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Electrospun and Cross-Linked Nanofiber Composite Anion Exchange Membranes

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S *Supporting Information*

ABSTRACT: A unique cross-linked nanofiber composite morphology was employed to create highly conductive and mechanically robust anion exchange membranes (AEMs) for alkaline fuel cells and electrodialysis separations. Chloromethylated polysulfone (CMPSF), the precursor for a tetramethylammonium ionomer, and an inert reinforcing polymer, poly(phenylsulfone) (PPSU), were simultaneously electrospun from separate spinnerets into dual fiber mats. The mats were processed into dense and defect-free nanofiber composite anion exchange membranes by cross-linking a portion of the chloromethyl groups in the CMPSF fibers with an aliphatic diamine, softening the PPSU so that it flowed and filled the void space around the CMPSF fibers, and quaternizing the remaining chloromethyl groups of CMPSF. The final network of ionomer fibers embedded in a PPSU matrix had a very high ion exchange capacity (3.1 mmol/g) but was insoluble in water due to the presence of cross-links. Membranes after processing were mechanically strong (in both the wet and dry states) with a very high hydroxide ion conductivity and moderate water swelling. Thus, a membrane containing 65 wt % ionomer fibers had a OH^- conductivity of 65 mS/cm in water at 23 °C, a stress at break of 14 MPa (for a water-equilibrated membrane at room temperature), and an equilibrium liquid water swelling of 144% at 23 °C. The AEM fabrication scheme is robust and can easily be extended to different base polymers, ion exchange groups, and cross-linking schemes.
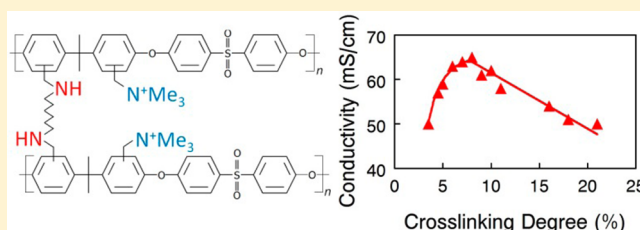
INTRODUCTION

Technological advancements and concerted research efforts worldwide in hydrogen/air proton exchange membrane fuel cell (PEMFC) development have been spurred, in part, by the excellent performance/properties of the Nafion perfluoronated polymer membrane used in such devices (e.g., a room temperature water-equilibrated proton conductivity of 90 mS/cm with good thermal and mechanical stability). Unfortunately, the acidic environment of a PEMFC requires expensive platinum group metals to catalyze the cathodic oxygen reduction and anodic hydrogen oxidation reactions.[1] Alkaline fuel cells are an attractive alternative to PEMFCs because they can potentially use less expensive nonprecious metal electrode catalysts, but a suitable polymeric membrane that possesses good mechanical properties, chemical stability, and moderate water swelling while maintaining high hydroxide conductivity has yet to be identified.[2,3]

Anion-exchange membranes (AEMs) for alkaline fuel cells usually contain tetramethylammonium cationic fixed charge groups, where the polymer backbone is polysulfone,[3–5] poly(arylene ether),[6,7] poly(phenylene),[8,9] poly(phenylene oxide),[10–12] polystyrene,[13–15] poly(ethylene),[1,16,17] or poly(ether−imide).[18,19] The OH^- ion conductivity of an AEM is generally lower than the H^+ conductivity of Nafion due to the lower mobility of hydroxide ions vs protons in water[20] as well as differences in the water-swollen morphology of Nafion vs a hydrocarbon-based AEM. For example, Varcoe and Slade

prepared mechanically robust poly(ethylene) based membranes with tetramethylammonium ion-exchange sites, where the ion exchange capacity (IEC) was 1.03 mmol/g (comparable to Nafion) but the hydroxide ion conductivity in water at 50 °C was only 34 mS/cm.[1] Another weakness of AEMs with tetramethylammonium ions is the potential loss in IEC during alkaline fuel cell operation due to quaternary ammonium group hydrolysis.[21] To address the issue of IEC stability, membranes with guanidinium,[22–24] imidazolium,[25–27] and phosphonium[28–30] cationic fixed charge groups were examined. For example, Noonan and co-workers synthesized AEMs with tetrakis(dialkylamino)phosphonium ion exchange sites on a poly(ethylene) backbone.[16] The membranes were highly stable in 1 M KOH at 80 °C, but the OH^- ion conductivity was low at 22 mS/cm in room temperature water due to a low membrane IEC.

A common strategy to increase the ion conductivity of an AEM is to raise its IEC by increasing the concentration of positively charged functional groups that are tethered to the polymer backbone.[4] As IEC increases, however, the mechanical properties of the membrane often suffer, with excessive swelling and poor strength when fully hydrated[27] and polymer brittleness when dry.[28] Of course, there is a limit as to how
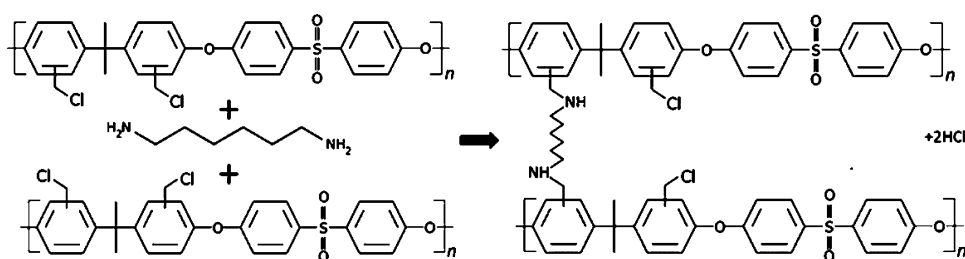
Scheme 1. Scheme for Reacting Chloromethylated Polysulfone (CMPSF) with Diamine (Pictured: Hexamethylenediamine) To Create Cross-Linked Polysulfone

high one can raise the IEC of an AEM, due to polymer chemistry and water solubility restrictions.[9] Even below the solubility limit, however, there could be adverse effects of IEC on ion conductivity, as demonstrated by Lee et al., who found that the OH⁻ conductivity of highly charged membranes (an IEC > 2.4 mmol/g) was low due to the volumetric dilution of polymer fixed charges by sorbed water (where the gravimetric swelling was >200 wt %).[31]

Recent research work on new AEMs for alkaline fuel cells has focused on novel polymer chemistries and membrane morphologies for improved conductivity with limited water swelling. Hibbs et al., for example, prepared charged and uncharged poly(phenylene) copolymer films with quaternary ammonium groups (1.57 mmol/g IEC) and achieved a hydroxide ion conductivity of 50 mS/cm in 30 °C water.[9] Tanaka et al. reported on an alkaline fuel cell membrane composed of multiblock poly(arylene ether)s, where some blocks were uncharged and others were functionalized with tetramethylammonium groups. At an IEC of 2.05 mmol/g, the membranes swelled 112% and exhibited an extraordinarily high hydroxide ion conductivity of 144 mS/cm at 80 °C, but polymer degradation was noted after immersion in hot water.[32] High conductivity AEMs have also been made from cross-linked ionomers. Gu et al. cross-linked a chloromethylated polysulfone material with a tris(2,4,6-trimethoxyphenyl)-phosphine cation and measured a membrane OH⁻ conductivity of 38 mS/cm and an equilibrium water swelling of 100% at room temperature.[30] Another cross-linked membrane was developed by Robertson and co-workers who used a ditetramethylammonium cation to both cross-link and provide ion-exchange sites to a ring-opened cyclooctene backbone, where the IEC and hydroxide ion conductivity were high (2.3 mmol/g and 69 mS/cm in 23 °C water).[33]

In the present study, a new AEM fabrication strategy was utilized where dual polymer fiber electrospinning was combined with polymer cross-linking to create anion exchange membranes with a phase-separated morphology of ionomer fibers embedded in an uncharged polymer matrix, where the ionomer fiber IEC is very high and where the uncharged polymer controls fiber swelling and imparts good mechanical properties to the membrane. Here, electrospinning is used as a "forced assembly" technique for dispersing/mixing two dissimilar polymers in the dry state and on the submicrometer scale. It is an alternative to the use of polymer blending or block copolymers for composite membrane fabrication. The work builds upon the prior successes of Ballengee and Pintauro, who developed a dual fiber electrospinning approach for preparing nanofiber composite proton-exchange membranes.[34] The present work is also a direct extension of a dual fiber AEM study that was recently published by Park and Pintauro, where

un-cross-linked polysulfone fibers with a moderate concentration of tetramethylammonium fixed charge sites were embedded in a poly(phenylsulfone) (PPSU) matrix.[35]

To make highly conductive fiber composite AEMs, a polymer cross-linking step was incorporated into the dual fiber membrane fabrication scheme. A mat containing chloromethylated polysulfone fibers (where the degree of chloromethylation was >95%) and PPSU fibers was immersed in an aliphatic diamine cross-linker (the polymer cross-linking reaction is shown in Scheme 1). The mat was then exposed to chloroform vapors which selectively softened the PPSU and allowed it to flow and fill the void space between the cross-linked chloromethyl-containing fibers. Finally, the chloromethyl groups were converted to tetramethylammonium ion exchange sites by reaction with trimethylamine. The cross-linking step was necessary because the IEC of the quaternized polysulfone fibers was far greater than their water solubility limit.[20]

The focus of the present study was on controlling the degree of cross-linking of the ionomer fibers, where all membranes were made from the same chloromethylated polysulfone (a degree of chloromethylation of 1.94, which would produce an ionomer IEC of 3.32 mmol/g after complete quaternization). Membranes were also made with different ratios of chloromethylated ionomer precursor to polyphenylsulfone to examine the effect of uncharged polymer content on membrane properties. Composite membranes were tested for ion exchange capacity, OH⁻ conductivity after equilibration in room temperature liquid water, equilibrium gravimetric water swelling, methanol permeability, mechanical properties, and chemical stability.

■ EXPERIMENTAL SECTION

Materials. Udel P-3500 polysulfone (MW = 80 000) and Radel R-5500 (MW = 63 000) poly(phenylsulfone) (henceforth denoted as PPSU) were obtained from Solvay Advanced Polymers, LLC, and dried at 140 °C for at least 2 h before further use. Dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP), acetone, 1,6-hexamethylenediamine 60 wt % aqueous solution, 1,2-ethanediamine, 1,4-butanediamine, 45 wt % aqueous trimethylamine, paraformaldehyde, chlorotrimethylsilane, tin(IV) chloride, and methanol were used as received from Fisher Scientific or Sigma-Aldrich.

Synthesis of Chloromethylated Polysulfone. Chloromethylated polysulfone (abbreviated as CMPSF) was synthesized from Udel polysulfone by a method adapted from Avram et al.[35] and as reported previously.[36,37] The degree of chloromethylation of the CMPSF, as determined from ¹H NMR, was fixed for the entire study at 1.94 (the maximum is 2.00). In a preliminary evaluation of the CMPSF material, after converting the CH_2Cl groups to tetramethylammonium fixed-charges (by exposure to trimethylamine), the measured IEC was 3.32 mmol/g and the ionomer was found to be completely soluble in 23 °C DI water.

Electrospinning. Chloromethylated polysulfone and polyphenylsulfone solutions were separately and simultaneously electrospun onto a common collector surface in a method similar to that described previously.[38] CMPSF was dissolved in dimethylacetamide (DMAc) at a CMPSF concentration of 20% w/w. Dry polyphenylsulfone pellets were dissolved in a 4:1 weight ratio mixture of N-methyl-2-pyrrolidinone (NMP) and acetone where the final polymer concentration was 25% w/w. Solutions of each polymer were loaded into separate syringes that were fitted with 22 gage needles from Hamilton Co. A separate high voltage power supply was used to apply the necessary bias potential to each needle (10.5 kV for CMPSF and 8.5 kV for PPSU). A rotating and laterally oscillating drum was used to collect the fibers, as was done in prior studies to ensure a uniform distribution of fibers throughout the entire mat. The flow rates of the polymer solutions were set by separate syringe pumps and were 0.8 mL/h for CMPSF and between 0.38 and 0.57 mL/h for PPSU. Each needle was placed 9 cm from the collector drum surface. The temperature and humidity during electrospinning were fixed at 23 °C and 35% RH.

Cross-Linking of Electrospun Fibers. Before cross-linking, residual NMP was removed from the dual fiber mat by soaking in methanol and drying for 2 h at 70 °C. Mat samples were then cross-linked by immersion in a 20 wt % diamine solution in a DMAc/water solvent for 3−30 min, where the diamine was either 1,2-ethanediamine, 1,4-butanediamine, or 1,6-hexamethylenediamine. To terminate cross-linking, the mats were removed from the diamine solution and quickly and thoroughly washed with DI water, followed by drying at 70 °C for 1 h. PPSU fibers were unaffected by the diamine solution.

Converting Dual Fiber Mats into Dense Membranes. Cross-linked CMPSF/PPSU dual fiber mat samples were processed into dense, defect-free anion exchange membranes by a three-step sequence: compaction, vapor exposure, and quaternization. Fiber mats were first compressed at 5000 psi for 20 s to increase the volume fraction of fibers in the mat from 0.25 to 0.6. These mats were then suspended over liquid chloroform in a sealed container at room temperature for 10−12 min, where chloroform vapor sorbed into PPSU fibers, softened the fibers, and allowed the polymer to flow and fill the void space between cross-linked CMPSF fibers (the CMPSF fibrous morphology was unaffected by chloroform vapor exposure). After vapor treatment, the membranes were immediately dried at 70 °C for 1 h to remove excess chloroform. Finally, the chloromethyl groups were quaternized by soaking in a 45% aqueous trimethylamine solution for 24 h at 40 °C. There was no protonation of primary or secondary amines, due to the high pH (12−13) of the trimethylamine solution. After quaternization, the membranes were washed in DI water to remove excess trimethylamine. Membranes were always stored in the Cl⁻ counterion form in DI water for later use. Prior to a characterization experiment, membrane samples were soaked in a 1 M KOH solution to replace Cl⁻ counterions with mobile OH⁻ ions, and thoroughly washed with DI water degassed with argon. The degassing step is necessary and commonly used with AEMs in the OH⁻ form to remove dissolved carbon dioxide from the DI soak solutions and prevent undesirable carbonate counterion formation.[5]

Membrane Characterization. Electrospun mats and anion exchange membranes were imaged using a Hitachi S-4200 scanning electron microscope (SEM). Samples were coated with gold using a Cressington gold sputter coater to enhance resolution of nonconductive membrane regions. An average fiber diameter was determined from SEMs using ImageJ software. Membrane cross sections were made after freeze fracturing samples by immersion in liquid nitrogen. ¹H NMR data were taken on a Bruker 400 MHz spectrometer and analyzed using Topspin software. Mechanical property data were collected on membranes equilibrated in liquid water and ambient air at 23 °C using a TA Instruments Q800 dynamic mechanical analyzer in tension mode. Controlled force experiments were performed where the constant rate of strain (40%/min) was applied until the sample yielded.

The degree of cross-linking in CMPSF fibers was determined in three ways. For the first method, the initial weight of a dry un-cross-linked mat was compared to the final weight of the same dry mat after cross-linking, where the observed weight gain was attributed to diamine cross-linking. The second way was based on measuring the difference in ionomer IEC before and after cross-linking, where it was assumed that all diamine molecules formed inter or intra chain cross-links (i.e., one diamine molecule always reacted with two chloromethyl groups). Membrane samples for this test were soaked a 1.0 M NaCl solution at neutral pH, where the measured concentration of membrane-bound chloride counterions was associated exclusively with the ionomer's tetramethylammonium fixed charge groups. The third method involved equilibrating membrane samples in a 0.1 M HCl solution, in which case the two amine groups of diamine cross-linker molecules are protonated and thus the titrated Cl⁻ ion concentration is a measure of both the tetramethylammonium fixed charge concentration and the total concentration of diamine cross-linkers in the membrane (where every bound diamine molecule has two protonated amine groups, regardless of whether one end or both ends are covalently bonded to a polymer chain). The difference between this protonated species IEC and the tetramethylammonium IEC determined at neutral pH was used to quantify the amount of cross-linker in the membrane.

IEC was calculated by a variant of the Mohr titration method.[5] Membrane samples were placed in 20 mL of 0.2 M sodium nitrate solution under stirring. The nitrate ions replaced the chloride ions in the membrane, releasing Cl⁻ into solution. Every composite membrane tested was soaked in two separate 20 mL solutions for 2 h each to ensure full nitrate substitution, for a total chloride solution volume of 40 mL. This solution was titrated with 0.1 M standard silver nitrate, using potassium chromate as an indicator. Chloride ion titration of anion exchange groups is preferred over titration with a OH⁻ solution because hydroxide counterions can react with CO_2 to form carbonates, which can lead to erroneous (low) IEC values.[39] The IEC of the un-cross-linked tetramethylammonium form of CMPSF was determined by ¹H NMR after dissolving a known weight of polymer in deuterated dimethyl sulfoxide.

In-plane hydroxide ion conductivity was measured using an AC-impedance method with a four probe Bekktech conductivity cell. Membrane samples were presoaked in degassed DI water, then quickly mounted in the conductivity cell and immersed in liquid water at room temperature (23 °C); all measurements were made within 2 min of sample removal from the degassed water to minimize carbonate formation. The conductivity of the membranes was calculated by eq 1,

$$\sigma = \frac{L}{Rw\delta} \tag{1}$$

where σ = conductivity [mS/cm], L = distance between working electrodes, R = resistance of the membrane [ohm], w = measured wet sample width [cm], and δ = measured wet membrane thickness [cm].

Equilibrium gravimetric water swelling of membrane samples at room temperature was determined immediately following a conductivity test, in accordance with eq 2,

$$\% \text{ swelling} = \frac{w_{wet} - w_{dry}}{w_{dry}} \times 100 \tag{2}$$

where (W_{wet}) = the weight [g] of a membrane sample after equilibration in liquid water and (W_{dry}) = the weight [g] of the same sample after drying at 70 °C for 1 h.

The volumetric concentration of fixed-charge sites in a wet membrane sample (χ, with units of mmol cation/cm³ of sorbed water) was found using the following equation:

$$\chi = \text{IEC}_{mem}\left[\frac{w_{wet}}{w_{wet} - w_{dry}}\right]\rho_{water} \tag{3}$$

where IEC_{mem} is the measured effective IEC of the composite membrane [mmol/g] and ρ is the density of water [g/cm³].

One potential application for the membranes fabricated in this study is in a direct methanol alkaline fuel cell. So methanol permeability was measured at room temperature in a custom-made glass two-chamber diffusion cell with 1.0 M methanol, as described elsewhere.[40]

Membrane stability was evaluated by soaking membranes in the hydroxide counterion form at 70 and 50 °C for up to 5 days. After measuring the initial OH$^-$ ion conductivity, membranes samples were immersed in heated and degassed DI water. Periodically, at regular time intervals, the membranes were removed from the water and conductivity was remeasured.

■ RESULTS AND DISCUSSION

Membrane Fabrication. Three aliphatic diamines were studied as cross-linkers in the present work: 1,2-ethanediamine, 1,4-butanediamine, and 1,6-hexamethylenediamine. These diamines react with chloromethyl groups to give uncharged secondary amine cross-links, which are not susceptible to the Hoffman elimination reaction. The percentage of chloromethyl groups that react during cross-linking, defined henceforth as the cross-linking degree of the CMPSF nanofibers, was controlled by varying the soaking time of an electrospun dual fiber mat in a diamine solution. The relationship between soak time and cross-linking degree for mat immersion in a hexamethylenediamine solution, for example, is shown in Figure 1. In the
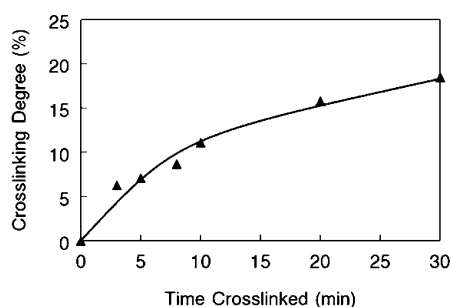

Figure 1. Cross-linking degree of CMPSF fibers as a function of time exposed to diamine cross-linking solution at 23 °C. Diamine solution concentration: 20 wt % in DMAc/water; base polymer was polysulfone with 1.94 degree of chloromethylation.

present study, between ~5% and ~20% of the total chloromethyl groups reacted with the diamine. For the samples used to collect the data in Figure 1, the diamine cross-linker was assumed to react on both ends to form either an interchain cross-link or an intrachain loop (where both ends of the diamine react on the same CMPSF chain). The possibility of an incomplete reaction, where a diamine molecule reacts only on one end, will be addressed below with regards to the results in Figure 3.

A photograph of the as-spun dual fiber mat is shown in Figure 2a. It was opaque due to the presence of interfiber voids (pores). Figure 2b is an SEM micrograph of this initial mat; the chloromethylated polysulfone and polyphenylsulfone fibers are indistinguishable and the average fiber diameter is ~700 nm. A photograph of a composite membrane after compaction and chloroform vapor exposure is shown in Figure 2c. The film is nearly transparent, which is a qualitative indicator of the absence of voids. A freeze-fractured cross section of this densified film is shown Figure 2d; the film appears to be free of voids. Because the fibers of CMPSF are not clearly distinguishable from those of PPSU in SEM micrographs, a sample of the film shown in Figure 2c was soaked in liquid chloroform to dissolve PPSU (thus revealing the network of cross-linked CMPSF fibers) and is shown in Figure 2e. Chloroform is a good solvent for both CMPSF and PPSU, but after the diamine cross-linking step, the CMPSF fibers retain their fibrous morphology upon chloroform vapor exposure. Figure 2e also
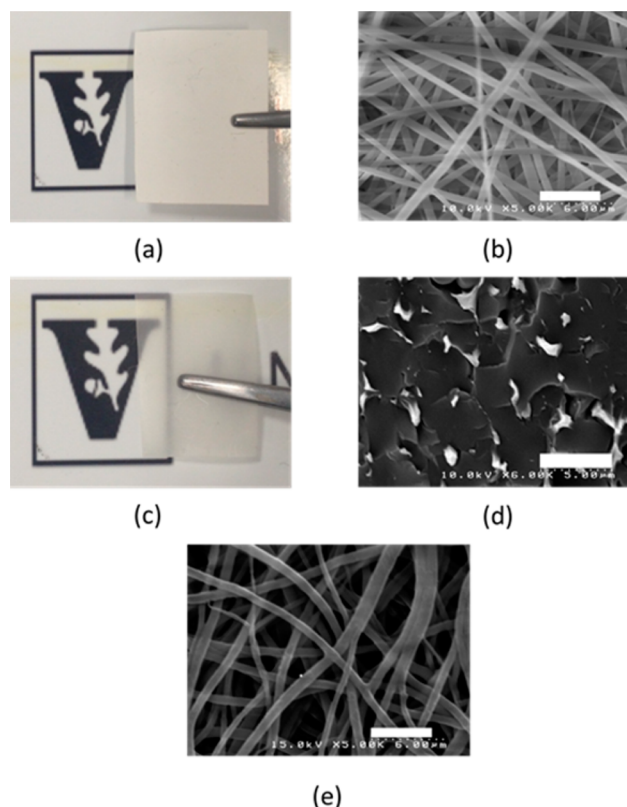

Figure 2. Optical and SEM images, respectively, of electrospun mat with cross-linked CMPSF fibers (a, b), final dense membrane where PPSU has filled void space around cross-linked CMPSF fibers (c, d), and cross-linked CMPSF fibers with PPSU removed (e). Scale bars for images b, d, and e are 5 μm.

shows that there is some fiber welding as a consequence of chloroform vapor exposure. It has been shown previously by Choi et al. that ionomer fiber welding is beneficial in terms of membrane mechanical properties and ion conductivity, for the case of proton conducting cation exchange composite nanofiber membranes.[41] So in the present study, the CMPSF fiber welds were not considered to be deleterious to the morphology. Also, based on SEM observations (but not shown here), the fibrous morphologies shown in Figure 2, parts c and e, were retained after quaternization of all remaining (un-cross-linked) CH$_2$Cl groups.

Fully processed membranes contained 65 or 55 wt % cross-linked ionomer and 35 or 45 wt % PPSU. 35 wt % (32 vol %) PPSU was chosen as the minimum amount of uncharged polymer in a composite membrane based on the prior work of Ballengee and Pintauro, who found that at least 30 vol % PPSU was needed to completely fill voids in nanofiber composite membranes where Nafion nanofibers were embedded in a polysulfone matrix.[42] In the present study, composite anion exchange membranes were also prepared with 45 wt % PPSU to assess the effect of increased uncharged/inert polymer on membrane properties.

The ion exchange capacity of ionomer fibers in composite membrane, as measured from titration experiments at neutral pH (and corrected for the amount of uncharged polymer in a fully processed membrane) was compared to that back-calculated from the initial degree of polysulfone chloromethylation and the measured fiber weight change after cross-linking with hexamethylenediamine. These two values of ionomer fiber

IEC (with units of mmol of fixed charges per gram of dry ionomer) are plotted in Figure 3 as a function of the degree of
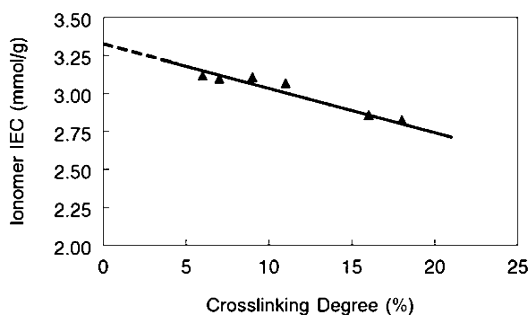

Figure 3. Dependence of ionomer fiber IEC on cross-linking degree with hexamethylenediamine: triangles, measured values from titration (from membranes with 35 wt % PPSU); solid line, values back-calculated from the total chloromethyl content and the weight change in a fiber mat after cross-linking. The initial polymer was chloromethylated polysulfone (1.94 degree of chloromethylation).

cross-linking, for membranes containing 35 wt % PPSU. As expected, the ionomer IEC decreases with an increase in the cross-linking degree. Also, there is very good agreement between the two determinations of IEC. If a measurable amount of diamine cross-linker reacted with only one chloromethyl group, the titrated IEC would be greater than that calculated from the weight change, as there would be more tetramethylammonium sites than expected. The amount of hexamethylenediamine cross-linker was further quantified by the difference between the measured IEC of membranes soaked in HCl (where protonated amine cross-linker groups and quaternary ammonium sites were associated with a chloride ion) and the IEC measured after soaking the membrane in neutral pH 1.0 M NaCl. These measurements were also found to be in good agreement with the diamine weight change data.

From a separate set of experiments, it was found that above a cross-linking degree of 4%, there was no measurable loss in ionomer when a membrane sample was equilibrated in room temperature water. Some polymer weight loss (ionomer dissolution) was seen when the cross-linking degree fell below 4%. Dissolution of poorly cross-linked ionomer fibers was not unexpected; the pristine polymer IEC was 3.3 mmol/g − well above the water solubility threshold of ∼2.5 mmol/g for tetramethylammonium functionalized PPSU. When the straight line best fit of the data in Figure 3 is extrapolated to 0% cross-linking degree, an IEC of 3.32 mmol/g is obtained, which is in excellent agreement with the measured ion exchange capacity of the un-cross-linked ionomer with 100% conversion of chloromethyl groups to tetramethylammonium (see Figure S1 in the Supporting Information).

Thus, from these results, it can be concluded that: (1) all bound diamine molecules have reacted with two chloromethyl groups, (2) there is no ionomer dissolution due to insufficient or nonuniform cross-linking when the cross-linking degree is >4%, and (3) all chloromethyl groups remaining after cross-linking are converted into tetramethylammonium ion fixed charge sites by reaction with trimethylamine. It is important to note that the range of effective membrane IEC surveyed in the present study was relatively small, between 1.52 and 2.05 mmol/g (as calculated by multiplying the IECs in Figure 3 by the weight fraction of ionomer in a final membrane). In this IEC range, however, membrane properties changed substan-

tially, as will be shown below, because the degree of ionomer cross-linking varied inversely with ion exchange capacity (i.e., when the ionomer IEC was high, the degree of cross-linking was low).

Membrane Performance. Gravimetric water swelling as a function of membrane cross-linking degree is shown in Figure 4
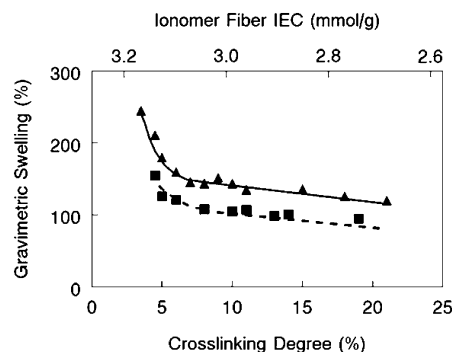

Figure 4. Dependence of gravimetric membrane swelling, measured in liquid water at 23 °C, on cross-linking degree for composite anion exchange membranes with 35 (▲) and 45 (■) wt % PPSU.

(no data is shown for a cross-linking degree <4% because these ionomer fibers partially dissolved in water during a swelling experiment). All of these membranes contained 35 or 45 wt % PPSU, which surrounded the ionomer fibers and to some extent limited membrane water uptake by the fibers. As can be seen, 35 wt % PPSU membrane water swelling dropped from 250% to 140% when the cross-linking degree increased from 4% to 7%, In this cross-linking range the ionomer fiber IEC was essentially constant (3.1−3.2 mmol/g), i.e., the hydrophilicity of the ionomer fibers was unchanged, so the reduction in swelling can be associated with the creation of additional cross-links. A similar effect is seen in membranes with 45 wt % PPSU. These results demonstrate the strong effect cross-linking has on the swelling of the quaternized PPSU in the 4−7% cross-linking region. Beyond 7% cross-links, there is only a modest decrease in water uptake with cross-linking degree, even though chloromethyl groups are consumed and the ionomer fiber IEC decreases (as per Figure 3). The consistent but small decrease in water uptake for 8−20% cross-linking is associated with the reduction in ionomer fiber IEC. When the uncharged polymer content of the membrane is increased to 45 wt % PPSU, membrane swelling is significantly reduced (e.g., from 144% to 108% at cross-linking degree of 8%) due to the replacement of some hydrophilic ionomer with hydrophobic PPSU. It is not clear at the present time if ionomer cross-linking or the presence of the PPSU matrix surrounding every fiber is the dominant factor in limiting membrane swelling. Future work will seek to quantify and contrast these two individual effects for different extents of cross-linking and different relative amounts of ionomer and uncharged polymer.

The data in Figures 3 and 4 were combined in order to calculate the concentration of cationic fixed-charge groups per unit volume of water in a nanofiber composite membrane. This parameter χ (given by eq 3, with units of mmol cation/cm^3 water sorbed), is a measure of the actual concentration of fixed charge sites in the water swollen ionomer fibers, as compared to IEC, which is always given on a dry ionomer basis and does not take into account how the ionomer swells. As shown in Figure 5, χ increases when the degree of ionomer cross-linking is
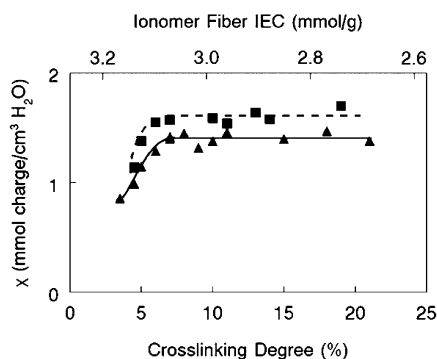
Figure 5. Dependence of tetramethylammonium ion fixed charge site concentration (χ) on the fraction of chloromethyl groups cross-linked in ionomer fibers for composite membranes with 35 (▲) and 45 (■) wt % PPSU, where all membranes were equilibrated in liquid water at 23 °C.

increased from 4% to 7%. Here, the small decrease in the membrane IEC due to an increase in cross-linking degree is offset by the substantial decrease in water swelling due to the presence of interchain cross-links; i.e., $w_{wet} - w_{dry}$ decreases faster than IEC_{mem} in eq 3. This result demonstrates that the cationic groups have been effectively concentrated in the ionomer fibers by interchain cross-linking. Above a cross-linking degree of 8%, there is no further change in χ with cross-linking. This unexpected result can be explained by a balance between the decrease in membrane IEC, due to increasing the number of cross-links, and a concomitant/identical decrease in $w_{wet} - w_{dry}$. Increasing the PPSU content from 35 to 45 wt % produces an increase in χ, indicating that the PPSU component in the membrane is effective at reducing swelling of the ionomer fibers.

The in-plane OH⁻ ion conductivity of composite membrane samples that were equilibrated in liquid water at 23 °C is shown in Figure 6 as a function of cross-linking degree for films
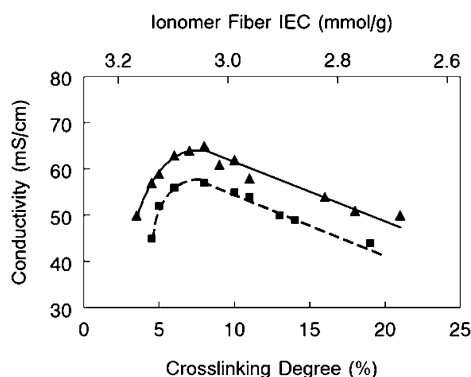

Figure 6. In-plane conductivity of cross-linked composite membranes at various cross-linking degrees with (▲) 35 wt % PPSU and (■) 45 wt % PPSU. Data was collected in liquid water at room temperature (23 °C).

containing 35 and 45 wt % PPSU. The highest conductivity was 65 mS/cm for a film where the ionomer fiber cross-linking degree was 8% and the PPSU content was 35 wt %. The conductivity is low for membranes with a cross-linking degree of 4% because of excessive water swelling, where χ, the volumetric concentration of cationic fixed charges in swollen ionomer fibers, is small (see Figure 5). As the degree of cross-linking increases from 4% to 7%, the fixed charge concentration (χ) increases, resulting in the observed increase in conductivity. For cross-linking degrees >8%, the hydroxide ion conductivity decreases linearly with cross-linking degree for membranes with either 35 or 45 wt % PPSU even though there is no measured change in χ (Figure 5). The observed decline in conductivity is attributed to an increase in tortuosity of diffusive pathways for hydroxide ions in ionomer fibers as the cross-linking degree increases. Finally, it should be noted that although χ for ionomer fibers in the 45 wt % PPSU membrane is higher than that in the 35 wt % PPSU membrane (Figure 5), the OH⁻ conductivity is lower for the membrane with the higher PPSU content due to the diluting effect of uncharged polymer.

For completeness, the length of the aliphatic backbone of the diamine cross-linker was varied to determine its effect upon the swelling and conductivity of composite membranes. 1,2-ethanediamine and 1,4-butanediamine, (denoted as C_2 and C_4 in Table 1), were investigated, where the amount of ionomer in the membrane and the cross-linking time were held constant at 65 wt % and 5 min, respectively, and where the degree of chloromethylation of the CMPSF fibers was fixed at 1.94. All diamine soaking solutions were of the same concentration, 8 mol %, in a mixture of DMAc and water. The properties of three cross-linked composite membranes with essentially the same measured effective dry polymer IEC are presented in Table 1. As can be seen, composite membranes made from 1,2-ethanediamine and 1,4-butanediamine had a higher gravimetric water swelling and a lower volumetric concentration of cations (χ), leading to a lower OH⁻ ion conductivity. These results were attributed to incomplete cross-linking with of the shorter diamine molecules (i.e., reaction of the diamine with only one chloromethyl group), which would reduce IEC without restricting swelling (leading to lower χ). It is clear that controlling swelling is important for a high χ value, and that high swelling correlates directly to low χ when the dry ionomer IECs are similar. These results lead us to the conclusion that hexamethylenediamine is a more effective cross-linker than ethanediamine or butanediamine; no further studies were performed with the shorter diamines.

Stress−strain curves for cross-linked composite membranes with 35% and 45 wt % PPSU are shown in Figure 7, where the films were equilibrated at 23 °C in either liquid water or in 50% relative humidity (RH) air. The cross-linking degree for the two films was 8%, which corresponds to an ionomer fiber IEC of ∼3.1 mmol/g, The OH⁻ ion conductivity for the two films in water was 65 mS/cm (35 wt % PPSU) and 57 mS/cm (45 wt % PPSU). The measured mechanical properties of both

Table 1. Properties of Composite Membranes with Different Cross-Linker Lengths Where the PPSU Content was 35 wt %

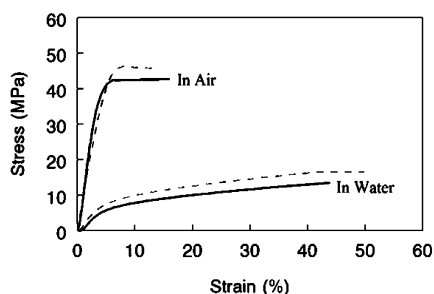| cross-linker carbon length	membrane IEC (mmol/g)	membrane gravimetric swelling[a] (%)	conductivity[a] (mS/cm)	χ (mmol charge/cm³ H₂O)
C_2	1.85	167	47	1.10
C_4	1.79	160	46	1.12
C_6	1.82	126	51	1.44

[a]In water at 23 °C.

Figure 7. Stress−strain curves for cross-linked fiber composite membranes when equilibrated at 23 °C in liquid water or equilibrated 50% RH in air. Shown are a membrane with 35 wt % PPSU and an effective membrane IEC of 2.01 mmol/g (solid lines) and a membrane with 45 wt % PPSU and an effective IEC of 1.67 mmol/g (dashed lines).

membranes are very good in the fully and partially hydrated states, which is important for possible fuel cell applications.[43] Water and air equilibrated films were soft and pliable. The sorption of liquid water decreased the membrane's tensile properties—a phenomena seen in other AEMs[8]—but the hydrophobic reinforcing PPSU matrix provides sufficient strength to the wet membrane for mechanical robustness. The elongation at break, when membranes were sorbed with liquid water, is consistent with data reported in the literature for other AEMs and shows that water is plasticizing ionomer fibers and reduces their brittleness.[44]

The properties of several anion exchange membranes reported in the literature are listed in Table 2, along with data for two cross-linked fiber composite membranes from the present study with a cross-linking degree of 8% (which maximizes conductivity for a given PPSU content). As can be seen, the OH⁻ ion conductivity of the composite films compare well with other anion-exchange membranes. The swelling of the cross-linked fiber membranes is somewhat high, but comparable to those films with similar conductivities. The tensile strength of water equilibrated cross-linked nanofiber composite membranes is similar to that reported by Varcoe et al.[1] (13−17 MPa) and Robertson et al.[33] (15 MPa) for membranes composed of a poly(ethylene) and cross-linked octene backbone, respectively. The fact that we observe the same conductivity as a membrane with greater IEC (2.01 vs 2.62 mmol/g reported by Wang et al.[3,45]) with a similar backbone suggests that the phase-separated morphology of cross-linked fiber composite membranes leads to well-ordered hydroxide ion

conducting channels and is an effective way to combine the need for hydrophilic (ion-conducting) and hydrophobic (mechanically reinforcing) domains.

There have been alkaline fuel cell studies where the fuel is an aqueous methanol solution,[1] so methanol permeability was measured in a small number of nanofiber composite films. Figure 8 shows the effect of ionomer cross-linking (the effective
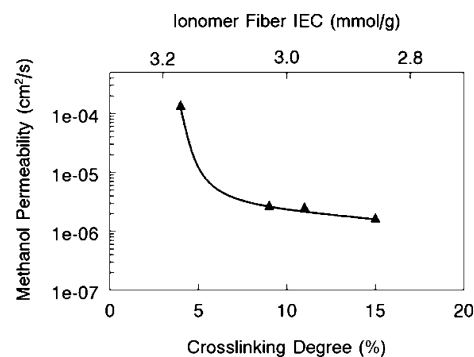

Figure 8. Methanol permeability at 23 °C of fully hydrated cross-linked nanofiber composite membranes with 35 wt % PPSU.

membrane IEC) on methanol permeability at 23 °C for films containing 35 wt % PPSU. As expected, the membrane with the lowest cross-linking degree (and highest IEC) has high methanol permeability, due to greater membrane swelling. The permeability data are comparable to those reported in the literature for other AEMs; for example, Hickner and Yan[5] report a permeability of $2.0(10)^{-6}$ cm²/s for a polysulfone-based AEM with tetramethylammonium groups (at an IEC of 2.1 mmol/g). The reasonable values of measured methanol permeability for the nanofiber films is also an important indicator that the processed composite membranes have no pinhole defects and no significant void volume between cross-linked ionomer fibers and reinforcing PPSU matrix.

The chemical and thermal stability of nanofiber composite membranes in the OH⁻ counterion form was assessed by soaking films in 50 and 70 °C water for 5 days. The results of these tests, as quantified by the change in membrane conductivity with time (designated as the ratio of conductivity to the initial conductivity), are shown in Figure 9. The conductivity of membranes in 50 °C water was stable over 5 days, whereas the membrane failed in the 70 °C soak test, with a linear and substantial decline in hydroxide ion conductivity with time. The latter result was not unexpected and is

Table 2. Anion Exchange Membranes with Tetramethylammonium Fixed Charges: Comparison of Literature Data and Present Work

| sample/reference	effective membrane IEC (mmol/g)	conductivity in water at 23−25 °C (mS/cm)	gravimetric swelling (%)	tensile strength at 23 °C (MPa)	
				in water	in air at 50% RH
35% PPSU	2.01	65	144	14	42
45% PPSU	1.67	57	108	17	45
Varcoe et al.[1] (un-cross-linked polyethylene)	1.03	27	40	13−17	−
Li et al.[46] (polysulfone block copolymer)	1.74	38	40	−	60
Robertson et al.[33] (cross-linked octene)	2.3	69	225	15	−
Wang et al.[45] (polysulfone block copolymer)	2.62	65	86	−	61
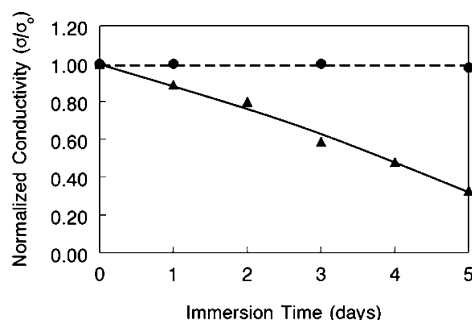
Figure 9. Change in conductivity of cross-linked composite membranes samples with 35 wt % PPSU and an effective membrane IEC of 2.01 mmol/g (see Table 2) after soaking in OH⁻ form at 70 °C (▲) and 50 °C (●).

attributed to quaternary ammonium group hydrolysis at the higher test temperature.[21] For both the high and low temperature soak tests, there was no evidence of membrane cracking, discoloration, or a change in mechanical properties. The water content of nanofiber composite membranes for all IECs was high enough to prevent accelerated degradation due to hydroxide nucleophilic attack.[47] The 50 °C stability results are encouraging, in light of published reports that such a temperature is adequate for alkaline fuel cell operation with either hydrogen or methanol fuel.[1]

CONCLUSIONS

A novel fabrication scheme has been devised for composite anion exchange membranes where cross-linked ionomer fibers with tetramethylammonium fixed charge sites are embedded in an uncharged polymer matrix of polyphenylsulfone. First, two different polymers—chloromethylated polysulfone (CMPSF) and poly(phenylsulfone) (PPSU)—were simultaneously electrospun into a dual-fiber mat. Then, CMPSF fibers were soaked in a diamine solution to cross-link a small fraction of the chloromethyl groups. Finally, the PPSU component was selectively made to flow and fill the void space around the cross-linked CMPSF fibers, and the remaining chloromethyl groups were quaternized with trimethylamine. When the cross-linking degree was >4%, the cross-linked ionomer fibers were insoluble in water but had an IEC much higher than that possible with un-cross-linked, water-insoluble quaternary ammonium polysulfone (3.1 vs 2.5 mmol/g). These cross-linked electrospun composite membranes had effective IEC in the range 1.52–2.05 mmol/g which was varied by changing: (1) the degree of cross-linking and (2) the percentage of inert PPSU by weight. Cross-linked nanofiber composite membranes exhibited excellent hydroxide ion conductivity (65 mS/cm when equilibrated in room temperature water) with reasonable swelling (144%) and very good mechanical properties.

ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectrum indicating complete reaction of all chloromethyl groups on polysulfone with trimethylamine. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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