on an electrode for the measurements. Probe leads were connected to the sample using silver paint for improved contact. To generate a temperature gradient, one electrode was heated using a furnace and another was cooled by supplying cold air inside a double-walled quartz tube attached to the electrode. The temperature gradient was established by controlling the flow rate of cold air. The Seebeck coefficients were measured using the Pt wires of the thermocouple through a digital multimeter featuring the measurement resistance in the range of 1 \(\Omega\) to 100 \(\Omega\). The Seebeck coefficients were measured using the ratio between the voltage difference generated and the temperature difference between the hot and cold terminals. For thermopower measurements, the steady-state direct current method was used. For conductivity measurements, the two-probe method was applied, in which a DC current was passed through the sample using one side of the thermocouples attached to Pt electrodes and the corresponding voltage between the contact points of Pt wires was measured. By varying the current from \(-1\) to 1 \(\mu\)A, the voltage was measured repeatedly. Using a linear current–voltage curve, the resistance was determined, and the Seebeck coefficient was evaluated from the linear temperature gradient–voltage data. Point data having a linearity over 90% were taken into account as the most reliable points. The measured resistances of the sample were 62 \(\pm\) 2 k\(\Omega\). Throughout the experiment, the temperatures at the hot and cold terminals were measured using a Pt wire thermocouple.

2.2.5. Fourier-transform infrared (FTIR) spectroscopy measurement. FTIR spectroscopy was used to analyse the chain interactions between the electrospun films and RTILs through the identification of absorption bands related to the vibrations of functional groups present in PVA, CS, EMIMCl and BMIMBr. A Perkin Elmer Spectrum 400 FTIR spectrometer was used to obtain the FTIR spectra with 1 cm^{-1} resolution in transmission mode in the wavenumber range of 450–4000 cm^{-1}.

**Table 1** Electrospinning parameters used to fabricate the PVA:CS nanofibers

<table>
<thead>
<tr>
<th>Wt% (PVA : CS)</th>
<th>Applied voltage (kV)</th>
<th>Tip-to-collector distance (cm)</th>
<th>Feed rate (mL h^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 : 1</td>
<td>7</td>
<td>10</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Table 2** The parameters applied to characterize ionic transference number of electrospun PVA:CS membrane immersed in EMIMCl and BMIMBr

<table>
<thead>
<tr>
<th>DC voltage</th>
<th>Time frame (s)</th>
<th>Maximum current limit (mA)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0–1000</td>
<td>20</td>
<td>303</td>
</tr>
</tbody>
</table>

![Fig. 2](image-url)  
Fig. 2 Schematic diagram of the Seebeck coefficient measurement experiment (adapted from the layout of the Ozawa Science RZ2000i manual).
3. Results and discussion

3.1. Morphological properties

Fig. 3 presents the SEM image of the electrospun PVA:CS membrane before immersing in RTILs. The microscopic image of the electrospun PVA:CS membrane shows that the diameters of the nanofibers are in the range of 250–500 nm. The scaffolded matrix of the polymer nanofibers provides high porosity/vacant space compared with gel or casted polymer membranes, which facilitates the sufficient trapping of RTILs and more frequent movements of ions. This leads to the enhanced conductivity. Therefore, the conductivity of the electrospun PVA:CS membrane was observed to increase from 6 × 10⁻⁶ S cm⁻¹ to 0.10 S cm⁻¹ after immersion in RTILs (details are reported in Table 3).

3.2. Conductivity measurement

The conductivity data obtained for the electrospun PVA:CS membrane immersed in RTILs are listed in Table 3. The conductivity was observed to increase with an increasing molar concentration of RTILs. The maximum conductivity of 0.10 S cm⁻¹ was achieved for the electrospun PVA:CS membrane immersed in 2 mol L⁻¹ EMIMCl. The most interesting observation in this study was the maximum electrical conductivity, which surpassed those of the corresponding pure RTILs. For instance, the conductivity of pure RTIL BMIMBr is 5.0 × 10⁻⁸ S cm⁻¹ (ref. 29) compared with the value of 4.32 × 10⁻⁷ S cm⁻¹ for the PVA:CS membrane immersed in 2 mol L⁻¹ BMIMBr, representing an increase in the conductivity beyond that of the pure RTIL. A possible explanation of this observation is the “breathing polymeric chain model”, in which the inherent folding and unfolding of the polymer chains induce fluctuations on a microscopic level inside the polymer matrix, which generates greater ionic motion than in the pure RTILs. In addition, the breathing in and out of the polymer chains constantly breaks the ion pairs, which induces more free charge carriers in the scaffolded matrix of the polymer nanofibers; thus, resulting in a significantly increased conductivity. When the concentration of the ILs was increased to more than 2 mol L⁻¹, there was the challenge of adequately drying the membrane. The hygroscopic nature of the ILs trapped the water molecules at high concentrations, thus causing high viscosity. Therefore, it was resolved that 2 mol L⁻¹ is the optimum concentration for the membrane.

3.3. Transference number analysis

The transference numbers corresponding to ionic (t_ion) and electronic (t_ele) transports were calculated for the electrospun PVA:CS membrane immersed in 2 mol L⁻¹ EMIMCl and BMIMBr, respectively, because they exhibited a higher conductivity compared with the other combinations. The transference numbers were calculated from the polarization current versus time plot. In this case the following equations were used:

\[ t_{ion} = \frac{(I_f - I_i)}{I_i} \]

and

\[ t_{ele} = 1 - t_{ion} \]

where, \( I_i \) = initial current, \( I_f \) = final current, and \( t_{ion} \) = ionic transference number. The transference numbers of ions \( t_{ion} \) for all the samples lies between 0.65 and 0.70, which in other words proves that \( t_{ion} > t_{ele} \) for the electrospun PVA:CS membrane immersed in RTILs. These results suggest that the charge transport in this system is dominated by ions. Table 4 lists the ionic transference numbers calculated for all the samples studied. Fig. 4 and 5 demonstrate the polarization current versus time plots of the electrospun PVA:CS membrane immersed in the RTILs EMIMCl and BMIMBr, respectively.

<table>
<thead>
<tr>
<th>RTIL</th>
<th>Thickness in 1 mol L⁻¹ (µm)</th>
<th>Thickness in 2 mol L⁻¹ (µm)</th>
<th>Conductivity in 1 mol L⁻¹ (S cm⁻¹)</th>
<th>Conductivity in 2 mol L⁻¹ (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIMCl</td>
<td>12.91</td>
<td>13.90</td>
<td>5.50 × 10⁻²</td>
<td>1.02 × 10⁻¹</td>
</tr>
<tr>
<td>BMIMBr</td>
<td>8.28</td>
<td>9.14</td>
<td>4.20 × 10⁻²</td>
<td>4.32 × 10⁻²</td>
</tr>
</tbody>
</table>

Fig. 3 SEM image of the electrospun PVA:CS nanofibers.
3.4. Thermoelectric potential of the electrospun ionic liquid membrane

In polymers, doping is an important means to yield high conductivity, and thus a higher optimized Seebeck coefficient. A significant advantage of doping is the conformation of the conducting host molecules, which consequently modify the carrier transport properties in the polymer matrix. For the Seebeck coefficient measurement, the PVA:CS membrane immersed in 2 mol L\(^{-1}\) EMIMCl was considered because it exhibits the maximum conductivity compared with other combinations, as reported in Table 3. The Seebeck coefficients were measured in the temperature range of 298 K to 318 K because polymer thermoelectric materials are usually targeted for the low temperature applications. A maximum Seebeck coefficient of 17.92 \(\mu\)V K\(^{-1}\) was obtained at 300.7 K with an average of 14.9 \(\mu\)V K\(^{-1}\). All the Seebeck coefficients were observed to be negative. The negative values of the Seebeck coefficients are thought to be due to the fact that the ionic liquid dissociates into cations and anions in the PVA:CS nanofiber scaffolded matrix, where the anions (Cl\(^-\)) are expected to have a higher mobility than the cations (C\(_6\)H\(_{11}\)N\(_2\)\(^+\)). This is in turn is thought to be due to the lower mass of the (Cl\(^-\)) ions, and thus the negatively charged anions act as the majority charge carriers, resulting in a negative Seebeck coefficient. However, for the practical implementation as a thermoelectric generator, a redox couple has to be incorporated with the RTILs to allow charge transfer from the electrospun membrane to the electrode and vice versa. Fig. 6 presents the Seebeck coefficient as a function of temperature.

3.5. FTIR analysis

In this study, extensive FTIR analysis has been carried out with all possible variations. Because both PVA and CS polymers are capable of forming hydrogen bonds, it is expected that some identical interactions could occur between the different molecular groups. The FTIR spectra of pure PVA, CS, and electrospun PVA:CS are shown in Fig. 7a. The FTIR spectra of electrospun PVA:CS and electrospun PVA:CS immersed in EMIMCl and BMIMBr are shown in Fig. 7b and c, respectively. For pure PVA, the stretching and bending of the hydroxyl (–OH) groups are observed at approximately 3300 cm\(^{-1}\) and 1377 cm\(^{-1}\), respectively. An asymmetric stretching vibration was noted at approximately 2945 cm\(^{-1}\), which represents the methylene group (CH\(_2\)). The band at approximately 1100 cm\(^{-1}\)

### Table 4 Transference number data for the electrospun PVA:CS membrane immersed in the RTILs EMIMCl and BMIMBr

<table>
<thead>
<tr>
<th>RTIL</th>
<th>Initial current (A)</th>
<th>Final current (A)</th>
<th>Ionic transference number</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIMCl</td>
<td>6.55 (\times) 10(^{-7})</td>
<td>1.92 (\times) 10(^{-7})</td>
<td>0.70</td>
</tr>
<tr>
<td>BMIMBr</td>
<td>1.07 (\times) 10(^{-5})</td>
<td>3.75 (\times) 10(^{-6})</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Fig. 4 DC polarization current versus time plots for the PVA:CS membrane immersed in 2 mol L\(^{-1}\) EMIMCl.

Fig. 5 DC polarization current versus time plots for the PVA:CS membrane immersed in 2 mol L\(^{-1}\) BMIMBr.

Fig. 6 Seebeck coefficients for the PVA:CS membrane immersed in 2 mol L\(^{-1}\) EMIMCl.
signifies C–O stretching and the band at approximately 1740 cm\(^{-1}\) corresponds to the C=O stretching of the acetyl groups that exist on the PVA backbone.\(^{38-41}\) In the spectra of pure CS, the saccharide structures, which are regarded as the main characteristic bands, were observed at approximately 1035 cm\(^{-1}\) and 1150 cm\(^{-1}\). Weaker amino group bands were observed at approximately 1250 cm\(^{-1}\). Strong characteristic amino bands were observed at approximately 3400 cm\(^{-1}\), 1672 cm\(^{-1}\), and 1595 cm\(^{-1}\), which correspond to –OH stretching, amide I, and amide II bands, respectively.\(^{18,21}\)

In the spectra of electrospun PVA:CS membrane, the absorption peak at 1250 cm\(^{-1}\) was absent, unlike in the FTIR spectra of pure CS. Furthermore, the bands at approximately 1028 cm\(^{-1}\) and 1093 cm\(^{-1}\) represent a primary amine and –OH group with polymeric association, which indicate the hydrogen bond conformation between the two polymers (PVA and CS) in the electrospun PVA:CS membrane.\(^{20,21}\) For pure EMIMCl, the peak at 3050 cm\(^{-1}\) was assigned to the asymmetric –CH\(_3\) group attached to the imidazolium ring. The peak at 2974 was assigned to the asymmetric stretching of the aliphatic –CH\(_2\) group and that at 2866 cm\(^{-1}\) was attributed to the symmetric stretching of the –CH\(_2\) group.\(^{43}\) A broad peak in the range of 3500–3250 cm\(^{-1}\) is due to the quaternary amine salt formation with a chlorine ion. Peaks at 1664 and 1330 cm\(^{-1}\) are due to C=C and C=N stretching, respectively.\(^{43}\) For pure BMIMBr, the peaks at 3082 cm\(^{-1}\) is represented by the asymmetric –CH\(_3\) group attached to the imidazolium ring. The aliphatic –CH\(_2\) and –CH\(_2\) groups resonated at 2961 and 2869 cm\(^{-1}\), respectively. A broad peak at 3600–3300 cm\(^{-1}\) represents the formation of the quaternary amine salt with a bromide ion. In addition, the EMIM\(^{+}\) cation was observed to be dominated by a strong isolated band at 1164 cm\(^{-1}\), whereas the band at 1170 cm\(^{-1}\) represents the BMIM\(^{+}\) cation.\(^{44-46}\) In the spectra of the electrospun PVA:CS immersed in EMIMCl and BMIMBr, we observed no specific chemical bonding between the polymer scaffolded nanofiber matrix and RTIL. The RTILs were physically dispersed in the polymer scaffold nanofiber matrix\(^{47}\) for the case of the PVA:CS nanofiber scaffolded membrane immersed in RTILs.

4. Conclusions

A novel approach to generate electrically conductive electrospun polymer membrane has been presented in this study. The following are the key findings of this approach:

- The electrospun polymer membrane was found to act as a scaffold for trapping the RTILs; thus, successfully enhancing the conductivity up to 0.10 S cm\(^{-1}\).
- The maximum electrical conductivities achieved through this method were found to surpass those of the corresponding pure RTILs, which is thought to be due to the folding and unfolding of the polymer chains.
- The ionic transference number results suggest that the charge transport in this system is dominated by ions.
- The FTIR results showed that the RTILs are physically dispersed in the polymer nanofiber matrix.
- By achieving a Seebeck coefficient of up to 17.92 µV K\(^{-1}\), the presented method shows potential as a polymer-based TE material, implying its feasibility for use in low-temperature/ flexible applications.

The advantage of this approach is that it provides a simple fabrication technique that may be used as a starting concept to produce highly electrically conductive polymers, which might
also be of use as materials for other energy conversion devices such as dye-sensitized solar cells and sensors.

Acknowledgements

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