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14. ABSTRACT

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a stress at break of 16 MPa. Composite membranes showed reasonably good chemical stability in 1.0 M KOH at 50? C, with a 20% loss in OH? conductivity after 3 days.

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Diol-Crosslinked Electrospun Composite Anion Exchange Membranes

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A dual fiber electrospinning procedure was employed to prepare composite anion exchange membranes, where an interconnected network of hexanediol-crosslinked polysulfone polyelectrolyte fibers with quaternary ammonium or imidazolium fixed charge groups was embedded in a polyphenylsulfone matrix. Chloromethylated/iodomethylated polysulfone nanofibers containing 1,6-hexanediol were electrospun simultaneously with polyphenylsulfone fibers and the resultant mat was processed into a dense and defect-free anion exchange membrane by: (i) physical compaction, (ii) heating to create diol crosslinks, (iii) exposure to chloroform vapor which softened the polyphenylsulfone and allowed it to fill the voids between crosslinked fibers, and (iv) functionalization of the chloromethyl/iodomethyl fibers with trimethylamine, 1-methylimidazole, or 1,2-dimethylimidazole. The presence of the polyphenylsulfone matrix and polyelectrolyte crosslinks controlled water swelling and allowed for good mechanical properties when the ion exchange capacity and hydroxide ion conductivity were high. For example, a room temperature water-equilibrated membrane containing 35 wt% polyphenylsulfone and 65 wt% crosslinked polysulfone fibers with 1,2-dimethylimidazolium fixed charge sites and 8% crosslinking degree exhibited a room temperature OH^- ion conductivity of 49 mS/cm, a gravimetric swelling of 96%, and a stress at break of 16 MPa. Composite membranes showed reasonably good chemical stability in 1.0 M KOH at 50°C, with a 20% loss in OH^- conductivity after 3 days.

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Fuel cells have emerged as viable candidates for portable, stationary, and automotive power applications. The hydrogen/air proton exchange membrane fuel cell (PEMFC) has been extensively studied in terms of component materials and system operations. Nafion perfluorosulfonic acid membranes are often used in PEMFCs as the solid electrolyte that separates the anode and cathode. Another fuel cell type that has attracted increased interest in recent years is the anion exchange membrane fuel cell (AEMFC). AEMFCs can employ less expensive non-precious metal electrode catalysts such as nickel or silver because the alkaline operating conditions are less corrosive to fuel cell components.[1] Significant efforts have been directed toward developing a suitable anion exchange membrane (AEM) for these fuel cells. Such a membrane should have a high hydroxide ion conductivity while being mechanically robust and chemically/thermally stable.[2]

An AEM is often made by reacting a solution-cast film of a chloromethylated precursor polymer with trimethylamine to give an anion exchange polymer with quaternary ammonium groups tethered to a polymer backbone.[3,4] AEMs that exhibit a high hydroxide ion conductivity typically have a high concentration of fixed charges, i.e., a high membrane ion exchange capacity (IEC).[2] Such membranes, unfortunately, swell excessively in water (or are water soluble) and the films are often brittle when dry.[5,6] Several groups have attempted to address the swelling problem by using block co-polymers[7] or by crosslinking the polyelectrolyte.[8] The present authors have recently shown that a dual nanofiber electrospinning approach (originally developed by Ballengee and Pintauro[9] for proton exchange membranes can be used to prepare high performance composite AEMs with a high hydroxide ion conductivity, where the anion exchange polymer fibers are crosslinked with an aliphatic diamine and the fixed charge groups are quaternary benzyl trimethylammonium moieties.[10,11] In the present paper, the dual fiber electrospinning approach was extended to fabricate a series of new anion exchange membranes where: (i) an aliphatic diol was used to create crosslinks in anion exchange polymer fibers and (ii) three different ion exchange group chemistries were investigated: benzyl trimethylammonium, 1-methylimidazolium, and 1,2-dimethylimidazolium (imidazolium cations were chosen based on their popularity as an alternative to benzyl trimethylammonium fixed charges).[5,12–15]

The general procedure for membrane fabrication is as follows. A precise stoichiometric amount of an aliphatic diol crosslinker molecule (1,6-hexanediol) is added to a solution of chloromethylated/iodomethylated polysulfone where the degree of chloromethylation is near its maximum. The solution is then electrospun simultaneously with a separate solution of polyphenylsulfone using two spinnerets to make a dual fiber mat. When the mat is subjected to heating, the diol reacts with chloro/iodomethyl groups to form di-ether linkages between polymer chains, as shown in Figure 1. Only a small fraction of the total chloromethyl/iodomethyl groups are consumed in the crosslinking reaction (between 8–20%); most remain intact for subsequent conversion to fixed charge anion exchange sites. The spun mat is compacted and exposed to chloroform vapor so that the polyphenylsulfone fibers soften and flow around and between the crosslinked fibers. The resulting dense (defect-free) film is then soaked in the appropriate free base solution to add fixed charges to the remaining chloromethyl/iodomethyl sites, where the final membrane has either benzyl trimethylammonium, 1-methylimidazolium, or 1,2-dimethylimidazolium ion exchange groups. In the present study, the polyelectrolyte precursor's degree of chloro/iodomethylation was held constant for all membranes at 1.94, as was the weight ratio of polyelectrolyte precursor to inert polysulfone polymer in the dual fiber mat (65:35). A series of dense membranes, with different degrees of crosslinking and with different anion exchange group chemistries were characterized in terms of hydroxide ion and chloride ion conductivity in water, equilibrium gravimetric water swelling, wet and dry membrane mechanical properties, and chemical stability in hot water and hot 1.0 M KOH.

Experimental

Materials.— Udel P-3500 polysulfone (MW_n = 80,000 g/mol) and Radel R-5500 polyphenylsulfone (PPSU, MW_n = 63,000 g/mol) were obtained from Solvay Advanced Polymers, LLC and dried at 140°C for 2 hours. Anhydrous tetrahydrofuran (THF) and dimethylsulfoxide (DMSO) solvents were used as received from Sigma Aldrich. A 45% aqueous trimethylamine solution, 1-methylimidazole, 1,2-dimethylimidazole, 1,4-butanediol, 1,6-hexanediol, *N*-methyl-2-pyrrolidinone (NMP), acetone, methanol, dimethylacetamide (DMAc), potassium iodide, paraformaldehyde, chlorotrimethylsilane, and tin (IV) chloride were all used as received from Fisher Scientific or Sigma Aldrich.

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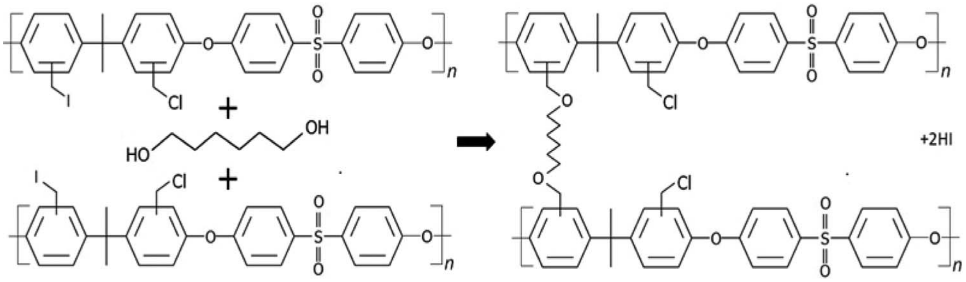


Figure 1. Reaction scheme for crosslinking chloromethylated/iodomethylated polysulfone with an aliphatic diol molecule.

Synthesis of chloromethylated polysulfone (CMPSF).— The chloromethylation of Udel polysulfone (PSF) was performed using a procedure adapted from the work of Avram et al.[16] with paraformaldehyde and chlorotrimethylsilane as the chloromethylation agents and tin (IV) chloride as a catalyst. The degree of chloromethylation, as determined by ^{1}H NMR, was either 1.91 or 1.94 (where the maximum degree of chloromethylation is 2.0, assuming one CH_2Cl group per aromatic ring). After quaternization to create benzyl trimethylammonium anion exchange sites, a 1.91 degree of chloromethylation translates into a polymer ion exchange capacity (IEC) of 3.3 mmol/g, well above the threshold for solubility in room temperature water.[2]

Iodomethyl group replacement on CMPSF.— To increase the crosslinking reactivity of the CMPSF with an aliphatic diol, a portion of the chloromethyl groups in some CMPSF samples was converted to iodomethyl moieties. This was accomplished via a modified version of the Finkelstein reaction[17] using a saturated solution of potassium iodide (1.4 g/100 mL) in dimethylacetamide (DMAc). 2.0 g of CMPSF was dissolved in 100 mL of the KI/DMAc solution (16% excess iodide) and the resulting mixture was stirred for 16 hours at room temperature. The polymer product was precipitated into water, filtered, and then dried under vacuum at 40°C for 12 hours to remove traces of water and DMAc (henceforth, the iodine-substituted chloromethylated polysulfone will be denoted as IMPSF). From NMR analysis, it was concluded that approximately 30% of the chloromethyl groups of CMPSF were converted to iodomethyl groups.

Crosslinking studies with dense films.— Homogeneous (dense) films of either CMPSF or IMPSF were prepared by first dissolving each polymer in DMAc to form a 10 wt% solution. 1,4-butanediol or 1,6-hexanediol was added to the polymer solutions at a stoichiometric ratio of between 2.5 and 10 mol% (relative to the moles of chloromethyl/iodomethyl side groups). Solutions were poured into glass casting dishes and heated at 40°C for 16 hr to evaporate DMAc solvent. The resulting films were then placed in closed containers and heated to a temperature of 110–140°C to crosslink the CMPSF/IMPSF polymer chains. Crosslinked film samples were re-equilibrated in DMAc to determine gravimetric swelling and possible polymer dissolution (both determinations were used to assess the crosslinking reaction), where swelling is given by

$$Swelling(\%) = \frac{w_{wet} - w_{dry}}{w_{dry}} \times 100 \qquad [1]$$

In Equation 1, W_{wet} and W_{dry} are the solvent-equilibrated and dry weights of a film sample. Membranes were then dried under vacuum at 40°C until there was no further change in the measured weight (typically 12 hours). Initial and final dry sample weights were compared to record any loss (DMAc solubilization) of uncrosslinked polymer.

Polymer electrospinning.— Polyphenylsulfone (PPSU) and chloro/iodomethylated polysulfone (IMPSF) were simultaneously electrospun from separate spinnerets into a dual fiber mat. PPSU was chosen as the reinforcing polymer because it has excellent mechanical properties and is chemically stabile in an alkaline environment.[9,11] In the present study, the diol crosslinking agent (1,6-hexanediol) was added directly to the IMPSF spinning solution at a concentration between 4.0 and 10.0 mol% with respect to the chloro/iodomethyl repeat units (this amount of diol will react with 8–20% of the iodo/chloromethyl groups of polysulfone during the crosslinking reaction). A heating step after mat fabrication was used to crosslink the IMPSF fibers, where the proper heating time and temperature were determined from a separate set of experiments with solution-cast dense films (using 1,4-butanediol and 1,6-hexanediol as the crosslinking agent and either CMPSF or IMPSF as the polymer to be crosslinked). The experimental conditions for electrospinning IMPSF and PPSU solutions are listed in Table I. Fibers were collected on a custom-built rotating drum collector that also oscillated laterally, as described elsewhere.[18] In all experiments, the final mats contained 65 wt% functionalized polysulfone fibers and 35 wt% PPSU fibers (35 wt% was found to be the minimum amount of PPSU needed to completely fill the void space between IMPSF fibers).

Membrane fabrication.— A dual fiber porous mat with an as-spun fiber volume fraction of ∼0.25 was compacted at 5,000 psi for ∼20 seconds to increase the volume fraction of fibers to ∼0.60. The mat was then heated to 110°C for 4 hours between glass plates to allow 1,6-hexanediol crosslinker to react with iodo/chloromethyl groups, with essentially no evaporation of the crosslinking agent. After crosslinking, the fiber mat was exposed to chloroform vapor at room temperature for 10 minutes, during which time: (i) the PPSU polymer fibers softened and flowed to fill the void space between crosslinked iodo/chloromethylated polysulfone fibers and (ii) the crosslinked polysulfone fibers fused at intersection points (as determined from SEM images of a mat after dissolving the PPSU matrix). The resulting composite membranes were fully dense and defect free, where a network of interconnected functionalized polysulfone fibers (crosslinked by an aliphatic diol) were surrounded by a reinforcing matrix of PPSU. The composite films were converted into anion exchange membranes with quaternary ammonium or imidazolium fixed charges by immersion for 16 hours at 40°C in a 45 wt% aqueous solution of trimethylamine or a 45 wt% solution of either 1-methylimidazole or 1,2-dimethylimidazole in methanol. The charged films were washed thoroughly in DI water and then soaked for 1–2 hours in 1.0 M KOH solution (exchanged twice) to replace

Table I. Electrospinning Conditions for Preparing Dual Fiber Mats for AEMs.

Polymer	Polymer Concentration (w/w)	Applied Voltage (kV)	Flow Rate (ml hr^{-1})	Spinneret/Collector Distance (cm)
Radel PPSU	25 (in 4:1 wt ratio NMP/ Acetone)	+8.5	0.43	9
IMPSF (+ diol crosslinker)	15 (in 85:15 wt ratio THF/DMSO)	+12	1.0	11

chloride/iodide fixed charge site counter-ions with OH^-. Membranes were washed three additional times in argon-degassed DI water to remove excess KOH and then stored in sealed containers with degassed DI water until further testing.

Membrane characterization.— The morphology of the initial fiber mats and final membranes was examined by scanning electron microscopy (Hitachi Model 2-4200). A thin layer of gold was deposited on samples, using a Cressington sputter coater, to prevent charging during scanning.

In-plane hydroxide ion and chloride ion conductivity of water-equilibrated membrane samples was determined using a standard four-electrode AC impedance method, where conductivity (σ, with units of S/cm) was determined from:

$$\sigma = \frac{L}{w\delta R} \qquad [2]$$

where L is the distance between the two working electrodes (cm), w is the width of the membrane sample (cm), δ is membrane thickness (cm), and R is the calculated ionic resistance (Ω). Both δ and w were measured on wet (liquid water equilibrated) membrane samples.

Gravimetric swelling in liquid water at 23°C was determined using Equation 1. Both conductivity and swelling were measured on membrane samples immediately after washing with degassed DI water to prevent/minimize carbonate poisoning.

Membrane ion exchange capacity was measured by a variant of the Mohr titration method.[19] Membranes in the chloride ion form were equilibrated in a 0.2 M sodium nitrate solution. Nitrate ions exchanged for chloride, where the Cl^- ions were released into solution. The concentration of chloride ions in the sodium nitrate solution (total of 40 mL) was found by titration with 0.01 M silver nitrate, using potassium chromate as the end point indicator. The membrane IEC was calculated by dividing the moles of silver nitrate titrated (i.e., the moles of Cl^- released by a membrane in the $NaNO_3$ solution) by the dry weight of the membrane sample.

The mechanical properties of water-soaked membrane samples at 30°C were determined using a TA-Instruments Q800 DMA in tension mode. An initial stress of 0.01 MPa was applied and the strain was ramped at a rate of 30%/min. until membrane failure.

The chemical stability of membranes was assessed by monitoring the in-plane hydroxide ion conductivity of a given film periodically during 100 hours of immersion in either water or a 1.0 M KOH solution at 50°C. For the latter experiments, membrane samples were washed thoroughly with degassed DI water to remove all traces of KOH prior to a conductivity measurement.

Results and Discussion

Crosslinking experimental with solution-cast dense films.— The efficiency of the diol crosslinking reaction shown in Figure 1 was evaluated first in homogenous solution-cast dense films of chloromethylated polysulfone (CMPSF) with no iodine substitution, where the degree of chloromethylation was 1.91. Two diol crosslinkers (1,4-butanediol and 1,6-hexanediol) at three different concentrations (2.5, 5.0 and 10.0 mol% with respect to total moles of chloromethyl groups) and four crosslinking times (4, 8, 12, and 24 hours) were evaluated at a crosslinking temperature of either 120°C or 140°C. To determine the extent of crosslinking, the films were re-equilibrated in DMAc (the original casting solvent for the films) and gravimetric solvent uptake and polymer weight loss (dissolution) after soaking were recorded.

As the heating time increased from 4 to 24 hours, polymer weight loss in DMAc decreased and membrane swelling in DMAc was reduced (see Figures 2 and 3). Samples with 5 mol% 1,4-butanediol lost polymer after a DMAc soak for all crosslinking times (up to 24 hours). Films with 5.0 mol% 1,6-hexanediol, on the other hand, exhibited a swelling plateau at 225% after 12 hours of heating with no polymer dissolution in DMAc solvent, indicating successful crosslinking. Films containing a lower amount of 1,4-butanediol or 1,6-hexanediol (2.5 mol%) lost some weight in DMAc, even after heating at 140°C for 24 hours. Similarly, all films for all heating times and diol concentrations lost weight after a DMAc soak when the crosslinking temperature was 120°C. The results of these experiments indicated that: (i) 1,6-hexanediol is a more effective crosslinking agent than 1,4-butanediol, (ii) the necessary crosslinking time and temperature to crosslink CMPSF with hexanediol is 12 hours at 140°C, and (iii) a hexanediol concentration > 2.5 mol% is required to crosslink a sufficient number of polymer chains for DMAc insolubility. Unfortunately, the crosslinked films cracked and broke apart when they were immersed in an aqueous trimethylamine solution to quaternize the CMPSF. Isothermal TGA analysis of the neat CMPSF polymer at 140°C showed the onset of polymer degradation after 6 hours, which may explain the observed film breakup in trimethylamine.

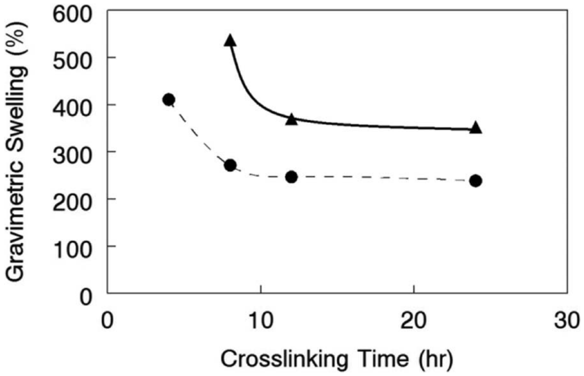


Figure 2. Gravimetric solution-cast membrane swelling in dimethylacetamide for dense CMPSF films that were crosslinked using: (▲) 1,4-butanediol or (●) 1,6-hexanediol. The diol concentration was 5.0 mol% and the crosslinking temperature was 140°C.

To facilitate diol crosslinking at a temperature below 140°C, iodide was partially substituted for chlorine on pendant CH_2Cl groups, where ∼30% of chloromethyl groups were transformed into iodomethyl moieties. The total amount of iodo/chloromethyl groups tethered to the polysulfone backbone remained constant. Representative NMR spectra of both the initial chloromethylated polysulfone (CMPSF) and an iodine-substituted chloromethylated polymer (IMPSF) are shown in Figures 4a and 4b, respectively, where the chloromethyl and iodomethyl peaks are identified (the ratio of the peak areas was used to determine the extent of iodine substitution). Gravimetric swelling in DMAc and weight loss results for an IMPSF film that was crosslinked with 5.0 mol% 1,6-hexanediol at 110°C is shown in Figure 5. After 4 hours of heating, there was no polymer weight loss and the gravimetric swelling in DMAc stabilized at 130%. After crosslinking, the remaining iodo/chloromethyl groups in films of IMPSF reacted

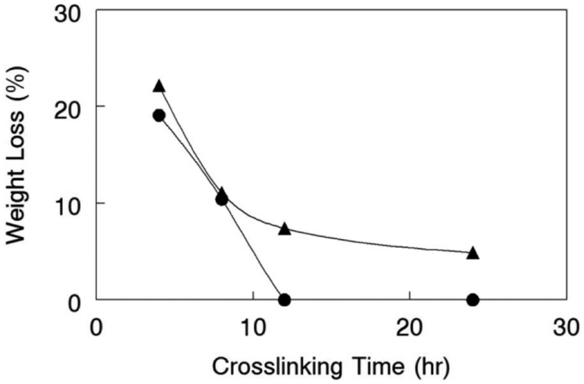


Figure 3. Weight loss of dense CMPSF films crosslinked at 140°C with: (▲) 1,4-butanediol or (●) 1,6-hexanediol (each at a concentration of 5.0 mol%). Weight loss was measured after removal from DMAc and complete drying.

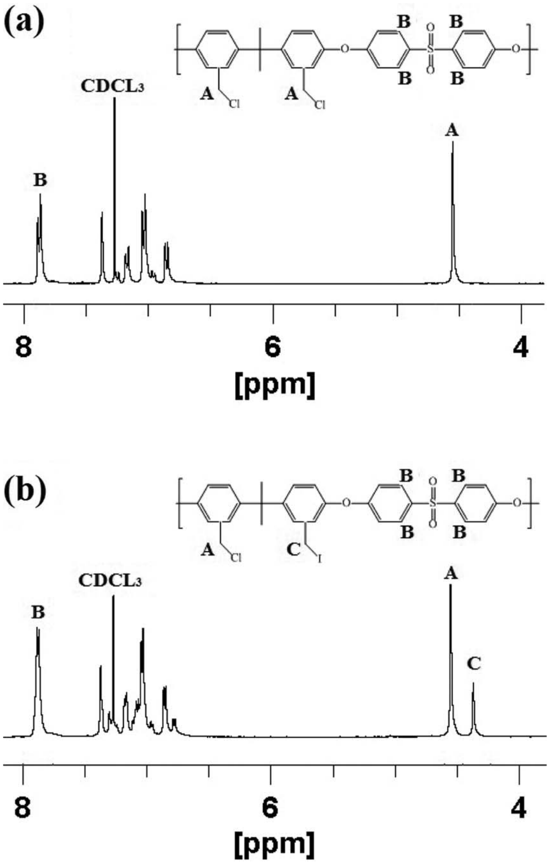


Figure 4. ^{1}H NMR spectrum showing hydrogens of chloromethylated polysulfone (Figure 4a) and polysulfone with chloromethyl and iodomethyl groups (Figure 4b). The initial degree of chloromethylation was 1.94. Chloromethyl groups are labeled as peak A, reference hydrogens adjacent to sulfone group are peak B, and hydrogens of iodomethyl groups are peak C (in Figure 4b only).

readily in a trimethylamine solution with no film break up. TGA confirmed that the polymer was stable when heated to 110°C for 4 hr. Also, after quaternization and hydroxide ion exchange, there was no measureable weight loss when films were immersed in room temperature water. Based on these results, all nanofiber composite membranes were prepared with IMPSF nanofibers (30% iodine substitution) that were crosslinked with 1,6-hexanediol by heating a dual fiber mat to 110°C for 4 hours.

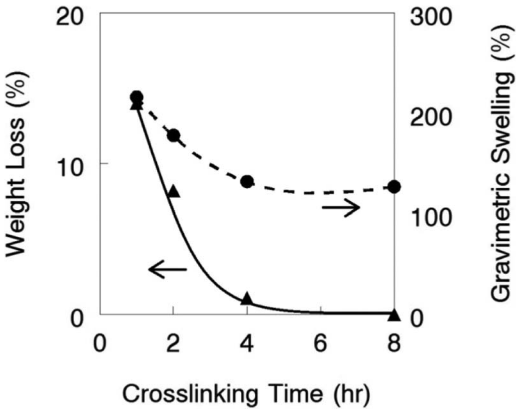
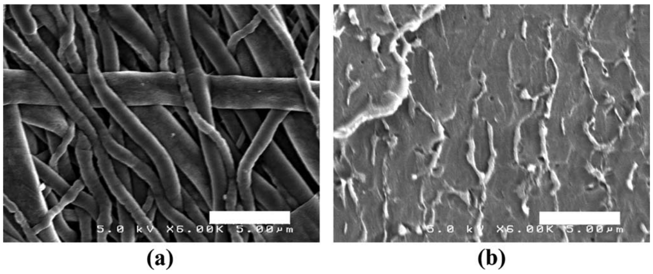


Figure 5. Swelling and weight loss of dense/homogeneous crosslinked IMPSF films. (●) Gravimetric membrane swelling in DMAc and (▲) membrane weight loss after soaking in DMAc. The crosslinker was 5.0 mol% 1,6-hexanediol. Crosslinking was carried out at 110°C.



(a) (b)

Figure 6. SEM micrographs of: (a) initial IMPSF + hexanediol/PPSU mat and (b) dense membrane after crosslinking, compaction, void space filling, and reaction with trimethylamine. Scale bars = 5 μm

Nanofiber composite membranes.— To further control polyelectrolyte fiber swelling beyond that which could be achieved solely by polymer crosslinking, IMPSF polymer fibers (with a degree of chloromethylation of 1.94, where 30% of the chloromethyl groups were converted to iodomethyl groups) were embedded in a polyphenylsulfone matrix. This step was accomplished by simultaneously and separately electrospinning IMPSF and PPSU nanofibers to create a dual nanofiber mat, where the mat contained 65 wt% polyelectrolyte precursor (with 4.0–10.0 mol% 1,6-hexanediol for crosslinking) and 35 wt% uncharged polyphenylsulfone. Figure 6a shows an SEM image of the as-spun dual fiber mat surface. The PPSU and polyelectrolyte precursor fibers are indistinguishable, with an average fiber diameter of 814 nm. NMR analysis of the $CDCl_3$ extract after soaking an electrospun fiber mat showed 1,6-hexanediol to be present at its initial concentration in the IMPSF fibers (i.e., there was no evaporation of crosslinker during electrospinning). An SEM image of a membrane cross-section (after crosslinking and chloroform exposure) is shown in Figure 6b. Visual inspection and SEM analyses indicated that the membranes were fully dense, without defects or pinholes. After reaction with trimethylamine, 1-methylimidazole, or 1,2-dimethylimidazole, those iodomethyl/chloromethyl groups remaining after the crosslinking step were converted into positively charged anion exchange sites.

The in-plane hydroxide ion conductivity and gravimetric water swelling of diol-crosslinked nanofiber composite membranes (equilibrated in liquid water at 23°C) with the three different ion exchange group chemistries are presented in Figures 7 and 8 as a function of the effective membrane IEC (this IEC takes into account the presence

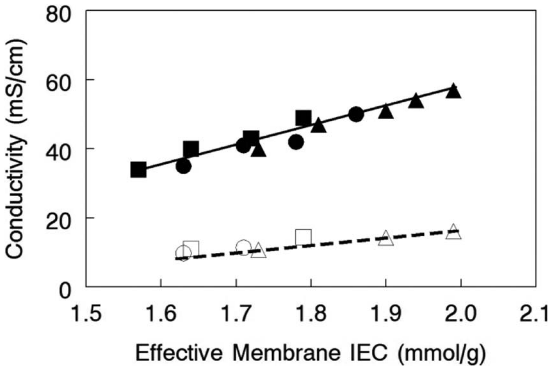


Figure 7. Dependence of in-plane OH^- ion (closed symbols) and Cl^- ion (open symbols) conductivity on the effective membrane IEC of diol-crosslinked electrospun composite membranes with: (▲,△) benzyl trimethylammonium, (●,○) 1-methylimidazolium, and (■,□) 1,2-dimethylimidazolium fixed charge groups. All measurements were made in liquid water at 23°C.

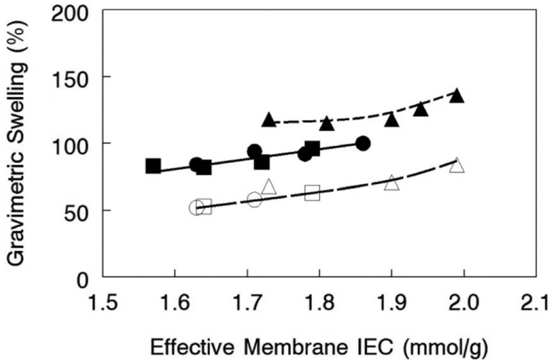


Figure 8. Dependence of gravimetric liquid water swelling at 23°C on the effective membrane IEC of diol-crosslinked electrospun composite membranes in the OH^- ion form (closed symbols) and Cl^- form (open symbols) with: (▲,△) benzyl trimethylammonium, (●,○) 1-methylimidazolium, and (■,□) 1,2-dimethylimidazolium fixed charge groups.

of the uncharged/inert polymer matrix). Since the ratio of polyelectrolyte to inert polymer was held constant in the present study (a weight ratio of 65:35), a composite membrane's effective IEC was altered by: (i) changing the concentration of 1,6-hexanediol in the electrospinning solution, where a greater mol% of diol translates into a lower fiber/membrane ion exchange capacity and (ii) changing the ion exchange group chemistry (the molecular weight of the ion exchange site moiety will impact the final membrane IEC). As expected, the conductivity and swelling data in Figures 7 and 8 exhibit a strong correlation with the dry membrane IEC. The highest conductivity and greatest water swelling were obtained with benzyl trimethylammonium cationic sites because the relatively low molecular weight of benzyl trimethylammonium (73 g/mol vs. 110 g/mol for 1,2-dimethylimidazolium, for example) led to a higher effective membrane IEC. At the same IEC, gravimetric water swelling was slightly higher for benzyl trimethylammonium functionalized membranes, because this cation has a larger hydration sheath (the ion is smaller in size with a more centralized charge as compared to the bulkier imidazolium moieties).[20] As more diol was added to the polyelectrolyte fibers, the degree of crosslinking increased, the effective membrane IEC decreased, and both conductivity and water swelling decreased for all membranes regardless of the cationic fixed charge site chemistry. The in-plane OH^- conductivity was found to be a maximum when the amount of diol crosslinker was 4.0 mol%, corresponding to a crosslinking degree of 8%, i.e., 57, 50 and 49 mS/cm for benzyl trimethylammonium, 1-methylimidazolium, and 1,2-dimethylimidazolium, respectively. This diol content is the minimum needed to eliminate polymer dissolution in DMAc (as discussed above). To enable comparison with other AEMs in the literature, conductivity and swelling of diol-crosslinked electrospun composite membranes were also measured in the chloride counterion form. As expected, the electrospun membranes exhibited a somewhat lower swelling and much lower conductivity for chloride vs. hydroxide counterions (see Figures 7 and 8), e.g., the conductivity dropped from 57 mS/cm for OH^- to 16 mS/cm for Cl^- (both measurements were taken in water at 23°C). The observed reduction in conductivity, by a factor of ~3.5, is consistent with other AEM studies in the literature.[21,22]

Table II. Properties of Diol-Crosslinked Homogeneous IMPSF Films with Benzyl Trimethylammonium Functional Groups.

Crosslinker Amount (mol%)	Theoretical IEC (mmol/g)	Measured IEC (mmol/g)	OH^- Conductivity (mS/cm)	Gravimetric Water Swelling (%)
5.0	2.95	2.8	50	400
10.0	2.66	2.53	38	274

The importance of the PPSU component in nanofiber composite films is confirmed by comparing the benzyl trimethylammonium membrane results in Figures 7 and 8 with the crosslinked polyelectrolyte homogeneous film data in Table II. It should be noted with regards to the results in Table II that: (i) the measured ion exchange capacities of the homogeneous crosslinked IMPSF films (2.8 mmol/g at 5.0 mol% diol, for example) compare well with the theoretical IECs (2.95 mmol/g), assuming complete reaction of added hexanediol during crosslinking and full quaternization of the remaining iodo/chloromethyl groups and (ii) the homogenous film IECs are well above the water solubility limit of 2.5 mmol/g for a quaternary ammonium polysulfone, indicating the polymer was successfully and sufficiently crosslinked. Thus, a homogeneous film with 2.8 mmol/g IEC had a lower conductivity (50 mS/cm) than the nanofiber composite AEM with 2.8 mmol/g IEC fibers (57 mS/cm), even though the effective dry film IEC of the composite membrane was only 2.0 mmol/g (due to the presence of uncharged PPSU). The low conductivity of the homogenous film is attributed to its very high water swelling (400% vs. 136% for the nanofiber composite film), which lowered the volumetric concentration of fixed charge groups.[20,23] This amplification in conductivity for a diol-crosslinked composite AEM, as compared to a homogeneous polyelectrolyte film, is consistent with our previous results with crosslinked and uncrosslinked quaternary ammonium polysulfone membranes.[10,11] It is clear that control of water swelling in high IEC AEMs is critical to achieving a high ionic conductivity. There was some reduction in water swelling (to 274%) with a decrease in OH^- conductivity (to 38 mS/cm) when the amount of diol crosslinker in a dense film was increased from 5.0 mol% to 10.0 mol%, but the high water uptake was still an issue (leading to poor membrane mechanical properties, as will be discussed below). The work shown here suggests that to maximize conductivity for a crosslinked electrospun composite membrane with a given amount of uncharged reinforcement polymer, one should use only enough crosslinks to prevent water solubility of the polyelectrolyte. However, it is possible that a membrane with less PPSU and more crosslinks could yield a higher hydroxide ion conductivity. Unfortunately, this membrane structure cannot be used with a dual fiber electrospinning protocol; 35 wt% is the minimum amount of PPSU for filling the void space between crosslinked polyelectrolyte fibers.[11] Such membranes could be prepared if only polyelectrolyte precursor fibers were electrospun and the inter-fiber void space were filled using a follow-on uncharged polymer impregnation step[20] (there was no attempt to make such membranes in the present study).

The mechanical properties of diol-crosslinked composite membranes are presented in Table III. Membranes were evaluated at two equilibrium conditions: (i) in liquid water at 23°C (wet), and (ii) in 23°C air at <10% RH (dry). The stress at break for wet electrospun composite membrane samples was 13–17 MPa, and the strain at break was 25–29%. The polyphenylsulfone matrix surrounding the polyelectrolyte fibers allowed for good mechanical reinforcement, independent of the fixed charge cation chemistry. When dry, all of the electrospun membranes exhibited excellent strength with a stress at break at or above 40 MPa. The composite membranes were much stronger than a homogeneous film of crosslinked polysulfone with benzyl trimethylammonium fixed charges (2.8 mmol/g IEC) in both

Table III. Mechanical Properties of Electrospun Composite Membranes with 4.0 mol% diol (8% Crosslinking Degree) and Three Different Fixed Charge Groups.

Cation Type	Stress at break (wet, MPa)	Strain at break (wet, %)	Stress at break (dry, MPa)	Strain at break (dry, %)
Benzyl trimethyl Ammonium	13	29	40	9
1-methyl imidazolium	17	25	45	8
1,2-dimethyl imidazolium	16	27	43	11

Table IV. Hydroxide Ion Conductivity, Water Swelling, and Tensile Strength of Recently Reported Anion Exchange Membranes Equilibrated in Water at Room Temperature (22-25°C).

Membrane	Cation[a]	Membrane IEC (mmol/g)	OH^- Conductivity (mS/cm)	Water Swelling (%)	Tensile Strength (MPa)	Ref.
Diol crosslinked nanofiber composite	TMA	1.99	57	136	13	This Work
Diamine crosslinked nanofiber composite	TMA	1.99	61	152	14	11
Poly(arlyene ether) copolymer	TMA	1.93	80	112	13[b]	7
Octene with di-ammonium crosslinker	TMA	2.3	69	150	15	8
poly(vinylidine fluoride)/vinyl benzyl chloride copolymer	TMA	2.25	52	151	18	27
Polysulfone	TMA	2.4	49	73	3	28
Polyfluorene	DIm	1.04	23	17	50	12
Poly(arylene ether ketone)	TMA	1.8	23	24	44	29

[a]: TMA = benzyl trimethylammonium and DIm = 1,2-dimethylimidazolium

[b]: Tensile strength taken at 80°C and 60%RH

the wet and dry states (films swelled so much in water that tensile tests could not be performed). As further evidence of the mechanical integrity of nanofiber composite membranes, a 2.0 mmol/g effective IEC film in the chloride counterion form was equilibrated in water, dried, and then re-hydrated without any visible damage or change in mechanical properties.

A survey of recent AEMs in the literature that report hydroxide ion conductivity, water uptake, and wet membrane tensile strength is presented in Table IV along with a diol-crosslinked membrane from this work and a diamine-crosslinked nanofiber composite membrane from reference 11. Comparing membranes with similar IECs, the properties of the nanofiber AEMs fall below some films, e.g., the block copolymer films reported in references 7 and 8, but are superior to the polysulfone and poly(arylene ether ketone) membranes in references 23 and 24.

The chemical stability of diol-crosslinked nanofiber composite membranes with different cation chemistries was assessed by separate 50°C soaking experiments, in water and in 1.0 M KOH. The testing temperature was chosen based on that used by others in their alkaline fuel cell experiments.[1,24] The results are presented in Figure 9, where the fraction of initial hydroxide ion conductivity (measured in degassed water at room temperature) is plotted vs. membrane immersion time. For membrane samples in hot water, no degradation was observed for soak times of at least seven days. After soaking in a hot KOH solution, on the other hand, all three nanofiber membranes lost ionic conductivity. Membranes with 1-methylimidazolium fixed charge groups exhibited a rapid decline in conductivity (a 75% drop after one day) due to hydroxide C-N ring-opening attack at the hydrogen of the 2-carbon on the imidazole ring, as reported by others.[24,25] The chemical stability of films was much improved when the fixed charge moieties were either 1,2-dimethylimidazolium or benzyl trimethylammonium. Thus, films with 1,2-dimethylimidazolium groups retained 80% of their initial hydroxide ion conductivity after three days in hot 1.0 M KOH and had twice the conductivity of benzyl trimethylammonium membranes after a 7 day soak in hot KOH. The mechanical properties of films did not change after KOH immersion, due to the excellent alkaline stability of the PPSU component which is not subject to mechanical degradation or embrittlement in a hot alkaline environment. In general, the chemical stability of nanofiber films compares well with other polysulfone-based AEMs in the open literature, e.g., Mohanty et. al reported on films that lost 19.5–38.7% of their quaternary ammonium groups after 6 hours in 1 M NaOH at 50°C.[26]

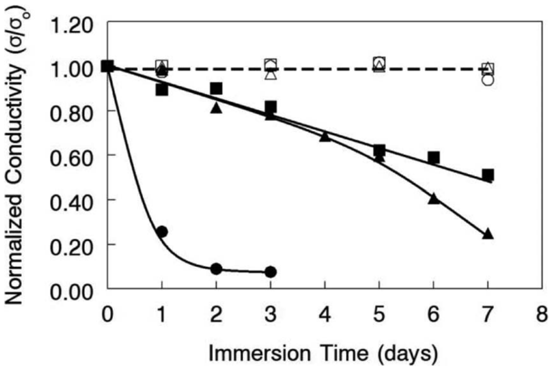


Figure 9. Change in OH^- ion conductivity after membrane soaking in hot water (open symbols) or 1.0 M KOH (closed symbols). All composite films contained 35 wt% polyphenylsulfone and the polyelectrolyte nanofibers were crosslinked with 4.0 mol% hexanediol and had (▲) benzyl trimethylammonium, (●) 1-methylimidazolium, or (■) 1,2-dimethylimidazolium functional groups.

Conclusions

Nanofiber composite alkaline fuel cell anion exchange membranes were fabricated and characterized, where an interconnected network of submicron diameter fibers of anion exchange polymer (crosslinked polysulfone with either benzyl trimethylammonium, 1-methylimidazolium, or 1,2-dimethylimidazolium fixed charge groups) was embedded in a polyphenylsulfone matrix. A dual fiber membrane fabrication procedure was employed, where chloromethylated/iodomethylated polysulfone nanofibers containing 4.0–10.0 mol% 1,6-hexanediol crosslinker were electrospun simultaneously with polyphenylsulfone fibers. The resultant dual fiber mat was subsequently processed into a dense and defect-free anion exchange membrane by heating to create diol crosslinks, exposure to chloroform vapor which softened the polyphenylsulfone and allowed it to fill the space between crosslinked fibers, and functionalization of the chloromethyl/iodomethyl fibers with trimethylamine, 1-methylimidazole, or 1,2-dimethylimidazole. All membranes contained 65 wt% polyelectrolyte fibers and 35 wt% polyphenylsulfone, where the ion exchange capacity of the crosslinked fibers was 2.5–3.0 mmol/g, well above the water solubility limit for uncrosslinked polysulfone with benzyl trimethylammonium or imidazolium fixed-charged groups. The in-plane OH^- ion conductivity of the resulting nanofiber composite membranes was high (up to 57 mS/cm in water at room temperature at 8% crosslinking degree). The presence of polyphenylsulfone matrix material reduced water swelling and improved membrane mechanical properties. As an example of overall membrane properties, a diol-crosslinked nanofiber composite film with 1,2-dimethylimidazolium charge sites exhibited a high OH^- conductivity in room temperature water (49 mS/cm), reasonable swelling (96%), good mechanical properties (16 MPa stress-at-break for a water equilibrated film), and reasonably good chemical stability.

Acknowledgments

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