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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.

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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.

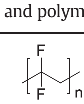
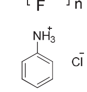
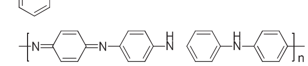
2.2. Preparation of PANI

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)