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Short Communication

Directly Copolymerized Disulfonated Poly(arylene ether sulfone) Membranes for Vanadium Redox Flow Batteries

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For the first time with this study, membranes from directly copolymerized disulfonated poly(arylene ether sulfone) (BPSH 35) were utilized to replace Nafion^{TM} in vanadium redox flow batteries (VRFB). Direct copolymerization provided exact control of the degree of disulfonation on the chemical structure. BPSH 35 showed higher proton conductivity (75 mS cm^{-1}), lower vanadium permeability (1.6x10^{-13} m^2 s^{-1}) and better selectivity (4.7x10^{13} S m^{-3} s) than N212. The water uptake values for N212 and BPSH 35 membranes were 28 and 40 % by weight, respectively. Higher proton conductivity and water uptake were observed due to the higher ion exchange capacity (IEC) values of BPSH35. In spite of high water uptake of BPSH35, it showed better resistance to vanadium permeation which was most probably because of the chemically bulky nature of the membrane. Moreover, higher columbic (98.9 %) and energy efficiencies (75.6-90.3 %) at the considered current densities than N212 were achieved. Consequently, BPSH 35 membranes were successfully demonstrated as an inexpensive energy efficient candidate for VRFB.

Keywords: Vanadium redox flow battery; disulfonated membrane; poly(arylene ether sulfone); direct copolymerization

1. INTRODUCTION

Vanadium redox flow batteries (VRFBs) are promising candidates for the grid and load leveling energy storage applications [1]. High energy efficiencies, long cycle life and also cost effectiveness of VRFBs have been reported extensively [1-4]. VRFBs also provide flexibility in design especially for high capacity storage applications [5]. Moreover, they are very suitable in backup systems due to their well-known fast response [3, 4].

Among the components of the VRFBs, the membrane assembled in the battery is the most important one. Although Nafion^{TM}, which is a perfluorinated copolymer, has been extensively used in

VRFBs, it suffers from low ionic selectivity and high vanadium permeability. Additionally, the high cost of the Nafion^{TM} makes resulted VRFB less cost effective. Therefore, inexpensive membranes with lower vanadium permeability, higher conductivity and ionic selectivity are required for VRFBs [1, 5, 6].

Post sulfonated polymers have been widely studied to meet these requirements due to their reasonable cost, low vanadium permeability and high proton conductivity [7-10]. Chen et. al. [7-9] studied post-sulfonated poly(arylene ether sulfone) copolymer membranes in VRFB. They showed that the performance of the membrane is related with the ion exchange capacity (IEC). Since IEC is proportional to the degree of sulfonation, the control on the sulfonation of the membrane is very important for the VRFB performance. Also, Kim et. al. [10] evaluated the performance of post sulfonated membranes in VRFB. However, the post sulfonation method has several drawbacks on the resulted membrane properties. For example, undesirable chain scission, branching and crosslinking can occur during post sulfonation. Morover, decrease in the intrinsic viscosity, insolubility and inability to produce ideal films may be resulted from post-sulfonation process. Additionally, the sulfonation degree can not be controlled in post sulfonation [11-13]. In order to provide exactly the same amount of sulfonation consistently on deactivated position enhancing the chemical stability due to the low electron density, it is crucial to use direct copolymerization of sulfonated monomers. Direct copolymerization has been extensively studied for especially fuel cells and desalination process [11-18]. For the first time with this study, membranes from directly copolymerized disulfonated poly(arylene ether sulfone) (BPSH) (Fig. 1) has been studied for VRFBs.

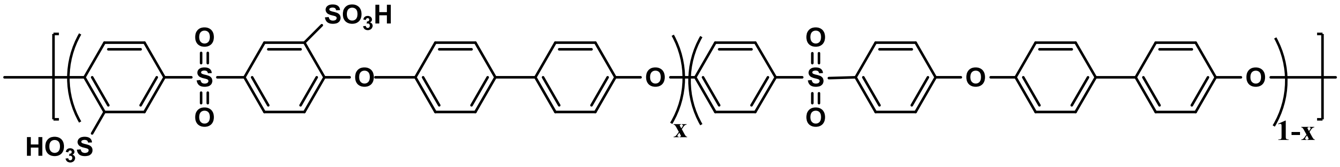


Figure 1. The chemical structure of BPSH copolymer

2. EXPERIMENTAL

2.1. Membrane Preparation

The direct copolymerization of BPSH 35 (35 molar percent degree of disulfonation) has achieved as described in our previous studies [12-14]. A 10 % of copolymer solution in N,N′-dimethylacetamide was prepared and casted on ordinary glass under IR lamp (about 60^0C) for 12 h. Membranes were acidified in boiling sulfuric acid (0.5 M) for two hours followed by two-hour reboiling in deionized water. Later, they were kept in water prior to further use in VRFBs [15-17].

2.2. Characterization of Membrane Properties

BPSH 35 copolymer was dissolved in dimethylsulfoxide having a 10% (w/v) solution for ^{1}H-NMR (Bruker Avance III 400 MHz) measurements. Fourier transform infrared (FTIR) spectrum was recorded using a Perkin Elmer Spectrum 100 FT-IR spectrometer. The water uptake of the membrane is calculated according to the equation given below:

$$\text{Water uptake (\%)} = \frac{W_w - W_d}{W_d} \times 100 \qquad (1)$$

where W_d and W_w are the weight of the dry and wet membrane which is kept in deionized water for 24 hours, respectively.

The proton conductivity of the membrane was measured by Bekktech BT-112 conductivity cell via electrochemical impedance spectroscopy in deionized water at 26^0C (Solartron 1260, 1287). The conductivity (σ) was then calculated by the equation:

$$\sigma = \frac{d}{RA} \qquad (2)$$

where d is the thickness, A is the surface area of the membrane and R is the resistance derived from the intercept of the high frequency complex impedance with the Re (Z') axis.

The VO^{2+} permeability test was conducted at 25^0C with a cell having two reservoirs separated by the membrane. One reservoir was filled with 50 ml of 1.0 M VO^{2+} in 3.0 M H_2SO_4. On the other hand, 1.0 M $MgSO_4$ in 3.0 M H_2SO_4 as vanadium blank solution was used in the other reservoir in order to equalize the osmotic pressure. Solutions were magnetically stirred during the experiment. The VO^{2+} concentration was determined by measuring its absorbance with a Perkin Elmer UV-Vis spectrophotometer. The VO^{2+} permeability, P, of the membrane was calculated by following equation:

$$P = \frac{V_B L}{A(C_A - C_B(t))} \times \frac{dC_B(t)}{dt} \qquad (3)$$

where V_B is the volume of $MgSO_4$, blank solution, L is the thickness, A is the effective area of the membrane, C_A is the initial VO^{2+} concentration in the VO^{2+} compartment, while $C_B(t)$ is the permeated VO^{2+} concentration in the $MgSO_4$ compartment as a function of time (t).

Ion exchange capacity, IEC, of the membrane was calculated according to the following equation:

$$IEC = \frac{2 \text{ x mole fraction of disulfonation}}{(MW_{\text{non-sulfonated unit}} \text{ x its mole fraction}) + (MW_{\text{sulfonated unit}} \text{ x its mole fraction})} \qquad (4)$$

where of $MW_{\text{non-sulfonated unit}}$ and $MW_{\text{sulfonated unit}}$ are the molecular weight of the non-sulfonated and sulfonated unit, respectively.

Selectivity of the membranes (Φ) (Eqn. 5) was defined as the ratio of the proton conductivity (σ) of the membrane to VO^{2+} permeability (P).

$$\Phi = \frac{\sigma}{P} \qquad (5)$$

2.3. Cell Performance

The electrolyte was 1.0 M $VOSO_4$ in 3.0 M H_2SO_4. Volumes of the electrolytes were 50 and 100 mL in the cathode and anode compartments, respectively. Electrolytes were pumped under N_2 environment to the cell continuously with a flow rate of 110 mL min^{-1}. Electrochemical measurements were conducted using Solartron system (1260A and 1287). For the charging and discharging processes, 0.7 and 1.7 V were selected as lower and upper limit voltages at constant currents, respectively. The coulombic (CE), voltage (VE) and energy efficiencies (EE) of the cell were calculated by the following equations (Eqn. 6-8):

$$\mathrm{CE}\ (\%)=\frac{t_d}{t_c}\mathrm{x}100 \qquad (6)$$

$$\mathrm{VE}\ (\%)=\frac{V_d}{V_c}\mathrm{x}100 \qquad (7)$$

$$\mathrm{EE}\ (\%)=\mathrm{CE\ x\ VE} \qquad (8)$$

where t_d and t_c are the discharging and charging time, respectively. On the other hand, V_d and V_c are the average discharging and charging voltages, respectively.

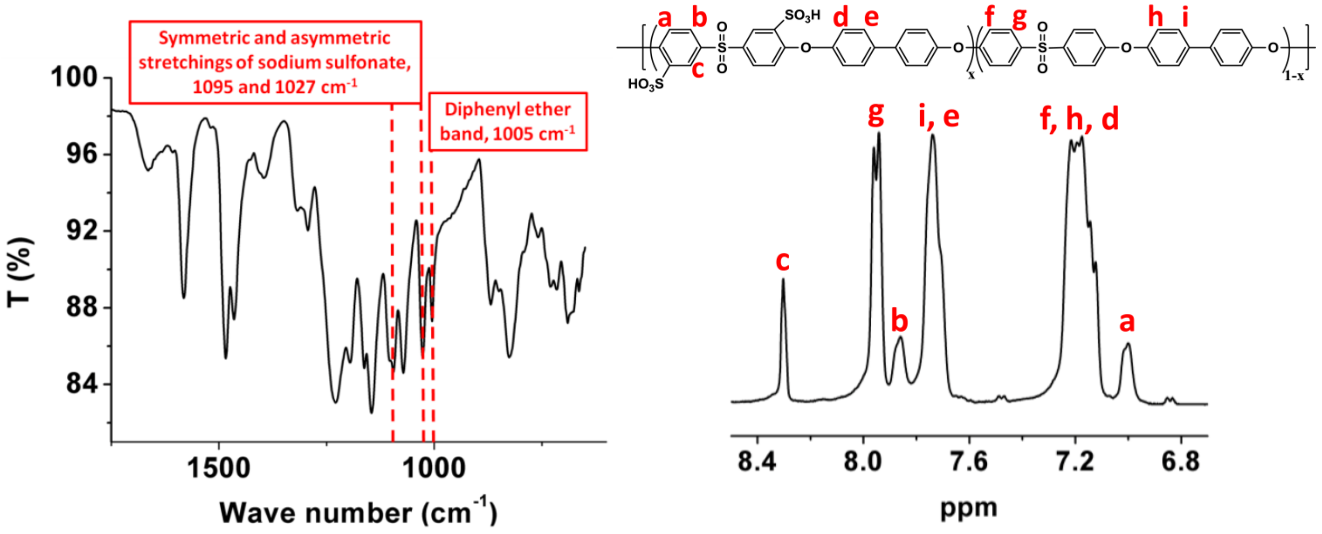
3. RESULTS AND DISCUSSION

The ion exchange capacity (IEC) of the membrane can be directly related to the cell performance of vanadium flow battery [7]. By varying IEC of the membrane, proton conductivity and electrolyte permeability can be tailored [15, 18]. Since the IEC is a function of the degree of sulfonation, precise controlling of the degree of sulfonation especially by direct copolymerization is an important issue for the proton exchange membranes [18]. The sulfonation of the polymer can be achieved in two ways, namely post sulfonation and direct copolymerization. The direct copolymerization has several advantages over the post sulfonation. The most important one is that sulfonation sequences can be exactly controlled by direct copolymerization [11, 18]. In other words, the IEC can also be simply varied by changing the ratio of disulfonated to nonsulfonated monomer in the copolymerization step.

3.1. Membrane Characterization and Properties

The chemical structure and degree of sulfonation (34.95 %) of BPSH 35 used in this study was confirmed by the FTIR and ^{1}H-NMR spectra (Fig. 2). FT-IR of BPHS 35 shows that monomers were successfully incorporated to the structure. The peak at 1005 cm^{-1} is the characteristic Ar-O-Ar diphenyl ether linkage. On the other hand, peaks at 1027 cm^{-1} and 1095 cm^{-1} are belong to the symmetric and asymmetric vibrational strechings of the sulfonic acid group salt respectively. ^{1}H-NMR spectrum of BPSH 35 indicates that almost 35 percent disulfonation as targeted was achieved.

IEC values were 1.54 and 0.48 mequiv g^{-1} for BPSH 35 and N212, respectively. Higher IEC value of BPSH 35 has resulted with higher proton conductivity (75 mS cm^{-1}) than N212 (40 mS cm^{-1}) (Table 1). Since Nafion^{TM} has fluorocarbon (Teflon^{TM} like) backbone, as expected that it shows lower water uptake than disulfonated copolymer. Additionally, the VO^{2+} permeability of BPSH 35 membrane was lower than that of N212 membrane. . This could be attributed to bulky backbone nature of the disulfonated copolymer. The stiff aromatic backbone produces a more closed structure reducing vanadium permeability, whereas Nafion^{TM} with its fluorocarbon backbone and β-relaxation below room temperature affords higher permeability. Similar behavior was observed for methanol permeabilities of BPSH copolymers [18]. Therefore, the selectivity of BPSH 35 was better than N212**.**



(a) (b)

Figure 2. The FT-IR (a) and ^{1}H-NMR spectra (b) of BPSH 35.

Table 1. Basic membrane properties of BPSH 35 and N212.

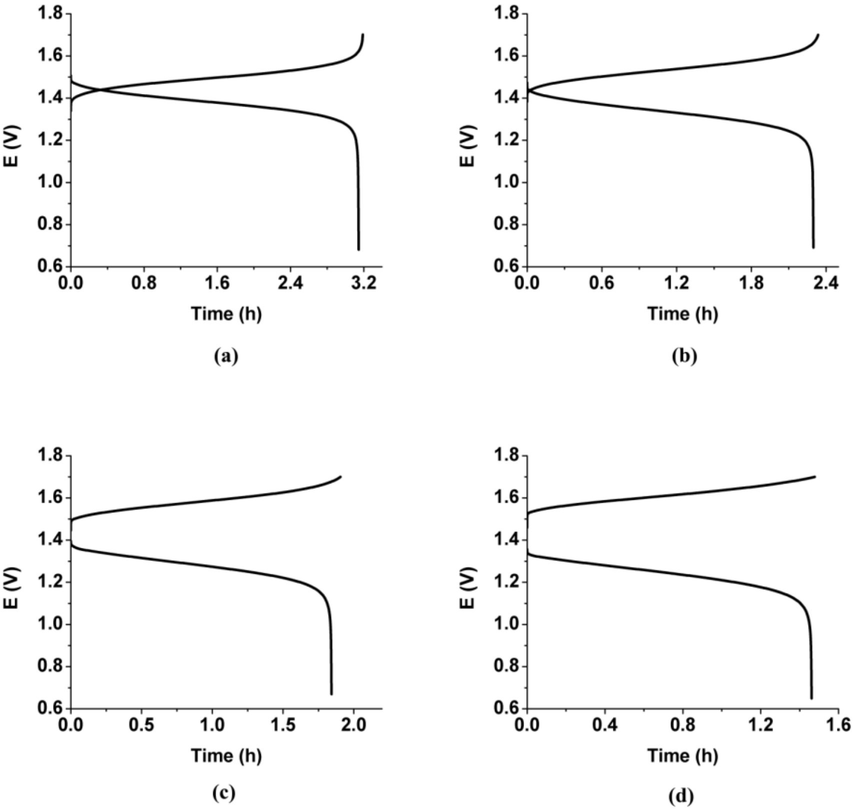
Membrane	IEC (mequiv g^{-1})	Proton Conductivity (mS cm^{-1})	Selectivity (S m^{-3} s)	Water Uptake (wt.%)	VO^{2+} Permeability (m^2 s^{-1})
BPSH 35	1.54	75	$4.7x10^{13}$	40	$1.6x10^{-13}$
N212	0.48	40	$3.1x10^{12}$	28	$1.3x10^{-12}$

3.2. VRFB Performance

In Fig. 3, the charge and discharge curves of the BPSH 35 are shown. The coulombic efficiency was reached about 98.9%. The increase in current density causes decreasing both charge and discharge time. This leads to lower the vanadium crossover for shorter charge and discharge time. Inspite of the fact that charge and discharge voltages decreases with lowering the cross over effect, one can easily notice that the ohmic polarization becomes dominant. Therefore, the difference in charge and discharge voltages increased with the current density [19].

As can be seen in Fig. 4a, the CE of BPSH 35 remained constant while the current density was varied from 20 to 80 mA cm^{-1}. However, the CE of N212 decreased from 94.2% to 87.6% due to the increase in vanadium permeation resulted with longer operational time. At all four current densities, the CE of BPSH 35 was higher than that of N212. This could be attributed to lower VO^{2+} permeability of the BPSH 35 copolymer when compared to the N212 (Table 1).

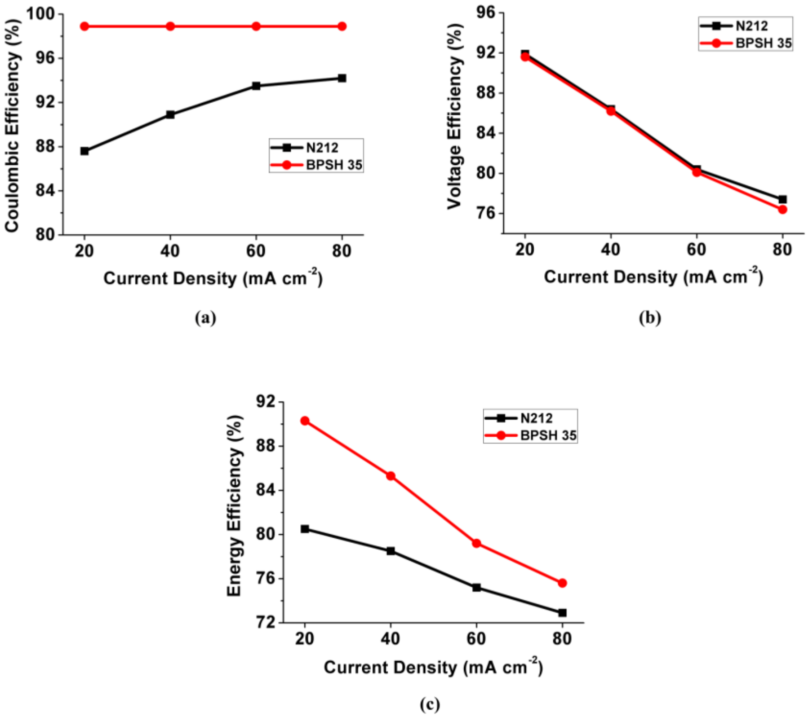
The VEs of the cells assembled with BPSH 35 and N212 can be seen in Fig. 4b. As current density increased, the VE of both cells decreased as expected due to the ohmic polarization effect. Despite proton conductivity of the BPSH 35 was higher and vanadium permeability was lower than N212^{TM}, VEs were comparable for almost all current densities. This behaviour has also been reported in other studies [1, 7].



(a) (b)

(c) (d)

Figure 3. Charge discharge curves of vanadium redox flow batteries assembled with BPSH 35 membrane at 20 mA cm^{-2} (a), 40 mA cm^{-2} (b), 60 mA cm^{-2} (c) and 80 mA cm^{-2} (d).



(a) (b)

(c)

Figure 4. Coulombic (a), voltage (b) and energy (c) efficiencies of the vanadium redox flow batteries assembled with BPSH 35 and N212.

The EE, which is the product of CE and VE, can also be described as the ratio of the output to input energy of the vanadium redox flow battery. The EEs of BPSH 35 and N212 was illustrated in Fig. 4c. The BPSH 35 copolymer membrane had higher EEs than N212 at all current densities because of its higher CE due to the lower VO^{2+} permeability. These results showed that BPSH 35 is more promising membrane compare to N212 especially in terms of the energy efficiency.

4. CONCLUSIONS

Disulfonated poly(arylene ether sulfone) copolymer (BPSH) with a 35% degree of sulfonation was synthesized and turned into an ionomeric membrane in order to be evaluated in the VRFB. The method of direct copolymerization of disulfonated comonomers has been proven to provide for the exact degree of disulfonation. Higher IEC, proton conductivity and lower vanadium permeability than N212 were observed for BPSH 35. Therefore, selectivity of the membrane was better than N212. Moreover, BPSH35 showed higher coulombic (98.9 %) and energy efficiencies (75.6-90.3 %) at all current densities than N212. This was due to its lower VO^{2+} permeability of BPSH35. These results showed that membrane from disulfonated poly(arylene ether sulfone) copolymer is a promising alternative of Nafion^{TM} for the VRFB applications.

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