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Abstract: Highly sulfonated poly(ether sulfone)s with densely populated flexible acid side chains were prepared for fuel cell applications by polycondensation of 3,3'-dihydroxybenzidine with bis(4-fluorophenyl)sulfone and 4,4'-biphenol, followed by postsulfonation using 1,4-butanedisulfone at room temperature. The sulfonated polymers gave tough, flexible, and transparent membranes by solvent casting. The membranes had high ion exchange capacity (IEC) values (2.47-2.95 mequiv/g) and displayed good proton conductivities in the range of $13.90\text{--}20.90 \times 10^{-2}$ and $1.08\text{--}2.21 \times 10^{-2}$ S/cm at 95% and 35% relative humidity (RH) (80 °C), respectively. In particular, the S-PES-55 membrane with the highest IEC value showed higher or comparable proton conductivity than that of Nafion 212 in the range of 35-95% RH. The morphologies of these membranes were investigated by STEM analysis, which exhibited well-connected hydrophilic channels due to their high IEC values and densely populated flexible acid side chains. In sharp contrast with many reported highly sulfonated polymers, the membranes showed good dimensional stability regardless of their high IEC values.

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August 3rd 2012

Subject: Submission of a full article to the *Journal of Membrane Science*
Title: Proton-conducting membranes from poly(ether sulfone)s grafted with sulfoalkylamine.
Authors: Chenyi Wang, So Young Lee (co-first author), Dong Won Shin, Na Rae Kang, Young Moo Lee*, Michael D. Guiver*

Dear Editor:

On behalf of my coauthors, I am pleased to submit a manuscript entitled "Proton-conducting membranes from poly(ether sulfone)s grafted with sulfoalkylamine " for consideration for publication as an article to the *Journal of Membrane Science*.

Poly(ether sulfone)s substituted with four flexible acid side chains per repeat unit were prepared by polycondensation using a diamino-substituted commercial bisphenol monomer 3,3'-dihydroxybenzidine. The polymer was subsequently treated with 1,4-butanedisulfone to introduce sulfoalkyl groups onto amine substituents. The resulting polymers gave tough membranes with unusually high ion exchange capacity (IEC) values (2.47-2.95 mequiv/g) and displayed good proton conductivities in the range of $13.90\text{--}20.90 \times 10^{-2}$ and $1.08\text{--}2.21 \times 10^{-2}$ S/cm at 95% and 35% relative humidity (80 °C), respectively. The morphologies of these membranes exhibited well-connected hydrophilic channels. In contrast with many reported highly sulfonated polymers, the membranes showed good dimensional stability, in spite of their high IEC values. We believe this is the first report of this approach to introduce multiple flexible acid side chains

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If you have any questions or require any more information, please feel free to contact me by email at michael.guiver@nrc-cnrc.gc.ca.

Yours sincerely

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Research Highlights

- High IEC PEMs having densely populated flexible sulfoalkylamine groups.
- Good dimensional stability regardless of high IEC values.
- Clear nanophase-separated structures
- Good proton conductivity over a range of relative humidity.

Graphic Abstract

Proton-conducting membranes from poly(ether sulfone)s grafted with sulfoalkylamine

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ABSTRACT:

Highly sulfonated poly(ether sulfone)s with densely populated flexible acid side chains were prepared for fuel cell applications by polycondensation of 3,3'-dihydroxybenzidine with bis(4-fluorophenyl)sulfone and 4,4'-biphenol, followed by postsulfonation using 1,4-butanedisulfone at room temperature. The sulfonated polymers gave tough, flexible, and transparent membranes by solvent casting. The membranes had high ion exchange capacity (IEC) values (2.47-2.95 mequiv/g) and displayed good proton conductivities in the range of $13.90\text{--}20.90 \times 10^{-2}$ and 1.08-2.21

1 $\times 10^{-2}$ S/cm at 95% and 35% relative humidity (RH) (80 °C), respectively. In
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3 particular, the S-PES-55 membrane with the highest IEC value showed higher or
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5 comparable proton conductivity than that of Nafion 212 in the range of 35-95% RH.
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7 The morphologies of these membranes were investigated by STEM analysis, which
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9 exhibited well-connected hydrophilic channels due to their high IEC values and
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11 densely populated flexible acid side chains. In sharp contrast with many reported
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13 highly sulfonated polymers, the membranes showed good dimensional stability
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15 regardless of their high IEC values.
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22 **Keywords:** Sulfonated polymer; high IEC values; Proton conductivity; Proton
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24 exchange membrane
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31 1. Introduction

32

33 Proton exchange membrane fuel cells (PEMFC) have been extensively
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35 investigated for their utility in automotive and portable electronic applications
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37 because of high efficiency and power density, quiet operation, and environmental
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39 friendliness [1-3]. The proton exchange membrane (PEM) is one of the key
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41 components of the PEMFC in terms of performance and production cost.
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43 Perfluorosulfonic acid (PFSA) polymers such as Nafion[®] (DuPont) have been the
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45 most widely used PEM materials in fuel cell applications due to their high proton
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47 conductivity and chemical stability, but well-known limitations such as high cost and
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49 fuel crossover, restricted operation temperature and environmental recyclability
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51 prevent their full commercial realization in PEMFC. These challenges have driven the
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1 investigation of aromatic hydrocarbon polymers as alternative PEM materials [4]. The
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3 most widely reported classes of aromatic PEMs include sulfonated derivatives of
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5 poly(arylene ether ketone)s [5,6], poly(arylene ether sulfone)s [7-9], poly(arylene
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7 sulfide sulfone)s [10-12], poly(arylene ether)s [13-15], and polyimides [16,17].
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9 Aromatic ionomers are advantageous in terms of thermal stability and gas
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11 impermeability, and some of them had good proton conductivities in the hydrated
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13 state. With some exceptions for PEMs exhibiting marked phase separated morphology
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15 inducing interconnected proton-conducting channels, proton conductivities at low
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17 hydration levels (or low relative humidity (RH)) are typically much lower than that of
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19 Nafion [18].
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28 Membrane morphology plays an important role for proton transport in PEMs.
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30 Phase separated structures on the nanometer scale with connected hydrophilic
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32 channels results in facile diffusion of protons and water molecules, leading to high
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34 proton conductivity [19]. Much research has been focused on improving the
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36 nanophase-separated structures and proton conductivity of aromatic ionomers under
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38 low RH [20-27]. One effective strategy is the design of linear multiblock PEM based
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40 on hydrophilic and hydrophobic oligomers incorporated into the copolymers. The
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42 sequential block structure of these PEM can promote the phase separation between
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44 hydrophilic and hydrophobic segments, thereby achieving much higher proton
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46 conductivity at low humidity in comparison with random sulfonated copolymers.
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48 Some multiblock PEM with long hydrophilic and hydrophobic block segment showed
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50 a clear lamellar morphology with well-connected hydrophilic channels and proton
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conductivity comparable to that of Nafion 212 at low humidity [24-26]. Block copolymer architecture in the form of comb-shaped [28] and triblock architecture [29] has also been shown to be a highly effective in inducing proton channel formation for good conduction at low RH. Another approach to enhance phase separated structures and PEM performance can be realized by introducing densely sulfonated structures into the aromatic polymer backbone [30-35]. The large difference in polarity between the densely sulfonated units and hydrophobic units of the polymers results in the formation of well-defined nanophase-separated structures and can induce efficient proton conduction.

In previous work, we reported side-chain-type poly(ether sulfone)s with pendant flexible sulfoalkyl groups [36,37]. This was demonstrated to be an effective approach in achieving good PEM performance; the membranes had good conductivity-swelling behavior in the wet state due to the hydrophilic sulfonic acid groups being flexible and distant from the hydrophobic polymer main chain. Some of the membranes also exhibited clear nanophase-separated morphology with interconnected hydrophilic clusters [38-43]. However, most of these side-chain-type PEM had low IEC values and the proton conductivity under low humidity conditions required additional improvement [42,43].

The IEC value is also an important indicator for high proton conduction in PEMs, because it is closely related to the amount of water in membranes, which functions as a carrier for proton transportation. Furthermore, high IEC values can enhance the contrast in polarity between sulfonated units and hydrophobic units, thus inducing

1 phase separated morphology. Several examples of PEMs with high IEC values, but
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3 having acceptable dimensional stability, for PEM materials have been reported by the
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5 introduction of highly hydrophobic structures [44,45]. A significant improvement in
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7 proton conductivity for these membranes could be achieved at low RH.
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11 To the best of our knowledge, the combination of the three aforementioned
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13 structural features for PEM materials, those being (1) side-chain-type structures with
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15 flexible sulfoalkyl group, (2) densely and locally populated sulfonic acid and (3) high
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17 IEC values, has never been reported so far. In the present study, we report the
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19 preparation of side-chain-type sulfonated polymers with densely populated flexible
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21 sulfoalkyl groups and high IEC values (IEC >2.4 mequiv/g). The sulfonated
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23 copolymers were prepared by a facile postsulfonation chemical grafting route. The
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25 phase-separated morphology and selected PEM properties such as proton conductivity,
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27 water uptake, dimensional change, thermal and chemical stability, and mechanical
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29 strength were investigated in detail.
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45 **2. Experimental**

46 **2.1. Materials**

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48 3,3'-Dihydroxybenzidine (DHBZ), 4,4'-biphenol (BP),
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50 bis(4-fluorophenyl)sulfone (BFPS) and 1,4-butanedisulfone were purchased from
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52 Sigma-Aldrich. N-Methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), and all
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54 other solvents and reagents were reagent grade and were used as received.
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2.2. *Synthesis of amino-substituted poly(ether sulfone)s (A-PES-xx)*

A typical synthetic procedure, illustrated by the preparation of A-PES-50 copolymer (xx: DHBZ / BP = 50/50), is described as follows. 1.514 g (7 mmol) DHBZ, 1.304 g (7 mmol) BP, 3.560 g (14 mmol) BFPS, 2.318 g (16.8 mmol) K₂CO₃, 20 mL NMP and 10 mL toluene were added into a 100 mL three-neck flask equipped with a mechanical stirrer, a Dean-Stark trap and a nitrogen inlet. The reaction mixture was refluxed at 140 °C for 2 h until water was removed from the reaction mixture by azeotropic distillation, and then excess toluene was distilled off. Then the mixture was stirred at this temperature for another 3-4 h to give a viscous solution. After the reaction, 5 mL of NMP was added to the mixture to reduce the solution viscosity. The solution was poured into 500 mL deionized water with vigorous stirring. The resulting fibrous copolymer was washed with deionized water and hot methanol several times, and dried at 100 °C under vacuum for 24 h.

2.3. *Sulfonation*

The sulfonation reaction was conducted by a similar method reported in our preceding studies [36,37]. A typical synthetic procedure, illustrated by the preparation of S-PES-50 copolymer, is described as follows. 2.0 g A-PES-50 and 50 mL of DMSO were added into a nitrogen-flushed reactor equipped with a mechanical stirrer. After complete dissolution, 2.0 mL 1,4-butanedisulfone was added to the solution and the reaction mixture was stirred for 10 min at room temperature; then 0.36 g NaH was added. The reaction mixture was allowed to proceed for another 5 h at room temperature before precipitation of the polymer in isopropanol. The copolymer was separated by filtration and dried in a vacuum oven at 100 °C for 10 h.

2.4. Membrane preparation

The dried sulfonated copolymers in the sodium salt form were readily dissolved as 8–12 wt % solutions in DMSO at 60 °C. The solutions were filtered, cast onto glass plates with a doctor blade, dried at 60 °C for 12 h, and then treated in vacuum at 100 °C for 10 h. The as-cast membranes were immersed into 2.0 M H₂SO₄ solution for 24 h at room temperature and then thoroughly washed with deionized water. Tough, ductile ionomer membranes were prepared with controlled thickness in the range of 50–70 μm, depending on the casting solution concentration.

2.5. Measurements

¹H NMR spectra were measured on a 300 MHz Bruker AV 300 spectrometer using DMSO-*d*₆ as solvent. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min. The gel permeation chromatographic (GPC) analysis was carried out with Tosoh HLC-8320 instrument (NMP as eluent and polystyrene as standard).

Ion exchange capacities (IEC) of the membranes were determined by titration. A sample membrane in proton form was immersed in 2M NaCl aqueous solution for 48 h to exchange the H⁺ ions with Na⁺ ion. Released protons were titrated by 0.01 M NaOH solution using phenolphthalein as an indicator.

The humidity dependence of water uptake was measured by placing a membrane in a thermo-controlled humidity chamber for 6 h. Then, the membrane was taken out and quickly weighed on a microbalance. Water uptake was calculated from: WU =

$(W_w - W_d)/W_d \times 100\%$, where W_d and W_w are the weights of dry and corresponding wet membranes, respectively. The dimensional changes of the membranes were measured in the thickness and in-plane direction, which were calculated by $\Delta T = (T_{\text{wet}} - T_{\text{dry}})/T_{\text{dry}}$, $\Delta L = (L_{\text{wet}} - L_{\text{dry}})/L_{\text{dry}}$, where T_{dry} , T_{wet} , L_{dry} , and L_{wet} are the thickness and length of dry and wet samples, respectively.

The proton conductivity (σ , S/cm) of each membrane coupon (size: 1 cm $\times$ 4 cm) was obtained according to methods used previously³⁷ using $\sigma = d/L_s W_s R$ (d : distance between reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively). The resistance value (R) was measured over the frequency range from 100 mHz to 100 kHz by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solartron 1260) and an electrochemical interface (Solartron 1287, Farnborough, Hampshire, UK). The membranes were sandwiched between two pairs of gold-plated electrodes. The membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1.0 cm. Conductivity measurements under fully hydrated conditions were carried out in a thermo-controlled chamber with the cell immersed in liquid water.

Transmission electron microscopy (TEM) observations were made similarly to our previously reported work [37]. Membranes were first treated with 0.5 M lead acetate aqueous solution, and then rinsed several times with deionized water, and dried in a vacuum oven for 12 h. After embedding in epoxy resin, the membranes were sectioned to 70 nm thickness with a RMCMTX Ultra microtome, and placed on

1 copper grids. Electron micrographs were taken with a Carl Zeiss LIBRA 120
2
3 energy-filtering transmission electron microscope using an accelerating voltage of
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6 120 kV.
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10 11 **3. Results and discussion**

12 13 **3.1. Synthesis of amino-substituted copolymers and sulfonation**

14
15 A series of amino-substituted poly(ether sulfone) copolymers (A-PES-xx, xx:
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17 mole ratio (%) of DHBZ) were prepared via a standard K_2CO_3 -catalyzed aromatic
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19 nucleophilic substitution polycondensation using various monomer feed ratios of
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21 DHBZ/BP, so that polymers with different molar percentage of amino groups were
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23 obtained. The polymerization reactions proceeded smoothly to high molecular weight,
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25 and no cross-linking was evident when the temperature was controlled by an oil bath
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27 (less than 150 °C) and the reaction time was about 3-4 h. GPC results (Table 1)
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29 showed that high molecular weight polymers ($M_n > 70,000$ g/mol) were obtained, and
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31 molecular weight distribution (PDI) ranged from 2.07 to 2.25, which is consistent
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33 with the results of typical polycondensation reactions.
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44 The A-PES-xx copolymers contained two primary amine groups in each
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46 repeating unit, which provided reaction sites to introduce various functional groups,
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48 such as sulfonated aliphatic side chains. Gieselman and coworkers have demonstrated
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50 that amine groups in aramid poly(p-phenyleneterephthalamide) (PPTA) could be
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52 sulfopropylated through direct attachment of aliphatic groups to the amine nitrogen
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54 with 1,3-propanesultone using NaH as a base [46]. Zhang and coworkers also
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prepared sulfonated poly(ether sulfone)s with one attached flexible sulfoalkyl group in each unit by a grafting reaction of 1,3-propanesultone or 1,4-butanedisulfone with an amine-substituted polymer [38]. Applying similar methodology to the present work, Scheme 1 shows the grafting reaction of sulfobutyl groups onto A-PES-xx by nucleophilic ring opening reaction with 1,4-butanedisulfone. A series of copolymers with different sulfobutyl content were obtained by adjusting the $-\text{NH}_2$ content in A-PES-xx copolymers, followed by reaction with an excess of 1,4-butanedisulfone. The sulfonation proceeded smoothly and completely using reasonable reaction times. No obvious polymer decomposition or crosslinking occurred under these reaction conditions, as indicated by the viscosity measurements and the mechanical properties of the resulting sulfonated membranes.

Scheme 1. Synthesis of A-PES-xx and S-PES-xx copolymers.

Table 1

Physical properties of A-PES-xx and S-PES-xx copolymers.

Copolymers	GPC Data ^a			η_{inh}	η_{inh}
	$M_n^a (\times 10^4 \text{ g/mol})$	$M_w (\times 10^4 \text{ g/mol})$	PDI	(dL/g) ^b	(dL/g) ^c
A-PES-40	7.57	17.03	2.25	0.62	0.84
A-PES-45	7.76	17.15	2.21	0.66	0.89
A-PES-50	8.15	16.88	2.07	0.65	0.93
A-PES-55	8.22	17.07	2.08	0.68	1.04

^a Measured at 25 °C using NMP as solvent and polystyrene standards.^b Viscosity before sulfonation; 0.5 g/dL in NMP solution at 30 °C.^c Viscosity after sulfonation; 0.5 g/dL in DMSO solution at 30 °C.

The chemical structures of the copolymers were confirmed by ¹H NMR spectra. Fig. 1 shows ¹H NMR stacked spectra of A-PES-45 and S-PES-45 copolymers with signal assignments. The spectra are consistent with the designed molecular structure. Marked changes in the ¹H NMR spectrum of S-PES-45 compared to that of the original polymer (A-PES-45) are observed. The signal at 5.02 ppm (amine protons) disappears completely, and new signals appear at 4.07 ppm, 3.58 ppm, 2.48 ppm and 1.62 ppm corresponding to sulfoalkyl protons, which confirms that all of the amine groups reacted with 1,4-butanedisulfone to produce N-alkylated product. Signal integration values are also consistent with the structure of these copolymers as well. Moreover, the obtained experimental IEC values (Table 2) for all sulfonated copolymers were close to the theoretical values, further indicating close to quantitative reaction yields for sulfobutylation.

Fig. 1. Comparative ^1H NMR spectra of A-PES-45 ($-\text{NH}_2$) and S-PES-45 (salt form) copolymers.

3.2. Morphological structures of S-PES-xx membranes

Hydrophilic/hydrophobic microphase separation in PEMs plays an important role in controlling water retention and dimensional swelling, and in enhancing proton conductivity. It has been demonstrated that some aromatic polymers substituted with sulfoalkyl groups can form well-defined hydrophilic/hydrophobic phase-separated

structures because the flexibility of the sulfoalkyl pendant chains facilitates ionic cluster formation [36-43]. In order to investigate the hydrophilic/hydrophobic morphology, S-PES-40, S-PES-50 and S-PES-55 membranes were studied by TEM and the microstructures are shown in Fig. 2. The dark lead-stained regions represent localized ionic domains and the light regions correspond to domains comprised of hydrophobic polymer backbones. As shown in the pictures, the phase images for all samples exhibit clear hydrophilic/hydrophobic nanophase-separated morphologies. The distinct ionic domain size and connectivity are highly dependent on their IEC values. In the case of S-PES-40, which has an IEC value of 2.47 mequiv/g, the image shows hydrophilic spheroidal clusters with diameter sizes in the range of 4-6 nm with the beginnings of interconnection each other, while S-PES-50, which has an IEC value of 2.81 mequiv/g, worm-like interconnected hydrophilic networks of narrow channels of about 5-7 nm in diameter were observed. For higher IEC value of S-PES-50 to S-PES-55 (IEC value 2.95 mequiv/g), the diameter size of the interconnected hydrophilic channels increased in the range of 10-15 nm. S-PES-55 also exhibited much clearer phase-separated structures and better interconnected hydrophilic networks compared with some reported polymers with side-chain type sulfoalkyl groups and those with low IEC values [36-43]. It is reasonable that the hydrophilic cluster became larger and the connectivity of hydrophilic domain increased with IEC due to increased concentration of sulfonic acid groups. Well-connected hydrophilic domains in these membranes should behave as proton transportation channels. The strategy of designing sulfonated polymer together with

high IEC values combined with densely populated flexible sulfoalkyl groups is effective in improving the formation of proton transportation channels, which contribute to high proton conduction over a wide range of relative humidity. These morphological considerations will be further discussed below, in consideration of the proton conductivity behavior.

Fig. 2. TEM photographs of S-PES-40, S-PES-50 and S-PES-55 membranes.

3.3. Water uptake and dimensional stability

Water uptake of membranes is a key factor for sustaining proton conductivity because water molecules play an important role as proton transportation carriers in membranes. However, dimensional swelling should be also considered in conjunction with water uptake, because excessive swelling significantly decreases the dimensional stability and mechanical properties of the polymer films.

The water uptake of S-PES-xx membranes after being equilibrated at 80 °C and

95% RH are summarized in Table 2. As expected, higher IEC membranes absorbed more water due to the increased hydrophilicity. The highest water uptake was 41.5 % at 95% RH ($IEC_w=2.95$ meq./g), which was much higher than that of Nafion membrane (12.0%). The humidity dependence of water uptake is shown at Fig. 3. The water uptake for some high IEC main-chain-sulfonated PEMs often shows a great dependence with RH, with sharp decreases observed from 95% RH to 70% RH [25,26,44,45]. In contrast with those PEMs, the water uptake of the present S-PES-xx membranes displays a lesser dependence with RH, showing a mild decline with RH decrease. This is likely to be attributable to the locally and densely populated flexible sulfoalkyl groups, which enable good hydrophilic/hydrophobic phase separation to occur and which consequently provide good water-retention properties. The dimensional stabilities of S-PES-xx membranes were evaluated by comparing their hydrated state with dry state at 80 °C (Table 2). As expected, the dimensional changes of S-PES-xx membranes followed the same trend with water uptake, and show a mild increase with IEC increase at 95% RH. S-PES-55 with the highest IEC value exhibited a slightly larger dimensional change than Nafion 212, while all the other membranes exhibited lower dimensional change. Considering that the S-PES-xx have such high IEC values, the dimensional stabilities of the membranes are good, and they are also better than other high IEC PEMs [25,26]. In general, it is apparent that side-chain-type PEMs having sulfonic acid units on flexible side chains are very effective in allowing phase separation to occur between the hydrophilic sulfonic acid groups and the hydrophobic polymer main chain. Thus, water molecules can be

restricted to hydrophilic domains in the membranes and separated from hydrophobic domains, leading to a suppression of the water swelling. It should be also noted that the polymer main chain of S-PES-xx copolymers are very hydrophobic because they contain a high content of biphenyl units, which can further enhance dimensional stability. The PEMs displayed mildly anisotropic membrane swelling, in which the dimensional change was larger in the thickness direction than in the planar direction, in common with that observed in many other phase-separated membrane morphologies.

Table 2

IEC, water uptake, dimensional swelling, and proton conductivity of the S-PES-xx membranes.

Copolymers	IEC (mequiv/g)		Water uptake ^b (%)	Dimensional Swelling ^b (%)		Proton Conductivity ($\times 10^{-2}$ S/cm) (80 °C)	
	calcd	expt ^a		Δl	Δt	RH 95%	RH 50%
S-PES-40	2.54	2.47	25.1	3.1	4.2	13.90	1.08
S-PES-45	2.73	2.64	29.1	4.5	6.0	14.81	1.39
S-PES-50	2.91	2.81	35.6	6.1	7.9	18.04	1.81
SPES-55	3.07	2.95	41.5	7.8	10.4	20.90	2.21
Nafion 212	—	0.90	12.0	7.3	8.7	13.60	2.10

^a Determined by acid-base titration.

^b In the hydrated state (80 °C and 95% RH).

Fig. 3. Relative humidity dependence of water uptake of S-PES-xx membranes and Nafion 212 at 80 °C.

3.4. Proton conductivity

Proton conductivity is one of the key properties for predicting PEM suitability, since high conductivity is necessary for their effective utilization in fuel cell devices. The proton conductivity of S-PES-xx membranes was measured at 80 °C in the range of 35–95% RH. As can be seen in Table 2 and Fig. 4, all the membranes show higher proton conductivity than that of Nafion 212 at 95% RH (13.60×10^{-2} S/cm). Although the proton conductivity is more dependent on relative humidity than that of Nafion 212, good proton conductivity (higher than 1.0×10^{-2} S/cm) is achieved for S-PES-xx membranes at 50% RH, which is attributable to their high sulfonic acid content and well-connected ionic channels evident in the TEM images. In particular, the proton conductivity of the S-PES-55 membrane at 50% RH (2.21×10^{-2} S/cm) is slightly higher than that of Nafion 212 (2.10×10^{-2} S/cm), and retains a relatively high conductivity of 0.62×10^{-2} S/cm at 35% RH.

Fig. 4. Proton conductivity of S-PES-xx membranes and Nafion 212 at 80 °C as a function of RH.

Sulfonated hydrocarbon PEMs often require a relatively high water content to achieve proton conductivity comparable with Nafion, because of the inherently lower acidity and non-connected hydrophilic ionic channels [18,19,32]. In order to explore the relationship between water uptake and proton conductivity, S-PES-55 and Nafion 212 membranes was investigated. In Fig. 5, proton conductivity is plotted against hydration number (λ), which is the number of water molecules per sulfonic acid group. As expected, both membranes exhibit increases in proton conductivity with increasing λ values. It is remarkable that the S-PES-55 membrane has comparable or higher proton conductivity than Nafion 212 at corresponding λ values over the wide range of 35–95% RH. Ueda also observed that some sulfonated polymers with high IEC values and having apparent proton pathway connectivity had comparable or even higher proton conductivity than Nafion at similar λ values [25,44]. The present results provide further support that the formation of well-connected proton transportation

channels is effective for improving proton transport at low water content.

Fig. 5. Relationship between proton conductivity and hydration number (λ) of S-PES-55 and Nafion 212 membranes at 80 °C.

3.5. Thermal and mechanical properties

The thermal stabilities as measured by TGA 5% weight loss temperatures are listed in Table 3. The TGA curves of all sulfonated copolymers are shown in Fig. 6. A three-step degradation profile was observed for S-PES-xx membranes in their acid form. There was no weight loss up to 200 °C, because the samples were preheated at 150 °C for 20 min to remove absorbed water. The first weight loss occurred from 220-250 °C, which is associated with the degradation of the sulfoalkyl groups, and the initial weight loss increased with increasing the content of sulfuric acid groups. The second and third steps starting at about 370 °C mainly correspond to the main chain decomposition.

Fig. 6. TGA curves of S-PES-xx (acid form) membranes from measurements run at 10 °C/min in N₂.

Table 3

Thermal and mechanical properties.

Copolymers	$T_{d5\%}$ (°C) ^a	Tensile Strength at Break (MPa) ^b	Young's Modulus (GPa)	Elongation at Break (%)
S-PES-40	237.6	38.5	0.75	26.3
S-PES-45	236.5	35.9	0.67	27.0
S-PES-50	233.1	34.1	0.59	18.7
S-PES-55	229.8	26.7	0.38	22.1
Nafion 212	—	23.2	0.26	>200.0

^a 5% weight loss temperature in N₂ gas (acid form membrane).

^b measured at room temperature and 50 % RH.

Good mechanical properties of the membranes are one of the necessary requirements for their effective use in PEMFC applications. The mechanical properties of S-PES-xx membranes and Nafion 212 were measured at room temperature and 50% RH. The stress–strain data are presented in Table 3. The membranes have tensile stress at maximum load of 26.7–38.5 MPa and elongation at break of 18.7–26.3% with the general trend of lower maximum stress for the higher IEC. Although S-PES-xx membranes had relatively high IEC values, they had greater

1 tensile strength and Young's modulus compared with Nafion 212, which was likely
2
3 attributable to their hydrophobic and rigid polymer backbone. The mechanical
4
5 properties indicated that the membranes were strong and tough for potential use as
6
7 PEM materials in a fuel cell.
8
9

10 11 12 13 **4. Conclusions** 14

15
16 High IEC values of sulfonated poly(ether sulfone)s with densely populated
17
18 pendant sulfoalkyl groups were prepared by a facile synthetic route and low cost.
19
20 These sulfonated membranes exhibited clear hydrophilic/hydrophobic phase
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22 separation with 5-15 nm width of the hydrophilic domains. All the membranes had
23
24 higher proton conductivity than that of Nafion 212 at 80 °C and 95% RH and their
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26 proton conductivities were higher than 0.01 S/cm at 50% RH. The side-chain structure
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28 and hydrophobic polymer main chain also resulted in these membranes having good
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30 dimensional stability, in spite of the high IEC values. Moreover, they displayed good
31
32 thermal and mechanical properties. Considering the facile and inexpensive synthetic
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34 route, these sulfonated poly(ether sulfone)s have promising proton exchange
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36 membrane properties for application in fuel cells.
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Notes.

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Scheme 1. Synthesis of A-PES-xx and S-PES-xx copolymers.

Fig. 1. Comparative ^1H NMR spectra of the A-PES-45 ($-\text{NH}_2$) and S-PES-45 (salt form) copolymers.

Fig. 2. TEM photographs of S-PES-40, S-PES-50 and S-PES-55 membranes.

Fig. 3. Relative humidity dependence of water uptake of S-PES-xx membranes and Nafion 212 at 80 °C.

Fig. 4. Proton conductivity of S-PES-xx membranes and Nafion 212 at 80 °C as a function of RH.

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Table 1 Physical properties of A-PES-xx and S-PES-xx copolymers.

Table 2 IEC, water uptake, dimensional swelling, and proton conductivity of the S-PES-xx membranes.

Table 3 Thermal and mechanical properties.

Figure
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