



Direct methanol fuel cell operation with pre-stretched recast Nafion®

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ABSTRACT

Direct methanol fuel cell operation with uniaxially pre-stretched recast Nafion® membranes (draw ratio of 4) was investigated and compared to that with commercial (un-stretched) Nafion®. The effects of membrane thickness (60–250 μm) and methanol feed concentration (0.5–10.0 M) on fuel cell power output were quantified for a cell temperature of 60 °C, ambient pressure air, and anode/cathode catalyst loadings of 4.0 mg cm⁻². Pre-stretched recast Nafion® in the 130–180 μm thickness range produced the highest power at 0.4 V (84 mW cm⁻²), as compared to 58 mW cm⁻² for Nafion® 117. MEAs with pre-stretched recast Nafion® consistently out-performed Nafion® 117 at all methanol feed concentrations, with 33–48% higher power densities at 0.4 V, due to a combination of low area-specific resistance (the use of a thinner pre-stretched membrane, where the conductivity was the same as that for commercial Nafion®) and low methanol crossover (due to low methanol solubility in the membrane). Very high power was generated with a 180-μm thick pre-stretched recast Nafion® membrane by increasing the cell temperature to 80 °C, increasing the anode/cathode catalyst loading to 8.0 mg cm⁻², and increasing the cathode air pressure to 25 psig. Under these conditions the power density at 0.4 V for a 1.0-M methanol feed solution was 240 mW cm⁻² and the maximum power density was 252 mW cm⁻².

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1. Introduction

DuPont's perfluorosulfonic acid Nafion® is the membrane of choice for H₂/air fuel cells that operate at a temperature ≤ 80 °C. Nafion® has also been used in direct methanol fuel cells (DMFCs), but high methanol crossover lowers the power output due to cathode depolarization. Research and development efforts have focused on new sulfonic acid-containing membrane materials for DMFCs with improved methanol barrier properties, including polysulfones, polyketones, and polyphosphazenes [1–3]. Also, Nafion® has been blended with a hydrophobic (inert) polymer, such as poly(vinylidene fluoride) or tetrafluoroethylene/hexafluoropropylene copolymer (Teflon®-FEP) [4–6], or mixed with inorganic particles [7–10] in order to slow methanol crossover. Fuel cell power densities with these new membranes were, at best, equal to that with commercial Nafion® and in many cases less power was produced due to unacceptably high IR losses (i.e., the improved methanol barrier property of the membrane was accompanied by a decrease in proton conductivity).

More recently, the present authors have reported on pre-stretched recast Nafion® for use in a direct methanol fuel cell, where uniaxial film elongation was carried out prior to polymer annealing [11]. Membrane stretching had no effect on proton conductivity (up to a draw ratio of 7, where the draw ratio is defined as the final membrane length divided by its initial length), but it did cause the methanol permeability to decrease, by a factor of 2.5 when the draw ratio was ≥ 4. In preliminary DMFC tests with 1.0 M methanol at 60 °C, elongated recast Nafion® performed significantly better than commercial Nafion® 117 due to a unique combination of high proton conductivity and low methanol permeability.

The present paper deals with a more in-depth evaluation of membrane preparation and properties and fuel cell operation with pre-stretched recast Nafion®. In particular, the following topics are covered in this paper: (i) the fabrication and properties (proton conductivity and methanol permeability) of thin and thick pre-stretched recast Nafion® membranes, (ii) the determination of methanol partition coefficients in pre-stretched Nafion® films, (iii) the effects of membrane thickness, methanol feed concentration, and methanol flow rate on fuel cell power output with pre-stretched Nafion®, and (iv) a high power output experiment with pre-stretched recast Nafion®. In a prior publication [11] we referred to our membrane material as “stretched recast Nafion®” herein, we changed this description to “pre-stretched

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recast Nafion[®],” to better characterize the fabrication process.

2. Experimental

2.1. Membranes preparation

2.1.1. Pre-stretched recast Nafion[®]

Two methods were used to fabricate pre-stretched recast Nafion[®] membranes: Method No. 1 for thin films (50–60 μm in thickness for a membrane with a draw ratio of 4, when equilibrated in water) and Method No. 2 for thicker films (130–190 μm wet thickness for a draw ratio of 4).

2.1.1.1. Method No. 1 (for thin membranes). Membranes were prepared from Nafion[®] polymer that was recovered after evaporating the solvent from a commercial Nafion[®] solution (Liquion 1115 from Ion Power, Inc.). The dried Nafion[®] material was fully dissolved in dimethylacetamide (DMAc) at room temperature and membranes were cast in a Teflon dish from the resulting 10 wt% solution. DMAc solvent was partially evaporated at 60 °C for ca. 18 h, resulting in a film that contained 10–15 wt% DMAc and was 200–300 μm in thickness. After the DMAc-swollen membrane was removed from the casting surface, it was placed in a stretching frame, heated to 125 °C, and then uniaxially elongated to a desired draw ratio. The membrane was kept in the stretching frame and heating was continued at 125 °C for 1 h to fully evaporate DMAc, followed by an annealing step at a temperature of 150–180 °C for 2 h. The membrane was removed from the stretching apparatus, boiled in 1.0 M H₂SO₄ for 1 h, and then boiled in deionized water for 1 h.

2.1.1.2. Method No. 2 (for thick membranes). In order to obtain a pre-stretched membrane with a final thickness in the 130–190 μm range (for a draw ratio of 4), the thickness of the film prior to stretching was increased to 450–600 μm . Films were cast into a Teflon disk from a 10% DMFC solution and solvent was partially evaporated at 60 °C for 48 h. The dish was then suspended above DMAc liquid in a sealed container. The container was heated to 60 °C and DMAc vapor was allowed to reabsorb into the membrane over a 24-h period. This procedure was required to insure a uniform distribution of DMAc solvent in the Nafion[®] film (without DMAc vapor re-equilibration, there was excessive drying of the membrane surfaces which resulted in membrane cracking/tearing during elongation). After the film was uniaxially stretched to a desired draw ratio at 125 °C, the membrane was vacuum-dried in the stretching frame at 125 °C for 12 h to fully evaporate residual DMAc solvent, followed by annealing at 180 °C for 2 h (a higher annealing temperature was required for the thicker pre-stretched films). The membranes were pre-treated by boiling in 1.0 M H₂SO₄ and deionized water before further use.

2.1.2. Commercial Nafion[®]

Commercial Nafion[®] 212, 115, 117, and 1110 samples (with a wet thickness of 64 μm , 160 μm , 215 μm and 320 μm , respectively) were pre-treated prior to use by boiling sequentially for 1 h in 3% H₂O₂, 1.0 M H₂SO₄, and then deionized water. All membranes (pre-stretched and un-stretched) were stored wet (in room temperature water) until further use.

2.2. Proton conductivity and methanol permeability

The proton conductivity tests (through-plane AC impedance measurements for water-equilibrated membranes at 25 °C) and methanol permeability determinations (1.0 M methanol and 60 °C)

were performed using the experimental procedures described elsewhere [3,11,12].

2.3. Methanol partition coefficient measurements

Membrane strips were immersed in 1.0 M methanol for 12–18 h (equilibration was carried out in sealed 20 ml vials that were completely filled with methanol solution). After the soak step, the membrane samples were removed from solution, quickly wiped dry, weighed, and returned to the vials. After one additional hour of soaking, the samples were removed, wiped dry, and transferred to septum-cap vials filled with deionized water (water completely filled the vials, in order to eliminate any head space where methanol vapor could accumulate). Methanol was allowed to desorb from each film for 3–5 h. Water samples were extracted from each closed vial with a syringe and analyzed for methanol by gas chromatograph (Thermo Finnigan Trace GC 2000). The membrane-phase concentration of methanol (mole g⁻¹ of solution) was determined from the measured methanol concentration in the water soak solution, the known volume of water in the vial, and the wet mass of a membrane sample after methanol equilibration.

2.4. MEA fabrication

MEAs were prepared using a two-layer catalyst structure for both the anode and cathode, where the total catalyst loading for each electrode was 4.0 mg cm⁻². The first anode catalyst layer contained 3.0 mg cm⁻² platinum–ruthenium alloy (1:1, Alfa Aesar) with 7 wt% Nafion[®] ionomer (from a 5-wt% solution, Sigma–Aldrich) which was deposited onto E-Tek A-6 ELAT/SS/NC/V2 carbon cloth. A second layer of PtRu (1.0 mg cm⁻² with 30 wt% Nafion[®] ionomer) was painted directly on the first. The two layer cathode was made using A-6 ELAT/SS/NC/V2 carbon cloth, where the first layer contained 3.0 mg cm⁻² Pt and 7 wt% Nafion[®] ionomer and the second layer contained 1.0 mg cm⁻² Pt and 40 wt% Nafion[®]. Both the anode and cathode were dried at 80 °C for 30 min and then hot pressed onto a membrane at 140 °C and 400 psi for 5 min. MEAs were soaked in 1.0 M H₂SO₄ for 12 h and washed thoroughly with de-ionized water prior to a fuel cell test. MEAs with pre-stretched recast Nafion[®] contained a single membrane or a stack of two, three, or four films, depending on the desired final membrane thickness. For the three and four membrane case, one or two pre-stretched recast Nafion[®] films were placed between two half-MEAs [3,11], made by hot pressing an anode and a cathode to separate membranes. The two membrane MEA was made in the same manner, without the inner stretched film.

2.5. Fuel cell experiments

Steady-state voltage–current density data were collected using a single cell test station (Scribner Series 890B) with mass flow and temperature control. The fuel cell (5.0 cm² geometric electrode area with single anode and cathode serpentine flow channels, 1 mm wide and 1 mm in depth) was operated at 60 °C with ambient pressure humidified air at 500 sccm. The anode feed was 0.5 M, 1.0 M, 3.0 M, or 10.0 M methanol. During a preconditioning break-in period, all MEAs except those with Nafion[®] 212 were operated for 2 h in the fuel cell test fixture at room temperature with 1.0 M methanol at a constant current density of 40 mA cm⁻². Nafion[®] 212 MEAs were preconditioned for 2 h at room temperature with 0.5 M methanol at a constant current density of 20 mA cm⁻². After the break-in period, the cell was heated to 60 °C and the preconditioning was continued for another 2 h with 1.0 M methanol. The methanol feed concentration and cell operating conditions (temperature, feed flow rates, and air backpressure) were then

appropriately fixed and the fuel cell was operated at a constant voltage of 0.4 V for 0.5 h. The steady-state current at 0.4 V was recorded, followed by collection of data for an entire voltage vs. current density plot at a scan rate of 0.05 V min⁻¹. Methanol crossover flux was determined by measuring the carbon dioxide concentration in the cathode air exhaust with a calibrated Vaisala GMM12B or GMM220A CO₂ detector.

3. Results and discussion

3.1. Membrane characterization

The critical DMFC membrane transport properties (through-plane proton conductivity and methanol permeability) for commercial Nafion[®]117, un-stretched recast Nafion[®] (draw ratio = 1), and pre-stretched recast Nafion[®] are shown in Fig. 1 (conductivities are reported at 25 °C and permeabilities at 60 °C). Proton and methanol transport in un-stretched recast and commercial Nafion[®] films were found to be the same, as would be expected. For the pre-stretched recast Nafion[®] films, however, there was a significant decrease in methanol permeability without an accompanying loss in proton conductivity. This behavior is unique for an ionomeric DMFC membrane and distinguishes pre-stretched recast Nafion[®] from any other fuel cell membrane material. Methanol permeability decreased with stretching up to a draw ratio of 4 (there was no further change in permeability for larger draw ratios), hence only membranes with this degree of elongation were used to prepare MEAs in the present study. Thin pre-stretched membranes, fabricated by Method No. 1 were less permeable to methanol than thicker films (from Method No. 2), but both thin and thick pre-stretched Nafion[®] exhibited essentially the same permeability vs. draw ratio dependence and both fabrication procedures resulted in membranes with the same proton conductivity (within experimental error). The difference in methanol permeability for Method Nos. 1 and No. 2, can not be fully explained at the present time but was tentatively associated with differences in the morphology of the DMAc-swollen recast Nafion[®] films immediately before stretching.

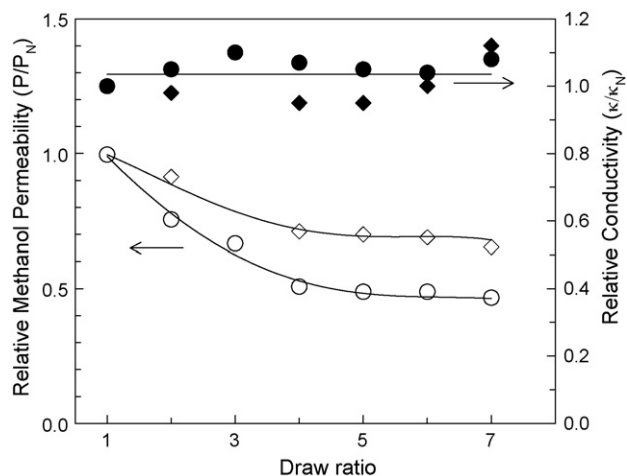


Fig. 1. Through-plane proton conductivity (water-equilibrated membranes at 25 °C) and methanol permeability (1.0 M methanol at 60 °C) as a function of draw ratio for un-stretched (draw ratio = 1) and two pre-stretched recast Nafion[®]: (●) through-plane proton conductivity of pre-stretched recast Nafion[®] (50–90 μm, made using Method No. 1); (◆) through-plane proton conductivity of pre-stretched recast Nafion[®] (120–200 μm, made using Method No. 2); (○) methanol permeability of pre-stretched recast Nafion[®] (50–90 μm); and (◇) methanol permeability of pre-stretched recast Nafion[®] (120–200 μm). κ_N and P_N are the measured proton conductivity and methanol permeability of commercial Nafion[®] 117 ($\kappa_N = 0.10 \text{ S cm}^{-1}$ at 25 °C; $P_N = 3.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 60 °C).

Rod-like polymer aggregates, which are known to be present in a Nafion[®]/DMAc solution [13], might be better aligned in a thinner cast film (prior to elongation), thus improving the stretched membrane nanostructure, with fewer molecular-level defects, better polymer chain packing, and greater polymer crystallinity upon annealing. Further investigations are planned to explain the permeability differences in thin/thick pre-stretched Nafion[®] and to elucidate the inter-relationship between membrane casting and elongation conditions, and the resultant morphology, and transport properties; such work will be the subject of a future publication. Although not shown in Fig. 1, the methanol permeability of a pre-stretched recast Nafion[®] film (60 μm in thickness) at 25 °C exhibited the same P/P_N vs. draw ratio dependence as that at 60 °C (where P_N , the methanol permeability in an un-stretched recast Nafion[®] membrane at 25 °C was $2.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$).

It is important to note that the morphological changes that lead to the desirable proton and methanol transport properties in Fig. 1 were permanent, as evidenced by long-term soak tests. For example, a pre-stretched recast Nafion[®] sample maintained its elongated physical dimensions after immersion in 10.0 M methanol at 60 °C for more than 60 days, whereas stretched commercial Nafion[®] 117 (draw ratio of 2) retracted to its original shape after a 12-h 60 °C soak in 10.0 M methanol.

To determine if the low methanol permeability in pre-stretched Nafion[®] was due to low methanol solubility in the membrane and/or a low methanol diffusion coefficient, methanol partition coefficients were measured for commercial Nafion[®] 212 and 117, and for un-stretched and pre-stretched recast Nafion[®] films. The results of these experiments are shown in Fig. 2 (for thin films made by fabrication Method No. 1). Here, the partition coefficient is defined as the ratio of the membrane phase methanol concentration to the external bulk solution concentration of methanol (both concentrations given as mole g⁻¹ of solution). The methanol partition coefficients in the two commercial Nafion[®] membranes and in un-stretched recast Nafion[®] are identical at a value of 1.05. This result is consistent with data in the literature [14–16] (within experimental accuracy) and indicates no preferential sorption of either water or methanol. In pre-stretched recast Nafion[®], there was selective absorption of water over methanol, with a decrease in the methanol partition coefficient. The shape of the curve in Fig. 2

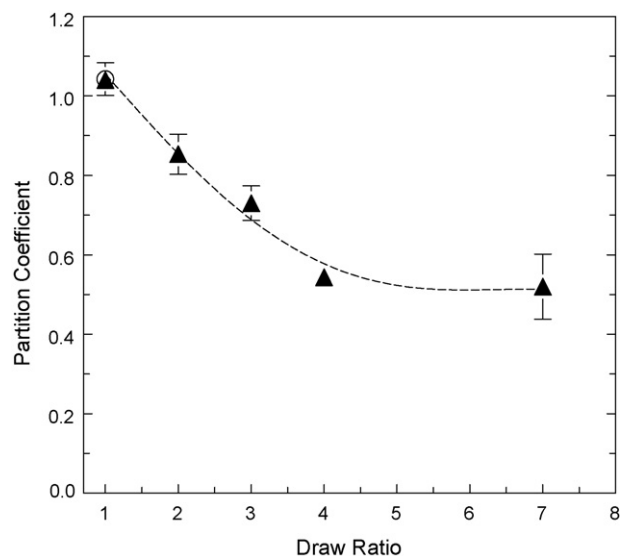


Fig. 2. Methanol partition coefficient as a function of draw ratio for commercial, un-stretched recast Nafion[®] (draw ratio 1) and pre-stretched recast Nafion[®] (made using Method No. 1). (▲) Pre-stretched recast Nafion[®]; (○) commercial Nafion[®].

mirrors the methanol permeability vs. draw ratio plot in Fig. 1 and the relative decrease in permeability with draw ratio is essentially identical to the decrease in methanol partition coefficient. Thus, it can be concluded that the methanol diffusion coefficient is independent of draw ratio in pre-stretched Nafion® and the decrease in methanol permeability is solely due to low methanol solubility at the membrane/solution interface. These results are in qualitative agreement with water self-diffusion coefficient in pre-stretched Nafion® [17], which was invariant with draw ratio and equal to that in commercial Nafion®. The solubility data are also consistent with low temperature differential scanning calorimetry results which showed that the amount of freezable water in pre-stretched Nafion® decreased and the amount of non-freezable (bound) water increased with draw ratio (up to a draw ratio of 4) [17]. Thus, the decrease in partition coefficient with draw ratio was associated with the presence of more bound water which strongly interacts with membrane fixed-charge groups in pre-stretched Nafion® and which will not be exchanged with methanol during equilibrium partitioning.

3.2. Single vs. multi-layer membrane MEAs

The effects of MEA design (a single thick membrane or a stack of thin membranes) on DMFC voltage–current density performance plots are shown in Fig. 3 (for pre-stretched Nafion® membranes of draw ratio 4). MEAs were made from one pre-stretched recast Nafion® membrane with a thickness of 185 μm , a three-layer stack of pre-stretched recast Nafion® films (three 60 μm thick membranes), and commercial Nafion® 117. The DMFC test conditions were 60 °C and 1.0 M methanol at 5 mL min⁻¹ with 500 mL min⁻¹ ambient pressure air. As can be seen, there was a significant improvement in the power output, over the entire voltage range, for the two MEAs containing pre-stretched recast Nafion®. The high open circuit voltage with pre-stretched Nafion® is indicative of low methanol crossover. Based on the methanol permeability data in Fig. 1, the three-layer stack was expected to perform better than a single pre-stretched film due to lower methanol crossover, but this was not the case. The MEA area-specific resistance, as measured by a current interrupt technique, was the same for both MEAs. The measured methanol crossover flux at the open circuit voltage

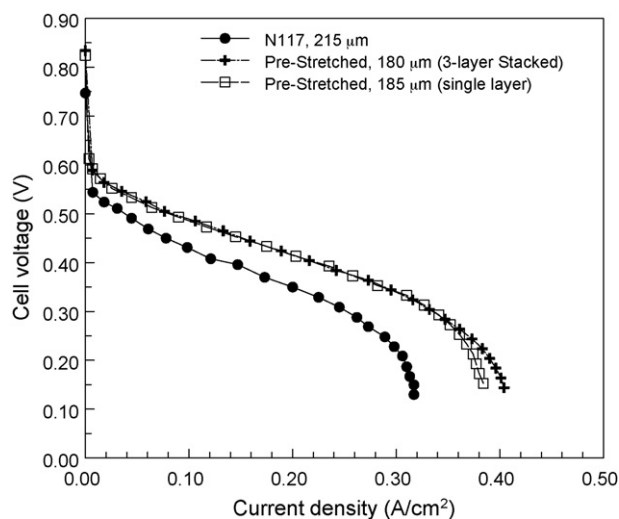


Fig. 3. Direct methanol fuel cell performance for MEAs made with pre-stretched recast Nafion® of draw ratio of 4 (a single membrane 185 μm in thickness, and a three-layer membrane stack with a total thickness of 180 μm), and with Nafion® 117. 4.0 mg cm⁻² catalyst loading for the anode and cathode, 60 °C, 1.0 M methanol, and 500 sccm humidified air at ambient pressure.

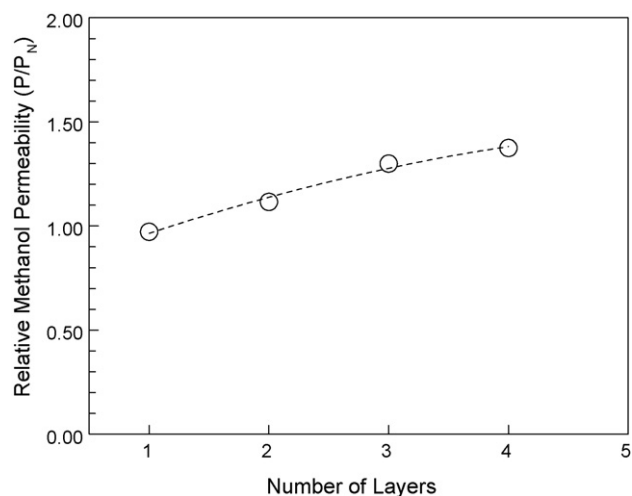


Fig. 4. Methanol permeability of stacked Nafion® 212 MEAs as a function of the number of layers in a DMFC MEA. Permeability was determined from the OCV methanol crossover. The test conditions were 60 °C, 1.0 M methanol, and 500 sccm humidified air at ambient pressure. P_N is the methanol permeability of commercial Nafion® 212 ($P_N = 3.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 60 °C).

($8.1 \times 10^{-6} \text{ mol cm}^{-2} \text{ min}^{-1}$) was the same and equal to that calculated using a membrane thickness of 185 μm and the methanol permeability data for Method No. 2 membranes in Fig. 1. The results suggested that there was an increase in the apparent methanol permeability of pre-stretched Nafion® when three thin membranes (made by Method No. 1) were stacked together in the fuel cell test fixture. To further investigate this observation, MEAs were prepared with 2, 3 and 4 layers of Nafion® 212. As shown in Fig. 4, the calculated methanol permeability at open circuit increased with the number of stacked layers (where the open circuit methanol crossover was converted to permeability using the total membrane thickness and a concentration difference across the membrane stack of 1.0 M). Such an increase in permeability was attributed to small gaps/spaces between the stacked layers where methanol diffusion was fast, thus increasing the effective methanol permeation rate (such small gaps did not affect proton conductivity, for reasons not well understood at this time). It should also be noted that the pre-stretched Nafion® current–voltage data in Fig. 3 differ slightly from those published previously by the present authors, due to a difference in the voltage scan rate (a slower and we believe more accurate scan rate of 0.05 V min⁻¹ was used in the present study vs. 0.02 V s⁻¹ in Ref. [11]).

3.3. Effect of membrane thickness on power output

There is conflicting data in the literature with regards to the optimum membrane thickness in a DMFC. Hikita et al. [18] showed that three commercial Nafion® membranes of difference thickness (Nafion® 112, 115, and 117) had a similar power density at 0.4 V, for 90 °C operation with 6 vol% (~1.5 M) methanol feed and ambient pressure air. Jung et al. [19], achieved a higher current density at 0.4 V with Nafion® 117, as compared to Nafion® 112 with 2.0 M methanol and O₂ at 50 °C. Liu et al. [20] also found that the DMFC power density at 0.4 V increased with membrane thickness at 40 °C with 4.0 M methanol and O₂ feed, whereas Kim et al. [21] reported that Nafion® 112 (the thinnest of a series of commercial Nafion® membranes that were tested) generated the highest power density at 0.4 V with 0.5 M methanol and air at 80 °C (a similar thickness effect was observed at temperatures above 110 °C when pure O₂ was supplied to the cathode with backpressure [22,23]). In light of the contradictory results in these prior studies, an in-depth study of

membrane thickness effects with pre-stretched Nafion® was performed.

A series of MEAs (4.0 mg cm^{-2} catalyst loading for the anode and cathode) were made from single and multiple layers of pre-stretched recast Nafion® (draw ratio of 4), such that the total membrane thickness ranged from $60 \mu\text{m}$ to $250 \mu\text{m}$ (e.g., single films for membranes with a thickness of $60\text{--}180 \mu\text{m}$; two stacked films for $120 \mu\text{m}$; three stacked films for $160 \mu\text{m}$, $180 \mu\text{m}$, and $200 \mu\text{m}$; four stacked films for $250 \mu\text{m}$). MEAs with four commercial Nafion® films (Nafion® 212, 115, 117, and 1110 with a wet thickness of $64 \mu\text{m}$, $160 \mu\text{m}$, $215 \mu\text{m}$, and $320 \mu\text{m}$, respectively) were also tested. DMFC voltage vs. current density data were collected at 60°C for 1.0 M methanol and ambient pressure air. Typical results are shown in Fig. 5 for five different MEAs. All of the MEAs with pre-stretched Nafion® performed well, with the $180 \mu\text{m}$ membrane working best (a high OCV, due to low methanol crossover, and good performance at high currents due to small IR losses). The caption in Fig. 5 lists the area specific resistance of each MEA, as determined from current interrupt experiments, and the methanol crossover flux at open circuit, relative to that for Nafion® 117. The MEA with a single sheet of pre-stretched recast Nafion® ($60 \mu\text{m}$ wet thickness) did not perform well at low currents due to high methanol crossover, but at high currents it out-performed commercial Nafion®, with a maximum power density of 103 mW cm^{-2} at 0.28 V , as compared to 76 mW cm^{-2} at 0.31 V for Nafion® 117 and 94 mW cm^{-2} at 0.26 V for Nafion® 212 (the Nafion® 212 data are not shown in Fig. 5).

The results of the membrane thickness experiments are summarized in Fig. 6 where the measured steady-state power density at 0.4 V is plotted against membrane thickness. All data with pre-stretched Nafion® (single and multiple membrane MEAs; thin and thick films made by Method Nos. 1 and 2) lie on the same parabolic curve. The data show that all of the pre-stretched recast Nafion® membranes, other than the $60 \mu\text{m}$ thick film, performed better than any commercial (un-stretched) Nafion® material. Within the accuracy of the fuel cell tests, the optimum thickness of stretched recast Nafion® for the DMFC operating conditions in this study was in the range of $130\text{--}180 \mu\text{m}$ (either single or multiple membrane MEAs),

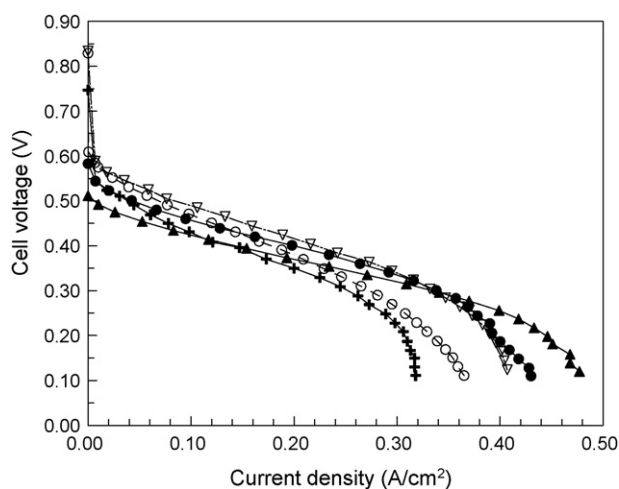


Fig. 5. Methanol fuel cell performance for MEAs made with pre-stretched recast Nafion® of different thicknesses and with Nafion® 117. 4.0 mg cm^{-2} catalyst loading for the anode and cathode, 60°C , 1.0 M methanol, and 500 sccm humidified air at ambient pressure: + Nafion® 117 ($215 \mu\text{m}$, 0.20 ohm cm^{-2} sheet resistance, OCV crossover flux = 1). Pre-Stretched recast Nafion®: (▲) $60 \mu\text{m}$ ($0.065 \text{ ohm cm}^{-2}$, OCV crossover flux = 1.81); (●) $90 \mu\text{m}$ ($0.080 \text{ ohm cm}^{-2}$, OCV crossover flux = 1.26); (▽) $180 \mu\text{m}$ (0.17 ohm cm^{-2} , OCV crossover flux = 0.83); and (○) $250 \mu\text{m}$ (0.21 ohm cm^{-2} , OCV crossover flux = 0.68).

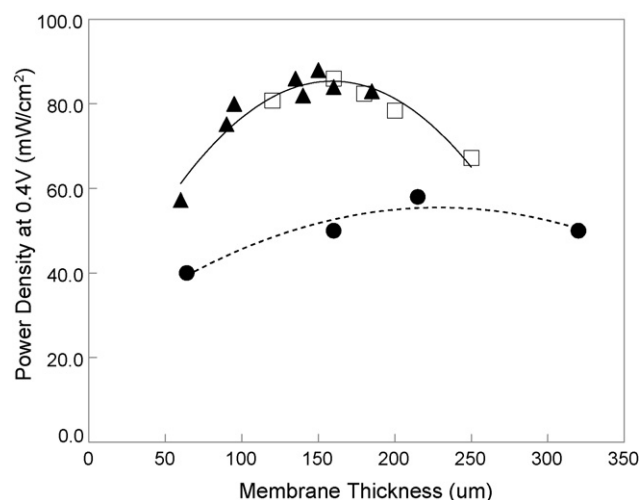


Fig. 6. Effect of membrane thickness on the steady-state DMFC power density at 0.4 V , 1.0 M methanol, 60°C , 4.0 mg cm^{-2} catalyst loading for the anode and cathode, 500 sccm air at ambient pressure. (▲) Pre-stretched recast Nafion® (single membrane MEA); (□) pre-stretched recast Nafion® (multiple stacked membranes in an MEA); and (●) commercial Nafion® membrane.

with a power density at 0.4 V of 84 mW cm^{-2} , which was 45% higher than that achieved with the optimal commercial Nafion® material (Nafion® 117, with a wet thickness of $215 \mu\text{m}$ and a power density of 58 mW cm^{-2}). The decrease in power at thicknesses greater than the optimum was associated with membrane IR losses, whereas high methanol crossover caused the power to decrease when the membrane thickness was less than the optimum.

The generally higher power densities for various membrane thicknesses of pre-stretched recast Nafion®, as compared to commercial Nafion®, was associated with the combined beneficial effects of a lower area-specific resistance and lower methanol crossover. For example, the MEA area-specific resistance at the optimal pre-stretched recast Nafion® thickness of $180 \mu\text{m}$ was 15% less than that of Nafion® 117 (see caption in Fig. 5 for resistance data). Similarly, the pre-stretched recast Nafion® MEA was a better methanol barrier than Nafion® 117, as shown in Fig. 7, where methanol crossover flux for Nafion® 117 and pre-stretched recast Nafion® (draw ratio 4, three-layer stack $180 \mu\text{m}$ film) is plotted as a function of current density during fuel cell operation. At

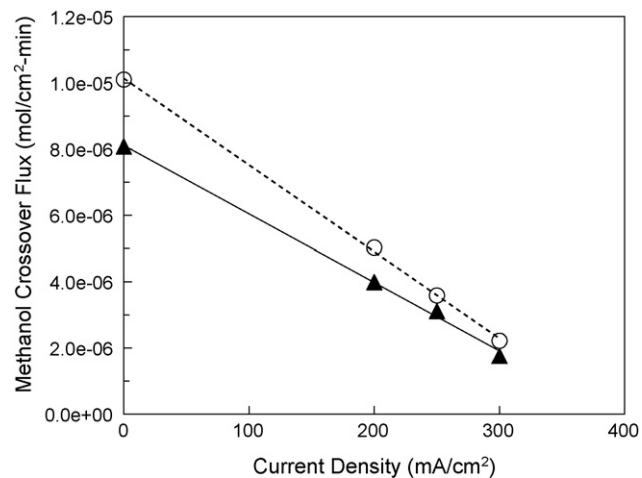


Fig. 7. Effect of current density on methanol crossover flux for Nafion® 117 and pre-stretched recast Nafion® (three-layer stack, $180 \mu\text{m}$ thickness, draw ratio of 4). 1.0 M methanol, 60°C , 4.0 mg cm^{-2} anode and cathode catalyst loading, 500 sccm air at ambient pressure. (▲) Pre-stretched recast Nafion®; (○) Nafion® 117.

0.4 V, which corresponding to 145 mA cm^{-2} for Nafion® 117 and 210 mA cm^{-2} for the $180 \mu\text{m}$ pre-stretched recast Nafion® MEA (see Fig. 5), the results in Fig. 7 indicate that the methanol crossover flux with pre-stretched Nafion® was 41% lower than that in Nafion® 117.

3.4. Effect of methanol feed concentration and flow rate on power output

The effect of methanol feed concentration on DMFC power density at 0.4 V was determined at 60°C for methanol feed solutions of 0.5 M, 1.0 M, 3.0 M, and 10.0 M, where the catalyst loading for each electrode was fixed at 4.0 mg cm^{-2} and the air flow rate was 500 sccm (at ambient pressure). During these experiments, the methanol flow rate was varied in the range of $0.02\text{--}18 \text{ mL min}^{-1}$ to find that combination of concentration and flow rate (for the single serpentine flow channel in the fuel cell test fixture) which maximized the power density at 0.4 V.

The results of these experiments (power density at 0.4 V vs. feed concentration) for pre-stretched recast Nafion® (draw ratio of 4, three-layer stack with a total wet thickness of $180 \mu\text{m}$) and Nafion® 117 are shown in Figs. 8 and 9. For all methanol concentrations, MEAs with pre-stretched recast Nafion® out-performed Nafion® 117, with 33–48% higher power densities. The optimum methanol feed concentration for Nafion® 117 was in the 1–3 M range, which agrees with results in the literature [24–26]. For pre-stretched recast Nafion®, the optimum methanol concentration was also in the same range. In the course of collecting the data in Fig. 8, the effect of flow rate on power density, for a given methanol feed concentration was quantified. The results in Fig. 9 indicate that there is an optimum flow rate for a given methanol feed concentration. Additionally, the power density at 0.4 V was less sensitive to flow rate at 0.5 M and 1.0 M methanol feed concentrations. Plots similar to those in Fig. 9 were obtained for Nafion® 117, with all curves shifted downward and slightly to the left (i.e., power densities were lower for Nafion® 117 and a lower flow rate was needed to maximize power at a given feed concentration because the methanol crossover was higher than that in pre-stretched recast Nafion®). The lower DMFC performance (power density) at the low flow rates was associated with depletion of methanol before the feed solution exited the serpentine anode flow channel, thus a portion of the anode was not being fully utilized for electrochemical oxidation of methanol. At high flow rates, there was incomplete consumption of

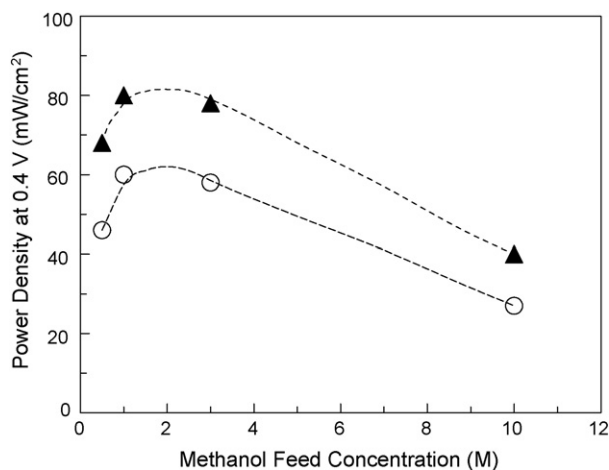


Fig. 8. Effect of methanol feed concentration on the DMFC power density at 0.4 V. 60°C cell temperature, 4.0 mg cm^{-2} catalyst loading for the anode and cathode, 500 sccm air at ambient pressure. (\blacktriangle) Pre-stretched recast Nafion® (draw ratio of 4, three-layer stack, with a total thickness of $180 \mu\text{m}$); (\circ) Nafion® 117.

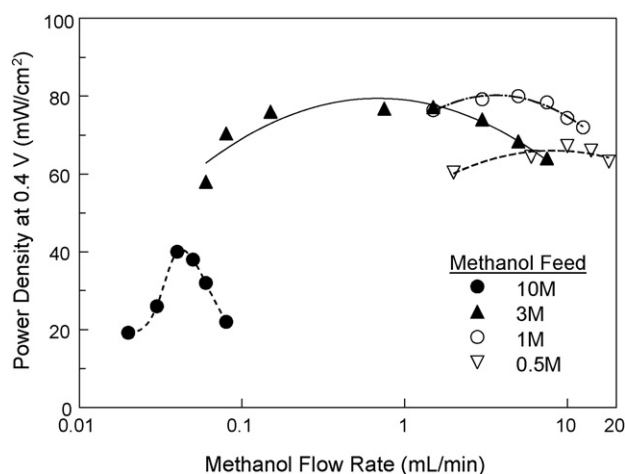


Fig. 9. Effect of methanol flow rate and feed concentration on DMFC power density at 0.4 V for a three-layer stack of pre-stretched recast Nafion® (draw ratio 4 and thickness of $180 \mu\text{m}$). 60°C cell temperature, 4.0 mg cm^{-2} catalyst loading for the anode and cathode, 500 sccm air at ambient pressure.

methanol within the fuel cell test fixture and the concentration of methanol in contact with the membrane was high, resulting in high methanol crossover and cathode depolarization. Such deterioration of performance was more severe when the feed concentration of methanol was high, as evidenced from Fig. 9. Although the maximum power density at 1.0 M and 3.0 M methanol feed were essentially identical, they were achieved at different methanol flow rates.

3.5. High power density experiments

To further demonstrate the superior performance of pre-stretched recast Nafion® in a DMFC, fuel cell tests were performed at conditions that would insure a very high power density, i.e., the MEA anode and cathode catalyst loadings were increased from 4.0 mg cm^{-2} to 8.0 mg cm^{-2} (using a two-layer electrode construct, as described in Section 2.4, with twice the catalyst loading in each layer), the temperature was increased from 60°C to 80°C , and the cathode air pressure was increased from ambient to 25 psig. Experimental DMFC results for Nafion® 117 and pre-stretched recast Nafion® (a stack of three membranes, $180 \mu\text{m}$ total thickness, a

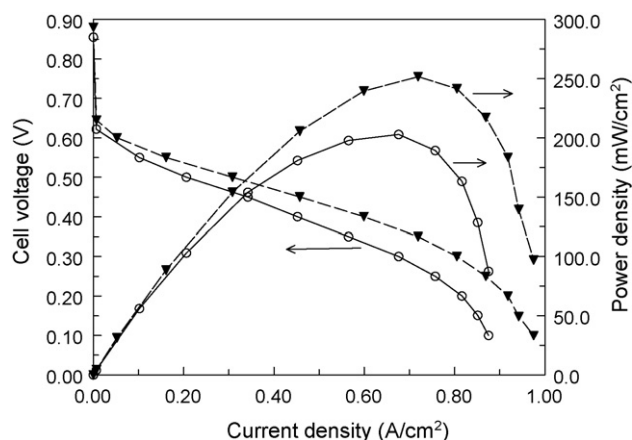


Fig. 10. Methanol fuel cell performance with air backpressure. (\blacktriangle) Pre-stretched recast Nafion® (three-layer stack, draw ratio 4, $180 \mu\text{m}$ thickness); (\circ) Nafion® 117 ($215 \mu\text{m}$ thickness). 1.0 M methanol, 80°C , 8.0 mg cm^{-2} catalyst loading, 500 sccm air at 25 psig.

Table 1

Comparison of power densities during direct methanol fuel cell tests with pre-stretched recast Nafion® (three-layer stack, 180 μm thick, a draw ratio of 4) and Nafion® 117

	Power density (mW cm ⁻²)			
	Pre-stretched recast Nafion®		Nafion® 117	
	@ 0.4 V	Maximum	@ 0.4 V	Maximum
4.0 mg cm ⁻² , 60 °C	86	107	56	72
4.0 mg cm ⁻² , 80 °C	170	176	112	137
8.0 mg cm ⁻² , 60 °C	110	117	82	91
8.0 mg cm ⁻² , 80 °C	204	207	144	155
4.0 mg cm ⁻² , 80 °C, 25 psig backpressure	197	202	143	153
8.0 mg cm ⁻² , 80 °C, 25 psig backpressure	240	252	181	203

Anode feed: 1.0 M methanol; cathode feed: 500 sccm humidified air.

draw ratio of 4) under these conditions are shown in Fig. 10, where cell voltage and power density are plotted against current density. Again, a very obvious and significant improvement in DMFC performance was observed for the pre-stretched recast Nafion® MEA; the open circuit potential was nearly 900 mV and the maximum power density was 252 mW cm⁻² (24% higher than the maximum with Nafion® 117). Additional data from these experiments are summarized in Table 1, where the effects of cell temperature (60 °C vs. 80 °C), catalyst loading (4.0 mg cm⁻² vs. 8.0 mg cm⁻²) and pressure (ambient vs. 25 psig) are contrasted separately in terms of the power density at 0.4 V and the maximum power density. As can be seen, pre-stretched recast Nafion® at 80 °C and 4.0 mg cm⁻² outperformed Nafion® 117 at the same temperature with twice the catalyst loading. Similarly, for 8.0 mg cm⁻² loading and 80 °C, a pre-stretched recast Nafion® MEA operating at ambient pressure generated more power than Nafion® 117 with backpressure.

4. Conclusions

Pre-stretched recast Nafion® membranes were prepared, characterized, and fabricated into membrane–electrode–assemblies for direct methanol fuel cell experiments. The low methanol permeability in pre-stretched Nafion®, as compared to that in a commercial Nafion® film, was associated with a decrease in the methanol partition coefficient, which decreased with increasing draw ratio up to a draw ratio of 4. Direct methanol fuel cell experiments were carried out with MEAs containing single and multiple layers of pre-stretched recast Nafion® with a draw ratio of 4. The effects of membrane thickness and methanol feed concentration on DMFC power density were determined and the DMFC performance was compared to that with commercial Nafion® films. For a feed solution of 1.0 M methanol at 60 °C with 500 sccm air at ambient pressure (4.0 mg cm⁻² catalyst loading for the anode and cathode), the optimum thickness for pre-stretched recast Nafion® was in the range of 130–180 μm, where the steady-state power density at 0.4 V was 84 mW cm⁻², as compared to commercial Nafion® 117, which generated only 58 mW cm⁻². Either a stack of three membranes or a single film was employed to achieve the optimal 130–180 μm thickness.

The effect of methanol feed concentration (0.5 M, 1.0 M, 3.0 M, and 10.0 M) on DMFC steady-state power output was determined for MEAs containing a three-layer stack of pre-stretched recast Nafion® (180 μm thickness) with 4.0 mg cm⁻² anode and cathode loadings, a cell temperature of 60 °C, and 500 sccm humidified air at ambient pressure. The highest power output at 0.4 V occurred when the feed concentration was in the 1–3 M range. Over the entire methanol feed concentration range, the pre-stretched recast Nafion® MEA outperformed Nafion® 117, with 33–48% higher power densities.

Very high power was generated in a DMFC with pre-stretched recast Nafion® (three-layer stack with a total wet thickness of 180 μm) by increasing the temperature (to 80 °C), cathode air backpressure (to 25 psig), and catalyst loading (to 8.0 mg cm⁻² for the anode and cathode). Under these conditions, the steady-state power density at 0.4 V and the maximum power density (for 1.0 M methanol) were 240 mW cm⁻² and 252 mW cm⁻², respectively, as compared to 181 mW cm⁻² and 203 mW cm⁻² for an MEA with Nafion® 117. DMFC performance with pre-stretched recast Nafion® at 4.0 mg cm⁻² anode/cathode catalyst loading and 80 °C was better than Nafion® 117 at 80 °C with 8.0 mg cm⁻² catalyst. Also, with a loading of 8.0 mg cm⁻² and a cell temperature of 80 °C, a pre-stretched recast Nafion® MEA (180 μm wet thickness) operating at ambient pressure generated more power than Nafion® 117 with 25 psig backpressure.

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