Synthesis and characterisation of superhydrophilic conductive heterogeneous PANI/PVDF anion-exchange membranes

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HIGHLIGHTS

- PANI/PVDF anion-exchange membranes are prepared by wet and dry phase inversions.
- The prepared PANI/PVDF membranes are superhydrophilic and highly conductive.
- Increase of the PANI ratio results in an increase in membrane ion exchange capacity.
- The transport number is affected by the water content and porosity of the membrane.
- Achieve a better understanding of the relationships among various properties.

ARTICLE INFO

ABSTRACT

In this research, polyaniline (PANI)/polyvinylidene fluoride (PVDF) heterogeneous conductive anion-exchange membranes are prepared by a solution-casting technique using 1-methyl-2-pyrrolidone (NMP) as solvent and wet and dry phase inversion methods, various properties of these casted PANI/PVDF membranes are characterized. Most of prepared membranes exhibit properties of superhydrophilicity, high conductivity, good anion exchange capacity and high water content. The effects of the ratio of PANI and PVDF in the mixture on the properties of the prepared membranes are studied, including ion-exchange capacity (IEC), fixed ion concentration (FIC), transport number and water content. It is found that the increase of the PANI ratio in casting solutions resulted in an increase in membrane conductivity and IEC. However, the membrane transport number which represents the pathways for ionic transport is not controlled solely by an increase in the IEC, but rather, is more influenced by the water content and membrane porosity. Further, the results from this work lead to a better understanding of the relationships between conductivity and IEC, water content and transport number, which help to develop more efficient anion-exchange membranes for water purification and other industrial applications.

1. Introduction

Desalination is an important strategy for supplying clean potable water for people worldwide. Developing efficient and cost-effective desalination technologies is the key for having a sustainable supply of fresh water into the future [1]. The common technologies used for seawater and brackish water desalination include reverse osmosis (RO), and thermal-assisted processes such as multiple-effect distillation (MED) and multiple-stage flash (MSF) vapour-compression distillation (VCD) [2–6]. More recent technologies include capacitive deionisation (CDI), electrodialysis (ED), electrodialysis reversal (EDR), and forward osmosis (FO) [7–9]. These technologies have emerged as alternative processes to the abovementioned common technologies for providing desalination solution in niche applications, for example, in regional and remote brackish water desalination, mining water treatment and reuse, and generation of ultrapure industrial-production water. CDI and ED both require the use of ion-exchange membranes (IEMs), and it has been reported that membrane capacitive deionisation (MCDI) combines the advantages of IEMs and CDI, and has a higher desalting efficiency than CDI without membranes [10]. The IEMs used in both CDI and ED processes need to be highly conductive, mechanically strong and chemically stable. Fouling of IEMs is a problem because of the presence of organic foulants in feed water [11]. The preparation of heterogeneous IEMs with high ion-exchange capacity (IEC), high conductivity and low fouling is critical for the successful application of IEMs in water purification and desalination. This research aims to develop

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conductive anion exchange membrane that will remove chloride ions, so it can be used together with cation exchange to remove both sodium ion and chloride ions in CDI or electrodialysis processes.

The ion exchange membranes prepared for desalination by MD or MCDI are: (1) homogeneous membranes, which are composed of fixed charge groups bound to some polymer; and (2) heterogeneous membranes consisting of a neutral polymer matrix such as silicon rubber filled with ion-exchange particles [12]. Unfortunately, trade-offs between the two kinds of membranes usually occur. For example, homogeneous membranes usually show good electrochemical properties, whereas heterogeneous membranes have more acceptable mechanical strength [13,14]. More recently, polyelectrolyte ion exchange membranes are also prepared using layer by layer assembly technique [15,16].

Polyaniline (PANI) is a conducting polymer with high IEC; it has been investigated extensively as a potential membrane material over the last 10 years. In some recent studies, membranes have been prepared by mixing PANI with other membrane materials, such as PANI/PVDF which were prepared by phase inversion in an aqueous solution of poly(styrenesulfonic acid) and PANI/PVC [17,18]. Furthermore, several studies have reported that the membrane conductivity and electrochemical properties have been enhanced by PANI membrane-surface modifications [19–22]. PANI polymer particles coated on the surface can increase IEC, water content and conductivity of the membranes [23,24]. Especially, using PANI or its derivatives as active anion exchange materials in membrane has been studied by several research groups. For example, poly (2-chloroaniline) anion exchange membranes were treated by plasma surface modification [25]. A recent publication reported about polyaniline (PANI)-co-multi-walled carbon nanotube (MWCNT) anion exchange membrane [17]. In addition, PANI can also be used in ion exchange membrane as cation exchange material. For example, PANI-assisted ion exchange membrane can help to remove calcium and magnesium by Donnan dialysis [26].

In this research, the anion exchange membranes were fabricated by casting the homogeneous polyaniline/poly(vinylidene fluoride)/1-methyl-2-pyrrolidone (PANI/PVDF/NMP) solution on a glass plate followed by phase inversion in ethanol/water solution, which is different from the previous research where an aqueous solution of poly(styrenesulfonic acid) was used for phase inversion of PANI/PVDF membrane and a thermal phase inversion method was used for PANI/MWCNT/PVC membranes [17, 18]. PVDF was selected as the membrane matrix material because it has many advantages, such as high mechanical strength, and good chemical and thermal stability. The anion exchange membranes prepared by our method showed markedly improved conductivity and hydrophilic property. Firstly, the conductive polymer PANI was synthesised by chemical oxidative polymerisation of aniline hydrochloride [27]. Then, the powder of PANI particles was blended with PVDF to prepare heterogeneous anion-exchange membranes by casting the solution on glasses followed by either wet phase inversion or dry phase inversion. Three different ratios of PANI/PVDF were employed to investigate properties such as the hydrophilicity, conductivity, IEC and pore properties of the resultant membranes.

2. Experiment

2.1. Materials

Aniline hydrochloride, ammonium persulfate, poly(vinylidene fluoride) (PVDF) and 1-methyl-2-pyrrolidone (NMP) were purchased from Sigma-Aldrich (Sydney, Australia). Ammonia solution (30%), silver nitrate solution (0.01 M) and potassium chromate solution (5%) used to determine the IEC by titration were supplied by Rowe Scientific (Adelaide, Australia). All the chemicals were used as received, without further purification.
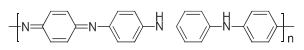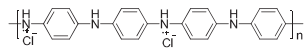
2.2. Preparation of PANI

The following oxidative polymerisation of ammonium persulfate with aniline hydrochloride was used to prepare PANI [27]. Aniline hydrochloride (0.4 mol) was dissolved in 500 ml hydrochloric acid, and then 0.5 mol ammonium persulfate was added while stirring at 5 °C. The reaction was constantly stirred for 1 h. 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. To obtain PANI in the emeraldine base form, part of the product was then further washed with deionised water and finally washed with 0.5 M ammonia solution. The wet powder was dried at room temperature for three days. The structures of these chemicals are presented in Table 1.

2.3. Membrane fabrication

PANI/PVDF heterogeneous anion-exchange membranes were prepared by either a wet phase inversion method or thermal phase inversion. The fabrication of PANI/PVDF heterogeneous membrane scheme is illustrated in Fig. 1(a), the image of the prepared membrane is shown in Fig. 1(b). PVDF particle powders were sieved to obtain the desired size and then added in NMP and mixed at room temperature in a Schott bottle for a week. After that, previously synthesised PANI powders were dissolved in the PVDF/NMP solution. Polyaniline (emeraldine) base and salt have different oxidized states, the emeraldine base can be doped by acid to emeraldine salt. The polyaniline in salt form is more conductive as well as more hydrophilic, so it is a more desirable form to be used in ion exchange membrane. However, PANI in base form can be dissolved more easily in NMP, so it is more feasible to obtain a homogenous casting solution, and prepare good quality membrane. In this study, more PANI in salt form is used. The solution was then mixed by a mechanical stirrer for about 2 h at room temperature to achieve uniformity and was then ultrasonicated for 15 min. A suitable amount of mixture was casted onto a clean, dry glass plate at room temperature. The phase inversion step was conducted in two approaches: 1) wet phase inversion: the assembly was immersed into a bath containing ethanol and deionised water at an appropriate ratio of 2:1. After a series of trials, it is found that PANI:PVDF ratio of 20:80 is the optimum value for membrane matrix, as further increasing of PANI content makes it difficult to cast a uniform membrane; and 2) dry phase inversion: the assembly was initially placed in a vacuum oven at 55 °C for solvent to evaporate and then immersed in 50 °C deionised (DI) water to complete the process. The fabricated membranes were stored in DI water. The membranes were named by their preparation methods. D represents dry phase inversion and W represents wet phase inversion. B stands for PANI emeraldine base forms in casting solutions and S stands for PANI emeraldine salt form in casting solution. The numbers relate to the percentage of PANI in the membranes. The membrane thickness was determined in a dry state using a digital calliper device. The compositions of the casting solutions and the ratios of PANI/PVDF are presented in Table 2. Based on the in-house trails of dissolving the PVDF pellets with NMP, it was found that 17% of PVDF can be dissolved efficiently in

Table 1
Chemical structures of aniline hydrochloride and polymers.

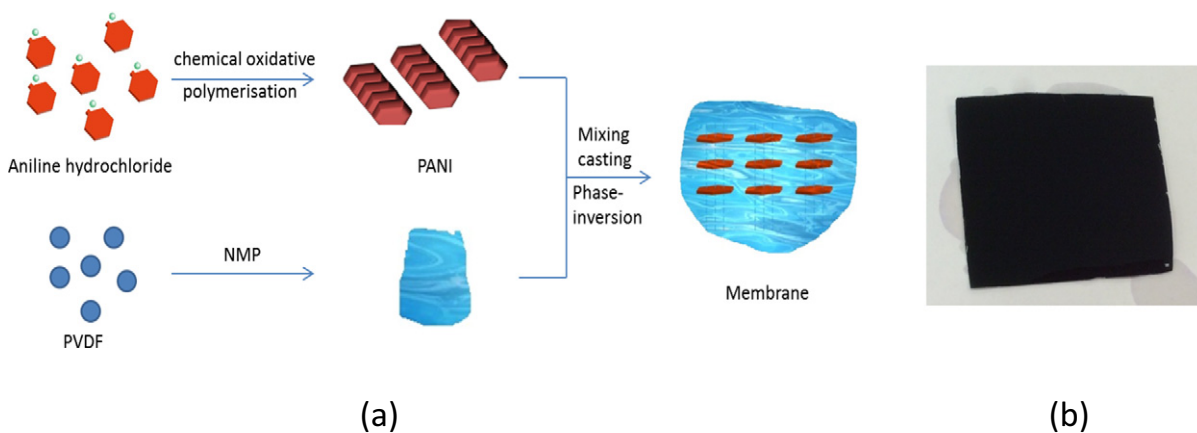| Poly(vinylidene fluoride) (PVDF)	
Aniline hydrochloride	
PANI$_b$ (PANI emeraldine base form)	
PANI$_s$ (PANI emeraldine salt form)	

(a)

(b)

Fig. 1. (a) The fabrication scheme of the membranes. (b) Photo of the prepared PANI/PVDF membrane.

NMP to form a homogenous solution, the viscosity of this solution can be casted into a good quality membrane.

2.4. Membrane characterisation

2.4.1. Membrane morphology

Scanning electron microscopy (SEM) was employed to image the cross-sectional morphology of the casted PANI/PVDF membranes.

2.4.2. Water contact angle

Samples were mounted on a glass microscope. DataPhysics OCA-200 Contact angle analyser was used to measure contact angle vs time as follows: firstly, a droplet of ultrapure DI water with volume ~19 μl was dropped on to the membrane from a height of ~5 mm. Secondly, videos (side view) of the drop on membrane surfaces were taken about 90 s. The analysis results were obtained from the images captured on videos, which can offer the membrane surface images and outline of the droplet. The contact angle on both sides (left and right) of the droplet and the average of these two results reported can be easily calculated from an elliptical shape droplet outline. Finally, the diagrams of contact angle(s) vs time were reported in the following. All experiments were performed at room temperature of approximately 20 °C and humidity of 31%.

2.4.3. Porosity

An AutoPore IV 9500 V1.09 Porosimeter (Micomeritics Instrument Corporation, USA) was used to characterise the membranes' porosity by applying various levels of pressure to a sample immersed in mercury. The intrusion volume is recorded with the corresponding pore size or pressure [28]. The apparatus has a practicable pressure range from 0 to 3300 psi. The pore size distributions can be obtained from the data of intruded volume and applied pressures.

2.4.4. Water content

The water content is defined as the mass differences between dried and wet membranes. To obtain the water content, the membrane wet

Table 2
Compositions of casting solutions to fabricate the PANI/PVDF membranes.

Membrane	Percentage of PVDF in NMP solution (w:w)	Ratio of polymer mixture PANI:PVDF (w:w)	Membrane Thickness (mm) ±0.01
WB5	17%	5:95	0.522
WB10		10:90	0.472
WB20		20:80	0.528
DB20			0.110
DS20			0.223

weight W_{wet} was obtained at first. Then, the wet membrane was dried in a vacuum oven at 45 °C for about 24 h until constant weight W_{dry}, which was determined by weighing the membrane between different times. The water content can be calculated by the following equation [29–32]:

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

2.4.5. Ion exchange capacity and fixed ion concentration

The IEC was measured by the following titration method: 1) the membranes were submerged in 1 M HCl solution for 72 h to convert PANI from the emeraldine base to the emeraldine salt and then washed with water to remove residual HCl; 2) the membranes were then placed in 2 M NaCl solution for 72 h and then washed with water until no visible residue from reacting with AgNO₃ and NaCl was observed; 3) the membranes were placed into 2 M NaNO₃ solution for 72 h to release the Cl⁻ into solution and then washed three times with deionised water; 4) the solution containing Cl⁻ was titrated with 0.01 M AgNO₃ standard solution with K₂CrO₄ indicator to obtain the amount of AgNO₃, *a* (mequiv); and 5) the membrane was wiped with absorbent paper and dried in a vacuum oven at 45 °C for 12 h until constant weight (W, g) was achieved [32]. The IEC can be calculated as follows:

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

The fixed ion concentration (FIC) can be calculated by the following equation:

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

2.4.6. Membrane potential and transportation number

Transport number was obtained from the different potentials between the two cells above. The electrical properties of the membrane along with the concentration and nature of the electrolyte solutions both determine the magnitude of this potential between two surfaces of the membrane. So an electrical potential across the membrane can be observed from the two surfaces of an anion-exchange membrane contacting with different concentrated solutions [32,33]. Indeed, the mobility of ions between the internal and external phases of the membrane both determines membrane potential the algebraic sum of the Donnan and diffusion potentials [34]. To get the membrane potential, a two-cell apparatus, a vertically positioned membrane separating two

solutions (0.5 M NaCl and 1 M NaCl), was applied, as shown in Fig. 2. The potential difference across the membrane ($E_{measure}$) was measured by a Biologic-VSP potentiostat connected to Ag/AgCl reference electrodes. The following Nernst equation can be used to express membrane potential as shown below [31,34–36]:

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

where t_i^m is the transport number of counter-ions in the membrane phase, R is the gas constant, T is the temperature (K), n is the electrovalence of counter-ion, and a_1 and a_2 are the activities of the NaCl solutions.

2.4.7. Membrane conductivity/resistivity measurement

The electrical resistance of an IEM is closely related to electrical energy consumption. Electrical resistance was measured in 0.5 M NaCl solution at 25 °C using electrical impedance spectroscopy in a three-electrode cell, as shown in Fig. 3. Titanium and platinum were used as the working and counter electrodes, with an Ag/AgCl reference electrode positioned next to the membrane surface. Using a Biologic-VSP potentiostat over a frequency range of 1 Hz to 1 MHz, the resistance of the cell with the membrane was measured (R_1). The electrical resistance (R_2) was measured again after membrane sample was removed from the cell above. The membrane electrical resistance (R_m) can be calculated as follows: $R_m = R_1 - R_2$ [34,35]. Based on the electrical resistance measurements, through-plane conductivity (σ, S·cm^{-1}) and area resistance (Ω·cm^2) can be calculated from the following equation [35,37]:

$$\sigma = \frac{L}{R_m A} \tag{5}$$

$$r = R_m A \tag{6}$$

where, r is the area resistance; L is the thickness of the membrane (cm) and A is the effective area of the membrane (cm^2).

2.4.8. Zeta potential measurement

The membrane surface charge information will confirm if the prepared the membrane is suitable for anion exchange. A streaming potential analyser (Anton Paar, Austria) with adjustable-gap cell apparatus was employed to determine the zeta potential values of the membranes. The streaming current was measured and the Helmholtz–Smoluchowski approximation was applied to evaluate the data. As described by the manufacturer, the resulting potential difference is detected by measuring electrodes that are connected at the electrolyte
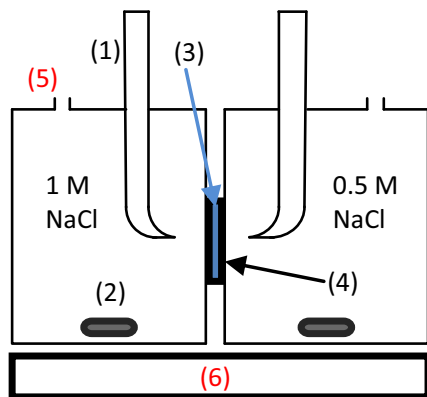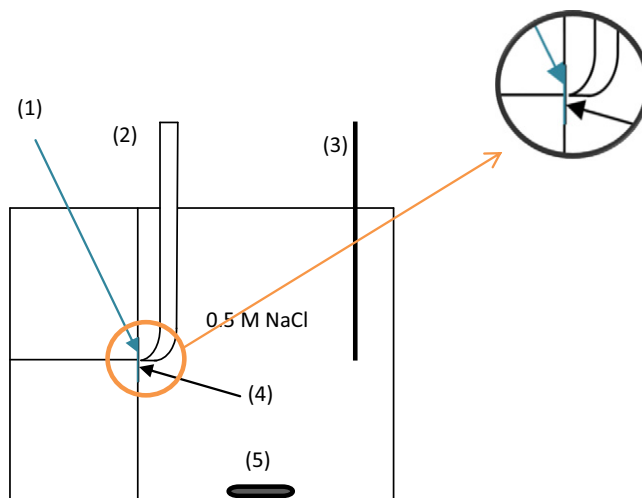

Fig. 3. (1) Titanium electrode; (2) Ag/AgCl reference electrode; (3) Pt electrode; (4) membrane; (5) magnetic stirring bar.

inlet and outlet of the measuring cell. A dual syringe pump system was prepared to dispense acid and base for pH adjustment, generating electrolyte flow, which causes an electrical charge separation in the flow direction along the cell. The charge results were calculated using VisioLab for SurPASS software. The initial pH was approximately 6.5, which was the pH value of the 10 mM KCl background solution. The tests were first carried out by automatically dosing 0.05 M HCl from an acid syringe to reduce the pH of the KCl solution from 6.5 to 3. After this, the samples were carefully rinsed with deionised water at least three times and the pH was adjusted to 6.5 again by using 10 mM KCl solution. A solution of 0.05 M NaOH from the base syringe was then automatically dosed to increase the pH from 6.5 to 11. The zeta potential values over the entire pH range of 3–11 were obtained by combining the results from these two runs. The instrument was set to measure the data at 0.5 pH intervals. At each pH value, four measurements were recorded and the average values of each pH were reported.

3. Results and discussion

3.1. Membrane preparation and membrane structure

In the present study, conductive PANI was synthesised at first, and then added into PVDF/NMP solution to cast the anion-exchange membranes. Membranes with different ratios of PANI/PVDF were hand casted, using wet or dry phase inversion methods. In general, the morphologies of the membranes were affected by the preparation conditions. Solvent/non-solvent exchange rate is one of the critical parameters for fabricating membranes. In our membrane-fabrication process, solutions with the ethanol/water ratio of 2:1 were found to be the most suitable condition and thus were used in the fabrication process. It was experimentally evident that if only water or ethanol was used as solvent, it cannot result in a uniform membrane structure. As a result, the ethanol/water mixture solution with the appropriate ratio is critical for the phase inversion process.

The SEM images of the prepared membranes were shown in Fig. 4. Images a_1, b_1 and c_1 are for membrane WB5; the images a_2, b_2 and c_2 are for membrane WB10; images a_3, b_3 and c_3 are for membrane WB20; images a_4, b_4 and c_4 are for membrane DB20; and images a_5, b_5 and c_5 are for membrane DS20. The pore structure, pore density and pore size distribution are shown in the cross-sectional images with varying magnifications. It can be clearly seen from SEM images that membranes (WB5, WB10 and WB20) prepared by wet phase inversion all present larger pore size and higher porosity than those (DB20 and DS20) prepared by the dry phase inversion method. This is because, in

Fig. 2. Schematic diagram of test cell: (1) Ag/AgCl reference electrode; (2) magnetic stirring bar; (3) membrane; (4) rubber gasket; (5) orifice and (6) magnetic stirrer.

the wet phase inversion process, the solvent escaped from the casting solution faster and left larger pores in membrane structure. Whereas in the dry phase inversion process, it took a longer time for solvent to be evaporated as a result the formed pores are smaller. It was found that the increased drying period during the phase inversion led to membranes with less porosity and denser structure [38].

3.2. Porosity results

To characterise the membrane porosimetry, the membrane samples were dried for 24 h in an oven at 50 °C before analysis. Prior to weighing, all the samples were placed into a closed sample cell and evacuated for 10 h at 10–3 mm Hg. The high purity mercury was pressed into the

membrane pores and voids. Pressures up to 3000 psi were sufficient to determine the expected pore sizes [39]. Representative intrusion and extrusion curves for sample WB5 are shown in Fig. 5. The measured membrane porosity results are shown in Table 3. It was found that although the PANI content and the PVDF concentration in casting solution are the main factors affecting the porosity and pore diameter, there are other factors in the process that are difficult to control also influence these parameters. The porosity results are also consistent with the observations of SEM images. The membranes prepared by the wet phase inversion method, i.e. WB5, WB10 and WB20, present larger pore size and higher porosity than membranes prepared by the thermal dry phase inversion method, i.e. DB20 and DS20. Apart from the solvent/water ratio and PANI/PVDF ratio, there are other random factors that
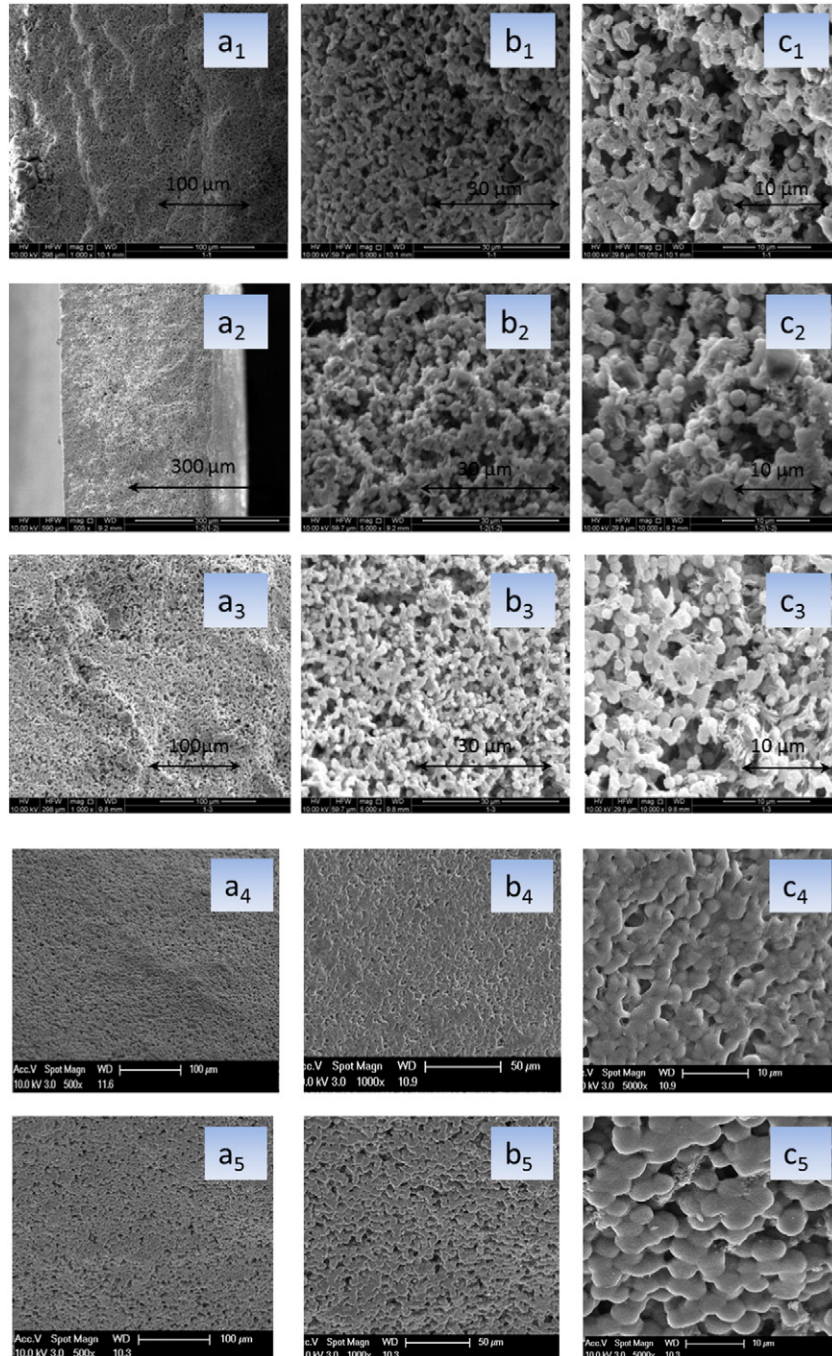

Fig. 4. Cross-sectional SEM images showing pore sizes of the PANI/PVDF anion exchange membranes with (a_1, a_2, a_3, a_4 and a_5) low; (b_1, b_2, b_3, b_4 and b_5) medium; and (c_1, c_2, c_3, c_4 and c_5) high magnifications.
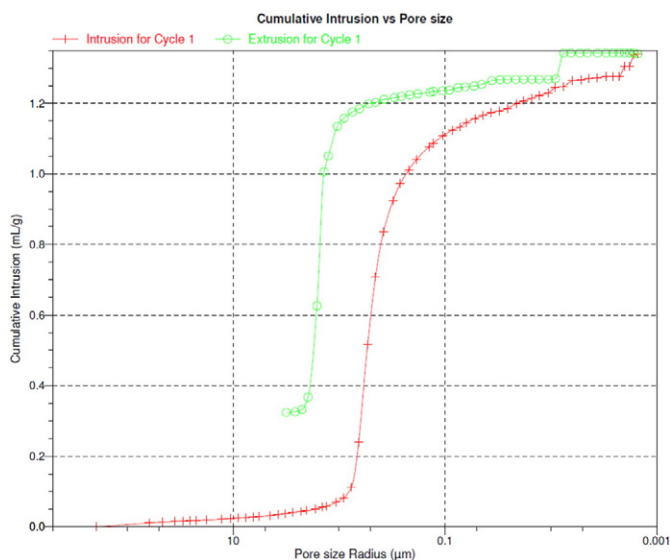
Fig. 5. Intrusion–extrusion curves given by the porosimeter for membrane WB5.

might affect the formation of the PANI ion exchange membranes. For example, the time that membrane was immersed in the phase inversion bath, may also need to be carefully controlled. The porosity result of membranes could be attributed to the random factors, which will be more carefully monitored and eliminated.

3.3. Water contact angle

Contact angle can provide information on interfacial force between a solid surface and a liquid surface. Water contact angle is commonly used to characterise the hydrophilicity of the membrane surface. Dynamic contact angles measured by a DataPhysics OCA-200 Contact angle analyser are presented in Fig. 6; three repeated measurements having an estimated $\pm 5\%$ induced error were conducted at room temperature of about 21 °C for each sample. It was found that membranes WB5, WB10, WB20 and DS20 were superhydrophilic and whereas sample DB20 has a constant water contact angle of about 66°. For sample WB5, after 223 s, no further decrease can be observed. For sample WB10, a sharp decrease occurred after 145 s. And the droplet of sample WB20 was not spreading but the height of the droplet decreased after 45 s. In addition, for DS20, the decrease only occurred after 60 s and the droplet finally disappeared at 358 s. As can be seen in Fig. 6, all samples but DB20 showed superhydrophilic membrane surface. It appears that membranes with larger pore and higher porosity, as shown in Table 3, can present stronger hydrophilicity. It is known that PANI in salt form has better hydrophilicity than PANI in base form [40]. So, membrane DB20 contains less PANI in salt form than DS20 which in turn shows less hydrophilic property. Furthermore, it is known that PVDF is a hydrophobic polymer and these results suggest that the added PANI in the membrane significantly increased the membrane hydrophilicity. This is because PANI possesses a large number of functional groups such as ammonium, which are distributed on the porous surface of the membrane and contribute to its hydrophilic property.

Table 3
The porosity results of prepared membranes.

	WB5	WB10	WB20	DB20	DS20
Average pore diameter (nm)	28.1	19.9	43.4	6.2	9.5
Apparent density (g/ml)	1.89	1.74	1.38	1.11	1.50
Porosity (%)	71.73	47.31	70.00	32.10	38.42

3.4. Water content

The water content of IEM is defined as the weight of water included in 1 g of swelled membrane soaked in pure water [31]. Water content measurements of the prepared membrane samples were shown in Table 4. The membranes prepared by wet phase inversion have similar water-content values: 249.8%, 263.5%, and 258.9% for WB5, WB10 and WB20 respectively. These values are at the similar levels for WB5, WB10 and WB20. The slight differences are not caused by the difference of the PANI content, instead it may be caused by other factors such as membrane thickness, where WB10 is a thinner membrane (0.472 mm) than WB5 (0.522 mm) and WB20 (0.528 mm), or affected by other uncontrollable factors. The results confirm that membranes prepared by the thermal phase inversion method have much higher water content than those prepared by dry thermal phase inversion. It is known that increase of membrane porosity results in increase of water content values [38]. It is most likely that membranes prepared by phase inversion in the ethanol/water bath resulted in larger pores and higher porosity and were able to adsorb more water than those membranes prepared by thermal-phase-inversion (which offered much lesser voids and cavities in the membrane matrix). For example, the membranes prepared by dry phase inversion have water content 2.13% for membrane DB20 and 17.2% for membrane DS20. Comparing the two membrane samples DB20 and DS20, as DS20 containing PANI in salt form and its surface is superhydrophilic, whereas sample DB20 containing PANI in base form and is the only sample has a less hydrophilic surface, as a result, the less hydrophilic DB20 attracts and retains less water within the membrane structure, ie lower water content.

The water contents of anion exchange membranes made of PPO have been reported at 0.302 to 0.673 [37] which are quite low comparing that of water contents in this study. It is well known that membranes with bigger pores or higher porosity can lead to improved conductivity and better channels for ion transportation, although they can also induce some disadvantages such as lower selectivity and more opened structure [38]. Furthermore, the high hydrophilicity also indicates that the added PANI contributed to an excellent hydrophilic characteristic of the membrane. Therefore, more hydrophilic IEMs can be prepared by blending PANI in the casting solution.

3.5. IEC and FIC

IEC is defined as the milli-equivalents of the anion-exchange group that are included in a 1 g dry membrane [29]. It indicates the density of ionisable hydrophilic groups in the membrane matrix, and is one of the important parameters of IEMs. As mentioned earlier, the fixed ion concentration (FIC) is the ratio of IEC over water content. The IEC and FIC values of the prepared heterogeneous anion-exchange membranes are presented in Table 4. It is clear that the increase in the amount of PANI (PANI:PVDF, w:w) from 5:95 to 20:80 in the casting solution resulted in an improvement of anion-exchange capacity from 0.86 to 1.72 (meq/g) in prepared membranes. This is because larger amount of functional groups present in the membrane matrix is responsible for the increase of the IEC and FIC. More polar amino groups can enhance the interaction (polar–polar interaction) between the membrane surface and solution to facilitate more efficient ionic transportation between the membrane and solution phase, and therefore, enhance the IECs. It is also seen that sample WB20 presents higher IEC than DB20 and DS20. This may be due to the fact that the larger pores and wider channels in the membrane matrix obtained by the wet phase inversion method provided more space for excellent interaction of counter ions with the functional groups on the membrane surfaces [38].

The FIC or equivalents of functional groups per gram of absorbed water control the transport pathways of counter-ions in the membrane. FIC, as shown in Table 4, can be used to optimise the relationship
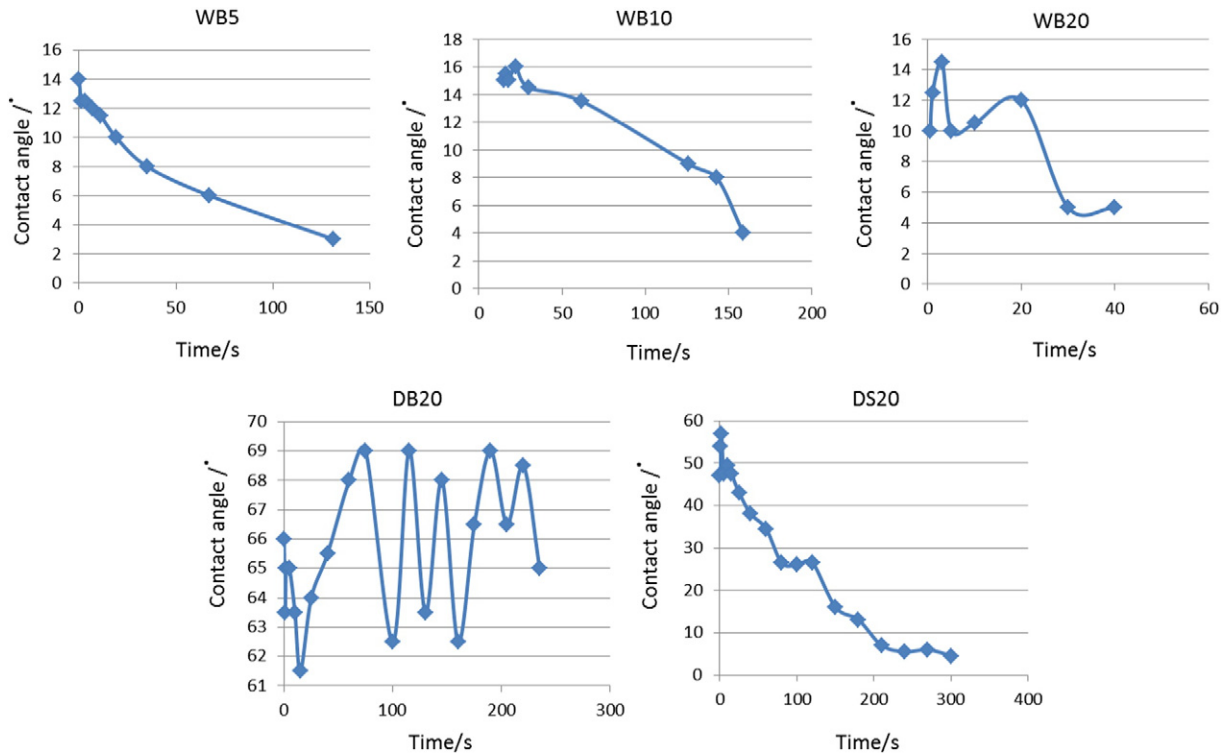
Fig. 6. The dynamic contact angles of prepared membranes.

between IEC and water content. Decrease of membrane water content or increase of PANI concentration in the membrane can lead to higher FIC.

3.6. Membrane conductivity and resistance

Ion exchange membrane conductivity or resistance is a particularly important property, as it directly relates to the energy consumption and operational costs of CDI and ED processes. The results of membrane conductivity and resistance are presented in Table 4. The conductivity of prepared membranes increased with increase of PANI content from sample WB5 to sample WB20. This is because a higher concentration of hydrophilic groups leads to a higher charge density in the membranes, so as to increase the ionic interaction and improve membrane conductivity. As is shown in Table 4, the membranes prepared by the wet-phase-inversion method achieved higher conductivity than membranes fabricated by the thermal-phase-inversion method. Membrane WB5 contains too little PANI content to help in conducting the electrons and forming the current. However, after PANI content is increased to 10% in WB10, the conductivity is significantly improved, further increase of the PANI content to 20% in WB20 only slightly further improved the conductivity, the improvement of conductivity is not linear promotional to the PANI content. On the other hand, the resistances of sample WB10 and sample WB20 were found to be lower than those of some commercial IEMs, for example, Neosepta ACS (area resistance: 3.8 $\Omega \cdot cm^2$) and Aciplex A201 (area resistance: 3.6–4.2 $\Omega \cdot cm^2$); while

sample WB5 exhibited higher resistance than these commercial membranes (at the measurement condition: 0.5 M NaCl solution at 25 °C) [37,41]. These results indicate that the membrane conductivity/resistance is influenced by the following two factors: 1) the amount of conducting polymer in the membrane matrix: the more added PANI in the casting solution, the more conductive the membrane is. 2) The connectivity of the pores formed by the phase inversion process: wet phase inversion resulted in high porosity and most importantly formed well connected pore channels, which led to better electric conductivity of the membrane.

Moreover, the prepared heterogeneous membranes were formed from finely powdered ion-exchange materials and a binder homogeneously blended in solution. The blended polymers presented a uniform distribution of fixed charges and had a more homogeneous nature. This yielded lower resistance for heterogeneous membranes. The uniform distribution of conductive additive PANI in the membrane matrix can effectively improve the conductivity of cast ion exchange membranes.

3.7. Transport number

In MCDI and ED processes, the membrane transport number is described as the current carried by counter-ions. A higher transport number means less energy is consumed in ion-exchange processes. The measured membrane transport numbers of prepared PANI/PVDF membranes are presented in Table 4. It is found that all membranes prepared by wet phase inversion (WB5, WB10, and WB20) exhibit higher

Table 4
The properties of the prepared anion exchange membranes.

Membrane	Water content (%)	IEC (meq/g)	FIC (meq/g absorbed water)	Conductivity (mS·cm^{-1})	Resistance area ($\Omega \cdot cm^2$)	Transport number (± 0.01)
WB5	249.8 ± 8	0.86 ± 0.2	0.344	14.33	3.642	0.879
WB10	263.5 ± 6	1.20 ± 0.3	0.455	46.61	1.013	0.870
WB20	258.9 ± 9	1.72 ± 0.2	0.664	55.59	0.950	0.868
DB20	2.1	1.04 ± 0.05	49.52	0.22	50.550	0.534
DS20	17.2	0.96 ± 0.05	5.581	0.60	36.952	0.735

transport numbers than those prepared by thermal phase inversion. This is because the former have a high porosity which provides more pathways to transfer ions, although higher water content related to the high porosity can also dilute the concentration of the anion-exchange groups and compromise the ion transportation. In addition, all these three membranes show similar transport numbers. This indicates that the pathways for ionic transport are not controlled solely by an increase in the IEC, but rather, are more influenced by the water content related to the membrane porosity. The transport numbers of DB20 and DS20 also agree with this analysis, DS has higher water content than DB20, as a result, the membrane transport number of DS20 (0.735) is higher than DB20 (0.534).

3.8. Zeta potential

Only PANI/PVDF membrane WB10 was chosen for the zeta potential analysis. Its zeta potential values (WB10) are presented in Fig. 7. The zeta potential values of the membrane were positive at a pH range of 3–10. The amine groups and positively charge nitrogen atoms may be contributed to the positive surface charge of the PANI/PVDF membrane. The value was decreased as the pH increased from about 56 mV at pH 3 down to 9.5 mV at pH 9. It passed through an isoelectric point (IEP) at approximately pH 10, and became negative at the pH range of 10–11.

4. Conclusion

The conducting polymer PANI was synthesised and then blended in a casting solution with PVDF/NMP to prepare heterogeneous anion exchange membranes. Ultrasonication was a critical step in achieving a uniformly distributed solution for casting the membrane. Five membrane samples were manually casted, then three of them were subjected to wet phase inversion in an ethanol/water bath (WB5, WB10, and WB20), and two were subject to dry phase inversion (DB20 and DS20).

The resultant PANI/PVDF membranes by wet phase inversion showed properties of superhydrophilicity (high water content), high conductivity and high ion exchange capacity, as well as a medium level of transport numbers. So the enhanced hydrophilicity has a double-sided effect: on one aspect, it would greatly increase the membrane water content and conductivity, so as to enhance the passage of ions through membranes, and as a result, higher hydrophilicity, water content and porosity can lead to higher conductivity; on another aspect, high hydrophilicity can reduce ion selectivity and compromise its applications such as reconcentration of useful resources in electrodialysis.

It is clear that the increase in the amount of PANI in the casting solution resulted in an improvement of anion-exchange capacity in prepared membranes. This is because larger amount of functional groups present in the membrane matrix is responsible for the increase of the IEC and FIC. It was found that the membranes casted by wet phase inversions have higher ICE than those prepared by the dry phase inversion method, this may be due to the fact that the larger pores and wider

channels in the membrane matrix obtained by the wet phase inversion method provided more space for excellent interaction between counter ions and the functional groups on the membrane surfaces.

All three membranes prepared by the wet phase inversion method show similar transport numbers. This indicates that the pathways for ionic transport are not controlled solely by an increase in the IEC, but rather, are more influenced by the water content related to the membrane porosity. It is believed that more future works need to be done to achieve the desirable membrane properties of high conductivity, high transportation number and appropriate water content.

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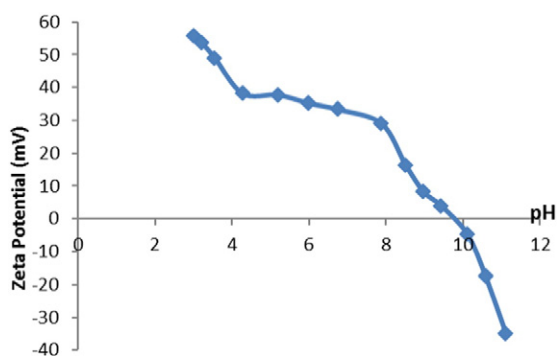

Fig. 7. Zeta potential for the membrane prepared.

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