Porous PVDF/PANI ion-exchange membrane (IEM) modified by polyvinylpyrrolidone (PVP) and lithium chloride in the application of membrane capacitive deionisation (MCDI)

Yiming Zhang, Wei Zhang and Luis F. Cházaro-Ruiz

ABSTRACT

In this work, polyvinylidene fluoride (PVDF)/polyaniline (PANI) heterogeneous anion-exchange membranes filled with pore-forming agents polyvinylpyrrolidone (PVP) and lithium chloride were prepared by the solution-casting technique using the solvent 1-methyl-2-pyrrolidone (NMP) and a two-step phase inversion procedure. Key properties of the as-prepared membranes, such as hydrophilicity, water content, ion exchange capacity, fixed ion concentration, conductivity and transport number were examined and compared between membranes in different conditions. The pore-forming hydrophilic additives PVP and lithium chloride to the casting solution appeared to improve the ion-exchange membranes (IEMs) by increasing the conductivity, transport number and hydrophilicity. The effects of increasing membrane drying time on the porosity of the as-prepared membranes were found to lower membrane porosity by reducing membrane water content. However, pore-forming agents were found to be able to stabilise membrane transport number with different drying times. As-prepared PVDF/PANI anion-exchange membrane with pore-forming agent is demonstrated to be a more efficient candidate for water purification (e.g. desalination) and other industrial applications.

INTRODUCTION

Since the first commercial cation exchange membrane developed by DuPont in 1970s, ion exchange membrane (IEM) has been utilised in a diversified range of areas, including separation and purification (Kumar et al. 2012), sensors (Castillo et al. 2002), energy conversion devices (Seo et al. 2013), desalination (Klayson et al. 2013), fuel cells (Peighambardoust et al. 2010), food processing (Bazinet et al. 1998), the drug industry (Tarvainen et al. 2013), the chemical process industry (Strathmann et al. 2013), biotechnology (Pourcelly & Bazinet 2009) and wastewater treatment (Rana et al. 2013) etc. Among those applications, IEM has recently been proved to be critical in improving the performance of capacitive deionisation (CDI) (Li et al. 2011; Mossad et al. 2013; Zhang et al. 2013; Jia et al. 2014; Jia & Zhang 2016), and considered to be an advantageous alternative to a number of traditional desalination technologies such as reverse osmosis (Qi et al. 2006), multiple-effect distillation and multi-stage flash vapour-compression distillation (Sen et al. 2011), electrodialysis (ED) (Fidaleo & Moresi 2013), electrodialysis reversal (Valero & Arbós 2010), and forward osmosis (Zhao et al. 2012).

IEMs can be classified into cation exchange membrane, anion exchange membrane, amphoteric IEM, bipolar IEM and mosaic IEM, based on the species and charge of fixed functional groups in the membranes (Sata 2004). In order to prepare various desired IEMs for different industrial processes and applications, a number of synthetic IEMs have been developed since the first synthetic IEM fabricated in 1920s (Sata 2004). Not only has the preparation of IEMs been extensively investigated in the last five decades (Vogel & Meier-Haack 2014), for example the membranes can be prepared by ion-exchangeable materials and binder blending (Hosseini et al. 2014a), polymerisation of monomers (Clark et al. 2009) and grafting of monomer on a
polymeric film etc. (Merle et al. 2011), but also the properties of IEMs have been significantly improved (Xu 2005; Nagarale et al. 2006). However, the drawbacks, such as high resistance and poor hydrophilicity, are still frequently encountered in some niche applications, especially CDI. Polyaniline (PANI) as a conducting polymer may present a viable solution for improving the conductivity and hydrophilicity of IEM (Hosseini et al. 2014b). Moreover, PANI possesses amino groups, which can increase the selectivity for different types of counter-ions (Nagarale et al. 2004).

In this study, polyvinylidene fluoride (PVDF) mixed with PANI was used to fabricate anion exchange membranes with the aim of improving membrane conductivity and hydrophilicity. PVDF, as one of the most popular membrane materials, has been studied widely due to its high mechanical strength and thermal stability (Liu et al. 2014). In addition, numerous strategies have been developed to obtain porous materials. The routes to making pores, including nanosized ones, can generally be divided into two groups: bottom-up and top-down. Pores generated by a bottom-up method are featured for their connectivity, i.e. the pores form a continuous phase and are uniformly distributed throughout the material matrix. In the top-down process, some parts or components of a solid substrate are selectively removed, leaving pores in the substrate. The top-down method is superior for its versatility of pore structure and ease of tuning the pore dimensions. There is a constant demand to obtain porous materials using a simple process that is highly efficient and of low cost (Wang and Li 2011). Recently, a new strategy was developed to obtain porous materials by using different block copolymers or polymers such as polyanilinopyrroldione (PVP). The pore-forming mechanism is based on a physical phenomenon that involves no chemical reactions. It is a relatively simple method: one needs only to immerse the materials which contain the polymer in a certain solvent for hours (sometimes less), and then remove them and evaporate the solvent to obtain the porous materials with ordered pore systems. This confined swelling-induced pore-making process has emerged recently as a new strategy to produce porous materials due to synergic advantages that include extreme simplicity, high pore regularity, no chemical reactions, no weight loss, reversibility of the pore-forming process etc.

Here we present a simple and efficient route for the synthesis of porous PVDF/PANI films using lithium chloride (LiCl) as pore-forming agent. LiCl is highly soluble in polar solvents, and so it can be uniformly mixed with the PVP solution. Another important aspect is that no chemical bond is formed between the LiCl and PVDF/PANI.

In addition, LiCl highly soluble in water and therefore very easy to remove from the films by dipping into water, thereby leaving pores in the films, as demonstrated by Pradhan et al. (2002) and Niyogi & Adhikari (2002) for the preparation of separation membranes. The pore-forming agents, PVP and LiCl, were added to the casting solutions to enable membranes with higher permeate flux and reduce macro-void formation (Fontananova et al. 2006).

**EXPERIMENT**

**Materials preparation**

All the chemicals in this work were applied as received. Aniline hydrochloride, ammonium persulphate, 1-methyl-2-pyrrolidone (NMP), LiCl and PVP (MW = 10,000) were supplied by Sigma-Aldrich (Sydney, Australia). Silver nitrate solution (0.01 M) and potassium chromate solution (5%) were purchased from Rowe Scientific (Adelaide, Australia). PANI was prepared by oxidative reaction of ammonium persulphate and aniline hydrochloride (Stejskal & Gilbert 2002): aniline hydrochloride (0.4 mol) was first dissolved in 500 ml hydrochloric acid, and then 0.5 mol ammonium persulphate was added while stirring at 5 °C and for 1 hour. After the reaction, the precipitate was filtered and collected. It was washed three times with 0.1 M HCl to obtain the PANI in emeraldine salt form. The wet powder was dried at room temperature for one week. The chemical structures of PANI in both forms are presented in Figure 1.

**Figure 1 | Chemical structure of monomers and polymers.**
Membrane fabrication

Figure 2 illustrates the step-by-step fabrication of the PANI/PVDF heterogeneous anion-exchange membranes in this work. First, PVDF powders were sieved to the desired mesh size and dissolved in NMP at room temperature for one week. Next, as-prepared PANI powders mixed with PVP and LiCl powders were dispersed in the PVDF/NMP solution. This suspension for casting membranes was mixed by a mechanical stirrer for about 2 hours at room temperature to obtain a uniform suspension and then given 15 min ultrasonication. Then a suitable amount of mixture was cast onto a clean, dry glass plate at room temperature; the assembly was then dried in a vacuum oven at 55 °C for a suitable time. The resulting membrane on the plate was immersed in 50 °C deionised water, where the solvent residues in the membrane were washed out. Finally, the membrane was immersed in 0.1 M HCl for 24 hours, followed by immersion in 0.5 M NaCl for 24 hours. Before testing, the membrane was thoroughly rinsed with water.

The membrane thickness was determined in the dry state using a digital calliper device. The basic physical parameters, compositions, ratios, oven drying time and membrane thickness of PANI/PVDF are presented in Table 1. The prepared membranes were named with letters and numbers: DP represents PVDF and PANI; TP stands for PVDF, PANI and PVP; L is for LiCl and the numbers are for the drying time (hours) in a vacuum oven.

Membrane characterisation

The morphology of the membranes was observed by scanning electron microscopy (SEM). The cross-section of the membrane was obtained by fracturing it in liquid nitrogen and then drying it at room temperature before imaging.

The surface wetting characteristics of the prepared membranes were investigated by measuring the dynamic contact angle between the water and the membrane surface using a contact-angle analyser (DataPhysics OCA-200 Contact angle analyser, Filderstadt, Germany). This measurement is usually applied for evaluating the hydrophilicity of the membrane surface. The results of the dynamic contact angle measurements were obtained by analysing the recorded videos (side view) where the drops on membrane surfaces were taken constantly until they disappeared. All experiments were carried out at a room temperature of approximately 20 °C and a humidity of 33% (Zhang et al. 2018).

The water content was calculated as the difference between the wet and dry membranes. The membranes were immersed in deionised water for 48 hours, water on the membrane surfaces was wiped off, and then the membranes were immediately weighed using a digital balance (Mettler Toledo). Subsequently, the membranes were dried in a vacuum oven at 45 °C for 24 hours until the weight of the membranes was constant. The dry membranes were then weighed again and the water content was calculated by the following equation (Li et al. 2005):

\[
\text{Water content \%} = \left(\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}}\right) \times 100 \quad (1)
\]

Table 1 | Basic physical parameters of PANI/PVDF membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>PVDF:NMP (w:w)</th>
<th>LiCl:PVDF (w:w)</th>
<th>PVP:PVDF (w:w)</th>
<th>PANI:PVDF (w:w)</th>
<th>Casting thickness (mm)</th>
<th>Membrane thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP5</td>
<td>17:83</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.187</td>
<td>0.526</td>
</tr>
<tr>
<td>TPL5</td>
<td>1:3</td>
<td>1:2</td>
<td>–</td>
<td>20:80</td>
<td>0.1</td>
<td>0.254</td>
</tr>
<tr>
<td>TPL10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.237</td>
</tr>
<tr>
<td>TPL48</td>
<td></td>
<td></td>
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</table>
where $W_{wet}$ and $W_{dry}$ represent the weight of the wet membranes and the weight after the membranes were dried in a vacuum oven, respectively.

The ion exchange capacity (IEC) was determined by titration. First, the membranes were submerged in 1 M HCl solution for 24 hours to convert PANI in the form of emeraldine base to emeraldine salt and then washed with water to remove residual HCl from the membranes surfaces. Secondly, the membranes were placed in 2 M NaCl solution for 48 hours, then the NaCl was washed out with enough deionised water. Third, the membranes were immersed in 2 M NaNO₃ solution for 48 hours to release the $\text{Cl}^-/\text{Na}^+$ from the membranes and then washed three times with deionised water. Fourth, the solution with $\text{Cl}^-$ was titrated with 0.01 M AgNO₃ standard solution and K₂CrO₄ indicator, so that the amount of AgNO₃, $\alpha$ (mequiv), could then be obtained. Finally, the membrane was wiped with absorbing paper and dried in a vacuum oven at 45°C for 24 hours until a constant weight (W, g) was reached. The IEC was calculated as follows (Hong 2011):

$$\text{IEC} = \left( \frac{\alpha}{W} \right)$$

The fixed ion concentration (FIC) was calculated by the following formula:

$$\text{FIC} = \left( \frac{\text{IEC}}{\text{water content}} \right)$$

Each surface of an anion-exchange membrane was in contact with solutions of different concentrations, and the electrical potential across the membrane could be observed. The magnitude of this potential depends on the electrical properties of the membranes and the concentration and nature of the electrolyte solutions (Hosseini et al. 2014a). The membrane potential is the algebraic sum of the Donnan and diffusion potentials, determined by the mobility of ions in the membrane phase and the electrolyte phase (Nagarale et al. 2004). The parameter transport number was calculated by measuring the membrane potential using a two-cell apparatus, in which a vertically positioned membrane separated two solutions of 0.5 M NaCl and 1 M NaCl. The potential difference across the membrane ($E_{\text{measure}}$) was measured by a BioLogic-VSP potentiostat connected to Ag/AgCl reference electrodes. This membrane potential was expressed by the following Nernst equation (Hosseini et al. 2010a, 2010b, 2014b):

$$E_{\text{measure}} = (2t^n_{\text{m}} - 1) \left( \frac{RT}{nF} \right) \ln \left( \frac{\alpha_1}{\alpha_2} \right)$$

where $t^n_{\text{m}}$ stands for the transport number of counter-ions in the membrane phase, $R$ represents the gas constant, $T$ is for the temperature, $n$ is the electrovalence of counter-ion, and $\alpha_1$ and $\alpha_2$ are the activities of the NaCl solutions.

The membrane conductivity was measured in 0.5 M NaCl solution at 25°C using electrical impedance spectroscopy in a three-electrode cell, and is closely related to electrical energy consumption. To obtain the membrane conductivity, titanium and platinum were used as the working electrode and counter electrode; Ag/AgCl as the reference electrode was positioned close to the membrane surface. A BioLogic-VSP potentiostat over a frequency range from 1 Hz to 1 MHz was applied to test the membrane resistance directly. The resistance of the cell with the membrane was measured ($R_1$) and the membrane was then removed to get the cell resistance ($R_2$). So the membrane electrical resistance ($R_m$) can be calculated as follows: $R_m = R_1 - R_2$ (Klaysom et al. 2011). Based on the electrical resistance measurements, through-plane conductivity ($\sigma$, S cm⁻¹) can be calculated from the following equation:

$$\sigma = \frac{L}{R_m A}$$

where $L$ is the thickness of the membrane (cm) and $A$ is the effective area of the membrane (cm²).

**Desalination experiment**

To study the desalination capacity of prepared membranes in CDI, a pair of RGO electrodes with a total mass of 1.8 g were used in the experiment with an external power supply through a CDI cell unit and different feeding solutions. The membrane capacitive deionisation (MCDI) unit cell was made of two RGO electrodes separated by a non-conductive spacer that prevents an electrical short and allows the feed solution to flow. The electrodes were connected to the two sides of the DC power supply using connecting leads. Two silicon sheets of 1 mm thickness lay between the outer sides of the
current collectors and the 10 mm thick Plexiglass plate to act as seals. An electrical voltage of 1.2 V was applied to the two electrodes, while total dissolved solids of the initial NaCl concentration 50 mg/L (108 μS/cm) were recorded every minute by a conductive meter at a constant flow of 25 ml/min at 25 °C. Therefore, salt removal efficiency (η) and sorption capacity (qe, mg/g) of the electrodes with or without prepared membranes can be calculated as follows:

$$\eta = \frac{C_0 - C_f}{C_0} \times 100\% \quad (6)$$

$$q_e = \frac{(C_0 - C_f)V}{W} \quad (7)$$

where C₀ and Cᵢ are the initial and final concentrations of the NaCl solution, V is the volume of the NaCl solution and W is the mass of electrodes.

RESULTS AND DISCUSSION

Effects of pore-forming agents

The hydrophilic pore-forming agents, PVP and LiCl, added to the casting solution can reduce macro-void formation, which can be explained by thermodynamic and kinetic relations (Fontananova et al. 2006). As a result, photographic images of prepared membranes in Figure 3 show that the surface of the membrane prepared from cast solutions filled with PVP and LiCl was smoother than those prepared from casting solutions without PVP and LiCl. Furthermore, SEM images in Figure 3 show membranes prepared with pore-forming agents (i.e. TPL5, 10, and 48) can provide a more uniform structure and higher porosity which should lead to improved transport number, conductivity and water content. Compositional and structural properties, water content, IEC, FIC, conductivity and

Figure 3 | Photographs of as-prepared membranes with and without pore-forming agents (DP5 and TPL10); cross-sectional SEM images showing pore size of as-prepared membranes (DP5, TPL5, TPL10 and TPL20) at lower and higher magnifications.
transport number of all the fabricated membranes with or without pore-forming agent are summarised in Table 2, where SEM porosity for the samples was calculated from processed SEM images. The following discussion used TPL5 and DP5 membranes as examples for comparison since they were prepared under the same conditions except for the addition of pore-forming agent in the casting solution. It is evidenced that sample TPL5 possessed higher conductivity, transport number and water content than DP5. It is well known that membrane structures play a critical role in membrane properties, such as membrane conductivity, selectivity and transport number. In this work, TPL5 possessed higher porosity than DP5, even though DP5 was more macroporous, as shown in Figure 3. TPL5 with higher porosities can provide more and bigger ion channels for counter and co-ion transportation (Klaysom et al. 2014), which together with its higher water content could account for its improved conductivity and increased transport number. However, it could be at the expense of lowered selectivity and loose structure of the membrane (Hosseini et al. 2014b). On the other hand, FIC was found to decrease with the increase of the porosity and water content of the membrane, while the IEC of the membranes were insignificantly affected by adding PVP and LiCl to the casting solution.

The interfacial force between a liquid and a solid surface can be studied by the dynamic contact angle. As shown in Figure 3, TPL5 with higher porosities can provide more and bigger ion channels for counter and co-ion transportation (Klaysom et al. 2011), which together with its higher water content could account for its improved conductivity and increased transport number. However, it could be at the expense of lowered selectivity and loose structure of the membrane (Hosseini et al. 2014b). On the other hand, FIC was found to decrease with the increase of the porosity and water content of the membrane, while the IEC of the membranes were insignificantly affected by adding PVP and LiCl to the casting solution.

Table 2 | The properties of as-prepared membranes

<table>
<thead>
<tr>
<th></th>
<th>DP5</th>
<th>TPL5</th>
<th>TPL10</th>
<th>TPL48</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water content (%)</td>
<td>40.0 ± 5.7</td>
<td>111.3 ± 8.1</td>
<td>82.8 ± 0.6</td>
<td>79.4 ± 1.2</td>
</tr>
<tr>
<td>IEC (mequiv/g)</td>
<td>0.51 ± 0.04</td>
<td>0.38 ± 0.01</td>
<td>0.33 ± 0.01</td>
<td>0.37 ± 0.02</td>
</tr>
<tr>
<td>FIC (mequiv/g water)</td>
<td>1.28</td>
<td>0.35</td>
<td>0.40</td>
<td>0.47</td>
</tr>
<tr>
<td>σ (mS/cm)</td>
<td>1.616</td>
<td>9.31</td>
<td>1.07</td>
<td>1.09</td>
</tr>
<tr>
<td>t\textsuperscript{th}</td>
<td>0.792</td>
<td>0.842</td>
<td>0.844</td>
<td>0.840</td>
</tr>
<tr>
<td>SEM porosity (%)</td>
<td>42.1</td>
<td>60.2</td>
<td>35.6</td>
<td>38.44</td>
</tr>
<tr>
<td>Surface porosity (cm\textsuperscript{2}/g)</td>
<td>1.69 × 10\textsuperscript{-3}</td>
<td>1.72 × 10\textsuperscript{-2}</td>
<td>6.90 × 10\textsuperscript{-3}</td>
<td>3.91 × 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Sorption capacity (mg/g)</td>
<td>1.21</td>
<td>1.51</td>
<td>1.49</td>
<td>1.46</td>
</tr>
<tr>
<td>Salt removal efficiency (%)</td>
<td>71.46</td>
<td>89.33</td>
<td>88.21</td>
<td>87.08</td>
</tr>
</tbody>
</table>

Figure 4 | Dynamic contact angle variations of different as-prepared membranes.

Effects of drying time in the phase inversion

Various properties of the prepared IEMs with different drying times (i.e. TPL5, TPL10 and TPL48) are shown in Table 2. It is noteworthy that prolonged oven drying time appeared to keep membrane transport number constant under different conditions, reduce water content and conductivity, and increase FIC. The transport numbers was unaffected significantly by different drying time in this work, probably because the pore-forming agent in the casting solution played a critical role in stabilising the formation of the membrane ion pathway and thus the transport number (Fontananova et al. 2006). Lowered membrane porosity with the increase in oven drying time at phase inversion was most likely to be responsible for reduced membrane water content and conductivity. As previously mentioned, higher porosity can provide a more interconnecting pore structure which can in turn enhance contact angle values at any time and the droplet on the surface of sample DP5 taking much longer to disappear.
membrane water content and conductivity (Klaysia et al. 2011). The FIC of a membrane is generally determined by its IEC and water content. In this research, FIC increased with increasing drying time because the IEC of three samples (i.e. TPL5, TPL10 and TPL48) was similar but the membrane water content decreased with increasing drying time. In general, lower FIC can worsen the pathway of counter-ion transportation in the matrix of a membrane and reduce the ionic selectivity (Hosseini et al. 2014a, 2014b).

In addition, among all the samples prepared with pore-forming agents, TPL5 featured a smaller contact angle than TPL10 and TPL48. This was probably due to the higher water content of TPL5, which made its surface more hydrophilic.

**Desalination performance in the application of CDI**

In Figure 5, Sample 1 was the result of graphene electrode CDI testing without ion exchange membranes, while Sample 2 represented the testing with an anion exchange membrane (AMH-PES, Ralex®) and a cation exchange membrane (CMH-PES, Ralex®). DP5, TPL5, TPL10 and TPL48 were tested with prepared anion exchange membranes and a cation exchange membrane (CMH-PES, Ralex®). As shown, the desalting performance of graphene electrode based MCDI with ion exchange membranes are compared with the CDI tested without any membranes under the same condition, which proved that using MCDI can lead to much better salt removal efficiency and sorption capacity. Comparing all the prepared membrane applied in MCDI, the desalting performance of the membranes fabricated with pore-forming agent improved measurably. In addition, this improvement was not affected significantly by the drying time in oven during the phase inversion.

**CONCLUSION**

We have showcased a modified solution-casting preparation of PVDF/PANI heterogeneous anion-exchange membranes filled with the pore-forming agents PVP and lithium chloride using the solvent NMP and a two-step phase inversion procedure. As-prepared anion-exchange membranes in different conditions were compared using key properties, such as hydrophilicity, water content, IEC, FIC, conductivity and transport number. Adding the pore-forming hydrophilic PVP and lithium chloride to the casting solution played a critical role in the improvement of IEM conductivity, transport number and hydrophilicity. Thermal phase inversion was proven to be a crucial step to control membrane porosity and pore size. By increasing membrane drying time in the vacuum oven at a constant temperature, membrane porosity was found to be lowered due to the reduction of membrane water content. In general, IEMs with higher water content can exhibit higher conductivity, but at the expense of transport number and mechanical stability. It was also experimentally evidenced that pore-forming agents can stabilise the transport number at different drying times. To sum up, as-prepared PVDF/PANI anion-exchange membranes filled with pore-forming agent possessed excellent salt removal efficiency and sorption capacity, which can help fabricate more efficient IEMs for water purification (e.g. desalination) and other industrial applications.

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