¹Effects of Sulfonated Side Chains Used in Polysulfone Based PEMs for VRFB Separator

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Abstract: (100-200 words)

Polysulfone (PSU) –based Proton Exchange Membranes (PEMs) were synthesized from different pre-sulfonated monomers and evaluated for use in a vanadium redox flow battery (VRFB). Two types of sulfonated monomers, containing either an allyl sulfonate or styrene sulfonate group, were synthesized by a Mizoroki-Heck reaction from a 4,4'-difluorodiphenyl sulfone derivative. These monomers were polymerized with 4,4'-(hexafluoroisopropylidene)diphenol to give partially fluorinated PSUs with controlled placement and content of sulfuric acid moieties. PEMs were then fabricated by solution casting and characterized against the membranes made from traditional backbone sulfonated PSU. The new PEMs revealed desirable physical properties and performance in a VRFB cell competitive with the Nafion membrane. Furthermore, each PEM with a different acid side-chain structure exhibited varying properties and performance depending on its acid content, providing a path to optimization.

Keywords: (a maximum of 5 relevant keywords)

Proton exchange membranes, Vanadium redox flow battery, Polysulfone, Conductivity, Heck reaction

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1. Introduction

Demand for devices capable of large scale energy storage has heightened as a result from the continuous growth of alternative energy and the need to store it. Redox flow batteries (RFB) have emerged as an option for grid-scale energy storage in view of their energy efficiency, rapid response to varying loads, durability shown in lengthy charge/discharge cycles and reasonable costs.[1] The all-vanadium redox flow battery (VRFB) in particular has drawn the most attention since its use of four vanadium species as redox couples allows for potential to minimize upkeep cost, as reflected by its many demonstration plants worldwide.[2] VRFBs utilize a central cell (or cell stack) containing an ion exchange membrane which separates two electrolyte solutions containing a mixture of V(IV)/V(V) and V(II)/V(III) in the positive and negative compartments, respectively. These solutions are circulated through the cell where a redox reaction occurs; allowing electrons to travel from the negative to the positive electrodes through an external circuit during discharge while the proton exchange membrane (PEM) allows for transport of ions to maintain charge balance (while both PEMs and anion exchange membranes have been used in RFBs,[3, 4] we focus here upon the former). The PEM also acts as a barrier material partly preventing crossover that could lead to side reactions and lower the energy efficiency of the battery. RFB efficiency is greatly dependent on the PEM. For baseline measurements, the most commonly used membrane at present is Nafion®. Despite its adequate performance, Nafion®'s high cost and modest ion selectivity has driven research aimed at identifying better performing, more cost-effective alternatives. Hydrocarbon based polymeric materials, e.g., sulfonated polyarylenes, have been studied for alternative PEMs over the past decades.[3-8] These hydrocarbon membranes are being sought after as a means of improving cost and performance in VRFB, while maintaining the chemical and mechanical integrity.

The selectivity of the membranes, that is their ability to perform as barriers with relatively free flow of protons, is considerably influenced by the morphology of these membranes. The hydrophilic sulfonic acid groups encourage uptake of water, which swells the membrane in wet/humid conditions. This results in the formation of nanosized pores through which protons can permeate. This phenomenon is typically seen, for example, in Nafion in which ca. 2 nm wide pores are present.[9, 10] Numerous efforts have revolved around alternating the placement of sulfonic acid groups in a variety of ways as a means of creating nanostructures to further improve performance.[11-14] Nanoscale morphologies formed in block copolymers with hydrophilic and hydrophobic blocks yielded some degree of improvement in proton conductivity.[15] Another report showed that clustering of the acid groups in random copolymers led to more defined nanostructures, promoting superior membrane performance.[16-18] PEMs with nanosize domains have been fabricated from polymers with sulfonic acid terminating side chains off the main backbone, ostensibly giving the sulfonic acids greater 'flexibility.[19-22]

Herein this work aims at studying structure-performance relationships of PEMs in VRFBs. For this study two novel monomers are synthesized containing different sulfonic acid

side chains, followed by polymerization to develop partially fluorinated sulfonated polysulfone (PSU) random copolymers, which then are cast into ductile membranes. These membranes are analyzed comparatively followed by testing in a VRFB cell to investigate the effect of the different side chains. We compare a group of three sulfonated polysulfones containing different sulfonated ‘spacer’ groups off the backbone: sulfonic acid directly on the backbone (sb-PSU), one separated by an allyl group (as-PSU) and another separated by a styrenyl group (ss-PSU). These have been prepared with a narrow IEC range to discern changes in performance.

2. Experimental

2.1. Materials

4,4'-Difluorodiphenyl sulfone (DFDPS) and 4,4'-(hexafluoroisopropylidene)diphenol (bisphenol AF) were purchased from Oakwood Chemicals and recrystallized twice from toluene. Palladium(II) acetate, sodium diphenylphosphinobenzene-3-sulfonate (TPPMS), sodium p-styrenesulfonate hydrate, and sodium allylsulfonate were purchased from TCI. Decafluorobiphenyl was purchased from Sigma Aldrich. Dimethyl sulfoxide (DMSO) and toluene were distilled over calcium hydride, and dimethylformamide (DMF) was purified by a Vacuum Atmospheres solvent purifier system. All other reagents were used as received.

2.2. Monomer Synthesis

Two novel monomers containing different sulfonated side chains were both prepared using a Mizoroki-Heck coupling reaction to give two new monomers with pendant acid side chains as shown in Fig. 1. The precursor dbDFDPS used for the Heck reaction was synthesized as reported in literature.[20] This precursor was then coupled with one of two presulfonated vinyl reagents, either sodium p-styrenesulfonate hydrate or sodium allylsulfonate giving pure disulfonated products for both.

Fig. 1. Monomer synthesis.

3,3'-Dibromo-4,4'-difluorodiphenyl sulfone (dbDFDPS): As a preliminary step to the coupling reaction to form the two acid-functionalized monomers, DFDPS was brominated as reported in the literature to yield dbDFDPS.[20] The details of the reaction are as follows: DFDPS (25 g, 98 mmols) was first dissolved in concentrated H₂SO₄ (160 mL). *N*-bromosuccinimide (40 g, 226 mmols) was added in 3 equal intervals to the flask over 30 minutes with vigorous stirring. After 6 h the reaction mixture was poured into 1 L of ice water and the precipitate was collected via Büchner filtration and washed multiple times with H₂O and hexanes (100 mL). The product was recrystallized three times from toluene to remove mono-reacted byproduct.

Bis[4-fluoro-3-(4-vinylbenzenesulfonate)phenyl]sulfone disodium salt (ss-DFDPS): To a 500 mL 3-neck round bottom flask equipped with nitrogen inlet and a condenser, dbDFDPS (8 g, 19.4 mmols), sodium *p*-styrenesulfonate (8.59 g, 41.7 mmols assuming 10 % H₂O), palladium(II) acetate (0.262 g, 1.07 mmols), TPPMS (0.212 g, 0.582 mmols), sodium carbonate (8.23 g, 50 mmols) were charged into the flask. Dry DMF (170 mL) was added to the nitrogen flushed flask with stirring followed by heating at 120 °C for 12 h. DMF was then rotary evaporated, and the residual precipitate was dissolved in DMSO, filtered, precipitated into chloroform, and finally recrystallized from water/alcohol mixture to give the resulting *trans* isomer, ss-DFDPS (2.81 g, 35 %). ¹H NMR: (499.7 MHz, DMSO-*d*₆) δ 8.47 (dd, *J* = 6.9, 2.2 Hz, 2H), 8.00 (ddd, *J* = 8.9, 4.8, 2.4 Hz, 2H), 7.34 (d, *J* = 16.7 Hz, 2H), 7.53 (dd, *J* = 10.1, 8.9 Hz, 2H), 7.56 (d, *J* = 16.8 Hz, 2H), 7.64 (q, *J* = 7.8 Hz, 4H).

Bis[4-fluoro-3-(prop-2-ene-1-sulfonate)phenyl]sulfone disodium salt (as-DFDPS): Using similar methodology to ss-DFDPS, sodium allylsulfonate (5.88 g, 40.8 mmol) was added in place of sodium *p*-styrenesulfonate. The same steps were followed to those in the similar reaction giving as-DFDPS (1.95 g, 30 %). ¹H NMR: (499.7 MHz, DMSO-*d*₆) δ 8.22 (dd, *J* = 7.0, 2. Hz, 2H), 7.93 (ddd, *J* = 8.7, 4.6, 2.4 Hz, 2H), 7.44 (dd, *J* = 10.6, 8.8 Hz, 2H), 6.59 (dT, *J* = 15.6, 6.7 Hz, 2H), 6.55 (d, *J* = 16.1 Hz, 2H), 3.41 (d, *J* = 6.1 Hz, 4H).

3,3'-Disulfonate-4,4'-difluorodiphenylsulfone disodium salt (sb-DFDPS): The monomer was synthesized according to the literature for a similar monomer.[23] DFDPS (6 g, 24 mmol) was dissolved in 17 mL of fuming sulfuric acid (20 % SO₃). The reaction mixture was flushed with nitrogen then heated at 105 °C overnight. The crude product was diluted with 60 mL of ice water and 15.5 g of NaCl was added with mild heating. After cooling, the precipitated crude product was collected by filtration. It was then redissolved in water and neutralized. The pure product was salted out by adding 15 g of NaCl with heating and cooling steps, and then collected and dried *in vacuo* before further polymerization.

2.3. Polymer Synthesis

Fig. 2. Synthesis of sulfonated side chain polymers by two step method.

Fig. 2 shows the synthesis scheme for acid-functionalized polysulfones. All polymers were synthesized under the same reaction conditions, only changing the monomer feed ratio of sulfonated acid monomer. Synthesized polysulfones and their membranes are referred to based on the side group type and theoretical IEC value (Low, Medium, High) by monomer feed ratios as listed in Table 1. A typical polymerization is as follows: for the synthesis of ss-PSU-L, ss-DFDPS (0.745 g, 1.124 mmol), DFPDS (0.191 g, 0.749 mmol), bisphenol AF (0.700 g, 2.082 mmol), and potassium carbonate (0.36 g, 2.6 mmol) were loaded into a 50 mL 3-neck flask equipped with a Dean-Stark, condenser, nitrogen inlet, and magnetic stirrer. The system was flushed with N_2 and dry DMSO (7 mL) and toluene (4.5 mL) were added. The reaction mixture was heated at 150 °C for 3 h then slowly heated to 180 °C for gradual removal of toluene. The vessel was then cooled to 55 °C after 3 h and decafluorobiphenyl (0.072 g, 0.214 mmol) was added with 7 mL of DMSO. After 12 h the reaction temperature was increased to 65 °C for 1 h and the viscous solution was precipitated into warm isopropyl alcohol, filtered, washed with hot water, and dried *in vacuo*.

2.4. Membrane formation

Each polymer was dissolved in DMSO (6-8 w/v %), centrifuged at 4500 rpm for 3 h to remove any insoluble impurities, cast onto a flat glass surface, and kept at 75 °C for 4-5 h. The cast plate was immersed in DI water to lift the membranes from the glass surface. The membranes were acidified in 1 M H_2SO_4 under reflux for 1 h followed by rinsing in boiled water for 1 h prior to any characterization.

Table 1. Acid-functionlized polysulfone synthesis

Series ^a	Acid side-group	Polymer ID (Membrane ID)	IEC Theoretical (meq g ⁻¹)	Feed ratio of sulfone monomers	
				acid monomer (mol %)	DFPDS (mol %)
sb		sb-PSU-L	1.45	50	50
		sb-PSU-M	1.62	57	43
		sb-PSU-H	1.77	63	37
as		as-PSU-L	1.45	53	47
		as-PSU-M	1.62	61	39
		as-PSU-H	1.77	69	31
ss		ss-PSU-L	1.45	60	40
		ss-PSU-M	1.62	70	30
		ss-PSU-H	1.77	80	20

^a Abbreviations are defined as: sulfonated backbone (sb), allyl sulfonate (as), and styrenyl sulfonate (ss).

2.5. Characterization

¹H NMR: NMR spectra were obtained on a Varian 500 MHz spectrometer in DMSO-*d*₆ to confirm the chemical structure of monomers and polymers.

Conductivity: Acidified membranes were cut into 5 x 0.75 cm² strips and soaked in deionized water, acid solution (1 to 3.3 M H₂SO₄), or electrolyte solution (1.7 M vanadyl sulfate in 3.3 M H₂SO₄) for at least 24 h prior to measurements. The strips were removed from the soaking solution, patted to remove surface water, and immediately placed into the cell. The resistance was then measured on a Biologic sp-150 potentiostat using a 4 pt. closed wall cell of a design described elsewhere.[24] Proton conductivity was then calculated using the following equation:

$$\sigma = \frac{L}{R \times A}$$

Where σ is the conductivity, L is the length between electrodes, R is resistance, and A is the cross-sectional area.

Water uptake: The water uptake of the membranes in acid form was calculated by the weight loss from wet and dry samples using the equation shown below:

$$\text{Water Uptake \%} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$

Where W_{wet} is the wet weight and W_{dry} is the dry weight. All samples were soaked in DI water for a minimum of 24 h then removed and excess water was patted off and quickly weighed to get W_{wet} . Samples were then dried in vacuum at 100 °C for 24 h then weighed to get W_{dry} .

IEC and hydration number: IEC was calculated by back-titration of the membranes in the acid form using membranes of known dry weight. Membranes were allowed to equilibrate in a known excess of base for 48 h, followed by titrating the excess base. Hydration number, λ , was calculated using the experimental IEC and wet and dry weights to calculate how many water molecules per SO_3H using the following equation where 18.02 is the mass of H_2O .

$$\lambda = \frac{(W_{wet} - W_{dry})/18.02}{IEC \times W_{dry}} \times 1000$$

Thermal analysis: All thermal measurements were performed using 1-3 mg of membrane in the acid form. Thermal Gravimetric Analysis (TGA) was done using TA Instruments Q50 under a nitrogen environment. Samples were first held at 150 °C for 1 hour then ramped from 30 °C to 700 °C at a rate of 10 °C/min. Differential Scanning Calorimetry (DSC) curves were collected using TA Instruments Q20. Under nitrogen the sample was kept at 120 °C for 20 min then cycled from -40 °C to 270 °C four times at a heating rate of 10 °C/min after every rapid cooling run (ca. -50 °C/min).

VRFB cell cycling test: Synthesized membranes were tested in vanadium redox flow battery single cells to determine their performance as an electrolyte separator. Membrane samples with thickness around 50 μm were chosen to allow direct comparison with commercial standard Nafion 212 membrane. The electrolyte solutions were prepared by two step charging from raw electrolyte with 1.7 M vanadyl sulfate (99.9% alfa aesar) and 3.3 M sulfuric acid (96~98%, Fisher Scientific). The charged electrolyte solutions (50 mL) were placed on positive and negative sides respectively. The 5 cm^2 flow battery cell hardware with serpentine flow field was supplied by Fuel Cell Technologies Inc.. A single layer of untreated SGL CP X-1 high surface area carbon paper compressed from 400 μm to 250 μm in thickness was used in each electrode. The electrolyte solutions were circulated between cell and reservoirs by a Masterflex peristaltic pump. A pair of cartridge heaters controlled by an Omega CSC32 temperature controller was installed in the battery cell to maintain a 30°C operation temperature of the cell. A current density of 200 $\text{mA}\cdot\text{cm}^{-2}$ was used during the cycling. The electrolyte flow rate was held at 50 $\text{mL}\cdot\text{min}^{-1}$ during cycling. To record the OCV decay, OCV was monitored across the battery cell after electrolytes were fully charged and the pump was stopped.

3. Results and Discussion

3.1. Monomer synthesis

The Heck coupling method gave nearly complete conversion with demonstrating both regio- and stereo-specific addition. The use of this coupling method, with its high conversion, allowed for relatively simple purification to remove excess sulfonated vinyl reagents. The structure of both monomers in the sodium salt form was confirmed by ^1H NMR as seen in Fig. 3. The Heck reaction was found to be sensitive to the typical bases; however, sodium carbonate gave little to no byproduct. Although high conversion was achieved, multiple recrystallizations were required to give high purity needed for polycondensation, that lowered the overall yield.

Fig. 3. ^1H NMR spectra of (a) as-DFDPS and (b) ss-DFDPS.

3.2. Polymer synthesis

Acid-functionalized polysulfones were synthesized via a two-step process: (i) synthesis of stoichiometry-controlled prepolymers, followed by (ii) *in situ* coupling to yield high molecular weight polymers. This coupling approach using decafluorobiphenyl was necessary to fabricate robust membranes for VRFB application. The prepolymers were synthesized using a specific feed ratio to give an average degree of polymerization of 9 by stoichiometric excess of bisphenol AF. Actual degree of polymerization of the prepolymers calculated by the ^1H NMR spectrum in Fig. 4a using the endgroup aromatic peak (peak 1 or 2) versus polymer backbone peaks revealed the molecular weight ranging from around 4000-6000 g/mol. A stoichiometric molar ratio of decafluorobiphenyl was then added at reduced temperature to couple the prepolymers, thereby maximizing molecular weight. Fig. 4b shows a spectrum of the typical post-coupling polymer in which the loss of the end group peak at around 6.8 ppm can be seen. Each of three types of acid polymers (sb-, as-, and ss-PSU) was synthesized with three different IECs: 1.45, 1.62, and 1.77. These theoretical IECs could be targeted by adjusting the feed ratio of acid- to nonacid- DFDPS monomer. Both as- and ss- side chains, gave polymers that were only soluble in DMSO and that

were not soluble in other aprotic polar solvents such as DMF, *N*-methyl-2-pyrrolidone (NMP), and dimethylacetamide (DMAc).

Fig. 4. ^1H NMR spectra of (a) the prepolymer with a structure and (b) the post-coupling ss-PSU.

3.3. Membrane characterization

The thin membranes, typically 40 to 70 μm in thickness, were prepared by solvent casting of the synthesized polymers. Membranes were characterized as summarized in Table 2. Experimental IECs were measured through titration and exhibited trends consistent with the theoretical IEC calculated by the monomer feed ratio, although experimental values were lower than those derived from the monomer feed values (theoretical IEC).

The conductivity and water uptake tend to increase as IEC increases for PSU membranes for most of side chain types, expected as an effect of the sulfonic acid group. These data were the average of measurements repeated at least 3 times for multiple strips ($n > 6$) from each membrane. Measurements were taken after the membranes were immersed in water for more than 24 hr and continuously up to 11 days for testing consistency and equilibrium state of the membranes. Fig. 5 shows the conductivity data against water uptake to examine correlation of these two properties. This graph revealed that all types of side chain PSU membranes have a linear correlation with a slightly different slope for the linear regression curve. Although ss-PSU membranes displayed lower conductivity and water uptake in comparison with sb- and as-PSU membranes, the higher slope indicates that ss-PSU membranes may transfer ions more efficiently when all membranes take up the same water amount (if more than 42 %). This slight difference

could be explained by the membrane morphology. The polymer membrane with the longest side-chain (ss-PSU) may have more complete segregation of the hydrophilic ionic channel from the hydrophobic and robust polymer domain when compared to the membrane of direct sulfonation (sb-PSU), as depicted in Fig. 6. Theoretically, longer sidechains can promote more defined channels by allowing the sulfonic acid groups to aggregate, the basis for this work. While these basic data indicate a difference in bulk physical properties, more localized effects related to structure of the pores might be reflected in actual battery test conditions in which the membranes are exposed to concentrated solutions of electrolytes. In that situation, the pores may play a larger role in overall proton mobility and crossover of vanadium ions reflected in its various efficiencies.

Table 2. Properties of PSU membranes with different acid side chains

Side-chain	Membrane ID ^a	IEC Theo. (meq/g)	IEC Exp. (meq/g) ^b	Water Conductivity (mS/cm) ^c	Water uptake (%)	Hydration number (λ)	Wet thickness (mm)	Electrolyte Conductivity (mS/cm) ^d
sb	sb-PSU-L	1.45	1.26	52	35	15	0.070	27
	sb-PSU-M	1.62	1.42	74	56	19	0.057	nd^e
	sb-PSU-H	1.77	1.59	88	70	23	0.060	34
as	as-PSU-L	1.45	1.31	58	39	12	0.063	24
	as-PSU-M	1.62	1.41	87	70	24	0.062	45
	as-PSU-H	1.77	1.57	83	62	22	0.060	nd^e
ss	ss-PSU-L	1.45	1.25	44	32	11	0.056	20
	ss-PSU-M	1.62	1.49	62	42	14	0.065	16
	ss-PSU-H	1.77	1.53	73	50	15	0.056	26
	Nafion 212	0.91	0.90	105	28	24	0.051	34 ^f

^a L/M/H represent low/medium/high content of acid-functional DPDFS monomer in all DPDFS monomers in feed.

^b Determined by titration.

^c Measured in DI water at RT (22 °C).

^d Measured in 1.7 M VOSO₄ / 3.3 M H₂SO₄ at RT (22 °C).

^e Not detected.

^f Data for Nafion 117.

Conductivity of all PEMs was measured in acid solution with different concentrations and then electrolyte solution containing 1.7 M VOSO₄ in 3.3 M H₂SO₄ as shown in Table 2. It was observed that the conductivity of membranes equilibrated in the electrolyte solution

significantly dropped for all membranes including Nafion when compared to the conductivity in H_2O . This phenomenon has been reported for Nafion 117.[25] The decrease is a result of several factors, including uptake of transition metal ions and dehydration of the membrane. Because transition metal cations have much lower mobility than protons in fully hydrated Nafion, membranes containing such cations generally have much lower conductivity than unexchanged proton-form membranes. We have also measured conductivity in H_2SO_4 solutions before obtaining electrolyte conductivity via the following sequence: DI water, 1 M H_2SO_4 , 2 M H_2SO_4 , 3.3 M H_2SO_4 , and finally 1.7 M VOSO_4 in 3.3 M H_2SO_4 . To compare the membranes with different side-chains, the results for the lowest IEC sb-, as-, and ss-PSU-L membranes are plotted in Fig. 7. Up to 3.3M, all membranes show minimal changes in conductivity., It was seen that ss-PSU-L exhibited appreciably lower conductivity in water as well as in acid solutions when compared to the other membrane types. However, interestingly the difference of electrolyte conductivity of all three membranes measured in 1.7 M VOSO_4 / 3.3 M H_2SO_4 became almost negligible as indicated by the points with open marks.

Fig. 5. The correlation of conductivity and water uptake for all PEMs.

Fig. 6. Schematic illustration of the proposed morphologies for sb- and ss-PSU membranes.

Fig. 7. Comparison of acid conductivity and electrolyte conductivity between sb, as, and ss-PSU-L (IEC=1.45) membranes. Measurements were done using same strips (n=3 for each) in sequence from DI water to increasing acid concentration with >24 hr equilibrium time before each measurement. The conductivity of membranes measured in 1.7 M VOSO₄ / 3.3 M H₂SO₄ are shown with open marks.

3.4. Membrane evaluation in VRFB cell

The membranes were subjected to an OCV decay measurement with results shown in Fig. 8. OCV decay correlates with the rate of exchange of vanadium species across the membranes. In previous studies of the effects of the equivalent weight (EW), [3, 4, 8] permeation through lower EW materials was slower than through high EW systems, presumably due to the higher degree of swelling of the latter when exposed to electrolytes. A similar trend was observed here: higher EW led to higher cross-over rates for each type of polymer. As indicated by the OCV decay, the as-PSU-L and as-PSU-M membranes exhibited high vanadium crossover rates and therefore the as-PSU-H membrane was not tested. The ‘ss’ series membranes showed the slowest overall vanadium crossover, according to Fig. 8. For the three side chain types, the OCV of cells with as-PSU-M, sb-PSU-M and ss-PSU-M dropped to 1.2 V at 2338, 5386 and 9346 s respectively after the pump was stopped. The voltage shoulder near 1.3 V on the OCV decay curve is caused by depletion of V²⁺ and V⁵⁺ in the pores of the electrode and flow field. To summarize this, for a given EW range, the vanadium permeability indicated in the OCV test increased in the order ss < sb < as.

In Table 2, the conductivity values in water for as-PSU-M, sb-PSU-M and ss-PSU-M are 0.087, 0.074 and 0.062 S/cm, respectively. Conductivity values in electrolyte have similar ordering and this in turn typically reflects the overall uptake of water or solution by the membrane. Given the similarity of the trends in water and electrolyte, we use the water conductivities here to analyze selectivity since we have complete data sets for these membranes. Because as-PSU has the lowest ratio of conductivity to rate of depletion of charged vanadium

species (the inverse of the times given), the ionic transport selectivity of this membrane is the least suitable for use as an electrolyte separator in a VRFB. According to the ionic selectivity index proposed by Tang et al,[4] ss-PSU-M and sb-PSU-M are 2.9 and 2.0 times more selective than as-PSU-M. The side chain structures on PSU membranes can influence their ionic transport properties. Perhaps the flexible (though shorter) side chain on the as-PSUs can lead to altered mechanical properties of the material, leading to ion cluster channels of larger size in swollen as-PSUs. As noted above, the overall higher conductivity and vanadium transport for ‘as’-form membranes likely reflect a higher degree of swelling. These can facilitate diffusion, especially for vanadium ions with large coordination structures. The key point is that the most effective membranes balance conductivity and permeability, as reflected in the selectivity index. A more detailed investigation of these aspects of membrane properties and morphology is in progress.

Fig. 8. The OCV decay on battery cell with 100% SoC electrolyte after electrolyte circulation was stopped.

Cell cycling tests in VRFB cells were performed on the series of membranes with Nafion 212 as a control. Fig. 9 shows efficiencies and areal specific resistance for 20 charge-discharge cycle tests for each membrane at a 200 mA/cm² current density. Overall, battery systems with PSU membranes showed excellent efficiencies with some membranes demonstrating superior performance over Nafion 212. For four PSU membranes, ss-PSU-H, ss-PSU-M, sb-PSU-H and sb-PSU-M, cells had energy efficiency of 86 to 87 %, higher than the 85% observed with Nafion 212 under the same test conditions. Cells using sb-PSU-L and as-PSU-M exhibited energy efficiencies close to that for Nafion-based cells, while as-PSU-L showed the lowest EE, around

83%. The performance of PSU membranes in cycling test demonstrated that they are suitable for use as electrolyte separators in VRFB.

Fig.9. Efficiency data for the membranes, sb-PSU (green), as-PSU (red), and ss-PSU (blue), in a VRFB cell for 20 cycles: (A) Voltage Efficiency, (B) Coulombic Efficiency, (C) Energy Efficiency, and (D) Area Specific Resistance after each cycle.

PSU membranes can contribute to enhanced battery performance with their high conductance in the VRFB environment. Although all PSU membranes tested are slightly thicker than Nafion 212, areal specific resistances (ASR) of all cells with PSU membranes are lower

than Nafion 212, except for cells using sb-PSU-L and as-PSU-L, as is shown in Fig. 9 (D). All proton-form PSU membranes are less conductive than Nafion in DI water (Table 2). Therefore, we anticipate that less electrolyte uptake is expected in PSUs to enhance ionic conduction to achieve lower ASR in VRFB environment. Details such as the uptake of ions and water by the membrane and the detailed mechanism of ionic transport in PSUs in equilibrium with strong electrolyte solutions are under investigation and will be reported elsewhere. Cells equipped with PSU membrane of ASR lower than Nafion 212 showed higher voltage efficiency than Nafion 212 (Fig. 9 (A)), because of lower ohmic loss by lowered internal resistance. The VE of each cell is dependent on its ASR in a roughly linear pattern, as presented below in Fig. 10. The ohmic potential loss is proportional to the cell ASR.

The coulombic efficiency achieved by each PSU membrane is consistent with the OCV decay measurement. All cells with PSU membranes have higher coulombic efficiency than Nafion 212 in the cycling, except for those with sb-PSU-H and as-PSU-M. The higher CE obtained in cycling measurements directly reflect the slower rate of vanadium crossover across the membrane in battery cell. For each side chain type, the ionic conductivity of both proton and vanadium in the membrane increases with its IEC. Generally, membranes of higher IEC and lower thickness are used to reduce the internal resistance of the battery. Although a VRFB system with low ASR and high CE is always desired, vanadium crossover can also be increased by using a membrane with high conductivity. In Fig. 10, the CE vs ASR of battery cell with PSU membranes is plotted to correlate the vanadium crossover with ASR. Apparently, as-PSU series and Nafion have lower ionic selectivity towards protons because they cause lower CE than the other membrane types at the same ASR level. The ss-PSU series have the highest ionic selectivity among all three types of membrane since it has the highest CE level. The high ionic selectivity in sb and ss-PSU suggests that their polymer structure is more favorable for proton transport than for vanadium ion transport. Since ss-PSU has a benzene- tethered side chain and sb-PSU has sulfonate directly attached on backbone, narrower and more branched ionic channels may form in the sb-form. These can be expected to slow down ion and water transport.

PSU membranes with ss and sb types of side chain structure show superior ionic selectivity to reduce vanadium crossover and maintain good conductivity in the VRFB. Fig. 11 shows the relative capacity of the cells over 20 cycles. The capacity decrease is much less with all hydrocarbon membranes than that with Nafion. This is a great sign of the higher ionic selectivity towards proton transfer. In particular, the membranes with the highest IEC such as ss-PSU-H and sb-PSU-H, which also gave the highest EE, showed the highest capacity retention of all membranes cycled.

Fig. 10. The comparison of coulombic and voltage efficiencies with respect to Area Specific Resistance of the battery with PSU membranes and Nafion 212. analysis.

Fig. 11. Capacity changes over 20 cycles in VRFB.

3.5. Thermal analysis

Thermal behavior of three types of membranes and stability of structure and properties after the cell cycling test were studied using TGA, DSC, ¹H NMR, and conductivity

measurements. TGA profiles of sb-, as-, and ss-PSU-H membranes are shown in Fig. 12. Thermal degradation of sb-PSU (green) shows 2-step process and that of as- (red) and ss-PSU (blue) indicates 3-step process. For these 'H' series with IEC 1.77, theoretical weight % of $\text{-SO}_3\text{H}$ in the polymer is 14 wt% for all three membranes. The first weight loss % in all membranes is corresponding to the degradation of sulfonic acid group, which also agrees with previous reports.[26] The 5% weight loss temperature, $T_d(5\%)$ of sb-, as-, and ss-PSH-H are 338, 254, and 320 °C, respectively. Significantly lower thermal stability of the $\text{-SO}_3\text{H}$ group in as-PSU is reasonable because it is an isolated group on the alkyl side chain unlike more stable conjugated acid form seen in sb- and ss-PSU. The as-PSU-H membrane displays distinct second degradation starting around 400 °C, that indicates degradation of propenyl side group (theoretical weight % of as-PSU side chain except $\text{-SO}_3\text{H}$: 7 wt%). The same second degradation is recognizable for ss-PSU, however it is slower process as seen in gentle slope. Finally, degradation of polymer backbone of all three membranes starts around 470 °C. Changes of the degradation profiles for all membranes before and after cell cycling test were negligible as shown in Fig. S2 (supporting info), indicating no appreciable degradation of polymers occurred in the VRFB cell.

DSC curves of three PSU-H membranes for their third heating runs are shown in Fig. 13. The T_g of all these polymers are expected to be between 200-300 °C, which is close to acid group degradation temperatures. Only one distinct T_g was observed at 245 °C in sb-PSU-H. Interestingly, exothermic transitions were observed at lower temperature for as- and ss-PSU-H membranes. Those thermal events were reversible for multiple runs after every rapid cooling from 270 to -40 °C. Since no such transition was observed for the backbone-sulfonated sb-PSU-H, the reversible exothermic events are probably caused by the orientation of side groups or ion complex formation with the side chain.

Fig. 12. TGA profiles of H-series (IEC = 1.77) membranes: heating at 10 °C/min.

Fig. 13. DSC profiles of H-series membranes: third heating run at 10 °C/min.

3.6 Chemical stability

Proton conductivity was re-evaluated for the membranes after cell cycling to observe any changes in performance. The original conductivity for sb-, as-, and ss-PSU-H were 88, 83, and 73 mS/cm, respectively. The conductivity values of the same membranes after the cell test were in the range of 60-99 mS/cm. This comparable conductivity ranges before and after cell cycling was indication that no major chemical or physical change took place, which agreed with the aforementioned thermal stability by TGA. It is, however, noted that all three types of membranes showed some degree of signs of wear after cycled in the VRFB cell, indicating that they were no longer as robust as they were prior to cycling. The more brittle nature of the membranes after cycling indicates polymer chain cleavage. ASR shows that the resistance in the cell only increased slightly through 20 cycles, complementing the minimal change in conductivity.

Finally, the detailed chemical structure of the polymers was studied using ^1H NMR by re-dissolving the membranes in DMSO-*d*₆ after the cell cycle test. The NMR spectra of sb-PSU-M before and after the cell were identical (Fig. S3). However, after the cell cycling the ss-PSU-M membrane was no longer completely soluble in the solvent. This is possibly due to a crosslinking reaction of the side groups under the VRFB cell conditions. As shown in Fig. 14, the ^1H NMR spectra of as-PSU-M before and after the VRFB cell cycling test revealed a noticeable decrease in non-aromatic alkene proton peaks (d, e) at 6.6 and 6.7 ppm as well as the related peaks (a, b, c, f) of the functional monomer unit, against the main chain peaks (g, h, i, j) in the spectrum (b). The integration of those acid monomer peaks appeared to be nearly 20% lower after the cell cycling test. Alkenes are generally sensitive to aqueous acid by way of hydration reactions or they can be oxidized by oxidizing agents. Even given this minor structure change, the electrolytes potentially could have morphology changes. Both 'as' and 'ss' side chain membranes are more susceptible to reactions under the given conditions than the direct backbone sulfonated polymer membrane. As expected, sb-PSU-M remained chemically unchanged shown by ^1H NMR (see Fig. S3). Overall, the three types of membranes in this study have shown satisfactory stability in their structures and performance based on the cycling studies. More detailed structural/morphological characterization and thermal/mechanical analysis are underway.

Fig. 14. ^1H NMR spectra of as-PSU-M membranes before (a) and after (b) cell cycling test.

4. Conclusion

Proton exchange membranes were prepared from polysulfone random copolymers containing three different side chains with a controlled range of IECs. The physical properties of the membranes were affected by the addition of a side group between a polysulfone backbone and the characteristic sulfonic acid groups. The use of a styrenyl group resulted in relatively lower water uptake without compromising its *in situ* performance compared to PSU sulfonated along its backbone. Coulombic, voltage, and energy efficiencies were measured in a VRFB cell and showed similar energy efficiency for most membranes despite large difference in conductivity and water uptake. Most of the membranes, regardless of their side chain, displayed high EE (up to ca. 86 %) which was higher than that of Nafion 212. Specifically, the membranes of PSU with a styrenyl sulfonic acid side group (ss-PSU) showed slightly higher proton conductivity than other membranes if comparing at same water uptake, and performed well in the VRFB cell with excellent VE and CE. This result would indicate the formation of the most favorable domain structure in the membrane by the longest and stable acid side group. It was demonstrated that the morphology and properties of polysulfone PEMs can be improved without sacrificing overall cell efficiency. The post-cell membranes showed no significant changes in structure and performances, however indicated a minor chemical transformation. Further characterization will be done on these membranes and ss-PSU series will be further explored due to its higher potential in VRFB membrane applications.

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