**A Novel Hybrid Poly (vinyl alcohol) (PVA)/
Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO)
Membranes for Reverse Electrodialysis Power System**

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Abstract

The ion exchange membrane (IEM) is a primary component in the reverse electrodialysis (RED) system for salinity gradient power generation. A great challenge exists in the selection of appropriate membrane materials and the design of proper RED membranes to optimize such an energy-producing process. This work presents a novel and cost-effective method for preparing hybrid cation exchange membranes by incorporating two organic polymers with fine film-forming ability. The functionalized poly (2,6-dimethyl-1,4-phenylene oxide) (sPPO) polymer with sulfated polyvinyl alcohol (sPVA) is proved to have great potential as a candidate for applications in RED. The prepared membranes showed that an optimal range of sPVA (2-10 wt%) improved the permselectivity (up to 87 %) and an area resistance (down to $1.31 \Omega \text{ cm}^2$), which is comparable to those obtained with commercially available FKS (Fumasep®, Germany) membranes. The hybrid membrane containing 5 wt% of sPVA achieved the highest gross power density at 0.46 W/m^2 . This study shows the potential of using organic-organic hybrid membranes for the RED power generation system.

1. Introduction

Renewable and sustainable energy sources are playing an important role and becoming increasingly important in view of the ongoing depletion of fossil fuels, growing environmental pollutions, and rising oil prices, in combination with increasing energy demands. Membrane technology provides an opportunity to gain non-polluting and sustainable energy from salinity gradients between seawater and river water, which has been recognized as a vital alternative to generate energy via reverse electrodialysis (RED) [1] and pressure retarded osmosis (PRO) [2, 3]. Each technology has its own

favorable salinity conditions for power generation: concentrated brines is favorable for PRO while seawater mixing with river water is more applicable in RED. PRO uses semi-permeable membranes (i.e., reverse osmosis, RO) to harvest energy through pressurized fluid created by osmotic pressure to drive turbine, while RED employs ion exchange membranes (IEM) to facilitate the transport of ions in two waters with different salinities, which can be converted to electricity [4, 5]. The theoretical amount of energy available for both technologies is comparable, but once operated in large-scale application, RED is considered as more energy efficient with less hydraulic losses. Also, the better chemical resistant of electrodialysis IEMs used in RED makes less sensitive to membrane fouling compared to RO membranes and, in particular, RO membranes are more susceptible to clogging, which may incur significant impact on the efficiency of a PRO process through interference with salt rejection [6, 7].”

RED converts chemical energy arising from the salinity gradient of concentrated and diluted salt solution into electrical power. In a typical RED system, an alternating series of cation exchange membranes (CEMs) and anion exchange membranes (AEMs) are stacked between two electrodes, as shown in Fig. 1.

Fig.1. Conceptual schematic view of energy produced by an RED stack. C is CEM, A is AEM and R is Resistance.

In RED, concentrated and diluted salt solution are pumped through each membrane compartment and allow transport of ions from concentrated to diluted compartments through selective ion exchange membranes. Electrode rinse solution in the electrode compartment is maintained via oxidation and reduction in the anode and cathode surface, respectively. As a result, an electron can be transferred from the anode to the cathode through an external electric circuit which generates an electrical current. A full stack in a RED system can be composed of numerous membrane cell pairs used to generate electrical power for an external load or energy consumer. Herein lies the mechanics behind the vision for large-scale energy conversion by RED.

RED has a great potential to play a vital role in the sustainable development of energy sources due to its technical and economical superiority when compared to fossil fuel systems or other new renewable energy sources such as solar and

wind energy. The RED application is currently limited by the absence of optimized IEMs, the high cost of IEMs, and an overall low power density.

IEMs have attracted great interest and much research across various fields ranging from water treatment [8, 9] to industrial separation [10-14], to power generation [11-13]. Normally, relevant functional physical and electrochemical properties of membranes have been required for each application. As a key component in the system, performance determining characteristics need to be studied. It is well known that electrochemical properties of the membranes have a significant effect on RED performance based on various commercially available membranes being tested and evaluated within a RED stack for generating power [4, 7, 15-18]. Lacey concluded that RED-specific membrane should have properties of low electrical resistance, high selectivity, long service life, acceptable strength, dimensional stability, and low cost [19]. Vermaas *et al.* demonstrated that power density of RED system could be improved through reducing membrane resistance and intermembrane distances [7]. However, it is still worthwhile to investigate the needed membrane properties for membranes with different chemistry formation and materials. Low area resistance, high charge density, high transport number, and high permselectivity are reported to be desirable for ion exchanging process such as RED [3, 15, 20, 21]. However, it is often challenging to tailor membranes for such features [22, 23]. Thus, it is essential to investigate the key membrane properties for maximizing power generation of RED and advance understanding if we are to further the development of RED-specific membranes.

To meet the demand for desired RED-specific membranes (i.e., low resistance, high selectivity, low cost, and ease of preparation), the selected polymers should be low cost

materials and stable for chemical modification. Here, we focus on the development of hybrid organic-organic RED membranes based on 2,6-dimethyl-1,4-phenylene oxide (PPO). The basic form of PPO consists of an aromatic ring, two methyl groups, and a phenol group (Fig. 2(a)).

Fig. 2. Basic chemical structures of (a) PPO and (b) PVA

As a commonly used polymer for forming membranes, which have been widely used in the areas of gas separation, RO, ultrafiltration, and ion exchange, PPO has significant membrane-forming properties with good chemical, thermal, and hydrolytic stability; high glass transition temperature; and low cost [24-27].

However, PPO hydrophobicity retards its dissolution in conventional dipolar solvents. To become ion-exchangeable, a conventional electrophilic substitution is needed to allow charged groups within the polymer matrix (i.e., anionic or cationic moieties) to blend with hydrophilic materials. PPO can become sulfonated poly 2,6-dimethyl-1,4-phenylene oxide (sPPO) and become highly hydrophilic by introducing sulfonate groups ($-\text{SO}_3^-$) to its polymer chain via a sulfonating agent such as chlorosulfonic acid. Until now, sPPO has been widely used for various industrial applications due to its excellent electrochemical characteristics [24, 28]. The sPPO-based IEMs can be modified to overcome the poor performance in aqueous separation processes by mixing with inorganic materials [29, 30]. However, in this case, the functionality of fixed charged

groups could be interfered in such heterogeneous structure, so the resistance may also increase due to its uncharged domains of the matrix.

In addition to inorganic particle blending of PPO membranes, PPO can also be blended or copolymerized with organic materials, which is potentially more stable in organic solvents with high membrane forming ability (e.g., polyvinyl alcohol, PVA). Research shows that hybrid membranes created by introducing soluble components into another organic polymer matrix are viable candidates for RED. Ion exchange capacity (IEC), thermal and mechanical stability, resistivity to organic solvents, and ion transport characteristics of PPO-based membranes can be enhanced by blending with PVA [31, 32].

As an odorless, non-toxic, and water-soluble polymer, PVA is very commonly used in practical applications because of its properties of easy preparation and biodegradability (Fig. 2(b)) [33-35]. PVA also has great properties such as high hydrophilicity, good chemical-resistance, good film formation, and low cost, which allow frequent uses in various applications [32, 34, 36-40]. Normally, PVA can be thermally cross-linked by heat treatment; thus, the density of a prepared membrane may increase under heat annealing process (thermal treatment) for a certain period of time [40].

However, the absence of charged ionic groups in pure PVA polymer results in poor conductivity. In order for PVA to possess reasonable ionic conductivity, chemical or physical modification is required, which allows the presence of charged ionic species in the PVA polymer matrix. PVA-based membranes can be modified by cross-linking, blending, and acid or base treatments. Generally, the electrophilic substitution process can be used to obtain desired conductivity for the PVA membrane by using either sulfonating or sulfating agents for CEMs or animating agents for AEMs [41]. For

example, sulfosuccinic acid (SSA) has been used as a crosslinking agent to introduce negatively charged groups ($-\text{SO}_3\text{H}$) on PVA for fuel cell applications. Obviously improved conductivity at a range of 10^{-3} to 10^{-2} S cm^{-1} has been exhibited for crosslinked PVA membranes with sulfonic groups. The IEC was also enhanced significantly as the SSA loading increased, reaching 2.24 meq g^{-1} with 30 wt% SSA [42].

As previously mentioned, blending sPVA into sPPO can be a promising approach to enhance the physical and electrochemical properties of membranes. However, to the best of our knowledge, no research exploring the use of sPVA in the sPPO polymer matrix has been reported in any field. The objective of this study is to introduce our design strategy for the development of a new type of RED-special membrane. This paper also presents our investigation into the effect of sPVA loading to optimize membrane performance in the RED system.

2. Experimental

PPO (Aldrich, analytical standard, M_w 30,000, M_n 20,000) was used as the base material. Chloroform (Aldrich, anhydrous, 99%) was used as a solvent for PPO sulfonation. Chlorosulfonic acid (Aldrich, 99%) and methanol (Aldrich, 99%) were used without purification. Sulfuric acid (Aldrich, 98%), ethyl alcohol (Aldrich, 99%) were also used as the reagent for PVA sulfating. Dimethylsulfoxide (DMSO) (ACS grade, 99.9%) was purchased from VWR. PVA (Aldrich, analytical standard) was used for sulfonation. sPPO was prepared by sulfonation of PPO according to the literature [43].

2.1. Preparation of hybrid membranes

2.1.1. Sulfonation of PVA

The powder of PVA was sulfated by concentrated H_2SO_4 (98%). The required amount of PVA was dissolved in DI water. Excess concentrated H_2SO_4 (98%) was slowly added to the PVA solution; then, the PVA solution was stirred vigorously in a water-bath over a period of 4 hours at 40 °C. As shown in Fig. 3, ethyl alcohol was slowly added to the PVA solution over a period of 30 min while stirring the solution vigorously at 25–30 °C until the sPVA was precipitated. Precipitation of sPVA was dried for 24 h at 50 °C in a vacuum oven.

Fig. 3. Synthesis route of sPVA

2.1.2. Membranes preparation

Hybrid RED membranes were prepared by the method of solvent evaporation. As shown in Fig. 4, sPPO polymers were dissolved in Dimethylsulfoxide (DMSO) to form a 20 wt% solution. 0–20 wt% of sPVA polymer (with the quality of sPPO polymer contrast) was dissolved in DMSO. Then the sPVA solution merged into the sPPO solution, and the mixed solution was stirred for 24 h at 40 °C. The mixed solution was then further mixed in an ultrasonic bath for 30 min to get sPVA dispersed uniformly in the solution. The well mixed solution was then cast onto a glass plate by the doctor blade to obtain the desired thickness of the membrane (near 50 µm). The obtained solid hybrid membrane was then put into a vacuum oven at 50 °C for 24 h and at 60 °C for another 6 h to fully remove solvents residing in the membrane. The prepared membrane was immersed in 40–50 ml

of warm water and then in 1 M HCl solution for 24 h. The membranes were further rinsed by DI water and were finally soaked in a 0.5 M NaCl solution for storing.

Fig. 4. Preparation process of the hybrid membranes

2.2. Membrane characterization

The chemical structures of the hybrid membranes were analyzed with Fourier transform infrared (FTIR) Spectrometer (Digilab FTS7000) equipped with a microscope (Digilab UMA600). The spectrum of the hybrid membranes were obtained with the average of 32 scans per sample at the resolution of 4 cm^{-1} and a spectral ranging of $4000\text{--}700\text{ cm}^{-1}$, together with the ambient air serving as the background spectrum.

Membrane morphology was observed using a scanning electron microscope (Zeiss Ultra60 FE-SEM). For the cross-sectional surface, liquid nitrogen was used to pretreat the membranes, which were manually cut to obtain a clear surface in the cross-section area. Samples were then dried overnight to preserve their structure.

Dry membranes and wet swollen membrane were accurately weighed to measure the swelling degree (SD) of hybrid membranes. The SD of a membrane was calculated in wt% by the following equation [44]:

$$SD = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (1)$$

where W_{wet} (g) and W_{dry} (g) are the weight of the wet and dry membrane, respectively.

IECs were measured through the back titration method [43]. Dry membranes were accurately weighed. The membranes were immersed in 1 M NaCl solution at least 15 h for converting free ions to H⁺ form. Excessive HCl was washed off with DI water, and then the membranes were immersed in 1 M NaCl solution for another 6 h. IECs were obtained by determining the decrease of HCl through back titration with 0.01 mol/L NaOH using phenolphthalein as an indicator. Then the fixed-charge density of membranes was acquired by the IEC over the SD. The IEC and the fixed-charge density of the membranes were calculated using the following equations:

$$IEC = \frac{C_{NaOH} \times V_{NaOH}}{W_{dry}} \quad (2)$$

$$C_{fix} = \frac{IEC}{SD} \quad (3)$$

where, C_{fix} is the fixed-charge density of the hybrid membrane, C_{NaOH} is the concentration of NaOH solution (mol.L⁻¹), V_{NaOH} is the volume of NaOH solution (L) used and W_{dry} is the dry weight (g) of the membrane.

The apparent permselectivity of the hybrid membranes was obtained by a static membrane potential measurement, which consisted of two cells separated by the membrane under investigation which has a 4.8 cm² effective area. Two solutions of 0.1 M and 0.5 M NaCl flowed through the separated compartment and their potential differences were measured with two Ag/AgCl reference electrodes (Hanna Instruments, USA) using a multimeter (Tektronix, USA) under room temperature [43]. These steps allowed the permselectivity of the membrane to be calculated as follows:

$$\alpha(\%) = \frac{\Delta V_{measured}}{\Delta V_{theoretical}} \times 100 \quad (4)$$

where, α is the membrane permselectivity (%), $\Delta V_{measured}$ is the measured membrane potential (V) and $\Delta V_{theoretical}$ is the theoretical membrane potential. $\Delta V_{theoretical}$ can be calculated from the Nernst equation, which is estimated to be 0.0379 V [45].

Electrical resistance is affected by temperature, so it decreased as the temperature rose. A two compartment cell filled with 0.5 M NaCl aqueous solution was used to measure the electrical resistance of the hybrid membranes at room temperature. We used two titanium electrodes with Ru–Ir metal oxides coating and potentiostat (Vertex, Ivium Technology) to measure the electrical resistances by Impedance spectroscopy (IS) [43]. The frequency range was from 10–10⁵ Hz with an oscillating voltage of 0.1 V amplitude.

2.3. RED membranes performance

The power performance of hybrid membranes was investigated by using a lab-scale RED in the study. As described in our previous study, the lab-scale RED stack consists of electrode rinse solution, woven fabric, simulated concentrated salt solution (0.5 M NaCl) and a diluted salt solution (0.017 M NaCl), together with four pieces of anion exchange membranes (FAS) (Fumasep®, Germany) and five pieces of cation exchange membranes (FKS (Fumasep®, Germany) or testing hybrid membranes) arranged at regular intervals between two endplates [43, 46]. A solution of NaCl (0.25 M) with K₄Fe(CN)₆ (0.05 M) and K₃Fe(CN)₆ (0.05 M) was used as an electrode rinse solution for facilitating the transfer of electrons. Woven fabric at a thickness of 250 μ m was applied to support and separate membranes; meanwhile, we had to determine the intermembrane distance of water compartments for the simulated seawater and fresh water to pass through. Each membrane had an effective area of 4 cm $\times$ 9 cm. Two silver wires placed half-into the stack between the spacers were used as the anode and cathode. A potentiostat in the

galvanostatic mode was used to measure E–I curves and calculate the gross power generation for evaluating the RED performance of the hybrid membranes. One peristaltic pump of double stream (Masterflex, Cole-Parmer) was used to feed the concentrated salt solution and the diluted salt solution through the RED system at various flow rates. Another peristaltic pump (Masterflex, Cole-Parmer) was used to feed an electrode rinse into the compartment between the shielding CEM and the endplates.

3. Results and Discussion

3.1. FTIR spectra study

The Fourier Transform Infrared Spectroscopy (FTIR) spectra of hybrid membranes are shown in Fig. 5. The broad bands appear in the range of 3200-3600 cm^{-1} , corresponding to the stretching vibrations of -OH groups. The bands at 2856 cm^{-1} , 1644 cm^{-1} and 942 cm^{-1} are from the stretching of –CH₂-, CH-groups and C–O–C stretch [47], which represent the original PPO polymer. The characteristic absorption band for the presence of the –SO₃H substitute for PPO aromatic rings appeared by the FTIR peak at 1060 cm^{-1} after it was formed from the sulfonation reaction. IR vibration bands for the characteristics of C–S–O stretching were observed at 1186 cm^{-1} . The FTIR peak at 3389 cm^{-1} was formed from stretch vibration absorption after shifting slightly from the hydroxyl of sPVA absorption peak (3434 cm^{-1}). This shift and subsequent peak was caused by hydrogen reaction between –OH groups and –SO₃H. Overall, these occurrences confirmed successfully merging the sPVA polymer to the sPPO polymer and a new hybrid compound being made.

Fig. 5. FTIR spectra of hybrid membranes

3.2. Morphology of the hybrid RED membranes

To attain the mixing behavior of sPVA and sPPO membranes, SEM was used to observe the morphology of hybrid RED membranes. The top surface and cross-section of the SEM were analyzed to observe the structure of the membrane skin layer. The SEM images of the surface and cross-section of the membranes are presented in Fig. 6 and Fig. 7, respectively.

As seen in the surface and cross section images of (b) sPPO-2% sPVA and (c) sPPO-5% sPVA hybrid membranes, relatively small pores were observed to be uniformly distributed within polymer matrix. However, for (d) sPPO-10% sPVA, (e) sPPO-15% sPVA, and (f) sPPO-20% sPVA, much bigger hollow structures are present. The cross-sections (Fig. 7) of these last three membranes confirm that compared to (a), (b), and (c), a less dense structure and possible defects are prevailing in (d), (e), and (f). This continuous change in morphology correspond well with the membrane properties that will be discussed in the following sessions.

Fig. 6. SEM surface morphology of (a) sPPO, (b) sPPO-2% sPVA, (c) sPPO-5% sPVA, (d) sPPO-10% sPVA, (e) sPPO-15% sPVA, and (f) sPPO-20% sPVA

Fig. 7. SEM cross section surfaces morphology of (a) sPPO, (b) sPPO-2% sPVA, (c) sPPO-5% sPVA, (d) sPPO-10% sPVA, (e) sPPO-15% sPVA, and (f) sPPO-20% sPVA

3.3. Electrochemical properties of the hybrid RED membranes

In this work, key characteristics of prepared hybrid RED membranes, including permselectivity, area resistance, IEC, SD, and C_{fix} were measured to evaluate their potential performance in the lab-scale RED system. The performance potential ratio was also presented by calculating the values of permselectivity (P^2) over area resistance (R) [43]. All values were measured three times to ensure reliable data and the error bars are in

all cases less than 5%. For comparison, the corresponding data of commercial CEM, FKS (Fumasep®, Germany), were also shown in the hybrid membrane tests.

3.3.1. Area resistance and SD of hybrid RED membranes

As one key parameter of RED membranes, the SD is dependent on the nature of the membrane structure and material, as well as the outer solution condition, which refers to the membrane's water content per unit weight [21, 46]. For example, SD can be restrained in a membrane with the increase of its cross-linking degree [48, 49]. On the other hand, the features of SD are also affected by the mechanical properties, dimensional stability, ion selectivity and electrical resistance of the membranes [50].

Electrical resistance is another key characteristic of RED membranes, which directly affects the gross power production in the RED system. The membrane resistance is highly influenced by the ion transport and IEC of the membrane. The temperature also alters the electrical resistance, i.e. lowers the resistance with temperature increase [45].

In our experiments, the SD values of hybrid membranes increased from 45.63% to 93.91% as the sPVA content increased, which indicated that the membranes had high hydrophilicity (Fig. 8). The increased hydrophilicity is mainly attributed to a reduced crosslinking degree. The hydrophilic nature of the membrane had great effects on its SD and area resistance [15]. And the SD is usually considered as a positive effect when striving to decrease membrane resistance in certain cases, especially for anion exchange membranes. Hence, membranes with a high SD are expected to have low area resistances [27, 45, 47, 51].

In our experiment, we observed a great decrease of area resistance along with SD increase, ranging from $2.11 \Omega \cdot \text{cm}^2$ (0 wt% sPVA) to $1.31 \Omega \cdot \text{cm}^2$ (10 wt% sPVA) (Fig. 8).

However, as the sPVA content increases further from 10 through wt% sPVA, the area resistance slightly reversed its tendency to increase by going back to $1.43 \Omega \cdot \text{cm}^2$. Thus, the lowest area resistance was achieved with the membrane containing 10 wt% of sPVA. Probable factors should be considered which may affect area resistance under the condition of SD achieving a certain degree, such as the charge density, the density of the polymer network and the morphology of the membrane itself. It has been reported that the pore formation and surface roughness of the composite also affects the transport of ions, permselectivity and conductivity [10].

Fig. 8. Area resistance and swelling degree (SD) of hybrid membranes. The triangles and circles are the SD and area resistance for custom-made membranes, respectively. The data of commercial membrane FKS has also been marked in horizontal line for comparison.

3.3.2 Effect of sPVA loading on C_{fix} and permselectivity

According to Donnan exclusion, ions with the same charge as the fixed ions are excluded and cannot pass through the membrane. On the contrary, oppositely charged ions can pass freely through the IEMs [52]. Fixed-charged groups containing mobile cations were attached to the polymer backbone in the hybrid membranes, which are often required to selectively separate some cations. Transport and permselectivity of mobile cations through the membrane are affected by the fixed-charge density in the membrane and the difference between the concentrations of the electrolyte solution in contact with the membrane. The permselectivity of the hybrid membranes describe the cations selectivity of the membranes from a solution containing anions and cations, which is determined by the type of the fixed ionic charges. In general, membranes with a lower fixed charge density have a lower selectivity as well [15].

Fig. 9. C_{fix} and Permselectivity of hybrid membranes. The triangles and circles are the C_{fix} and permselectivity for custom-made membranes, respectively. The data of commercial membrane FKS has also been marked in horizontal lines for comparison

Fig. 9 presents the membrane permselectivity and C_{fix} of the investigated hybrid membranes as a function of sPVA loading. As the amount of sPVA loading increased, we observed a great decrease of C_{fix} in the hybrid membranes, from 4.54 (0 wt% sPVA) to 1.68 (20 wt% sPVA) (Fig. 9). In a swollen state, the distance between ion exchange groups increase thus reducing the fixed charge density [15].

Although the charge density has a strong influence on the permselectivity, no straight forward relationship can exist between these properties. Therefore, other factors must be considered, such as the density of the polymer network, the hydrophilicity of the polymer matrix, and the morphology of the membrane. In this study, the loading of 5 wt% sPVA achieved the highest membrane permselectivity (Fig. 9).

3.3.3 Effect of sPVA loading on IEC

For the hybrid IEMs prepared using hydrophobic polymers as a base material, the SD values increased with a decrease in IEC as sPVA loading increased. As the hydrophilic nature of the membrane kept it expanding, more swelling occurred. As the swelling increases, the density of ion exchanging groups decreases (i.e., lowering the IEC) possibly due to disruption of the charged functional groups in the polymer matrix. The decreased IEC weakened the ion conductivity of the sPVA, which also decreased the transport properties. Consequently, the IEC and other ionic transport properties were affected by excess sPVA loadings, which decreased the overall membrane performance.

Fig. 10. IEC of hybrid membranes. The squares are the IECs for custom-made membrane. The horizontal dash line marks the IEC of FKS membrane.

Similarly, for the commercial FKS membrane, having high IEC did not result in low area resistance. In our experiment, no apparent signs of a direct relationship between IEC and resistance were exhibited (Figs. 8 and 10). Therefore, the relationship of IEC and resistance may not always lead to the trend of inverse correlation [15, 53].

3.3.4 Effect of sPVA loading on performance potential ratio

Based on Kirchhoff's law, we can yield the maximum power density output ($P_{\max}$) per unit membrane area of the RED system, which predicts the theoretical membrane stack power output. The $P_{\max}$ equation can also relate individual membrane properties, which can be used as a tool to compare different IEMs with respect to their performance in a RED stack [7, 45, 50, 54]. The $P_{\max}$ of the testing membrane is shown in the following equation:

$$P_{\max} = \frac{[\alpha RT / F \ln(\alpha_c / \alpha_d)]^2}{AR_{\text{stack}}} \quad (5)$$

where, R is the gas constant ($\text{Jmol}^{-1}\text{K}^{-1}$), T is the absolute temperature (K), F is the Faraday constant (Cmol^{-1}), α is the average apparent permselectivity of the membrane (%), a_c is the activity (molL^{-1}) of the concentrated salt solution, a_d is the activity (molL^{-1}) of the diluted salt solution, A is the membrane area (m^2), and R_{stack} is the stack resistance. This equation is based on the hypothesis that the RED system can generate a maximum power under the load when the state of the resistance is equal to R_{stack} [54, 55].

According to the Equation (5), permselectivity and resistance are the key properties for a $P_{\max}$ per unit membrane area in the RED system. Thus, P^2/R can be an indication of the best-performing membranes for power generation to a certain extent. Without considering other constants, which membrane property dominates RED system performance is not yet fully known and the relationships between these properties are not clearly understood. In our experiment, the loading of 5–15% sPVA achieved the highest level of P^2/R and decreased as more sPVA dosages were applied (Fig. 11), which indicates that the maximum power density level may lie on such range.

Fig. 11. Performance potential ratio of hybrid membranes. The custom-made membranes are marked as squares. The horizontal dash line marks the IEC of FKS membrane.

3.4. RED performance of hybrid IEMs

Power density of the membranes was tested by using five CEMs and four AEMs. Commercial CEMs from FKS (Fumasep®, Germany, thickness of 50μm) and AEMs FAS (Fumasep®, Germany, thickness of 50μm) were tested in RED stacks under the flow rate of 0.8 cm/s as a reference. Then under the same condition, FKSs were replaced by sPPO-sPVA membranes, and the gross power density was estimated from the product of E-I (voltage-current) curve we obtained. The results are shown in Fig. 12.

Fig.12. Power density of hybrid membranes. The custom-made membranes are marked as squares. The horizontal dash line marks the IEC of FKS membrane.

With the increase dosage of sPVA in the hybrid RED membranes, the gross power density of the membranes increased from pure sPPO membrane (0 wt%) to sPPO containing 5% sPVA. When sPVA loading continued to increase, the power density of the membrane dropped dramatically down to 0.35 W/m². The performance of the membrane reached its peak at the ratio of 5%, which can provide power of 0.462 W/m². Compared to the commercial FKS membranes, three membranes (i.e., 0 wt% sPPO, 2 wt% sPVA and 5wt% sPVA) achieved a higher power density, and the 5 wt% sPVA membrane achieved the highest power performance, which exceeded the power achieved with the commercial membrane by about 14%. Test results showed that these hybrid RED-special membranes have great potential for generating electricity, more so than the commercial IEMs in view of low cost and easy membrane-forming process. The relatively high permselectivity of 87.17%, low area resistance of 1.54, and high IEC may have played a

crucial role in determining the power output. The hybrid membrane (15 wt% sPVA) had the poorest results in power generation. As mentioned above, the amount of sPVA incorporated inevitably affects the polymer matrix and its inherent properties, which imposes influence on power density. Questions still remain as to the long-range effects of hybrid RED-special membranes for power generation impact, the mechanics of their mutual electrochemical relationships (IEC, area resistance, SD, and permselectivity) and the effects of physical properties (porosity). More research is needed to obtain a reliable interpretation of how these RED hybrid membranes can be used as a sustainable replacement for fossil fuels in the next generation of energy providers. However, the design presented herein of hybrid organic-organic RED special membrane represents great progress towards achieving the desired synthesis of RED membranes, which draws us closer to the promotion of its commercial application.

4. Conclusions

This work focused on membrane characteristics and the great importance they have toward achieving commercial power generation within in a RED system. A novel design of hybrid organic-organic cation exchange membranes was conducted and its electrochemical and physical properties were tested to investigate its performance in the power generation process. In order to enhance the membranes' properties that are vital for RED system performance, a small amount of sPVA was mixed with sPPO polymer matrix. The effect of sPVA loading to the membrane properties like IEC, SD, area resistance and permselectivity was also studied in great detail with the aim to optimize membrane performance. The membranes performed best at a sPVA range of 0–20 wt%. By controlling the sPVA loading amount, the hybrid membrane had its greatest performance

at 5 wt% sPVA, which reached the power density of 0.46 W/m^2 , achieving a 14% higher power generation output than what is currently available from FKS membranes. Therefore, this kind of hybrid membrane shows great potential for power generation use in a RED system. Comparatively high performance, cheap raw materials and the simple film-forming process of the hybrid RED-special membrane also indicates its superiority in economy over current commercial membranes used in RED system. Even though it has significant advantages, further investigations are necessary to better understand the effect of hybrid organic-organic polymer on RED performance as well as the correlation of key membrane properties for other compositions. At the same time, further investigation on economic comparisons of various membranes is necessary to provide an accurate financial forecast on cost savings.

Acknowledgments

This research was partially supported by the Litree Purification Company and the U.S. National Science Foundation (CBET-1235166).

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