

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.

Key words | ion-exchange membranes, membrane capacitive deionisation, PANI, PVDF, water purification

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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 (Klaysom *et al.* 2013), fuel cells (Peighambardoust *et al.* 2010), food processing (Bazinnet *et al.* 1998), the drug industry (Tarvainen *et al.* 1999), 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.* 2011). 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 polyvinylpyrrolidone (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).

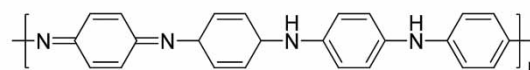
EXPERIMENT

Materials preparation

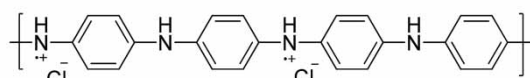
All the chemicals in this work were applied as received. Aniline hydrochloride, ammonium persulphate, 1-methyl-2-pyrrolidone (NMP), LiCl and PVP (MW = 10,000) were supplied by Sigma-Aldrich (Sydney, Australia). Silver nitrate solution (0.01 M) and potassium chromate solution (5%) were purchased from 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.



Poly(vinylidene fluoride) (PVDF) Aniline hydrochloride



PANI (emeraldine base)



PANI (emeraldine salt)

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.

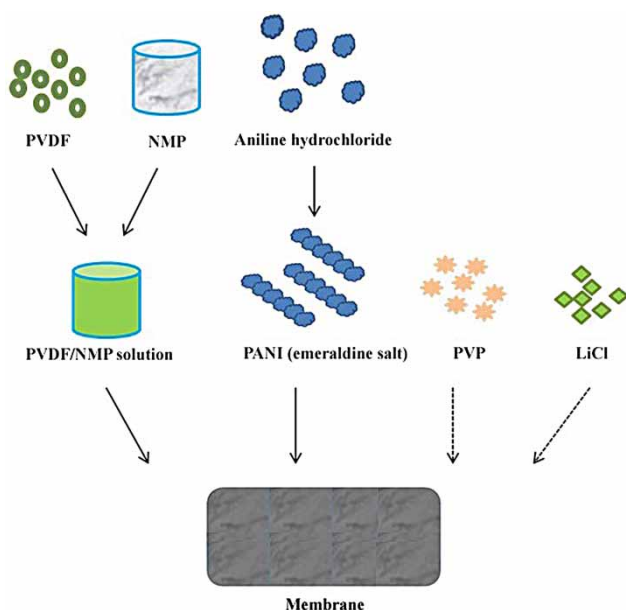


Figure 2 | The procedure for membrane fabrication in this work.

Table 1 | Basic physical parameters of PANI/PVDF membranes

Membrane	PVDF:NMP (w:w)	LiCl:PVDF (w:w)	PVP:PVDF (w:w)	PANI:PVDF (w:w)	Casting thickness (mm)	Membrane thickness (mm)
DP5		–	–			0.187
TPL5	17:83			20:80	0.1	0.326
TPL10		1:3	1:2			0.254
TPL48						0.237

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. 2015).

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):

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

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 Cl⁻ from the membranes and then washed three times with deionised water. Fourth, the solution with Cl⁻ was titrated with 0.01 M AgNO₃ standard solution and K₂CrO₄ indicator, so that the amount of AgNO₃, a (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):

$$IEC = \left(\frac{a}{W} \right) \quad (2)$$

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

$$FIC = \left(\frac{IEC}{\text{water content}} \right) \quad (3)$$

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_{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):

$$E_{\text{measure}} = (2t_i^m - 1) \left(\frac{RT}{nF} \right) \ln \left(\frac{a_1}{a_2} \right) \quad (4)$$

where t_i^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 a_1 and a_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 (σ , S·cm⁻¹) can be calculated from the following equation:

$$\sigma = \frac{L}{R_m A} \quad (5)$$

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 μ S/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 (q_e , 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 C_0 and C_f 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

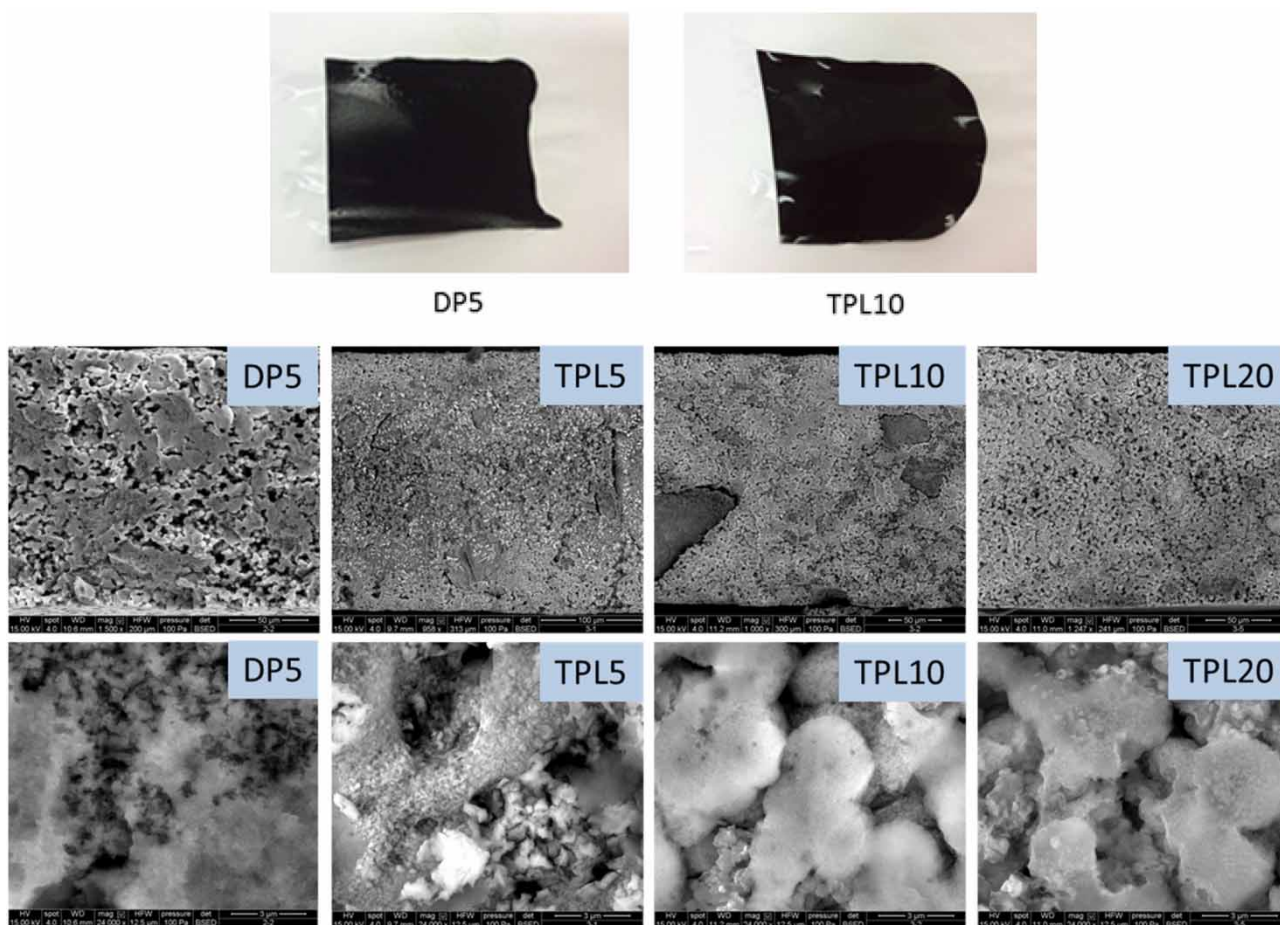


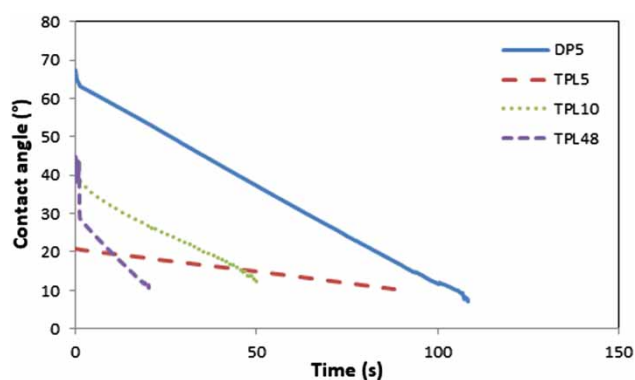
Figure 3 | Photographs of as-prepared membranes with and without pore-forming agents (DP5 and TPL10); cross-sectional SEM images showing pore size of as-prepared membranes (DP5, TPL5, TPL10 and TPL20) at lower and higher magnifications.

Table 2 | The properties of as-prepared membranes

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

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. 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.

The interfacial force between a liquid and a solid surface can be studied by the dynamic contact angle. As shown in Figure 4, it was clear that all the membranes prepared by the two-step method with or without pore-forming agents were hydrophilic because the droplet on the membrane surface decreased over time until its disappearance. Furthermore, membranes prepared with pore-forming agents (i.e. TPL5, TPL10 and TPL48) possessed even more improved hydrophilicity compared with the one without pore-forming agents (i.e. DP5), which were evidenced by their constantly smaller

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

contact angle values at any time and the droplet on the surface of sample DP5 taking much longer to disappear.

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

membrane water content and conductivity (Klaysom *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.

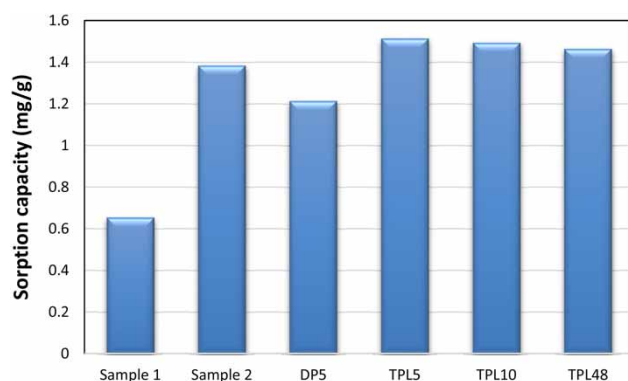


Figure 5 | Salt sorption capacity of CDI testing with and without IEM.

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.

ACKNOWLEDGEMENT

The authors acknowledge the scholarship and financial support received from the University of South Australia.

REFERENCES

- Bazinet, L., Lamarche, F. & Ippersiel, D. 1998 Bipolar-membrane electro dialysis: applications of electro dialysis in the food industry. *Trends in Food Science & Technology* **9**, 107–113.
- Castillo, E., Granados, M. & Cortina, J. L. 2002 Chemically facilitated chromium (VI) transport throughout an anion-exchange membrane: application to an optical sensor for chromium (VI) monitoring. *Journal of Chromatography A* **963**, 205–211.
- Clark, T. J., Robertson, N. J., Kostalik IV, H. A., Lobkovsky, E. B., Mutolo, P. F., Abruña, H. D. & Coates, G. W. 2009 A ring-opening metathesis polymerization route to alkaline anion exchange membranes: development of hydroxide-conducting thin films from an ammonium-functionalized

- monomer. *Journal of the American Chemical Society* **131**, 12888–12889.
- Fidaleo, M. & Moresi, M. 2013 Concentration of trisodium citrate by electrodialysis. *Journal of Membrane Science* **447**, 376–386.
- Fontananova, E., Jansen, J. C., Cristiano, A., Curcio, E. & Drioli, E. 2006 Effect of additives in the casting solution on the formation of PVDF membranes. *Desalination* **192**, 190–197.
- Hong, J. H. 2011 Preparation and characterization of weak-base anion exchange membrane. *Journal of Industrial and Engineering Chemistry* **17**, 208–212.
- Hosseini, S. H., Madaeni, S. S. & Khodabakhshi, A. R. 2010a Preparation and characterization of ABS/HIPS heterogeneous anion exchange membrane filled with activated carbon. *Journal of Applied Polymer Science* **118**, 3371–3383.
- Hosseini, S. M., Madaeni, S. S. & Khodabakhshi, A. R. 2010b Preparation and characterization of ABS/HIPS heterogeneous cation exchange membranes with various blend ratios of polymer binder. *Journal of Membrane Science* **351**, 178–188.
- Hosseini, S. M., Gholami, A., Koranian, P., Nemati, M., Madaeni, S. S. & Moghadassi, A. R. 2014a Electrochemical characterization of mixed matrix heterogeneous cation exchange membrane modified by aluminum oxide nanoparticles: Mono/bivalent ionic transportation. *Journal of the Taiwan Institute of Chemical Engineers* **45**, 1241–1248.
- Hosseini, S. M., Jeddi, F., Nemati, M., Madaeni, S. S. & Moghadassi, A. R. 2014b Electrodialysis heterogeneous anion exchange membrane modified by PANI/MWCNT composite nanoparticles: preparation, characterization and ionic transport property in desalination. *Desalination* **341**, 107–114.
- Jia, B. & Zhang, W. 2016 Preparation and application of electrodes in CDI: a state of art review. *Nanoscale Research Letters* **11**, 64.
- Jia, B., Wang, Q., Zhang, W., Lin, B., Yuan, N., Ding, J., Ren, Y. & Chu, F. 2014 A new oil/water interfacial assembly of ultrathin graphene films. *RSC Advances* **4**, 34566–34571.
- Klaysom, C., Moon, S. H., Ladewig, B. P., Lu, G. Q. M. & Wang, L. 2011 Preparation of porous ion-exchange membranes (IEMs) and their characterizations. *Journal of Membrane Science* **371**, 37–44.
- Klaysom, C., Ladewig, B. P., Lu, G. Q. M. & Wang, L. 2013 Recent Advances in ion Exchange Membranes for Desalination Applications, in: *Functional Nanostructured Materials and Membranes for Water Treatment*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, pp. 125–161.
- Kumar, M., Khan, M. A., Al-Othman, Z. A. & Choong, T. S. Y. 2012 Recent developments in ion-exchange membranes and their applications in electrochemical processes for in situ ion substitutions, separation and water splitting. *Separation & Purification Reviews* **42**, 187–261.
- Li, X., Wang, Z., Lu, H., Zhao, C., Na, H. & Zhao, C. 2005 Electrochemical properties of sulfonated PEEK used for ion exchange membranes. *Journal of Membrane Science* **254**, 147–155.
- Li, H., Zhang, W., Zou, L., Pan, L. K. & Sun, Z. 2011 Synthesis of TiO₂-graphene composites via visible-light photocatalytic reduction of graphene oxide. *Journal of Materials Research* **26**, 970–973.
- Liu, F., Hashim, N. A., Liu, Y., Abed, M. R. M. & Li, K. 2011 Progress in the production and modification of PVDF membranes. *Journal of Membrane Science* **375**, 1–27.
- Merle, G., Wessling, M. & Nijmeijer, K. 2011 Anion exchange membranes for alkaline fuel cells: a review. *Journal of Membrane Science* **377**, 1–35.
- Mossad, M., Zhang, W. & Zou, L. 2013 Using capacitive deionisation for inland brackish groundwater desalination in a remote location. *Desalination* **308**, 154–160.
- Nagarale, R. K., Gohil, G. S., Shahi, V. K., Trivedi, G. S. & Rangarajan, R. 2004 Preparation and electrochemical characterization of cation- and anion-exchange/polyaniline composite membranes. *Journal of Colloid and Interface Science* **277**, 162–171.
- Nagarale, R. K., Gohil, G. S. & Shahi, V. K. 2006 Recent developments on ion-exchange membranes and electro-membrane processes. *Advances in Colloid and Interface Science* **119**, 97–130.
- Niyogi, S. & Adhikari, B. 2002 Preparation and characterization of a polyimide membrane. *European Polymer Journal* **38**, 1237–1243.
- Peighambardoust, S. J., Rowshanzamir, S. & Amjadi, M. 2010 Review of the proton exchange membranes for fuel cell applications. *International Journal of Hydrogen Energy* **35**, 9349–9384.
- Pourcelly, G. & Bazinet, L. 2009 *Developments of Bipolar Membrane Technology in Food and bio-Industries*. CRC Press, Boca Raton, FL, USA, pp. 581–633.
- Pradhan, N. C., Sarkar, C. S., Niyogi, S. & Adhikari, B. 2002 Separation of phenol–water mixture by membrane pervaporation using polyimide membranes. *Journal of Applied Polymer Science* **83**, 822–829.
- Qi, D., Hu, E. & Zou, L. 2006 Reverse osmosis membrane fouling and its control. *Research Journal of Chemistry and Environment* **10**, 95–101.
- Rana, D., Matsuura, T., Kassim, M. A. & Ismail, A. F. 2013 Radioactive decontamination of water by membrane processes – a review. *Desalination* **321**, 77–92.
- Sata, T. 2004 *Ion Exchange Membranes Preparation, Characterization, Modification and Application*. Royal Society of Chemistry, Cambridge.
- Sen, P. K., Sen, P. V., Mudgal, A., Singh, S. N., Vyas, S. K. & Davies, P. 2011 A small scale multi-effect distillation (MED) unit for rural micro enterprises: Part I – design and fabrication. *Desalination* **279**, 15–26.
- Seo, S. J., Kim, B. C., Sung, K. W., Shim, J., Jeon, J. D., Shin, K. H., Shin, S. H., Yun, S. H., Lee, J. Y. & Moon, S. H. 2013 Electrochemical properties of pore-filled anion exchange membranes and their ionic transport phenomena for vanadium redox flow battery applications. *Journal of Membrane Science* **428**, 17–23.
- Stejskal, J. & Gilbert, R. G. 2002 Polyaniline. Preparation of a conducting polymer. *Pure Applied Chemistry* **74**, 857–867.

- Strathmann, H., Grabowski, A. & Eigenberger, G. 2013 Ion-exchange membranes in the chemical process industry. *Industrial & Engineering Chemistry Research* **52**, 10364–10379.
- Tarvainen, T., Svarfvar, B., Åkerman, S., Savolainen, J., Karhu, M., Paronen, P. & Järvinen, K. 1999 Drug release from a porous ion-exchange membrane in vitro. *Biomaterials* **20**, 2177–2183.
- Valero, F. & Arbós, R. 2010 Desalination of brackish river water using Electrodialysis Reversal (EDR): control of the THMs formation in the Barcelona (NE Spain) area. *Desalination* **253**, 170–174.
- Vogel, C. & Meier-Haack, J. 2014 Preparation of ion-exchange materials and membranes. *Desalination* **342**, 156–174.
- Wang, Y. & Li, F. 2011 An emerging pore-making strategy: confined swelling-induced pore generation in block copolymer materials. *Advanced Materials* **23**, 2134–2148.
- Xu, T. 2005 Ion exchange membranes: state of their development and perspective. *Journal of Membrane Science* **263**, 1–29.
- Zhang, W., Mossad, M. & Zou, L. 2013 A study of the long-term operation of capacitive deionisation in inland brackish water desalination. *Desalination* **320**, 80–85.
- Zhang, Y., Zou, L., Ladewig, B. P. & Mulcahy, D. 2015 Synthesis and characterisation of superhydrophilic conductive heterogeneous PANI/PVDF anion-exchange membranes. *Desalination* **362**, 59–67.
- Zhao, S., Zou, L., Tang, C. Y. & Mulcahy, D. 2012 Recent developments in forward osmosis: opportunities and challenges. *Journal of Membrane Science* **396**, 1–21.

First received 12 December 2017; accepted in revised form 22 March 2018. Available online 5 April 2018