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**Nafion/PVDF Nanofiber Composite Membranes for
Regenerative Hydrogen/Bromine Fuel Cells**

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Abstract

Nanofiber composite proton exchange membranes were fabricated and their properties measured, for possible use in a regenerative hydrogen/bromine fuel cell. The membranes were prepared from dual nanofiber mats, composed of Nafion[®] perfluorosulfonic acid (PFSA) ionomer for proton transport and polyvinylidene fluoride (PVDF) for mechanical reinforcement. Two composite membranes structures containing Nafion volume fractions ranging from 0.30 to 0.65 were investigated: (1) Nafion nanofibers embedded in a PVDF matrix (N(fibers)/PVDF) and (2) PVDF nanofibers embedded in a Nafion matrix (N/PVDF(fibers)). The in-plane conductivity for films equilibrated in water and 2.0 M HBr scaled linearly with Nafion volume fraction for both morphologies. The through-plane proton conductivity of N(fibers)/PVDF membranes in water was lower than that of N/PVDF(fibers) films with the same Nafion content for films with less than 55 vol.% Nafion, *e.g.*, 0.03 S/cm for N(fibers)/PVDF membrane vs. 0.04 S/cm for N/PVDF(fibers) membrane at 40 vol.% Nafion. N(fibers)/PVDF membranes exhibited excellent Br₂/Br₃⁻ barrier properties with a reasonable membrane resistance, *e.g.*, a N(fibers)/PVDF membrane with 40 vol.% Nafion and a thickness of 48 μm had the same area-specific-resistance as Nafion[®] 115 (0.13 Ωcm²) but its steady-state Br₂/Br₃⁻ crossover flux was 3.0 times lower than that of Nafion 115 (1.43×10⁻⁹ mol/s/cm² vs. 4.28×10⁻⁹ mol/s/cm²).

Keywords

Nafion; PVDF; proton exchange membrane; electrospinning; regenerative hydrogen bromine fuel cell

1. Introduction

Hydrogen/bromine regenerative fuel cells are being developed for use in grid-scale load leveling applications and for energy-storage coupling with intermittent renewable energy sources like wind and solar [1–3]. This type of fuel cell utilizes a membrane-electrode-assembly (MEA) which separates hydrogen gas and aqueous HBr compartments. The MEA is composed of a polymeric cation (proton)-exchange membrane separating thin-layer electrodes that are pressed onto the membrane's opposing surfaces. During charging, Br^- is oxidized to Br_2 in the HBr compartment and H^+ migrates across the membrane where it is reduced to form H_2 gas. Most of the electro-generated bromine reacts further with bromide ions in solution to produce a Br_3^- complex (the equilibrium constant for the reaction $\text{Br}^- + \text{Br}_2 = \text{Br}_3^-$ is 17 [4–6]). During discharging, H_2 and bromine products, which are stored in external tanks, are pumped into the fuel cell and allowed to react spontaneously to generate HBr and electricity. Compared to regenerative H_2/O_2 fuel cells, the H_2/Br_2 system has several advantages: (i) the fast kinetics of the bromine oxidation/reduction reactions contribute to low voltage losses, high roundtrip efficiencies, and very high power densities ($>1.5 \text{ W/cm}^2$ versus 0.7 W/cm^2 for H_2/O_2 system) [7,8] and (ii) mass transfer limitations are essentially nonexistent during fuel cell operation due to the high solubility of Br_2 in the hydrobromic acid electrolyte.

The membrane in a regenerative H_2/Br_2 fuel cell has several important functions; it physically separates the two electrodes and minimizes unwanted Br_2 and Br_3^- crossover while providing pathways for inter-electrode proton transport (high bromine crossover results in coulombic losses and degradation of the hydrogen electrode's platinum catalyst) [4,8–10]. Several studies have shown that a perfluorosulfonic acid (PFSA) membrane such as Nafion possesses the requisite thermal/mechanical/chemical stability and proton conductivity for use in a hydrogen-

bromine fuel cell, but bromine species crossover is too high, thus limiting the concentration of $\text{Br}_2/\text{Br}_3^-$ during charging [4,9–12]. To prevent $\text{Br}_2/\text{Br}_3^-$ crossover, a highly charged cation-exchange membrane with good anion exclusion properties is needed. Unfortunately, polymers with a high concentration of fixed charges swell excessively in water and aqueous salt solutions, thereby decreasing the effective volume-based ion-exchange capacity which in turn lowers the film's ability to reject co-ions (anions). Membranes with a high concentration of fixed charges may also be brittle when dry and mechanically weak when fully swollen.

In the present study, a series of nanofiber composite cation exchange membranes were fabricated and evaluated for possible/eventual use in a hydrogen/bromine regenerative fuel cell. Choi et al. were the first to prepare this type of proton exchange membrane, where a mat of electrospun, interconnected ionomer fibers was infiltrated with a photo-curable liquid prepolymer followed by UV light exposure [13–15]. In follow-on studies, Ballengee and Pintauro showed that two distinct bicontinuous composite membrane morphologies could be generated from the same dual fiber electrospun mat (various mixtures of perfluorosulfonic acid ionomer and uncharged polyphenylsulfone nanofibers), without the need for a separate polymer impregnation step [16]. Membranes composed of uncharged reinforcing polymer fibers surrounded by an ionomer matrix worked exceedingly well in hydrogen/air fuel cell MEAs, with high conductivity, low gas crossover, and low in-plane swelling, with excellent durability in accelerated wet/dry cycling experiments [16–18].

Nanofiber composite membranes were fabricated via dual fiber electrospinning and the resulting films were characterized for use in a H_2/Br_2 regenerative fuel cell. The membranes were composed of Nafion[®] perfluorosulfonic acid ionomer to provide facile proton transport and poly(vinylidene fluoride) (PVDF), as the uncharged polymer for mechanical reinforcement and swelling control. PVDF was chosen because it is known to have excellent chemical resistance

against bromine degradation and good mechanical properties [12,19]. Separate solutions of Nafion and PVDF were electrospun simultaneously to create a dual nanofiber mat, where the volume fraction of the two polymer fibers was varied over a range of Nafion/PVDF volume ratios. Mats were processed into defect-free dense membranes with two distinct structures: (1) Nafion nanofibers embedded in a PVDF matrix and (2) Nafion matrix reinforced with a PVDF nanofiber network. The ion conductivity, the $\text{Br}_2/\text{Br}_3^-$ steady-state permeability, diffusion coefficient, and partition coefficient were determined and correlated with respect to membrane composition (Nafion content) for the two composite membrane morphologies. Properties of electrospun membranes were then compared to those of commercial and solution-cast Nafion membranes and solution-cast Nafion/PVDF films.

2. Experimental

2.1. Solution-cast Nafion and Nafion/PVDF membranes

Dry Nafion 1100 EW powder was obtained by evaporation of solvent from an Ion Power Inc. LIQUION 1115 solution. To prepare a solution-cast membrane of neat Nafion, the powder was dissolved in N,N-dimethylacetamide (DMAc) at 25°C to obtain 20 wt.% solution which was then spread on a glass substrate using a doctor blade. The film was dried at 70°C for 12 h and annealed at 150°C for 2 h under vacuum. The resultant membrane was boiled in 1.0 M H_2SO_4 and water each for 1 h. and then stored in 25°C deionized (DI) water until further use.

Solution-cast Nafion/PVDF membranes containing 40-60 vol.% Nafion, were prepared as follows: solutions of 20 wt.% Nafion and 20 wt.% poly(vinylidene fluoride) (PVDF) were prepared separately by dissolving Nafion powder and PVDF powder (Kynar[®] 760, from Arkema,

with a molecular weight of 444 kDa) in DMAc. The appropriate amounts of the two solutions were mixed to obtain 20 wt.% total polymer concentration. The resultant mixture was cast onto a glass plate using a doctor blade, followed by film drying at 70°C for 12 h and annealing at 150°C for 2 h under vacuum. Membranes were pre-treated by boiling for 1 h in 1.0 M H₂SO₄ and in deionized (DI) water.

2.2. Electrospinning Nafion and PVDF

Dual nanofiber mats of Nafion and PVDF were prepared by simultaneously electrospinning PVDF and 1100 EW Nafion PFSA containing poly(ethylene oxide) (PEO) as a carrier polymer. The electrospinning solution for Nafion/PEO fibers was prepared as follows: solutions of 35 wt.% Nafion and 5.0 wt.% PEO were prepared separately by dissolving 1100 EW Nafion powder and PEO powder (Sigma-Aldrich, 400 kDa MW) into a 2:1 weight ratio mixture of n-propanol:water. The proper amounts of the two solutions were then mixed to make a Nafion/PEO mixture with 20 wt.% total polymer concentration and a 99:1 weight ratio of Nafion to PEO. PVDF was electrospun from a 20 wt.% polymer solution that was prepared by dissolving PVDF powder (Kynar[®] 760, from Arkema, with a molecular weight of 444 kDa) in a 7:3 weight ratio of DMAc:acetone.

All electrospinning experiments were carried out using a custom-built rotating drum collector apparatus [16] that was placed in a chamber where the relative humidity was fixed at 35% $\pm$ 2%. Nafion/PEO and PVDF solutions were electrospun simultaneously from separate hypodermic needle spinnerets placed horizontally on opposite sides of the drum. The Nafion/PEO solution was electrospun at the following conditions: 4.2 kV applied voltage between the needle spinneret tip and the grounded drum collector, 6.5 cm spinneret-to-collector

distance, and a solution flow rate of 0.2 ml/h. The 20 wt.% PVDF solution was electrospun at an applied voltage of 8.5 kV, where the spinneret-to-collector distance was 7.0 cm and the solution flow rate was varied from 0.06 to 0.2 ml/h to create dual fiber mats (and final membranes) with a different PVDF content. At the start and end of preparing a dual fiber mat, only Nafion/PEO fibers were electrospun to create thin surface layers of ionomer after mat processing for better contact to electrodes during testing (the Nafion surface layers will also improve membrane-electrode contact when fabricating membrane-electrode-assemblies for hydrogen/bromine fuel cells).

2.3. Dual nanofiber mat processing

2.3.1. Preparing membranes with Nafion fibers surrounded by PVDF

Electrospun mats were compressed four times (10 s each) at 875 psi and 25°C and then annealed at 150°C for 1 h under vacuum. It has been shown previously that intersecting Nafion fibers weld during polymer annealing, thus creating a 3-D interconnecting ionomer network. The annealed mats were then soaked in a 2.0 M NaCl solution for 24 h to replace H⁺ counterions with Na⁺ (this ion exchange step was necessary to ensure the chemical stability of Nafion in a subsequent high temperature hot-pressing step). After removing excess salt by numerous water washings, the membranes were dried at 70°C for 12 h and then at 100°C in vacuum for 2 h. The dry membranes were hot-pressed at 177°C and 6,000 psi for ~40 s to soften the PVDF and force it to fill the voids between Nafion fibers. The resulting dense films were boiled for 1 h each in 1.0 M H₂SO₄ and in deionized (DI) water, to remove residual PEO and to re-protonate all ion-exchange sites. Membranes were prepared with 30-65 vol.% Nafion.

2.3.2. Preparing membranes with PVDF fibers surrounded by Nafion

The procedure described by Ballengee and Pintauro [16] was employed. The dual fiber mat was compressed at 6,000 psi and 120°C for ~30 s and then annealed at 150°C in vacuum for 2 h. The high pressure and temperature pre-compaction step decreased the distance between ionomer fibers so that Nafion softened and flowed between PVDF fibers during the high temperature annealing step (the annealing temperature was too low for PVDF to soften and flow). Membranes were pre-treated by boiling for 1 h in 1.0 M H₂SO₄ and in deionized (DI) water. Membranes were prepared with 30-65 vol.% Nafion.

2.4. Membrane characterizations

2.4.1. SEM microscopy

The surface of electrospun mats and the cross sections of fully processed (final) membranes were imaged with a Hitachi S-4200 scanning electron microscope. Dry membrane samples were manually fractured after cooling in liquid nitrogen. Individual fiber diameters and the fiber diameter distribution of an electrospun mat were obtained from SEM images using the processing software ImageJ (<http://rsbweb.nih.gov/ij/index.html>).

2.4.2. Ion-exchange capacity

Membrane ion-exchange capacity (IEC) was determined by the standard method of acid exchange and base titration. A membrane sample of known dry weight in the acid form was soaked in multiple 20 ml aliquots of 1.0 M NaCl over a period of 3 h under stirring to exchange

Na⁺ for H⁺ (the NaCl solution was replaced repeatedly until there was no further proton extraction). The amount of H⁺ released into all of the NaCl soak solutions was determined by titration with 0.01 N NaOH. The IEC of a membrane sample was calculated by,

$$IEC \text{ (mequiv / g)} = \frac{V N}{m_{dry}} \quad (1)$$

where IEC (mequiv/g) is the ion-exchange capacity (on a dry polymer weight basis), V (ml) is the volume of the NaOH titrating solution, N (mol/L) is the normality of the NaOH titrating solution, and m_{dry} (g) is the dry mass of the membrane sample. The Nafion volume fraction in a Nafion/PVDF composite membrane was determined from the measured IEC, as per Equation 2 [16].

$$Nafion \text{ volume fraction} = \frac{IEC_{composite}}{IEC_{Nafion}} \times \frac{\rho_{composite}}{\rho_{Nafion}} \quad (2)$$

where IEC_{composite} and IEC_{Nafion} are the measured ion-exchange capacities of a nanofiber composite membrane and a solution-cast Nafion film, respectively, and ρ_{composite} and ρ_{Nafion} are the measured dry densities of the composite membrane and Nafion film (where ρ_{Nafion} = 1.96 g/cm³ and IEC_{Nafion} = 0.91 mequiv/g).

2.4.3. Ion conductivity measurements

Ion conductivity was measured in both the in-plane and through-plane directions, using an AC impedance technique. In-plane ion conductivity was measured using a BekaTech 4-electrode cell (Model – BT110, BekaTech, LLC) at 25°C with membrane samples equilibrated in water or 2.0 M HBr. For water measurements, the entire conductivity cell was immersed in DI water. For measurements with 2.0 M HBr, membranes samples were pre-soaked in electrolyte for 3 h, removed from the solution, and then quickly loaded into the conductivity cell after removing

excess electrolyte from the membrane surfaces. For all in-plane measurements, the membrane resistance was determined at a single frequency (1 kHz) and membrane conductivity was calculated using the following equation,

$$\sigma = \frac{L}{Rw\delta} \quad (3)$$

where σ (S/cm) is ion conductivity, L (cm) is the distance between the potential sensing electrodes in the conductivity cell, R (Ω) is the measured membrane resistance, w (cm) is the width of the wet membrane sample, and δ (cm) is the wet membrane thickness.

Through-plane conductivity of membrane samples equilibrated in liquid water at 25°C was determined using the custom-built two-electrode cell shown schematically in **Fig. 1**, which is similar in design to that reported by Cooper et. al. [20]. Membrane samples were clamped between two polished copper electrodes with an active area of 0.0507 cm² (the area was kept small in order to minimize impedances generated by the two electrodes). The clamping pressure on the membrane, measured by a Hookean spring (Gardner GC480-038-0875) and displacement indicator dial, was fixed at 310 psi; this applied pressure was chosen based on prior work with Nafion films [20]. In the present study, changing the clamping pressures in the range of 12-360 psi had no effect on the measured conductivity. Through-plane conductivity ($\sigma_{\text{through-plane}}$, S/cm) was calculated from Equation 4,

$$\sigma_{\text{through-plane}} = \frac{\delta}{(R_{\text{membrane}} - R_{\text{non-membrane}})A} \quad (4)$$

where δ (cm) is the wet membrane thickness, R_{membrane} (Ω) is the measured membrane resistance, $R_{\text{non-membrane}}$ (Ω) is the non-membrane resistance, and A (cm²) is the electrode area. The measured

membrane resistance (R_{membrane}) was found via AC impedance experiments as the value of the real impedance when a plot of real vs. imaginary impedance was extrapolated to an imaginary impedance of zero in the high-frequency region. The zero-thickness intercept of a linear R_{membrane} vs. membrane thickness plot was taken as the non-membrane resistance. For this part of the analysis, nanofiber and blended membranes of different thickness were prepared by stacking films. It was assumed that the interfacial membrane-membrane resistance within a stack was negligibly small. This assumption was validated by comparing conductivity data from a small number of stacked Nafion and Nafion/PVDF membranes (with a total thickness in the range of 50-350 μm) to that obtained from solution-cast single films of the same composition and thickness. Both systems gave the same through-plane conductivity.

Fig. 1. Schematic diagram of the through-plane conductivity apparatus [21].

2.4.4. Membrane swelling

Mass, volume, linear (in-plane), and thickness swelling of membrane samples in 2.0 M HBr were determined at 25°C. Fully protonated composite membranes, solution-cast Nafion films and commercial Nafion membranes were equilibrated in electrolyte solution for at least 24 h. Membranes were then removed from solution, quickly wiped with filter paper, and then their mass, length, area, and thickness were measured. Next, the membranes were soaked in multiple volumes of deionized (DI) water to remove HBr and dried in a convection oven (60°C for 12 h followed by 2 h at 100°C). After drying, the mass, length, area, and thickness were re-measured. Swelling was calculated from.

$$\text{Membrane swelling (\%)} = \frac{x_{wet} - x_{dry}}{x_{dry}} \times 100 \quad (5)$$

where x is the membrane's mass, volume, length, or thickness.

2.4.5. Determination of bromine diffusivity, permeability, and partition coefficient

A transient electrochemical breakthrough method was used to measure the diffusion coefficient of $\text{Br}_2/\text{Br}_3^-$ species in membrane samples [4,5,22,23]. A schematic diagram of the two-compartment glass cell is shown in **Fig. 2**. The downstream compartment contained a platinum wire counter electrode and a saturated calomel reference electrode. A carbon paper sensing electrode and Pt mesh current collector were physically pressed onto the back side of a sample membrane (a composite film, a solution-cast Nafion or a commercial Nafion 115 membrane). The two compartments of the cell were filled with an aqueous 2.0 M HBr solution and the carbon paper working electrode was polarized to +0.3 V vs. the saturated calomel reference electrode. Once the current stabilized at 1 μA , the electrolyte in the feed compartment was rapidly drained

and replaced with a pre-mixed solution of 2.0 M HBr with 0.14 M Br₂. Bromine species (Br₂/Br₃⁻) which diffused through the membrane into the downstream compartment were electrochemically reduced within the carbon paper electrode. The resultant current transient curve was recorded for further analysis using a Gamry Potentiostat (Reference 3000TM). All experiments were carried out at 25°C with well-stirred solutions.

Fig. 2. Schematic diagram of the two compartment cell for determining membrane diffusion coefficients.

The diffusivity of bromine species in a sample membrane was determined by matching measured current vs. time data to a theoretical transient diffusion model based on Fick's Second Law, with boundary and initial conditions that matched the experimental set-up,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (6)$$

$$C = C^b \text{ for } x = 0 \text{ at } t \geq 0 \quad (7)$$

$$C = 0 \text{ for } x = \delta \text{ at } t \geq 0 \quad (8)$$

$$C = 0 \text{ for } 0 \leq x \leq \delta \text{ at } t < 0 \quad (9)$$

where x is distance measured from the upstream membrane surface in contact with the HBr solution, δ is the wet (2.0 M HBr) membrane thickness, and C^b is the upstream concentration of $\text{Br}_2/\text{Br}_3^-$ ($C^b = 0.14$ M). The first term of the series solution to Equations 6-9 is:

$$\frac{J_t}{J_\infty} = \frac{2\delta}{(\pi Dt)^{1/2}} \exp\left[-\frac{\delta^2}{4Dt}\right] \quad (10)$$

where J_t is the current density at time t (A/cm^2), J_∞ is the steady-state current density (A/cm^2), D is diffusion coefficient (cm^2/s), and t is time (s). The steady-state permeability of bromine species (P , with units of cm^2/s) was calculated from the measured value of J_∞ and membrane thickness,

$$P = \frac{J_\infty \delta}{nFC^b} \quad (11)$$

where n is the number of electrons involved in the $\text{Br}_2/\text{Br}_3^-$ reduction reaction and F is Faraday's constant.

From the measured value of diffusivity and permeability, the $\text{Br}_2/\text{Br}_3^-$ partition coefficient (K) was determined, where K is defined as the concentration ratio of bromine species in the membrane (C^m) to that in the external bulk solution (C^b).

$$K = \frac{C^m}{C^b} = \frac{P}{D} \quad (12)$$

where K has the units of $\frac{\text{mol} / \text{cm}^3 \text{ membrane}}{\text{mol} / \text{cm}^3 \text{ solution}}$.

To determine the $\text{Br}_2/\text{Br}_3^-$ diffusion coefficient in a membrane sample, a computer optimization program was used to find the value of D that minimized the error between one set of experimental data points and the model prediction given by Equation 10. Initial experiments were carried out with commercial Nafion membranes to establish the accuracy and limitations of the method. Typical fits of experimental data to a theoretical breakthrough curve are shown in **Fig. 3**

for a Nafion 115 membrane and a solution-cast Nafion film. The value of D that matches the Nafion 115 data in **Fig. 3a** is $1.45 \times 10^{-6} \text{ cm}^2/\text{s}$, which is close to the value of $1.43 \times 10^{-6} \text{ cm}^2/\text{s}$, from reference 19. The average error (difference) between theory and experiments after matching an entire breakthrough curve was typically $\leq 5\%$ (the errors in **Fig. 3a** and **Fig. 3b** are 4.5% and 2.5%, respectively). The method was also reproducible; duplicate experiments using membranes of identical composition and thickness gave the same diffusivity within $\sim 6\%$.

In some cases (for thin membranes where bromine species transport is fast), transient current data could not be fitted accurately to the model because the breakthrough time was too short (< 10 s) and it was difficult to fix the start time of a transient experiment. This point is demonstrated in **Figs. 4** and **5**, where simulated current vs. time curves are shown for membranes of different thicknesses and for different values of bromine diffusivity. As can be seen in **Fig. 4**, the breakthrough time of a thin ($60 \text{ }\mu\text{m}$) membrane with a diffusivity of $1.45 \times 10^{-6} \text{ cm}^2/\text{s}$ is approximately 1 s, with the attainment of a steady-state current in *ca.* 10 s. These times are all short as compared to the time to completely fill the feed chamber with Br_2 -containing electrolyte during a diffusion experiment. Similarly, the simulated results in **Fig. 5** show that reasonably long breakthrough times will occur for a $60 \text{ }\mu\text{m}$ thick membrane when the bromine species diffusivity is $< 1.9 \times 10^{-7} \text{ cm}^2/\text{s}$.

Fig. 3. Comparison of the fit of experimental data (■) to the transient theoretical breakthrough model (—) for an electrolyte of 2.0 M HBr with 0.14 M Br₂. (a) a Nafion 115 membrane (140 μm thick), where the best fit value of D is $1.45 \times 10^{-6} \text{ cm}^2/\text{s}$ and (b) a solution-cast Nafion membrane (150 μm thick), where $D=1.90 \times 10^{-6} \text{ cm}^2/\text{s}$.

Fig. 4. Simulated transient breakthrough curves for a constant species diffusivity ($1.45 \times 10^{-6} \text{ cm}^2/\text{s}$) and membrane thickness of (—) 60 μm , (---) 140 μm , and (···) 190 μm .

Fig. 5. Simulated transient breakthrough curves for a constant membrane thickness (60 μm) and species diffusivities of (—) $1.46 \times 10^{-6} \text{ cm}^2/\text{s}$., (---) $1.9 \times 10^{-7} \text{ cm}^2/\text{s}$., and (···) $7.0 \times 10^{-8} \text{ cm}^2/\text{s}$.

3. Results and Discussion

3.1. Properties of commercial Nafion membranes, solution-cast Nafion films, and solution-cast Nafion/PVDF blended membranes

The properties of commercial and solution-cast Nafion and blended Nafion/PVDF membranes were used as base-line reference data when evaluating nanofiber composite membranes. In-plane ion conductivity in 2.0 M HBr and in water, mass and volumetric swelling in 2.0 M HBr, $\text{Br}_2/\text{Br}_3^-$ diffusion coefficient, and steady-state bromine species permeability for membrane samples are listed in **Table 1**. The following conclusions can be made from the results: (1) gravimetric and volumetric swelling for solution-cast Nafion membrane were greater than those for the commercial Nafion 115 and 212 membranes and for the Nafion/PVDF blends, and (2) the greater water/electrolyte uptake of solution-cast Nafion films led to a higher ion conductivity, $\text{Br}_2/\text{Br}_3^-$ diffusivity, and bromine species steady-state permeability. The difference in properties between commercial Nafion films and in-house solution-cast Nafion membranes is associated with different fabrication protocols.

With regards to the three solution-cast Nafion/PVDF films listed in Table 1, membrane (i.e., Nafion ionomer) swelling in 2.0 M HBr decreased with increasing PVDF content, with an accompanied decrease in $\text{Br}_2/\text{Br}_3^-$ diffusivity, steady-state permeability, and in-plane ion conductivity. For example, the steady-state $\text{Br}_2/\text{Br}_3^-$ permeability at 50 vol.% Nafion ($0.40 \times 10^{-7} \text{ cm}^2/\text{s}$) was ~11 times lower than that in Nafion 212 ($4.45 \times 10^{-7} \text{ cm}^2/\text{s}$), but its ion conductivity was only ~7 times lower than Nafion 212 in 2.0 M HBr. Thus, the membrane selectivity, which is the ratio of conductivity to permeability, was higher for blend membranes as compared to commercial films. Unfortunately, the significant drop in membrane conductivity upon addition of PVDF is problematic. For practical applications, one would like the area-

specific resistance (membrane thickness divided by conductivity) of Nafion/PVDF blended membranes to be low (comparable to that of commercial Nafion films). This is not the case for the blends in Table 1; the area-specific resistance of a Nafion/PVDF membrane with 50 vol.% PVDF is $0.34 \Omega\text{-cm}^2$, whereas that for Nafion 212 (55 μm in thickness) is only $0.05 \Omega\text{-cm}^2$. This means that one would need to prepare an 8 μm thick blended film to achieve the same operational resistance as Nafion 212. It is difficult to fabricate defect-free films of such low thickness and then to convert the films into membrane-electrode-assemblies for a hydrogen/bromine regenerative fuel cell. Consequently, a major focus of the electrospun composite membrane work was to prepare films with a high selectivity and low sheet resistance.

Table 1. Experimentally measured mass swelling, volume swelling, ion conductivity, $\text{Br}_2/\text{Br}_3^-$ diffusion coefficient and steady-state bromine species permeability of commercial Nafion membranes, solution-cast Nafion films, and solution-cast Nafion/PVDF membranes. All measurements were made at 25°C . Mass and volume swelling were measured in 2.0 M HBr; ion conductivities were measured in 2.0 M HBr and DI water; diffusion coefficients and steady-state permeabilities were measured in a 0.14 M Br_2 -2.0 M HBr solution.

Sample	Membrane swelling in 2.0 M HBr (%)		In-plane ion conductivity (S/cm)		Diffusion coefficient (cm^2/s)	Steady-state permeability (cm^2/s)
	mass	volume	2.0 M HBr	water		
Nafion 115	23	30	0.107	0.084	1.45×10^{-6}	4.26×10^{-7}
Nafion 212	25	33	0.122	0.088	—	4.45×10^{-7}
Solution-cast Nafion	36	48	0.125	0.092	1.90×10^{-6}	5.64×10^{-7}
<u>Solution-cast Nafion/PVDF</u>						
60 vol.% Nafion	13	16	0.037	0.036	0.82×10^{-6}	1.17×10^{-7}
50 vol.% Nafion	9	12	0.017	0.015	0.51×10^{-6}	0.40×10^{-7}
40 vol.% Nafion	7	9	0.009	0.007	0.42×10^{-6}	0.29×10^{-7}

3.2. Properties of electrospun composite membranes

3.2.1. Membrane morphology

Fig. 6(a) shows a surface SEM image of an electrospun dual fiber mat with 55 vol.% Nafion fibers and 45 vol.% PVDF. The Nafion and PVDF nanofibers are visually indistinguishable but are presumed to be distributed uniformly, as per prior dual fiber membrane studies [16]. The average fiber diameter is 400 nm. The mat was processed into a dense and defect-free membrane using one of two strategies: (i) the PVDF fibers were selectively melted to fill voids between Nafion nanofibers, resulting in a membrane where Nafion fibers were embedded in PVDF matrix; hereinafter, referred to as N(fibers)/PVDF, or (ii) the Nafion fibers were selectively melted to fill the voids between PVDF fibers, where a Nafion matrix is reinforced with PVDF fibers; hereafter, referred to as N/PVDF(fibers). A freeze-fractured cross section of the fully processed membrane with N(fibers)/PVDF is shown in **Fig. 6(b)**. The film is free of voids or pinholes, indicating that the PVDF fibers properly softened and flowed to form a continuous matrix within the final membrane. Although PVDF softening (hot-pressing) was performed at 177°C, the Nafion nanofibers remained intact because the ionomer was in the Na⁺ counterion form (the glass transition temperature for Nafion in the Na⁺ form is ~235°C) [24]. A freeze-fractured SEM cross section of a N/PVDF(fibers) membrane is shown in **Fig. 6(c)**. The presence of PVDF nanofibers throughout the membrane thickness is evident and the Nafion appears to completely fill the interfiber void space. **Fig. 6(d)** is a freeze-fractured SEM image of the cross section of a solution-cast blended membrane. A uniform morphology can be seen, with well-dispersed Nafion and PVDF and no significant macroscopic phase separation. Due to insufficient resolution of the image, it was impossible to identify the PVDF and Nafion phases.

Fig. 6. SEM images of (a) an electrospun Nafion/PVDF dual nanofiber mat, (b) freeze-fractured cross section of a 55 vol.% N(fibers)/PVDF membrane, (c) freeze-fractured cross section of a 55 vol.% N/PVDF(fibers) membrane, (d) freeze-fractured cross section of a 55 vol.% Nafion solution-cast blended membrane.

3.2.2. In-plane and through-plane proton conductivity in water

Measured in-plane and through-plane proton conductivities of nanofiber composite membranes and solution-cast Nafion/PVDF films that were equilibrated in water at 25°C are plotted in **Fig. 7** as a function of Nafion content. In-plane conductivities of both membrane morphologies were the same and increased linearly with increasing Nafion content, as expected based on a simple linear mixing rule with Nafion volume fraction (solid line in **Fig. 7** connecting points for 0 S/cm at 100% PVDF and the conductivity of a solution-cast Nafion film, 0.092 S/cm). This type of correlation was observed previously for Nafion/polyphenylsulfone nanofiber

composite films [16]. The conductivity of nanofiber composite membranes was higher than that of a solution-cast blended Nafion/PVDF membrane at the same Nafion vol.% (*e.g.*, 0.036 S/cm for a solution-cast Nafion/PVDF membrane with 60 vol.% Nafion versus 0.055 S/cm for a nanofiber composite membrane at the same Nafion content). Through-plane and in-plane conductivities of N/PVDF(fibers) films and solution-cast Nafion/PVDF membranes were identical, but the through-plane conductivities of N(fibers)/PVDF membranes were lower than expected for Nafion contents < 55 vol.% and exhibited a slight non-linear dependence vs. Nafion vol.%, where the difference between in-plane and through-plane conductivity grew with increasing PVDF content (*e.g.*, the ratio of in-plane to through-plane conductivities was 1.12 at 50 vol.% Nafion, and 2.04 at 30 vol.% Nafion). This result suggests that there is a disruption (partial disconnection) in the through-plane interconnectivity of the Nafion phase due to an overabundance of PVDF (> 50 vol.%) for the N(fibers)/PVDF membrane morphology.

3.2.3. In-plane ion conductivity in 2.0 M HBr

As shown in **Fig. 8**, the measured in-plane conductivities for both nanofiber composite membrane morphologies were a linear function of Nafion contents and were also greater than those measured in water at a given membrane composition due to the presence of additional charge carriers in the membrane (mobile H^+ and Br^-). It is important to note that the in-plane ion conductivity of solution-cast Nafion/PVDF membranes in 2.0 M HBr was much lower than that of the nanofiber composite membranes, due presumably to poor ionomer interdomain connectivity within the cast film as compared to that in an electrospun membrane.

Fig. 7. Proton conductivity of dual-nanofiber composite membranes and solution-cast Nafion/PVDF membrane as a function of Nafion volume fraction at 25°C. (○) In-plane conductivity of N(fibers)/PVDF membrane; (●) Through-plane conductivity of N(fibers)/PVDF membrane; (Δ) In-plane conductivity of N/PVDF(fibers) membrane; (▲) Through-plane conductivity of N/PVDF(fibers) membrane; (□) In-plane conductivity of solvent-cast Nafion/PVDF membrane; (■) Through-plane conductivity of solvent-cast Nafion/PVDF membrane; (—) predicted in-plane conductivity based on a simple mixing rule with Nafion volume fraction; (---) data guideline.

Fig. 8. In-plane ion conductivity of dual-nanofiber composite membranes as a function of Nafion volume fraction at 25°C after their equilibration in 2.0 M HBr (closed symbols) and in water (open symbols); (●) N(fibers)/PVDF membrane; (▲) N/PVDF(fibers) membrane; (■) solution-cast Nafion/PVDF membrane; (○) N(fibers)/PVDF membrane (data copied from **Fig. 7**); (Δ) N/PVDF(fibers) membrane (data copied from **Fig. 7**); (□) solution-cast Nafion/PVDF membrane (data copied from **Fig. 7**); (—) predicted in-plane conductivity based on a simple mixing rule with Nafion volume fraction (0.125 S/cm for solution-cast Nafion in 2.0 M HBr and 0.092 S/cm for solution-cast Nafion in water); (---) data guideline.

3.2.4. Membrane swelling in 2.0 M HBr

Mass and volumetric swelling of the two Nafion/PVDF composite membrane structures and solution-cast films after equilibration in 2.0 M HBr at 25°C are shown in **Fig. 9** as a function of Nafion vol.%. Three important conclusions can be drawn from the results: (1) swelling of the electrospun membranes was independent of the type of morphology (Nafion fibers or PVDF fibers), (2) mass and volume swelling decreased linearly with increasing PVDF content, as was observed in other Nafion dual fiber composite membranes [16], and (3) both the mass and volume

swelling were lower than would be expected based on a simple linear mixing rule with Nafion volume fraction, as shown by the solid line in **Fig. 9**, which connected points for 0% swelling at 100% PVDF and the measured swelling of a solution-cast Nafion film (36% and 48%, for the mass and volume swelling, respectively). It is also evident that the gravimetric and volumetric swelling of a solution-cast Nafion/PVDF membrane were lower than those of both nanofiber composite membrane types at a given PVDF content, which is consistent with the lower proton conductivity of the cast blends, as discussed above.

In contrast to the data in **Fig. 9**, membrane swelling in the lateral (in-plane) and thickness directions differ for the two nanofiber composite morphologies, as shown in **Fig. 10**. For N(fibers)/PVDF films, the thickness and lateral direction swellings are nearly identical (*i.e.*, near isotropic swelling) due to the continuity/connectivity of the PVDF reinforcing matrix in the thickness and in-plane directions. For the N/PVDF(fibers) membrane case, a more pronounced swelling anisotropy is observed, *e.g.*, at 60 vol.% Nafion the thickness direction swelling exceeds 15% while the lateral swelling is only ~2%. During electrospinning, PVDF fibers are deposited in a layer-by-layer fashion. Water/electrolyte uptake by ionomer causes the PVDF fiber layers to separate in the thickness direction, whereas the PVDF fiber network structure in the lateral membrane direction, which appears to be of a closed-form cell structure, resists Nafion swelling. The low in-plane swelling data reported here are consistent with previous results for Nafion dual fiber membranes with polyphenylsulfone as the uncharged reinforcing polymer [16].

Fig. 9. 2.0 M HBr swelling of dual-nanofiber composite membranes as a function of Nafion volume fraction at 25°C. (a) Mass swelling and (b) volumetric swelling. ($\circ$) N(fibers)/PVDF membrane; ($\blacktriangle$) N/PVDF(fibers) membrane; ($\square$) solution-cast Nafion/PVDF membrane; (—) predicted mass and volume swelling based on a simple mixing rule with Nafion volume fraction; (---) data guideline.

Fig. 10. In-plane swelling (a) and thickness swelling (b) of nanofiber composite membranes as a function of Nafion volume fraction at 25°C in 2.0 M HBr. (○) N(fibers)/PVDF membrane; (▲) N/PVDF(fibers) membrane; (---) data guideline.

3.2.5. Bromine species ($\text{Br}_2/\text{Br}_3^-$) diffusion coefficients, steady-state permeabilities, and partition coefficients

The determination of bromine species diffusivity and permeability was carried out using an electrolyte of 2.0 M HBr with 0.14 M Br_2 . This solution was chosen for the following reasons: (i) the HBr concentration needed to be moderately high to simulate conditions in a regenerative fuel cell (ii) the Br_2 concentration needed to be sufficiently low so that essentially all of the bromine in 2.0 M HBr would complex to form Br_3^- (at 0.14 M Br_2 , 97% of the bromine is converted to the tri-bromide complex, based on an equilibrium constant for complexation of 17), and (iii) 0.14 M Br_2 lies within the range of bromine concentrations (0.10-0.50 M) examined in related/previous studies [4–6].

A typical match of experimental current vs. time data to the theoretical breakthrough curve for a nanofiber composite membrane (N(fibers)/PVDF) is shown in **Fig. 11** for a film 70 μm thick film with 50 vol.% Nafion. The data fit was excellent when D was fixed at $3.78 \times 10^{-7} \text{ cm}^2/\text{s}$. A summary of measured bromine species ($\text{Br}_2/\text{Br}_3^-$) diffusion coefficients for the two nanofiber composite membrane morphologies at different Nafion/PVDF compositions are listed in **Table 2**. From these results, the following conclusions can be made: (1) The $\text{Br}_2/\text{Br}_3^-$ diffusion coefficient decreases with increasing PVDF content in all nanofiber composite membranes, (2) the $\text{Br}_2/\text{Br}_3^-$ diffusion coefficients in N(fibers)/PVDF membranes were always lower than those in N/PVDF(fibers) films, with a much more pronounced dependence of diffusion coefficient on membrane PVDF content, *e.g.*, a 9-fold decrease in $\text{Br}_2/\text{Br}_3^-$ transport when the PVDF content was doubled from 35 to 70 vol.%, and (3) diffusion coefficients in all composite films were lower than that in commercial Nafion 115 sample, *e.g.*, the diffusion coefficient of N(fibers)/PVDF

membrane with 50 vol.% Nafion ($3.84 \times 10^{-7} \text{ cm}^2/\text{s}$) was ~ 3.8 -times lower than that in Nafion 115 ($1.45 \times 10^{-6} \text{ cm}^2/\text{s}$, from Table 1).

Fig. 11. Fit of experimental data (■) to the transient breakthrough model (—) for 50 vol.% N(fibers)/PVDF membranes with 70 μm thickness. The resulting value of bromine species diffusion coefficient is $3.78 \times 10^{-7} \text{ cm}^2/\text{s}$.

Table 2. Experimentally determined bromine species diffusion coefficients in Nafion/PVDF nanofiber composite membranes. All measurements were made at 25°C. Diffusion coefficients were measured for an electrolyte of 0.14 M Br_2 + 2.0 M HBr.

Composition	Thickness (μm)	Br ₂ /Br ₃ ⁻ Diffusion coefficient (cm^2/s)	
		N(fibers)/PVDF	N/PVDF(fibers)
65 vol.% Nafion 35 vol.% PVDF	50	—	—
	65	7.38×10^{-7}	9.35×10^{-7}
	75	7.00×10^{-7}	8.84×10^{-7}
50 vol.% Nafion 50 vol.% PVDF	55	3.80×10^{-7}	7.02×10^{-7}
	65	3.95×10^{-7}	6.72×10^{-7}
	70	3.78×10^{-7}	6.68×10^{-7}
40 vol.% Nafion 60 vol.% PVDF	40	2.20×10^{-7}	5.62×10^{-7}
	55	2.31×10^{-7}	5.96×10^{-7}
	60	2.07×10^{-7}	5.68×10^{-7}
30 vol.% Nafion 70 vol.% PVDF	30	0.90×10^{-7}	3.95×10^{-7}
	48	0.84×10^{-7}	4.25×10^{-7}

Measured steady-state permeabilities are plotted in **Fig. 12** as a function of Nafion volume fraction for the two types of nanofiber composite membranes and also for the solution-cast Nafion/PVDF blended films. As expected, the bromine species permeation rate decreased with increasing PVDF content, due to the combined effects of an increase in tortuosity of Nafion pathways, a decrease in the cross-sectional area for transport, and a decrease in membrane swelling. The effect of composition on permeation for nanofiber composite membranes and solution-cast Nafion/PVDF blended films was further examined and quantified using Maxwell's equation for the analysis of species permeation through barrier films containing impermeable flakes [25,26]. Assuming that PVDF is dispersed in nanofiber composite membranes as impermeable flat domains (flakes) oriented parallel to the membrane surface, the relative change in permeability with PVDF content was expressed as:

$$\frac{P_o}{P} = 1 + \frac{\alpha^2 \Phi^2}{1 - \Phi} \quad (13)$$

where P_o is the measured $\text{Br}_2/\text{Br}_3^-$ permeability of a solvent cast Nafion film with no PVDF ($5.64 \times 10^{-7} \text{ cm}^2/\text{s}$ from **Table 1**), P is the permeability of a nanofiber composite membrane, Φ is the volume fraction of PVDF in the nanofiber composite film, and α is the aspect ratio of flake-like PVDF domains (length divided by thickness). In the present analysis, the aspect ratio (α) was used as a fitting parameter to match Equation 13 separately to experimental permeabilities for N/PVDF(fibers), N(fibers)/PVDF, and solution-cast blended membranes.

Fig. 12. Steady-state permeability of bromine species ($\text{Br}_2/\text{Br}_3^-$) in dual-nanofiber composite membranes of different Nafion volume fractions at 25°C in 0.14 M Br_2 -2.0 M HBr. (○) N(fibers)/PVDF membrane; (▲) N/PVDF(fibers) membrane; (□) solution-cast Nafion/PVDF membrane; Solid lines are the best fit of the Maxwell Equation (Equation 13).

The fit of theory and measurements is shown as the solid lines in **Fig. 12** and the resulting values of α are listed in **Table 3**, where the aspect ratio of PVDF domains in the membranes follows the order: blended solution-cast films > a N(fibers)/PVDF membranes > N/PVDF(fibers). When comparing the $\text{Br}_2/\text{Br}_3^-$ permeability in nanofiber composite membranes with that of a solution-cast blended Nafion/PVDF membrane, it can be seen that the latter is lower throughout the entire membrane composition range. This difference can be attributed to lower membrane swelling and higher tortuosity of the solution-cast blended film, where tortuosity scales with α . It should also be noted that the aspect ratio (α) does not denote the size of PVDF domains, so the results in **Table 3** do not contradict the differences in membrane morphology shown by the SEMs in **Fig. 6(b-d)**.

Table 3. The effective aspect ratio (α) of PVDF domains in Nafion/PVDF nanofiber composite and solution-cast blended membranes (from force-fitting Equation 13 to the experimentally permeabilities in **Fig. 12**, where α is defined as the length/thickness ratio of the PVDF domains).

Membrane	α
N(fibers)/PVDF membrane	2.99
N/PVDF(fibers) membrane	2.00
Solution-cast blended membrane	4.14

For a polymeric membrane, species permeability is defined as the product of diffusion coefficient and partition coefficient ($P=D \times K$), according to Equation 12. In the present study, bromine species partition coefficients were back-calculated from the data in **Table 2** and **Fig. 12**. The resulting values of K are plotted as a function of Nafion vol.% in **Fig. 13** for the two different nanofiber composite membrane morphologies. For all nanofiber composite films, the partition coefficient was constant at 0.29 and equal to the partition coefficient measured for both a solution-cast Nafion membrane and a commercial Nafion 115 film. These results indicate that: (1) the $\text{Br}_2/\text{Br}_3^-$ concentration within all membranes (including Nafion 115) is much less than that in the bulk solution, as expected due to the co-ion exclusion properties of the perfluorosulfonic acid Nafion ionomer and (2) the constant value of K for all membranes (including Nafion 115) is attributed to the fact that the nanofiber composite membranes had thin ($< 2 \mu\text{m}$ thickness) surface layers of neat Nafion. With a constant partition coefficient, the decrease in $\text{Br}_2/\text{Br}_3^-$ permeability with increasing PVDF content for nanofiber composite membranes (**Fig. 12**) can now be attributed solely to a reduction in the $\text{Br}_2/\text{Br}_3^-$ diffusion coefficient. Partition coefficients for solution-cast Nafion/PVDF blended films, calculated from the data in **Table 1** and plotted in **Fig. 13**, are significantly lower than those of commercial Nafion and nanofiber-based membranes.

Additionally, these partition coefficients decrease from 0.15 to 0.075 when the PVDF content was increased from 40 vol.% to 60 vol.% due to a reduction in membrane swelling. So the decrease in $\text{Br}_2/\text{Br}_3^-$ permeability with increasing PVDF content for blended films is caused by a reduction in both the bromine species diffusion coefficient and partition coefficient.

Fig. 13. Partition coefficient of bromine species ($\text{Br}_2/\text{Br}_3^-$) in dual-nanofiber composite membranes of different Nafion volume fractions at 25°C in 0.14 M Br_2 -2.0 M HBr. (○) N(fibers)/PVDF membrane; (▲) N/PVDF(fibers) membrane; (□) solution-cast Nafion/PVDF membrane; (—) Nafion 115; (---) data guideline.

4. Conclusions

Nanofiber composite membranes were fabricated from electrospun Nafion/PVDF dual-fiber mats for use in regenerative hydrogen bromine (H_2/Br_2) fuel cells. The Nafion polymer volume fraction content of composite membranes ranged from 0.30 to 0.65. Two membrane structures were investigated: (1) an interconnecting network of Nafion nanofibers embedded in an

uncharged PVDF matrix (denoted as N(fibers)/PVDF membrane) and (2) a PVDF fiber mat embedded in a continuous Nafion matrix (N/PVDF(fibers) membrane). Both membrane structures exhibited similar in-plane conductivity, where the conductivity scaled linearly with Nafion volume fraction. N/PVDF(fibers) membranes exhibited isotropic in-plane vs. through-plane ion conductivity while anisotropic conductivity was observed for N(fibers)/PVDF membranes when the Nafion content fell below 55 vol.%. The incorporation of PVDF into the membranes restricted membrane swelling and reduced $\text{Br}_2/\text{Br}_3^-$ permeation. N(fibers)/PVDF membranes were a better barrier to $\text{Br}_2/\text{Br}_3^-$ permeation than N/PVDF(fibers) membranes. For use in a H_2/Br_2 fuel cell, a N(fibers)/PVDF membrane is preferred because the drop in its permeability for bromine species upon addition of PVDF, exceeded the drop in its ion conductivity. This is in contrast to what was observed for a N/PVDF(fibers) membrane where the drop in proton conductivity was comparable to the drop in permeability, resulting in practically no gain of selectivity (the ratio of conductivity to permeability) relative to a commercial Nafion membrane. The selectivity of N(fibers)/PVDF membranes was also higher than that of solution-cast Nafion/PVDF blended films, due to the low ion conductivity of the latter. When compared to commercial Nafion[®] 115, a N(fibers)/PVDF membrane with 40 vol.% Nafion had a modestly lower ion conductivity (36% that of Nafion) with excellent bromine barrier properties (8.3 times lower than that of Nafion 115). Thus, a nanofiber composite film with a thickness of 48 μm has an area-specific resistance equal to that of Nafion 115 ($0.13 \text{ } \Omega\text{-cm}^2$) but its $\text{Br}_2/\text{Br}_3^-$ crossover flux is 3.0 times lower than that for Nafion 115 ($1.43 \times 10^{-9} \text{ mol/s/cm}^2$ vs. $4.28 \times 10^{-9} \text{ mol/s/cm}^2$).

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