Preparation and characterization of polysulfone/PEG heterogeneous ion exchange membrane for reverse electrodialysis (RED)

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Abstract. Heterogeneous cation-exchange membrane is synthesized using solution casting method. The casting solution is prepared by dispersing finely ground cation-exchange resin particles in N,N-dimethylacetamide (DMAc) solutions of polysulfone (PSf) while polyethylene glycol (PEG400) is used as a modifier. The results show that the PEG400 can increase water uptake, conductivity, and ion-exchange capacity (IEC) of the heterogeneous cation-exchange membrane due to the hydrophilic nature of PEG400. The more hydrophilic membrane results in higher water uptake and wider access for functional sites. However, when the concentration of PEG400 is increased further, the IEC and conductivity tend to decrease. This tendency is more pronounced when the ion-exchange resin particle is increased from 50 to 60%-wt. It could be attributed to the washed out of some ion-exchange particle during membrane immersion due to lower bonding between membrane matrix and the particles.

1. Introduction
Ion-exchange membrane (IEM) has been widely used in a number of different applications such as desalination and seawater pre-concentration, production of chlorine-alkaline, production of organic acids and organic salts, production of ultrapure water, wastewater treatment, and energy generation [1-8]. One of the applications of IEM membrane in energy generation is in reverse electrodialysis (RED). RED unit is very similar to conventional electrodialysis wherein a number of anion and cation exchange membranes are stacked together in an alternating pattern between a pair of electrode (anode and cathode). Due to the gradient salinity of two different solutions (e.g. seawater or brine water with river water) fed into RED cells, the chemical potential is converted to electrical energy by transporting ions from high salinity into low salinity solution called concentrate and diluate, respectively [9]. This technology can be combined with desalination plant such as seawater reverse osmosis (SWRO) in an integrated SWRO-RED system [10, 11]. It is found from the study that the brine from SWRO plant provides a better source for energy recovery. Moreover, the discharged brine can be controlled for minimizing environmental impact due to dilution effect during the process of RED [12]. Development of IEM with improved properties is required to achieve a better performance since IEM is the key of the process. Conductivity and pemselectivity of IEM are crucial properties in order to get a high power density in RED.

In general, commercial IEMs can be classified into homogeneous and heterogeneous membranes with their typical properties and advantages [13]. The homogeneous membrane exhibits better electro-
chemical properties than the heterogeneous [14]. On the other hand, heterogeneous IEMs have better mechanical strength, easier preparation procedure, and lower production cost [15, 16]. Recently, a number of works have been reported in the development of the heterogeneous IEMs which has been driven by the need to obtain IEMs with better properties, lower production cost, and easier preparation procedure [13]. Several modifications methods are proposed to improve the characteristic of heterogeneous IEM or even to obtain a specific property. The modifications methods include additive blending, surface modification, and special treatment after fabrication of a base membrane.

Introduction of additive into membrane solution or the additive blending method is a simple method for improving membrane characteristics. It has been used in many works especially for incorporating inorganic particles [17-25]. In this method, additives are blended together with a polymer and solvent. This solution is then cast into a pre-formed membrane and the solvent is separated through solvent evaporation, solution immersion, or combined process. This blending method is also applied in membrane preparation using extrusion [26]. The properties of the additive such as electrical conductivity, hydrophilicity, and adsorption capacity can be utilized to produce a membrane with better electrochemical characteristics.

In this study, polysulfone-based cation-exchange membrane is prepared using phase inversion method and solution casting technique. The effects of polyethylene glycol (PEG400) and ion-exchange resin content on the membrane characteristics were studied and evaluated in terms of water content, ion-exchange capacity, and membrane conductivity.

2. Materials and method

2.1. Materials
Poly sulfone (PSf) supplied by Solvay Advanced Polymers (Udel PSf P-3500 LCD) was used as a polymer binder. N,N-dimethylacetamide (DMAc) from Shanghai Jingsan Jingwei Chemical Co., Ltd was employed as the solvent. Strong acid cation-exchange resin (Amberlite® IR120-Na) was used in membrane preparation as functional groups. Polyethylene glycol (PEG400) was used as additive. Demineralized water is used throughout the experiment.

2.2. Membrane preparation
The heterogeneous cation-exchange membrane is prepared by phase inversion method and solution casting technique (figure 1). Prior to the membrane preparation, ion-exchange resins were dried in an oven at 60 °C for 24 hours, then pulverized into fine particles and sieved into the desired mesh size (-325+400). The polymer solution was prepared by dissolving PSf and PEG400 into DMAc and stirred until the solution was optically homogeneous. The concentration of PEG was varied from 0 to 45% by weight in a total polymer (PSf/PEG400). The concentration of polymer was maintained at 25% by weight (polymer/solvent). This was followed by dispersing a specific quantity of resin particles (50 and 60 %-wt in total solid or PSf/PEG/resin) and mixing until homogeneous. Afterwards, the mixture was casted onto a glass plate, dried at ambient temperature for 24 hours, and immersed in demineralized water. The thickness of the membranes was about 0.35 (±0.07) mm.

![Figure 1. Membrane preparation steps](image-url)
2.3. Characterization

Water uptake (Wu, g water/g dried membrane) was measured as weight difference between the dried (in oven 60 °C for 24 hours) and wetted membrane as follows:

\[ \text{Wu} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \]  

(1)

In equation (1), \( W_{\text{wet}} \) and \( W_{\text{dry}} \) are the weight of the wetted and dried membrane, respectively.

Ion exchange capacity (IEC) of the membrane was determined by using titration method. First, the membrane tip was immersed in a hydrochloric acid solution for 24 hours. Then, the membrane was immersed in a saturated NaCl solution for 48 hours at room temperature to change the H\(^+\) ions with Na\(^+\) ions. The H\(^+\) ions in the solution are titrated with NaOH 0.01 M while phenolphthalein is used as an indicator. The IEC was calculated by using the following equation:

\[ \text{IEC} = \frac{C \times V}{W_{\text{dry}}} \]  

(2)

Where IEC is ion-exchange capacity (meq.g\(^-1\)), C is molar concentration of the titrant (M), V is titrant volume (ml), and \( W_{\text{dry}} \) is dry weight of the membrane sample (g).

The measurement of membrane conductivity, \( \sigma \) (\( \Omega^{-1}.\text{cm}^{-1} \)), was conducted by using LCR Meter instrumentation with a frequency range from 20 Hz to 2 MHz. To characterize the membrane conductivity, the membrane samples were immersed in the deionized water for 24 h until they were wet enough and saturated. Each sample was cut according to the electrode size used in the measurement cell. The measurement process was conducted at room temperature. The conductivity of the membrane was calculated by using the following equation:

\[ \sigma = \frac{L}{R_{\text{m}}A} \]  

(3)

Where \( L \) is membrane thickness and \( A \) is membrane effective area.

3. Results and discussion

The effects of PEG400 and resin concentration on Wu and IEC are shown in figure 2. Figure 2 shows that the water content is increased with increasing PEG concentration either for the membrane with 50%-wt and 60%-wt of resin. In addition, the membranes with 50%-wt resin have higher water content than that with 60%-wt of resin. Meanwhile, the IEC of the membrane is increased when the PEG concentration is 15%-wt and decreased again for higher PEG concentration. The effect of resin concentration on IEC has a similar trend with the water content.

The increasing water content is attributed to the hydrophilic nature of PEG. As the PEG concentration is increased, the hydrophilicity of the membrane is improved which results in an increase of water adsorption of the membrane. The increasing water content then improves the accessibility of the functional site inside the membrane matrix. As the result, the IEC of the membrane with 15%-wt of PEG is increased.
However, the increase of water content is not always accompanied by the increase of IEC. When the PEG concentration is above 15%, it has a negative effect on IEC. This may be due to washed-out of some resin particles during the membrane immersion. This washed-out of the particles could be the results of lower bonding between resin particles and polymer matrix or binder. Since PEG replaces some portion of PSf, the structure of the membrane becomes weaker. The lower bonding between polymer and resin particles is also observed when the resin concentration is higher (60%-wt). Therefore, the prepared membrane with higher resin concentration exhibits less water content and lower IEC.

The membrane conductivity in various PEG400 and resin concentration is shown in figure 3. It can be observed that the highest conductivity is obtained when the PEG concentration is 15%-wt. This highest conductivity is associated with the high water content and high IEC of the prepared membrane. The adsorbed water inside the membrane contributes to electrical current transfer. The more adsorbed water also indicates the higher conductive part of the membrane instead of the inert or hydrophobic part. Therefore, the high water content results in high electrical conductivity. Meanwhile, IEC represents the amount of functional sites inside the membrane. These functional sites provide the active sites for bridging an electrical current transfer. As the functional sites are increased, the available active media involved in the electrical current transfer is also increased that yields in higher conductivity.

It is indicated in figure 2 and 3 that the electrical conductivity is affected by water content and IEC. However, the role of IEC in improving membrane conductivity is more dominant than the water content. The highest conductivity is obtained from the highest IEC (15%-wt of PEG and 50%-wt of resin). A relationship between IEC and membrane conductivity is elucidated in figure 4. It could be explained from the figure that the conductivity is increased with increasing IEC. It has been explained by the microheterogeneous model that there are two phases which have a contribution to membrane conductivity [27]. Those are a gel phase or the polymeric phase of the membrane and inter-gel phase or the solution phase filling a gap in the membrane matrix. Moreover, the gel phase could be further divided into (i) pure gel phase or the polymeric part with has the functional sites and (ii) inert phase. According to the model, the membrane conductivity ($\sigma$) is expressed by the following equation (if the conductive phase is randomly distributed) [27]:

$$\sigma = \sigma^f_1 \sigma^f_2$$
Where \( \sigma_1 \) and \( \sigma_2 \) are conductivity of the gel and the inter-gel phase, respectively. Meanwhile, \( f_1 \) and \( f_2 \) are fractions of the first and the second phase, respectively.

It is indicated in equation (4) that both phases have the proportional effect on membrane conductivity. Since the measurement of electrical conductivity was conducted using membrane wetted with demineralized water, the functional sites inside the membrane had more contribution in electrical current transfer than the water content. The contribution of the inter-gel phase would be increased if the membrane used in a solution containing high concentration of ions.

\[
\log \sigma (\Omega \cdot \text{cm}^{-1})
\]

**Figure 3.** Conductivity of membrane with various PEG concentration.

\[
\log \sigma (\Omega \cdot \text{cm}^{-1})
\]

**Figure 4.** Membrane conductivity in various IEC and Wu.

4. Conclusion
The PSf-based heterogeneous cation-exchange membrane is synthesized using solution casting method and PEG400 is used as a modifier. The membrane is prepared in the various concentration of PEG and resin particles. The results show that the PEG400 can increase Wu, IEC, and conductivity of the
heterogeneous cation-exchange membrane due to the hydrophilic nature of PEG400. The more hydrophilic membrane results in higher water content and wider access for functional sites. However, when the concentration of PEG400 is increased further, the IEC and conductivity tend to decrease. This tendency is more pronounced when the ion-exchange resin particle is increased from 50 to 60%-wt. It could be attributed to the washed out of some ion-exchange particle during membrane immersion due to lower bonding between polymer binder and the particles.

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