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Electrospun Composite Membranes for Alkaline Fuel Cells

A.M. Park and P.N. Pintauro

Department of Chemical and Biomolecular Engineering, Vanderbilt University,
Nashville, Tennessee 37235, USA

Electrospun fiber composite anion exchange membranes were created by electrospinning two polymers: a chloromethylated polysulfone that would ultimately serve as the hydroxide ion conductor, and an uncharged polyphenylsulfone to limit water swelling and provide mechanical strength to the final membrane. After electrospinning, the chloromethyl groups were converted into quaternary ammonium moieties for hydroxide ion conduction. The polyphenylsulfone fibers were then selectively made to flow and fill the void space in the dual fiber mat, thus forming a dense, defect free membrane. The final membrane morphology was a quaternized polysulfone interconnecting fiber network embedded in a polyphenylsulfone matrix. For a membrane containing 63 vol% anion-exchange polymer fibers (with a fiber IEC of 2.5 mmol g⁻¹), the OH⁻ ion conductivity was high (40 mS cm⁻¹ in 23°C water) and the equilibrium water swelling at room temperature was low (70 vol%).

Introduction

Alkaline anion-exchange membrane fuel cells (AAEMFCs) are a potentially significant technology that could compete with the more popular and well-studied proton exchange membrane (PEM) class of fuel cells for a variety of applications (1). The primary driving force for investigating AAEMFCs is the prospect of replacing platinum group metals in the electrodes with a less expensive non-noble metal, such as nickel or silver (2-4). Most commercial dialysis/electrodialysis anion exchange membranes (AEMs), however, were not designed to withstand the harsh highly alkaline and high temperature operating environment of an AAEMFC (5). Thus, a major challenge in AAEMFC development has been the identification of a suitable polymer electrolyte membrane that possesses high hydroxyl ion conductivity with good mechanical properties, moderate water swelling, and long-term chemical stability (6). A fundamental drawback of all anion-exchange membranes is the weak basicity of fixed-charge sites, as compared to the acidity of sulfonic acid groups in proton-exchange membranes. Also, hydroxide anions have a lower inherent mobility than protons which also affects ionic conduction in an anion-exchange membrane (6). To compensate for these two problems, membrane researchers have focused their attention on the use of high ion-exchange capacity polymers, but this strategy exacerbates the problems of membrane brittleness in the dry state and poor mechanical strength when the membrane is fully hydrated (7).

There are numerous reports in the literature on the fabrication and testing of AEMs with mechanical and transport properties that may be suitable for AAEMFCs. The

most common backbone materials include polysulfones (6, 8-14), poly(arylene ether)sulfones (4, 15-20), polyphenylene, (6) and polyphenylene oxide (6, 21). The fixed-charge ion-exchange sites are normally quaternary ammonium groups, but phosphonium moieties have also been investigated (8-10). For the case of a quaternary ammonium polysulfone (QAPSF), an IEC as high as 2.5 mmol g⁻¹ can be achieved before polymer dissolution in water (6).

In order to make functional membranes with dimensional stability (controlled water swelling) and good mechanical properties from highly charged polymers, a new electrospun fiber composite membrane morphology and fabrication scheme has been devised by Pintauro and co-workers (22-24). Proton conducting fuel cell membranes were successfully prepared by electrospinning a fiber mat from a sulfonated aromatic hydrocarbon polymer or from a perfluorosulfonic acid material, followed by filling the inter-fiber voids with an inert, uncharged polymer. In such a forced assembly electrospun system, the polymer material and nanostructure for ion conduction is decoupled from the polymer that is used to impart mechanical strength to the membrane. The use of a fiber composite membrane morphology for PEMs significantly improved membrane mechanical properties while reducing water swelling (22). Recently, Ballengee and Pintauro have shown that a fiber composite membrane can be made without a separate polymer impregnation step (25, 26). Here, two polymers (the ionomer and the uncharged polymer) are electrospun simultaneously followed by mat processing steps where one of the polymers softens, flows, and fills the inter-fiber voids while the fibrous morphology of the second polymer remains intact.

In the present study, we show for the first time that electrospinning methods can be used to fabricate an electrospun fiber composite AEM. Specifically, we have used the dual fiber electrospinning method of Ballengee and Pintauro to fabricate a two-component membrane morphology, where charged fibers composed of quaternized polysulfone are surrounded by uncharged polyphenylsulfone. A series of membranes with different effective IECs were made and then characterized by hydroxyl ion conductivity, equilibrium water uptake, and mechanical property analysis.

Experimental

Materials

Dual fiber composite membranes were fabricated using an uncharged/inert polymer, Radel[®] polyphenylsulfone (from Solvay Advanced Polymers, LLC) and a chloromethylated form of Udel[®] polysulfone (MW=35,000 g mol⁻¹), also from Solvay Advanced Polymers, LLC. After mat processing, the chloromethylated Udel polysulfone was converted into a quaternary ammonium anion-exchange polymer and then the mat was processed into a non-porous defect-free membrane. All reagents discussed below were used as received, without further purification.

Chloromethylation

Chloromethylated polysulfone (CMPSF) was synthesized by the procedure described by Avram and co-workers (27). 4.5 g of pre-dried polysulfone was dissolved in 225 mL of chloroform, to which 3.06 g of paraformaldehyde was added. After raising the temperature of the solution to 50°C and sparging the solution with nitrogen gas, 10.2 g of

chlorotrimethylsilane and 0.53 g of tin (IV) chloride were added, the headspace was blanketed with nitrogen, and the reaction vessel was sealed under a reflux condenser. Reaction times between 24 and 72 hours yielded polysulfones with different extents of chloromethylation.

Electrospinning

The electrospinning conditions for preparing a dual fiber mat with polyphenylsulfone (PPSU) and CMPSF are listed in Table I. The same conditions were used for CMPSFs with different degrees of chloromethylation. We found that the quaternary ammonium form of polysulfone could not be electrospun into a fiber mat; the polymer solution only electrospayed into micron-size droplets. In the present study, all mats contained 63 vol% CMPSF and 37 vol% PPSU.

Table I. Electrospinning conditions for making a dual-fiber AEM mat

	Polymer Concentration (w/w)	Applied Voltage (kV) ^a	Flow Rate (mL hr ⁻¹)	Spinneret/Collector Distance (cm)
Radel PPSU	25 (in 4:1 wt. ratio NMP/Acetone)	+8.5	0.7	9
Udel CMPSF	25 (in DMF)	+10.5	1.0	9

a – Needle tip voltage relative to a grounded fiber collector

Membrane Processing

After electrospinning, the total fiber volume fraction of a dual fiber mat was ~0.25. The mat was compacted at 2,000 psi to increase the volume fraction of fibers to ~50%, then exposed to chloroform vapor for 2.25 minutes to weld intersecting CMPSF fibers. After drying at 70°C to remove excess chloroform, the mats were soaked in an aqueous solution of 50% trimethylamine (TMA) for 48 hours, to convert the chloromethyl moieties of CMPSF to quaternary ammonium fixed-charge sites. The mat was then washed with deionized (DI) water to remove TMA, compressed at 15,000 psi for a few seconds to further increase the fiber volume fraction, and then exposed to tetrahydrofuran (THF) vapor at room temperature for 20 minutes. During the last vapor exposure step, uncharged PPSU fibers selectively softened and flowed to fill the void space between quaternary ammonium polysulfone (QAPSF) fibers, thus forming a dense and defect-free membrane. The resulting AEM was soaked in 1 M KOH solution exchanged several times over a 24 hr period to substitute hydroxide ions for Cl⁻ on all quaternary ammonium anion-exchange sites. The membranes were then washed in de-gassed DI water several times over 24 hours to remove excess KOH, then stored until further testing in sealed containers containing de-gassed DI water.

Characterization and Measurements

¹H NMR spectra for CMPSF and QAPSF polymers were collected on an AV-400 Bruker spectrometer. Solutions of both polymers were ~1% w/v in deuterated chloroform (for CMPSF) or dimethylsulfoxide (for QAPSF). NMR spectra were used to calculate the degree of chloromethylation for CMPSF and the IEC for QAPSF.

The morphology of the membranes at various stages of processing was monitored/characterized by SEM micrographs using a Hitachi 2-4200 instrument. The average fiber diameter of an electrospun mat was determined from SEM micrographs using ImageJ software. At least 80 fibers were included in an average fiber diameter calculation.

The in-plane hydroxyl ion conductivity of membranes was measured by electrochemical impedance spectroscopy, using a Gamry potentiostat and a four-probe Bekktech conductivity cell. Data were collected in room temperature (23°C) liquid water. Conductivity was calculated by the following equation:

$$\sigma = \frac{L}{w \cdot \delta \cdot R} \quad [1]$$

where σ = conductivity (S cm⁻¹), L = distance between the two working electrodes (cm), w = width of the membrane sample (cm), δ = membrane thickness (cm), and R is the calculated ionic resistance (Ω). Both δ and w are wet-state dimensions.

Liquid water uptake was calculated on a volumetric basis by comparing the physical dimensions (thickness and area) of a dry membrane with those of the same sample after water equilibration. All water uptake measurements were performed at 23°C.

Mechanical property data were taken on a TI-Instruments DMA in tensile mode. The strain rate was 0.1 N/min, equilibrated at 30°C.

Results and Discussion

Polymer Characterization

Before electrospinning, four synthesized CMPSF polymers were analyzed in terms of their degree of chloromethylation and their IEC after quaternization. The number of tethered chloromethyl groups per repeat unit of polysulfone (the degree of chloromethylation) was determined from ¹H NMR spectra of polymer samples. A typical spectrum is shown in Figure 1. Labeled in the figure are peaks associated with the four hydrogens surrounding the sulfone group in the PS backbone (peak 'a'), the six hydrogens in the *bis*-phenyl-A component of the polysulfone backbone (peak 'b'), and the peak at 4.6 ppm (peak 'c') for hydrogens associated with the chloromethyl groups. From a simple ratio of these three peaks, the degree of chloromethylation was determined. Similarly, the IEC of QAPSF could be found by comparing the hydrogen peak from quaternary ammonium groups at 3.1 ppm to the same hydrogen signals from PS backbone groups.

Four chloromethylated PS polymers were prepared in the present study. Values for the degree of chloromethylation and the polymer IEC after quaternization are listed in Table II. None of the quaternized polymers was soluble in water.

SEM micrographs of the dual fiber mat surface before and after quaternization are shown in Figures 2a and 2b. The fibers are indistinguishable in terms of polymer composition. The average fiber diameter was 950 nm before quaternization, and 1050 nm afterward. This slight increase in fiber diameter is associated with water vapor sorption by the hydrophilic QAPSF mats. No attempt was made in the present study to decrease/minimize the fiber diameter. A top-down SEM of a fully processed composite

Table II. Characterization of CMPSF polymers used for electrospinning.

Batch	Degree of Chloromethylation	Neat Film IEC (mmol g ⁻¹)
1	1.08	2.02
2	1.14	2.17
3	1.28	2.39
4	1.33	2.47

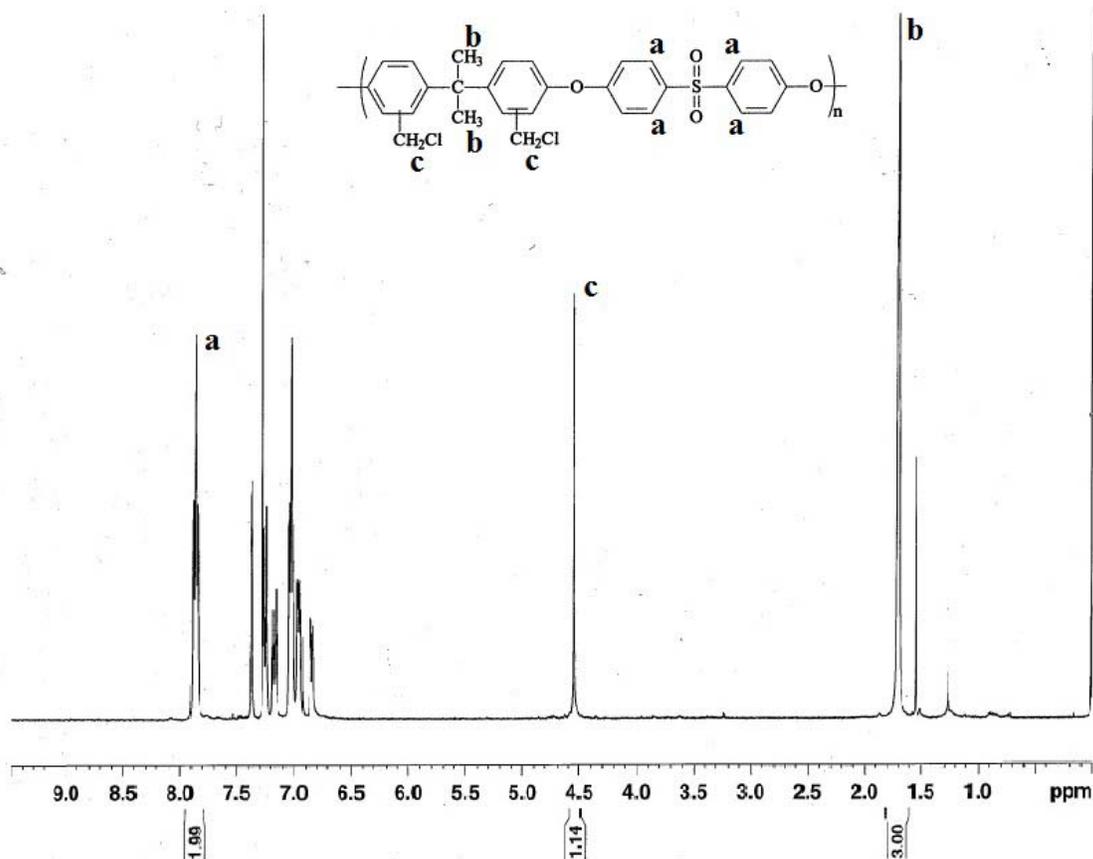


Figure 1. NMR spectrum of a chloromethylated polysulfone (CMPSF), showing peaks and the corresponding molecular hydrogens.

membrane, after PPSU melting and void volume filling, is shown in Figure 2c. No defect voids or pin holes are visible; individual QAPSF fibers, however, cannot be observed. To prove that the QAPSF fibers remain intact after mat processing, the membrane in (c) was soaked in liquid THF to selectively dissolve the PPSU matrix while leaving QAPSF intact. The resulting QAPSF fiber network is shown in Figure 2d.

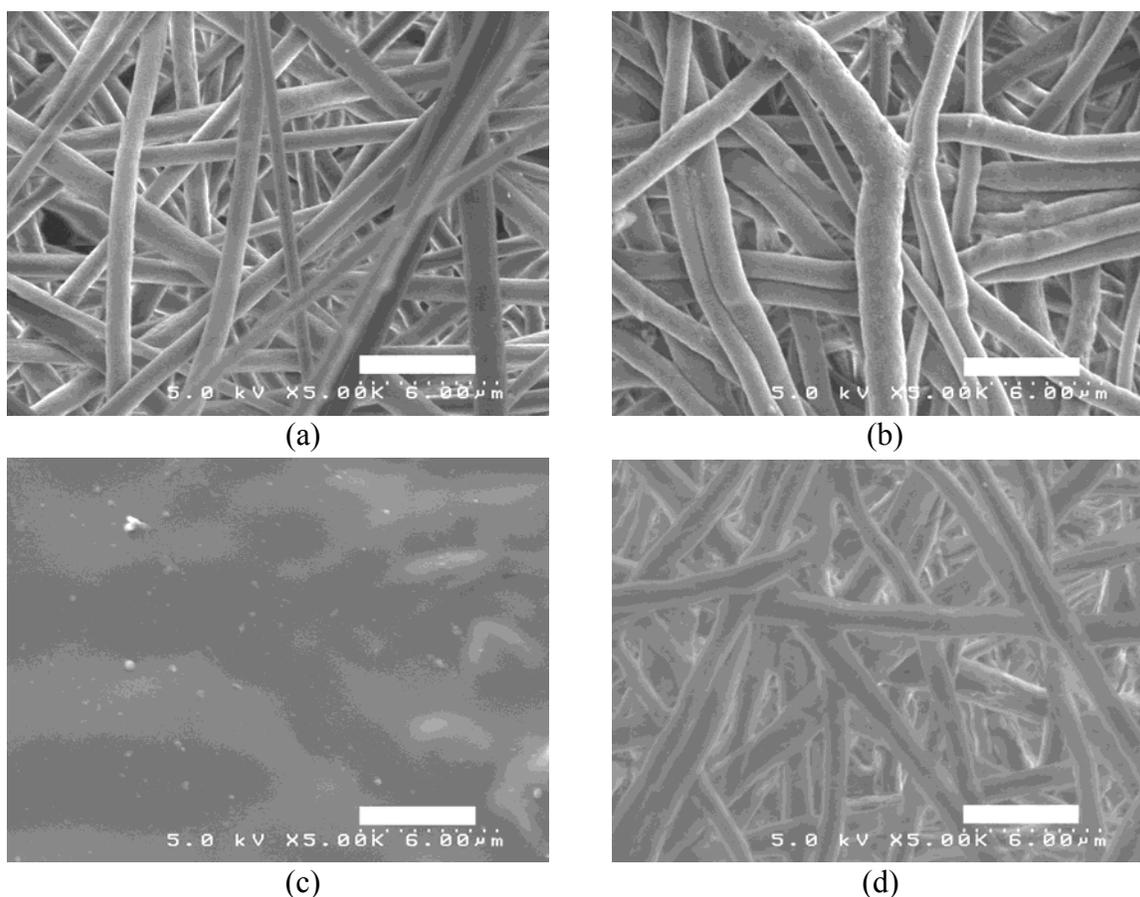


Figure 2. SEM micrographs of: (a) as-spun dual fiber mat of CMPSF and PPSU, (b) dual fiber mat of QAPSF and PPSU (post-quaternization), (c) surface of composite membrane after PPSU has filled the void volume between QAPSF fibers, and (d) QAPSF fiber network after dissolving PPSU matrix with THF from the composite membrane in (c). All scale bars = 5 μm .

Membrane Characterization

Measured in-plane hydroxyl ion conductivities for the composite membranes are plotted as a function of effective membrane ion-exchange capacity (given as the product of the QAPSF fiber volume fraction and the fiber IEC) in Figure 3. For comparison purposes, the properties (OH^- conductivity and water swelling) of neat QAPSF solution cast membranes are listed in Table III. For the two composite membranes with the lowest effective IEC, the conductivity scaled linearly with QAPSF volume fraction in the membrane. For the two higher IEC fiber films, the conductivity was greater than expected, based on the fiber IEC, the volume fraction of fibers in the composite membrane (0.63), and the conductivity of a neat/homogeneous high IEC QAPSF film (see Table III). This result is associated with the lower water uptake of high IEC fibers in a composite membrane (due to the presence of the inert PPSU matrix) which results in a higher volumetric concentration of fixed-charges and a higher OH^- conductivity.

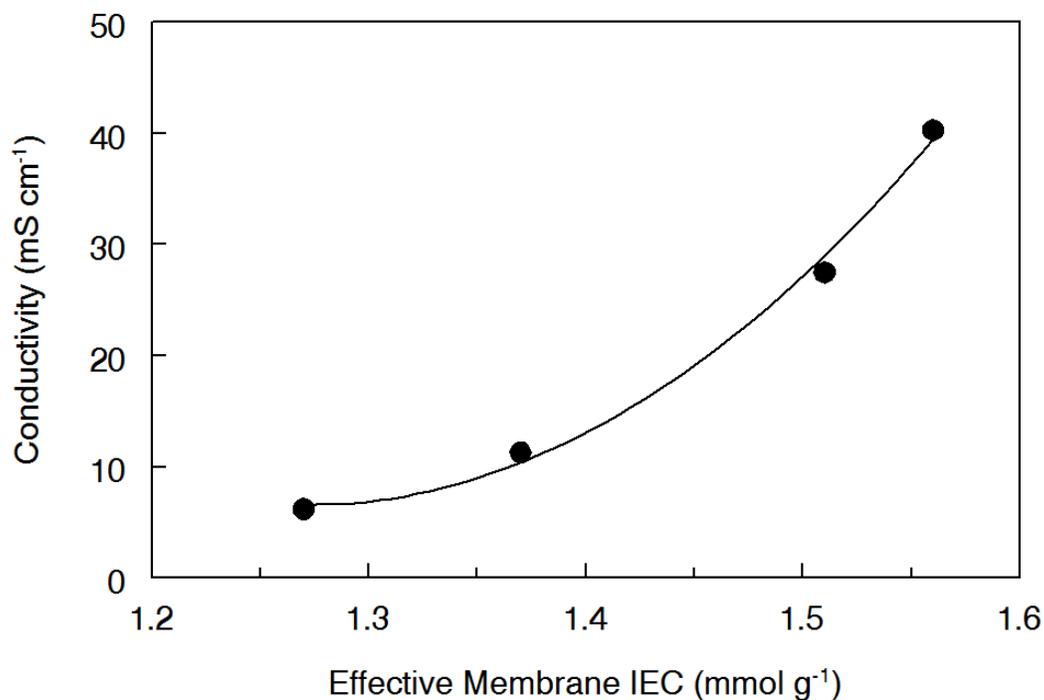


Figure 3. In-plane OH⁻ ion conductivity in water at 23°C versus membrane IEC for the composite membranes.

Table III. Conductivity and Water Swelling Properties of Neat/Homogeneous Membranes from Quaternized Polysulfone.

Neat Film IEC (mmol g ⁻¹)	OH ⁻ Conductivity ¹ (mS cm ⁻¹)	Equilibrium Water Swelling ² (%)
2.02	9.8	48
2.17	15.0	70
2.37	29.6	141
2.49	32.6	170

¹⁻ In-plane conductivity, measured in water at 23°C

²⁻ Volumetric liquid water swelling at 23°C

Membrane water swelling is plotted as a function of effective membrane IEC in Figure 4. At all IECs, membrane swelling by water is reduced by the inert PPSU matrix that surrounds the QAPSF fiber network. The best gains in water swelling (the greatest difference in swelling between the neat polymer and composite membranes) occurred at the higher IECs, where swelling is reduced by a factor of ~2.5. Thus, water swelling of the composite membranes was less than expected, based on the membrane volume fraction of fibers, the fiber IEC, and the inherent swelling of QAPSF polymer at a given IEC.

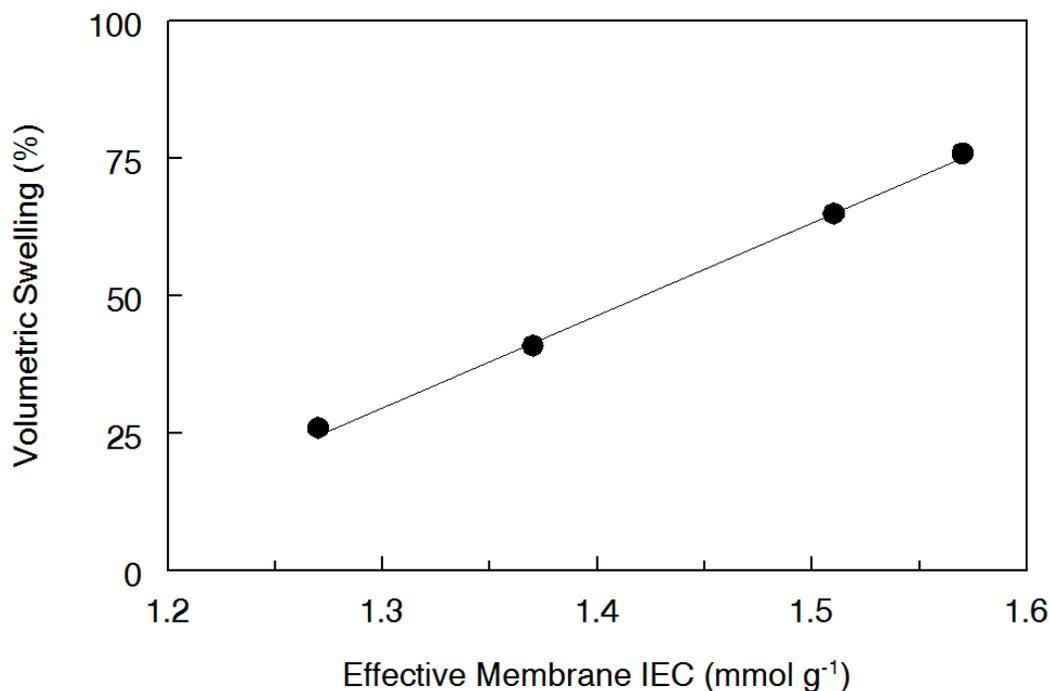


Figure 4. Equilibrium volumetric water swelling of membranes at 23°C vs. IEC for the composite membranes.

Stress/strain data were collected on the composite membrane with the highest IEC (an effective IEC of 1.57 mmol g⁻¹, where the membrane fibers are 2.49 mmol g⁻¹ QAPSF). After drying in an oven at 70°C to remove water, the membrane exhibited good strength (a stress at break of 17 MPa), but its elongation at break was only 2.5%. When the same test was performed on a water-equilibrated membrane, the stress at break increased to 25 MPa and the elongation at break increase to 7%. While the composite membranes are stiff with a low strain at break, they are significantly more flexible and more robust mechanically than a homogenous membrane composed of the same anion-exchange polymer as the fiber network. For example, a homogeneous quaternized polysulfone membrane with an IEC of 2.49 mmol g⁻¹ could not be tested for mechanical properties in either the wet or dry states; dry, cast film samples shattered on handling, and wet samples swelled to gel-like proportions and lost all mechanical strength.

Conclusion

Anion-exchange membranes composed of an interconnected network of submicron diameter quaternary ammonium polysulfone (QAPSF) fibers embedded in polyphenylsulfone (PPSU) have been fabricated and characterized. A dual fiber electrospinning approach was used to make the membranes, where chloromethylated polysulfone and polyphenylsulfone were separately and simultaneously electrospun into a dual fiber mat. The mat was then transformed into a dense and defect-free membrane by the following processing steps: mat compression, welding and then quaternization of chloromethylated fibers, a second mat compression to further increase the fiber volume fraction, and finally mat exposure to THF solvent to allow the polyphenylsulfone fibers to soften, flow, and fill the void volume between the charged fibers. All membranes had a

quaternized polysulfone volume fraction of 0.63 and a polyphenylsulfone volume fraction of 0.37. The effective ion-exchange capacity of the final membrane was varied by using different chloromethylated polysulfones during electrospinning (different extents of chloromethylation). When a highly chloromethylated polysulfone was employed, the final composite membrane IEC (1.57 mmol g^{-1}) and conductivity (40 mS cm^{-1} in 23°C water) were high, but the equilibrium water swelling was exceptionally low (70% at 23°C vs. 170% for a homogeneous membrane with the same IEC as the fibers in the composite film). The low water swelling was attributed to the presence of the polyphenylsulfone matrix which limited water uptake by the charged fibers. Additionally, electrospun fiber composite membranes with a high effective IEC exhibited improved mechanical properties when wet and dry, as compared to homogenous films of quaternized polysulfone. The resulting membranes are excellent candidates for use in alkaline fuel cells.

Acknowledgements

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