PRE-STRETCHED RECAST NAFION FOR
DIRECT METHANOL FUEL CELLS

by
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*We also certify that written approval has been obtained for any proprietary material contained therein.
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Pre-Stretched Recast Nafion for Direct Methanol Fuels

Abstract

by

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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/cm². Pre-stretched recast Nafion in the 130-180 μm thickness range produced the highest power at 0.4 V (84 mW/cm²), as compared to 58 mW/cm² 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/cm², 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/cm² and the maximum power density was 252 mW/cm².
Water uptake and mobility data were collected and analyzed for pre-stretched films with draw ratios ranging from 1 to 7 in order to better understand the transport characteristics and fuel cell performance of these materials. Macroscopic gravimetric water uptake and the water self diffusion coefficient (by NMR) in pre-stretched films were found to be identical to that in commercial Nafion 117 films, regardless of the extent of elongation. The ratio of freezable/nonfreezable water in pre-stretched recast Nafion, the water electro-osmotic drag coefficient, and the spin-lattice relaxation time constant of deuterated water, however, decreased with increasing film elongation, up to a draw ratio of 4. The combined water results indicated that there are a greater number of smaller ionic/hydrophilic domains in pre-stretched recast Nafion, as compared to commercial Nafion. This result was confirmed by transmission electron microscopy of pre-stretched membrane cross sections. Equilibrium methanol sorption experiments revealed that the low methanol permeability in pre-stretched recast Nafion was associated with a decrease in the methanol partition coefficient.
1. Introduction

1.1 What is a Fuel Cell

A fuel cell is a device that converts the chemical energy of fuel directly into DC electricity. The components of a fuel cell include an anode, a cathode and an ionic conducting electrolyte that separates the two electrodes. Fuel, e.g., hydrogen or methanol, is fed continuously to the anode where the oxidation reaction occurs while the oxidant (oxygen or air) is supplied to the cathode where the reduction reaction occurs. During fuel cell operation, the fuel is oxidized to release ions and electrons. The ions migrate from one electrode to the other through the ionically conductive electrolyte while the electrons travel from the anode to the cathode through an external circuit, creating an electric current. Fuel cells have many unique characteristics that make them attractive:[1]

i. Promise of high efficiency—The efficiency of fuel cells is higher than that of conventional power sources and internal combustion engines where the maximum efficiency is dictated by the Carnot limit.

ii. Promise of low emission—The only exhaust from a hydrogen fuel cells is water.

iii. Promise of long life—Unlike batteries, the fuel cell is capable of producing electrical energy as long as reactants are supplied to the electrodes.

iv. Quiet and simple—Because fuel cells do not have moving parts, they are inherently quiet. More power may be generated simply by the combination of several fuel cells into a stack configuration. Mass produced fuel cells may be significantly less expensive than traditional power plants.
Variety—Fuel cells may be made from microwatt to megawatt sizes. Such an advantage makes them useful in a variety of applications, from powering electronic devices to providing electricity to the grid.

Usually distinguished by the electrolyte material, a variety of different fuel cells exist, including alkaline fuel cells (AFC), solid oxide fuel cells (SOFC), molten carbonate fuel cells (MCFC), phosphoric acid fuel cells (PAFC), hydrogen/oxygen proton exchange membrane fuel cells (PEMFC), and direct methanol fuel cells (DMFC) (Table 1.1.) [2]. Among them, PEMFC and DMFC have drawn the most attention because of their simplicity, viability, quick start-up and low weight and volume. Both PEMFC and DMFC employ a “membrane-electrode assembly” (MEA) structure that consists of a polymeric cation exchange membrane with both sides bonded to a very thin layer of catalyst electrodes. The major difference between PEMFC and DMFC lies in the fact that a PEMFC uses hydrogen as fuel whereas DMFC employs methanol as the fuel.

### 1.2 Details on Direct Methanol Fuel Cell (DMFC)

A schematic diagram of a DMFC is shown in Figure 1.1 During DMFC operation, methanol is oxidized electrochemically at the anode to produce protons, electrons and carbon dioxide. Protons migrate through the membrane to the cathode where they react with oxygen and electrons to generate water. Electrons produced at the anode move through the external circuit and generate a electrical current. For DMFCs, the half cell and overall reactions are as following:
## Table 1.1. Different types of fuel cells

<table>
<thead>
<tr>
<th>Fuel cell type</th>
<th>Electrolyte</th>
<th>Conducting ions</th>
<th>Operating temperature (°C)</th>
<th>Fuels</th>
<th>Oxidant</th>
<th>Efficiency/ application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline</td>
<td>Potassium hydroxide (KOH)</td>
<td>OH⁻</td>
<td>50~200</td>
<td>Hydrogen</td>
<td>Oxygen</td>
<td>50~70%/ space, military</td>
</tr>
<tr>
<td>Solid oxide</td>
<td>Ceramic oxide</td>
<td>O₂⁻</td>
<td>900~1000</td>
<td>Hydrogen, natural gas</td>
<td>Oxygen/air</td>
<td>45~60%/ stationary power, office</td>
</tr>
<tr>
<td>Molten carbon</td>
<td>Alkali-carbonates (Li,K)CO₃</td>
<td>CO₃²⁻</td>
<td>650~700</td>
<td>Hydrogen, reformed methane</td>
<td>Oxygen/air</td>
<td>40~55%/ stationary power</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>Phosphorous (H₃PO₄)</td>
<td>H⁺</td>
<td>100~200</td>
<td>Hydrogen</td>
<td>Oxygen/air</td>
<td>35~50%/ stationary power, office</td>
</tr>
<tr>
<td>H₂/O₂ Proton exchange membrane</td>
<td>Solid polymer membrane</td>
<td>H⁺</td>
<td>60~100</td>
<td>Hydrogen</td>
<td>Oxygen/air</td>
<td>35~60%/ automobiles, portable power</td>
</tr>
<tr>
<td>Direct methanol</td>
<td>Solid polymer membrane</td>
<td>H⁺</td>
<td>60~100</td>
<td>Methanol solution</td>
<td>Oxygen/air</td>
<td>35~40%/ portable power, military, UPS</td>
</tr>
</tbody>
</table>
Figure 1.1. Cell components and reactions of Direct Methanol Fuel Cell
Anode: \[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \]

Cathode: \[ \frac{3}{2} \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \]

Overall: \[ \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad E_{\text{cell}}^0 = 1.21 \text{ V} \]

DMFCs do not have the fuel storage problems, as do PEMFCs when operate on hydrogen gas. Methanol is an attractive fuel because it is a liquid under atmospheric conditions and has a higher volumetric energy density than hydrogen. Methanol is also easier than hydrogen gas to transport and it is relatively easy to modify the current fuel distribution infrastructure to deliver methanol to consumers (hydrogen fuel needs to either be stored at very high pressures or an onboard fuel reformer is needed to convert a liquid fuel into hydrogen). Furthermore, since methanol is usually fed with large amount of water to the anode, it also avoids complex humidification and thermal management problem associated with a PEMFC [3]. These distinct characteristics make DMFCs an exciting technology for portable electronics, including cellular phones and laptop computers, and for auxiliary power for instrumentation.
1.3 Membranes for Direct Methanol Fuel Cells

At the heart of DMFC is a polymeric proton exchange membrane that has some unique capabilities, namely [4] :

i. It physically separates the anode and cathode to prevent an electrical short circuit.

ii. It prevents the fuel from mixing with the oxidant to prevent a chemical short circuit.

iii. It provides a facile pathway for the flow of protons.

The general requirements of a proton exchange membrane in a DMFC are as following [4, 5] :

i. High ionic conductivity and zero electronic conductivity under cell operating conditions.

ii. Low methanol and oxidant crossover, i.e. low methanol and oxygen diffusion coefficients in the membrane.

iii. High chemical and mechanical durability, especially at elevated temperatures.

iv. Good mechanical strength, preferably with resistance to swelling.

v. Interfacial compatibility with the catalyst layers in an MEA.

vi. Low cost.

Among many membranes investigated for DMFC use, Nafion® has been the most studied. Figure 1.2 shows the chemical structure of Nafion. Its polytetrafluoroethylene (PTFE) backbone provides high chemical resistance whereas the side chains, which consist of perfluorinated vinyl polyethers attached to
Figure 1.2. Chemical structure of Nafion (perfluorosulfonic acid – PFSA)
the PTFE backbone through an ether oxygen and terminate in sulfonic acid groups, 
(SO$_3$H), give Nafion its proton exchange capability. Although Nafion has a 
relatively high proton conductivity (0.1 S/cm at 25°C), it does not perform well in 
DMFCs because of its high methanol permeability. The high methanol crossover has 
several unfavorable effects on DMFC operation [3-5] :

i. A drop in fuel efficiency due to the consumption of methanol and oxygen 
without electricity generation.

ii. A loss of voltage efficiency because of depolarization (methanol oxidation 
at the cathode leading to depolarization of the oxygen electrode).

iii. Poisoning of the cathode catalyst (platinum) caused by carbon monoxide, 
generated from the partial oxidation of methanol on the cathode.

iv. Excessive water generation at the cathode, due to the oxidation of the 
permeated methanol, which blocks the electro-catalyst reaction sites.

Numerous materials have been investigated as a replacement for Nafion in 
DMFCs, including sulfonated polysulfones, polyimides, polyphosphazenes, and 
poly(ketones) [6-10]. In some cases, these polymers were crosslinked, blended with 
methanol barrier materials, or impregnated into an inert hydrophobic support [11-15]. 
Other approaches to lower the methanol permeation in Nafion include incorporating 
the inorganic particles (e.g., silica, titanium oxide, zeolites, and montmorillonite clay) 
[16-19] and blending with a inert (hydrophobic) polymer such as poly(vinylidene 
fluoride) [20, 21] or Teflon FEP [22]. In all of these studies, a reduction on the 
methanol permeability was always accompanied by a drop in the proton 
conductivity of the membranes.
1.4 Prior Work on Pre-Stretched Recast Nafion

In a previous study [23], a promising DMFC membrane, pre-stretched recast Nafion, was prepared by uniaxially elongating recast Nafion prior to polymer annealing. Membrane stretching had no effect on proton conductivity (up to a draw ratio of 7), but it did cause the methanol permeability to decrease up to 50% when the draw ratio was ≥ 4 [23]. DMFC power densities with pre-stretched recast Nafion (draw ratio of 4) were 50% higher than those with commercial Nafion 117, at 60°C with 1.0 M methanol and ambient pressure air [23]. The key innovative membrane fabrication steps were film stretching prior to polymer annealing and annealing the film under tension. Film elongation without annealing or annealing prior to stretching did not produce a membrane with good DMFC properties. Without annealing, recast membranes lacked the requisite mechanical properties and stretched recast membranes retracted to their original shape after a few hours of exposure to a hot methanol solution if film elongation were carried out after polymer annealing. The previous work focused primarily on pre-stretched recast Nafion with a thickness up to 60 µm (a draw ratio of 4). A single layer membrane of such thickness would not achieve a satisfactory DMFC performance (methanol crossover would be too high). So thicker pre-stretched membranes would be desirable. Additionally, the prior study only measured proton conductivity and methanol permeability, other properties of the membrane were not determined.

1.5 Water Transport in Nafion®

The uptake and mobility of water within an ion-exchange membranes is intimately related to proton conduction, electro-osmotic drag, methanol permeability,
and the film’s mechanical properties [24]. In Nafion, there is nano-phase segregation of the nonpolar fluorinated (Teflon®-like) backbone and the hydrophilic side chains (which terminate in sulfonic acid cation-exchange groups) prior to and during exposure to water. The hydrophilic domains in a fully hydrated film form an interconnecting proton conductive network with a characteristic dimension of ≈5 nm [25], whereas the semi-crystalline hydrophobic phase imparts mechanical strength to the membrane. Various models have been proposed to describe the nano-morphology of water-swollen Nafion, including a network of interconnecting water-filled inverted spherical micelles [25, 26], layered lamella [27, 28], rod-like structures [29-31] and, more recently, inverted-micelle cylinders [32], where the 5 nm dimension corresponds to the diameter of the sphere of cylindrical micelle or the distance between lamella sheets. Within Nafion’s hydrophilic domains, researchers have broadly identified two states of water [23]: (i) freezable water (water that is not or only weakly interacting with polymer fixed charges and which exhibits freezing/melting transitions in differential scanning calorimetry) and (ii) non-freezing water (water that is strongly bound to the polymer backbone or the ionic groups associated with the polymer).

1.6 Objectives of the Master’s Thesis

In this Master’s degree research project, there are three specific aims:

First, a method was developed to prepare 130~190 µm thick pre-stretched recast Nafion films (for the membrane with a draw ratio of 4). A more in-depth evaluation of direct methanol fuel cell operation with pre-stretched recast Nafion was performed, where the effects of membrane thickness and methanol feed concentration on fuel cell power output were compared to that with commercial
Nafion films. High power output experiments with pre-stretched recast Nafion in a DMFC were also performed.

Second, four water sorption/transport experiments were carried out to better study the extent of water adsorption and the physical states of water in pre-stretched recast Nafion membranes: macroscopic equilibrium water uptake, low temperature differential scanning calorimetry of water-equilibrated films, water self-diffusion coefficient as determined by pulsed-field gradient NMR and spin-lattice relaxation time of deuterated water (carried out by Dr. Jun. Lin), and the measurement of the electro-osmotic drag coefficient of protons in fully hydrated pre-stretched recast films. The water data was combined with transmission electron micrographs of membrane cross section (carried out by Dr. Zhiqing) to provide the insights into the nano-morphology of pre-stretched recast Nafion and the interaction of water molecules with the membrane, which in turn will shed light on the performance properties of such films when they are used in a DMFC.

Third, equilibrium methanol sorption experiments were performed to reveal whether the unusual reduction of methanol crossover in the pre-stretched recast Nafion films is due to a lower methanol partition coefficient or a decrease in methanol diffusivity inside the membrane.
2. Experimental

2.1 Membrane Preparation

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 2~7, when equilibrated in water) and Method No. 2 for thicker films (130-190 µm wet thickness for a draw ratio of 4).

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 approximately 18 hours, resulting in a film that contained 10-15 wt% DMAc and was 200-300 µm in thickness. After the membrane was removed from the casting dish, it was placed in a stainless steel stretching frame, heated to 125°C, and then uniaxially elongated to a desired draw ratio (where the draw ratio is defined as the final membrane length divided by its initial length). The membrane was kept in the stretching frame and residual DMAc was evaporated at 125°C for 1 hour, followed by polymer annealing at 150-180°C for 2 hours. The membrane was removed from the stretching apparatus, boiled in 1.0 M H₂SO₄ for one hour, and then boiled in deionized water for one hour.

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 partially dried film prior to stretching was increased to 450-600 µm. Films were cast into a Teflon disk from a 10% DMAc solution and solvent was partially evaporated at 60°C for 48 hours. 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 hour period. This procedure was required to obtain a uniform distribution of DMAc solvent in the Nafion film (without vapor re-equilibration, there was excessive drying of the membrane surfaces which resulted in membrane cracking during elongation). After the film was uniaxially stretched at 125°C, the membrane was vacuum-dried in the stretching frame at 125°C for 12 hours to fully evaporate residual DMAc solvent, followed by annealing at 180°C for 2 hours (a higher annealing temperature was required for the thicker pre-stretched films). The membranes were pre-treated by boiling for one hour in 1.0 M H₂SO₄ and boiling in deionized water for one hour before further use.

Commercial Nafion—Commercial Nafion 212, 115, 117 and 1110 samples (with a wet water-equilibrated thickness of 64 µm, 160 µm, 215 µm and 320 µm, respectively) were pretreated prior to use by boiling sequentially for one hour in 3% H₂O₂, 1.0 M H₂SO₄, and then deionized water. All membranes (pre-stretched and unstretched) were stored in deionized water at room temperature until further use.

2.2 Equilibrium, Macroscopic Water Uptake

Equilibrium absorption of deionized water in membranes was determined at room temperature. The wet weight (W_	ext{wet}) was measured immediately after
removing residual water from the film surfaces. Membrane dry weight ($W_{dry}$) was obtained after drying at 120°C for 1 hour. Water uptake, given as the number of water molecules per sulfonic acid site ($\lambda$), was calculated from

$$\lambda(H_2O/SO_3^-) = \left[ \frac{W_{wet} - W_{dry}}{W_{dry}} \right] \frac{1}{[IEC][MW_w]}$$

Eq (1)

where IEC denotes the membrane ion-exchange capacity (0.909 x 10^{-3} mol/g for Nafion) and MW$_w$ is the molecular weight of water (18 g/mol).

2.3 Proton Conductivity

In-plane and through-plane proton conductivity of water equilibrated pre-stretched recast and unstretched Nafion membranes were measured at room temperature by an ac impedance technique (Agilent 4338 milliohm meter, with all measurements made at 1kHz), using a custom-build open-frame two-electrode conductivity cell. For the through-plane measurements, membranes were stacked together with a thickness of at least 1mm to minimize surface capacitance effects (Preliminary through-plane conductivity of stacked commercial Nafion membranes was proved successful by using such an approach [22]).

2.4 Methanol Permeability

Methanol permeability in pre-stretched recast Nafion was measured at 60°C using a two-compartment glass diffusion cell (Figure 2.1) [33]. The membrane was clamped vertically between the two compartments, one of which was filled with 1.0M
Figure 2.1. Experimental apparatus used for methanol permeability measurements
methanol solution. The other (receiving) compartment contained deionized water. Concentrations of methanol in the receiving compartment were collected in real time by circulating continuously the receiving compartment solution through a differential refractometer, Data was collected using Personal DaqView acquisition software. Methanol permeability (P) was found to from slope of the following plot derived from Fick’s first law [33]:

\[
\ln \left[ \frac{1}{1 - \frac{C_R(t)}{C^O_L} \left(1 + \frac{V_R}{V_L}\right)} \right] \quad \text{VS} \quad t
\]

where \( C_R(t) \) is the methanol concentration in the receiving compartment at a given time \( t \) after the start of a permeation experiment, \( C^O_L \) is the initial methanol concentration in the feed compartment, \( V_L \) is the solution volume in the upstream methanol compartment of the permeation cell, \( V_R \) is the total volume in the downstream (receiving) compartment including the refractometer recirculation loop. The calculated slope was then inserted into the following permeability formula

\[
P = \frac{(\text{Slope}) \times \delta}{A \times \left( \frac{1}{V_L} + \frac{1}{V_R} \right)} \quad \text{Eq (2)}
\]

where \( A \) is the membrane area and \( \delta \) is the water-equilibrated membrane thickness.
2.5 Membrane-Electrode-Assembly (MEA) Fabrication

A two-layer catalyst structure was used for the anode and cathode, where the total catalyst loading for each electrode was 4.0mg/cm². The first anode catalyst layer contained 3.0 mg/cm² platinum-ruthenium alloy (1:1, Alfa Aesar) and 7 wt% dry Nafion ionomer (from a 5 wt% solution, Sigma-Aldrich) and was painted onto E-Tek A-6 ELAT/SS/NC/V2 carbon cloth. After the electrodes were dried at 80°C for 30 minutes, a second layer of Pt-Ru (1.0 mg/cm² with 30 wt% dry Nafion ionomer) was painted directly on the first. The electrodes were dried at 80°C for another 30 mins. As for the cathode, platinum black was used instead of Pt-Ru alloy with the same catalyst loading for both first and second layers. After both the anode and cathode were annealed at 140°C for 5 minutes, they were hot pressed onto a membrane at 140°C at 400 psi for 5 minutes. MEAs were soaked in 1.0 M sulfuric acid for 12 hours and washed thoroughly with deionized 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 stacked membrane cases, one or two pre-stretched recast Nafion films were placed between two half MEAs [13, 33], 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 pre-stretched recast Nafion film.

2.6 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 2 mm in depth) was operated at 60°C with ambient pressure humidified air at 500 sccm. The anode feed was either 0.5, 1.0, 3.0 or 10.0 methanol. During a preconditioning break-in period, all MEAs (except Nafion 212) were operated for 2 hours in the fuel cell test fixture at room temperature with 1.0 M methanol at a constant current density of 40 mA/cm². Nafion 212 MEAs were preconditioned for 2 hours at room temperature with 0.5 M methanol at a constant current density of 20 mA/cm². After the break-in period, the cell was heated to 60°C and the preconditioning was continued for another 2 hours with 1.0 M methanol. The methanol feed concentration and cell operating conditions (temperature, feed flow rate, and air backpressure) were then appropriately fixed and fuel cell performance data (voltage and current were collected) operated at a constant voltage of 0.4 V for 0.5 hour. The stead-state current at 0.4V was recorded, followed by collection of data for an entire voltage vs. current density plot at a scan rate of 0.05 V/min. Methanol crossover flux was determined by measuring the carbon dioxide concentration in the cathode air exhaust at open circuit with a Vaisala GMM12B or GMM220A CO2 detector [33].

2.7 Methanol Partition Coefficient Measurements

Membrane strips were immersed in 1.0 M methanol for 12-18 hours (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 a head space where methanol vapor might accumulate). Methanol
was allowed to desorb from each film for 3-5 hours. Water samples were extracted from each closed vial with a syringe and analyzed for methanol by gas chromatography (Thermo Finnigan Trace GC 2000). The membrane-phase concentration of methanol (mole/g 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.

2.8 Differential Scanning Calorimetry (DSC)

Low temperature DSC experiments were performed using a Mettler Toledo DSC822e configured with an intra-cooler capable of reaching temperatures of -70°C. Fully hydrated membranes were carefully blotted to remove surface water and then transferred to sealed aluminum pans. The samples were quickly placed in the calorimeter and cooled to -60°C. The samples were then heated to 50°C at a rate of 5°C/min. The water melting endotherms were integrated to calculate the amount of freezable water in a sample, based on the heat of fusion for bulk water. The weight percentage of freezable water in a given membrane, as compared to the total water content in the sample, was calculated using the following equation (3):

\[
\text{Freezable Water \%} = \left( \frac{\Delta H}{\Delta H_f} \right) \frac{1 + \beta}{\beta} \times 100\%
\]

Eq (3)

Where \( \Delta H \) is the integrated enthalpy from the DSC melting endotherm based on the total sample weight, \( \Delta H_f \) is the heat of fusion for bulk water (334 J/g) [34], and \( \beta \) is the gravimetric water uptake of the sample \( \beta = \frac{m_w}{m_d} \), where \( m_w \) and \( m_d \) are the total mass of water in the wet and dry membrane, respectively.)
2.9 Electro-osmotic Drag of Water

The electro-osmotic drag coefficient of water in commercial and pre-stretched recast Nafion membranes was measured using the procedure reported in the literature by Ren and Gottesfeld [35]. MEAs with a geometric electrode area of 5.0 cm² and catalyst loadings of 4.0 mg/cm² (for both the anode and cathode) were prepared as previously described in Section 2.5. An MEA was loaded into the fuel cell test fixture (with single anode and cathode feed serpentine flow channels) and operated at high current densities (≥200 mA/cm²), so that the electro-migration of water from the anode to the cathode far exceeded any back diffusion of water. The methanol concentration and flow rate were 1.0 M methanol and 1.5 ml/min, respectively, and the cathode gas was dry oxygen at a flow rate of 250 sccm. A backpressure of 25 psig was applied to both the anode and cathode, to minimize water transport due to a hydraulic pressure difference across the membrane. Water in the cathode oxygen exhaust was trapped in Schwartz U-shaped drying tube containing Drierite (W.A. Hammond Drierite Company Ltd.). The methanol crossover flux during current flow was found by measuring the carbon dioxide concentration in the cathode oxygen exhaust stream (after water was removed in the U-tube), using a calibrated Vaisala GMM12B or GMM220A CO₂ detector. The water flux due to electro-osmotic drag was calculated by subtracting the water produced by the primary cathodic oxygen reduction reaction (as determined from the current density and electrode area) and the water generated by methanol oxidation at the cathode as a consequence of methanol crossover (as determined from the concentration of CO₂ in the oxygen exhaust and oxygen gas flow rate) from the total water flux as determined by the weight of water trapped in the U-tube for a given time period. From the constant applied current density and the flow rate of
water transported across the membrane per unit time, the electro-osmotic drag coefficient (with units of H₂O/H⁺) was determined.

2.10 Transmission Electron Microscopy (these experiments were performed by Dr. Zhiqing Shi)

Samples for transmission electron microscopy (TEM) examination were prepared using a series of steps. Membrane samples, 1 mm X 5 mm in size, were stained by soaking for 12 hours in a saturated lead acetate solution. The samples were rinsed thoroughly with deionized water and then dried under vacuum at 60°C for 2 hours. The membranes were embedded in a block template using Spurr’s epoxy resin and cured at ~60°C for 12 hours. The blocks were sectioned to yield slices 50-75 nm in thickness, using a Leica Ultracut ultramicrotome, and the slices were collected on copper grids. Images were obtained using a Hitachi H7600 Transmission Electron Microscope with an accelerating voltage of 80 kV.
3. Results and Discussion

3.1 Membrane Characterization

The critical DMFC membrane transport properties (through-plane proton conductivity at 25°C and methanol permeability at 60°C) for commercial Nafion 117, unstretched recast Nafion (draw ratio = 1) and pre-stretched recast Nafion are shown in Figure 3.1 Proton and methanol transport in recast and commercial Nafion films were found to be the same, as would be expected. For the pre-stretched recast Nafion film, however, there is a significant decrease in methanol permeability without an accompanying loss in proton conductivity. This behavior is unique for an ionomeric methanol fuel cell 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). It is not known at the present time why methanol permeability stops decreasing for a draw ratio ≥4. 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 Methods No. 1 and No. 2, can not be explained at the present time but was tentatively associated with differences in the morphology of the DMAc-swollen recast Nafion films immediately before stretching. Rod-like polymer aggregates, which are known to be present in a Nafion/DMAc solution [36], might be better aligned in a thinner
**Figure 3.1.** 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); ◊ Methanol permeability of pre-stretched recast Nafion (120-200 µm). $\kappa_N$ and $P_N$ are the measured proton conductivity and methanol permeability of commercial Nafion 117 ($\kappa_N = 0.10$ S/cm at 25°C; $P_N = 3.6 \times 10^{-6}$ cm²/s at 60°C).
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. Although not shown in Figure 3.1, 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 $2.6 \times 10^{-6}$ cm²/s).

It is important to note that the morphological changes that lead to the desirable proton and methanol transport properties in Figure 3.1 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 hour 60°C soak in 10.0 M methanol.

### 3.2 Single vs. Multi-Layer Membrane MEAs

The effects of MEA design (a single thick membrane or multiple thin membranes stack) on DMFC voltage-current density performance plots are shown in Figure 3.2 (for the pre-stretched Nafion membranes, the raw ratio was 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 with 500 mL/min ambient pressure air. As can be seen, there was a significant improvement in the power output over the entire voltage
Figure 3.2. 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/cm² catalyst loading for the anode and cathode, 60°C, 1.0 M methanol, and 500 sccm humidified air at ambient pressure.
range for the two MEAs containing pre-stretched recast Nafion. The high open
circuit voltage with pre-stretched Nafion was due to low methanol crossover. Based
on the methanol permeability data in Figure 3.1, 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 during a fuel cell test, was the same for both MEAs.
The measured methanol crossover at the open circuit voltage (8.1×10^{-6} \text{ mol/cm}^2\text{-min})
was the same and equal to that calculated using a membrane thickness of 185 \mu m
and the methanol permeability data for Method No. 2 membranes in Figure 3.1.
These 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 commercial Nafion 212.
As shown in Figure 3.3, 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).

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 and co-workers [37] showed that three
Figure 3.3. 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 ($P_N = 3.6 \times 10^{-6} \text{ cm}^2/\text{s}$ at 60°C).
commercial Nafion membranes of different thickness (Nafion 112, 115 and 117 with a wet thickness of 64, 160, 215 μm, respectively) had a similar power density at 0.4 V, for 90°C operation with 6 vol% (~1.5M) methanol feed and ambient pressure air. Jung et al. [38], achieved a higher current density at 0.4 V with Nafion 117, as compared to Nafion 112 (64 μm thick) with 2.0 M methanol and O₂ at 50°C. Liu et al. [39] 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. [40] reported that Nafion 112 (the thinnest of a series of commercial Nafion membranes that were tested) generated the highest power density at 0.4V 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 [41, 42]). 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/cm² 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 was between 60 μm and 250 μm (single films from 60 to 90 μm; two stacked films for 120 μm; three stacked films for 160 μm and 180 μm; four stacked films for 250 μm). MEAs with four commercial Nafion films (Nafion 212, 115, 117, and 1110 with a wet thickness of 64, 160, 215 and 320 μm, respectively) were also tested. DMFC voltage vs. current density data were collected at 60°C for 1.0 M methanol at 5mL/min and 500 sccm ambient pressure air. Typical results are shown in Figure 3.4 for five different MEAs. It can be seen that all of the MEAs performed well, with the 180 μm stacked pre-stretched recast Nafion MEA working best, with a high OCV due to low methanol crossover, and good performance at high currents due to small IR losses (the figure caption lists the area specific resistance of the MEA, as determined from
Figure 3.4. Methanol fuel cell performance for MEAs made with pre-stretched recast Nafion of different thicknesses and with Nafion 117. 4.0 mg/cm² catalyst loading for the anode and cathode, 60°C, 1.0 M methanol, and 500 sccm humidified air at ambient pressure: + Nafion 117 (215 µm, 0.20 ohm-cm² sheet resistance, OCV cross. flux =1). Pre-Stretched recast Nafion: ▲ 60 µm (0.065 ohm-cm², OCV cross. flux = 1.81); ● 90 µm (0.080 ohm-cm², OCV cross. flux= 1.26); ▽ 180 µm (0.17 ohm-cm², OCV cross. flux = 0.83); ○ 250 µm (0.21 ohm-cm², OCV cross. flux = 0.68).
current interruption 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 µm 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/cm² at 0.28 V, as compared to 76 mW/cm² at 0.31 V for Nafion 117 and 94 mW/cm² at 0.26 V for Nafion 212 (Nafion 212 data are not shown in Figure 3.4).

The results of all membrane thickness experiments are summarized in Figure 3.5 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 and thin and thick films made by Methods 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 µm thick film, performed better than any commercial (unstretched) Nafion material. Within the accuracy of the fuel cell tests, the optimum thickness of pre-stretched recast Nafion for the DMFC operating conditions in this study was in the range of 130-180 µm, with a power density at 0.4 V of 84 mW/cm², which was 45% higher than that achieved with the optimal commercial Nafion material (Nafion 117, with a wet thickness of 215 µm and a power density of 58 mW/cm²). The decrease in power at thicknesses greater than the optimum was associated with IR losses (a high area-specific resistance of the membrane), 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 can be associated with the combined beneficial effects of a lower area-specific resistance of the
Figure 3.5. Effect of membrane thickness on the steady-state DMFC power density at 0.4 V. 1.0 M methanol, 60°C, 4.0 mg/cm² 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 membrane MEAs), ● Commercial Nafion membranes.
membrane and lower methanol crossover. For example, the MEA area-specific resistance at the optimal pre-stretched recast Nafion thickness of 180 µm was 15% less than that of Nafion 117 (see caption in Figure 3.4 for resistance data). Similarly, the pre-stretched recast Nafion MEA was a better methanol barrier than Nafion 117, as shown in Figure 3.6, where methanol crossover flux for Nafion 117 and pre-stretched recast Nafion (draw ratio of 4, three-layer stack 180 µm film) is plotted as a function of current density during fuel cell operation. At 0.4 V, which corresponding to 145 mA/cm² for Nafion 117 and 210 mA/cm² for the 180 µm pre-stretched recast Nafion MEA (see Figure 3.4), the methanol crossover flux with pre-stretched Nafion was 41% lower than that in Nafion 117.
Figure 3.6. Effect of current density on methanol crossover flux for Nafion 117 and pre-stretched recast Nafion (three layer stack, 180 µm thickness, draw ratio of 4). 1.0 M methanol, 60°C, 4.0 mg/cm² anode and cathode catalyst loading, 500 scem air at ambient pressure.
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, 1.0, 3.0, and 10.0 M, where the catalyst loading for the anode and cathode was fixed at 4.0 mg/cm² and the air flow rate was 500 sccm (at ambient pressure). During these experiments, the methanol flow rate was varied in the range of 0.02-18 ml/min 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 µm) and Nafion 117 are shown in Figure 3.7 and Figure 3.8. 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 both commercial Nafion 117 and pre-stretched recast Nafion was in the 1-3 M range, which agrees with results in the literature [43-45]. In the course of collecting the data in Figure 3.7, the effect of flow rate on power density, for a given methanol feed concentration, was quantified. The results in Figure 3.8 indicate that there is an optimum flow rate for a given methanol feed concentration. It can also be seen that the power density at 0.4 V was less sensitive to flow rate at 0.5 and 1.0 M methanol feed concentrations. Similar power vs. flow rate plots 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
Figure 3.7. Effect of methanol feed concentration on the DMFC power density at 0.4 V. 60°C cell temperature, 4.0 mg/cm² catalyst loading for the anode and cathode, 500 scem air at ambient pressure. ▲ Pre-Stretched recast Nafion (draw ratio of 4, three layer stack, with a total thickness of 180 µm); ○ Nafion 117.
Figure 3.8. 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 µm). 60°C cell temperature, 4.0 mg/cm² catalyst loading for the anode and cathode, 500 sccm air at ambient pressure.
methanol crossover was higher than that in pre-stretched recast Nafion). The Nafion results are shown in Figure 3.9.

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 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. The deterioration in performance with high/low flow rate was more severe when the feed concentration of methanol was high, as evidenced from Figure 3.8. 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 to 8.0 mg/cm² (using a two-layer electrode construct, as described in Section 2.5, with twice the catalyst loading in each layer), the cell 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 μm total thickness, draw ratio of 4) under these conditions are shown in Figure 3.10, where cell voltage and power density are plotted against current density. Again, a very obvious and
Figure 3.9. Effect of methanol flow rate and feed concentration on DMFC power density at 0.4 V for Nafion 117, 60°C cell temperature, 4.0 mg/cm² catalyst loading for the anode and cathode, 500 sccm air at ambient pressure.
Figure 3.10. Methanol fuel cell performance with air backpressure. ▲ Pre-Stretched recast Nafion (three layer stack, draw ratio 4, 180 μm thickness); ○ Nafion 117 (215 μm thickness). 1.0 M methanol, 80°C, 8.0 mg/cm² catalyst loading, 500 scem air at 25 psig.
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/cm² at 0.35 V (24% higher power than what is achievable with Nafion 117). Additional data from these experiments are summarized in Table 3.1, where the effects of cell temperature (60 vs. 80°C), catalyst loading (4.0 vs. 8.0 mg/cm²) 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/cm² outperformed Nafion 117 at the same temperature with twice the catalyst loading. Similarly, for 8.0 mg/cm² loading and 80°C, a pre-stretched recast Nafion MEA operating at ambient pressure generated more power than Nafion 117 with a backpressure.
<table>
<thead>
<tr>
<th>Power Density (mW/cm²)</th>
<th>Pre-Stretched Recast Nafion</th>
<th>Nafion 117</th>
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<tr>
<td></td>
<td>@ 0.4 V Maximum</td>
<td>@ 0.4 V Maximum</td>
</tr>
<tr>
<td>4.0 mg/cm²</td>
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<tr>
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<td>181</td>
</tr>
<tr>
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<td>252</td>
<td>203</td>
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<tr>
<td>25 psig backpressure</td>
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**Table 3.1.** 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. Anode feed: 1.0 M methanol; Cathode feed: 500 sccm humidified air.
3.6 Equilibrium, Macroscopic Water Uptake & Low Temperature Differential Scanning Calorimetry of Water-Equilibrated Pre-Stretched Recast Nafion Films

Equilibrium (macroscopic) gravimetric water uptake (swelling) at 25°C for commercial Nafion 117, solution cast Nafion, and pre-stretched recast Nafion (with a draw ratio of 2~7) is shown in Figure 3.11. Water absorption for unstretched recast Nafion was essentially constant at 19 H₂O/3SO₃⁻ (30 wt% uptake), independent of draw ratio, and slightly lower than that measured for commercial Nafion 117 (λ=21). Scatter in water uptake data is due to some variability in experimental procedure, in particular the wiping of excess water from the membrane surface with filter paper (the measurement step is difficult to reproduce identically every time). Uniaxial film elongation of semi-crystalline polymers often leads to an increase in crystallinity [46, 47]. If the pre-stretched films were substantially more crystalline, there might be a reduction in water uptake (crystallites would create physical crosslinks that would limit membrane swelling). Preliminary X-ray diffraction data [23] however, indicate that the increase in crystallinity upon membrane elongation was small and did not affect the water swelling behavior of the pre-stretched recast Nafion films.

Low temperature DSC water-melting endotherms for unstretched Nafion (draw ratio of 1) and pre-stretched recast Nafion (draw ratio of 2~7) are shown in Figure 3.12. The data were used to elucidate the different types of water (freezable vs. nonfreezable) in the fully hydrated membrane samples. The most striking feature of these plots is the monotonic decrease in the size of the water melting peak with increasing draw ratio. Clearly, there is less freezable water in Nafion upon stretching
Figure 3.11. Equilibrium water content of pre-stretched recast Nafion at 25 °C for different draw ratio.
Figure 3.12. Low temperature differential scanning calorimetry thermograms of water-equilibrated pre-stretched recast Nafion (DR denotes draw ratio).
a recast film (although not shown in Figure 3.12, the water endotherm for Nafion 117 was almost identical to that for un-stretched recast Nafion). A depression of the temperature at which the freezable water crystallizes in pre-stretched Nafion samples is also evident in Figure 3.12. Whereas thermograms of unstretched Nafion revealed the presence of sharp endothermic component at 0°C indicating the existence of water with bulk-like properties, freezable water in pre-stretched recast Nafion melted at a temperature below 0°C (e.g., about -10°C for a draw ratio of 4). This change in the melting point of water was associated with an increase in the local sulfonic acid concentration within the membrane. Such a change in the melting temperature of water has been observed previously for partially swollen Nafion, i.e., membranes exposed to low relative humidity (RH) air and was associated with a decrease in the size of water domains and/or a colligative effect where the membrane fixed charges are considered to be the solute. For example, Siu et al. [48] reported on a 10°C suppression in the melting point for water in commercial Nafion 117 that was equilibrated with 95% RH air, where $\lambda=11-14$ and where the membrane sulfonic acid concentration (based on the total volume of water in the membrane) before freezing was about 1.4 M, as compared to 1.1 M for a membrane fully swollen with liquid water. In the present study, the melting point temperature depression is seen under fully hydrated conditions (total $\lambda=19$) and, thus, is associated with morphological changes in the membrane polymer.

Histograms of the freezable and nonfreezable water (given as the number of water molecules per sulfonic acid site) in Nafion 117, unstretched and pre-stretched recast Nafion (for draw ratios of 1-7) are shown in Figure 3.13, where $\lambda_{\text{nonfreeze}} = \lambda_{\text{total}}$ (from Figure 3.11) - $\lambda_{\text{freeze}}$ (as determined from the data in Figure 3.12). The value of 12 for $\lambda_{\text{freeze}}$ in a water-equilibrated Nafion 117 membrane is
Figure 3.13. Freezable and nonfreezable water content of pre-stretched recast Nafion membranes at different draw ratio (the solid line denotes the dependence of the freezable water content on draw ratio).
comparable to that reported in the literature ($\lambda_{\text{freeze}} = 9$, in reference [48]). As can be seen, there is a steady and substantial decrease in the amount of freezable water in recast Nafion as it is elongated, up to a draw ratio of 4. In commercial Nafion 117 and unstretched recast Nafion (draw ratio of 1), approximately 60% of the total membrane water freezes, whereas only 26% of the water freezes in pre-stretched recast Nafion (draw ratio equal to or greater than 4). The general shape of the freezable water content vs. draw ratio curve mirror the dependence of methanol permeability on film elongation (Figure 3.1). This result is consistent with prior studies, which concluded that methanol permeability in proton exchange membranes is a function of the membrane’s freezable water content [8].

Based on the DSC and macroscopic water uptake results, a picture emerged as to the nanomorphology of pre-stretched recast Nafion. The DSC data indicated less freezable water in pre-stretched recast Nafion, which meant that there was more water in close proximity to the sulfonic acid ion-exchange sites. On the other hand, the total water content in pre-stretched Nafion was constant (independent of draw ratio and equal to that in an unstretched film). These two apparently contradictory results can be reconciled if there were a greater number of smaller hydrophilic ionic domains in a pre-stretched recast Nafion membrane (with the domain size decreasing and the number of domains increasing with draw ratio) (Figure 3.14). In an inverted-micelle cylinder nanomorphology with sulfonic acid groups on the wall of the cylindrical pores, for example, freezable water will only exist in the center region of the pore, where the pore-wall electric field (generated by $\text{SO}_3^-$ groups) that polarizes water molecules is negligibly small. In pre-stretched Nafion, with smaller ionic domains, the percentage of pore water that is unaffected by the wall charges is reduced, thereby
Figure 3.14. Schematic cartoon of ionic domains for unstretched recast Nafion and pre-stretched recast Nafion.
decreasing the amount of freezable water. To check whether this morphology actually exists, transmission electron micrographs of pre-stretched recast membrane cross sections were collected. The TEM results are shown in Figure 3.15, where the membrane cross sections are perpendicular to the stretched direction (i.e., stretching is perpendicular to the x-y plane of the page). As correctly hypothesized, the size of the ionic domains (darkened regions in Figure 3.15) was smaller and the number of such domains increased with increasing film elongation. Additionally, both the size and distribution of the ionic domains in the pre-stretched films were highly uniform (i.e., water is spread out more uniformly in pre-stretched recast Nafion). The decrease in domain size for a high draw ratio was significant; at a draw ratio of 7, for example, the ionic (hydrophilic) domain dimension was approximately 2 nm, as compared to about 8 nm for an unstretched recast film. Although the TEMs are of dry membrane samples, the general morphology should be preserved upon exposure to water [49], with an increase in both pre-stretched and unstretched domain size upon water sorption.
Figure 3.15. Transmission electron micrographs of unstretched recast Nafion and pre-stretched recast Nafion membrane cross sections. Dark regions are the ionic domains.
In light of the DSC results for water in pre-stretched recast Nafion and the supporting evidence provided by the TEM images in Figure 3.15, a discussion of proton conductivity (constant conductivity with draw ratio, as shown Figure 3.1) in relation to membrane morphology is warranted. Numerous studies with commercial Nafion membrane have shown that the proton conductivity decreases with decreasing total water content, where the amount of sorbed water was varied by equilibrating a membrane sample with humidified air at a water activity < 1. For example, Gavach et al. [50] found that the conductivity of perfluorosulfonic acid membranes increased significantly when the average number of water molecules per sulfonic acid site was > 6 (In this study it was assumed that $\lambda=6$ represents the minimum number of water needed to create a primary hydration shell on the SO$_3$H ion-exchange groups and a continuous, percolating water of hydration phase. Similarly, when Nafion 117 was equilibrated in 95% RH air at 25°C (where $\lambda=12$), the proton conductivity at 25°C was $\approx$0.06 S/cm vs. 0.09-0.10 S/cm for a liquid water-equilibrated film [51]. The data in Figures 3.1 and 3.11 for pre-stretched Nafion are consistent with our general understanding of proton mobility in Nafion (i.e., the high water content of pre-stretched recast Nafion, for all draw ratios, translates into a high proton conductivity).

The interpretation of the conductivity data in terms of the freezable/nonfreezable water contents in Figure 3.13 is more complex. Clearly, proton conductivity is not dependent on the amount of freezable water in pre-stretched recast Nafion. Such behavior has never before been observed in a proton conducting fuel cell membrane like Nafion because it was not possible to reduce the freezable water content without also lowering the total amount of sorbed water. It has generally been thought that proton conductivity in Nafion above 0°C scales directly with freezable water content, since the presence of bulk-like water
increases proton mobility in fully hydrated membranes [48]. The results in Figures 3.1 and 3.13 contradict this generally held belief. Thus, a pre-stretched recast Nafion film with as little as 1/3 the amount of freezable water as compared to Nafion 117 (i.e., a draw ratio of 4 with $\lambda_{\text{freeze}}=5$), maintains its high proton conductivity. The combined DSC, and conductivity results suggest that: there is a different proton conduction mechanism in the water-filled pores of pre-stretched recast Nafion. In fact, theoretical studies have indicated that proton hopping can occur via water bridging between two sulfonic groups if they are close enough to one another [52-54]. Smaller domains of the pre-stretched Nafion should result in closer spacing of sulfonic groups which could promote pore surface diffusion via a proton hopping mechanism. The interesting and unique proton conductivity behavior of pre-stretched recast Nafion vis-à-vis its membrane water properties has important implications for hydrogen/oxygen fuel cells. For example, the results imply that the proton conductivity in a highly pre-stretched recast Nafion film (draw ratio $>> 7$) containing no freezable water will remain high (although it is not clear how one might create such a film in light of the plateau in the freezable water content with draw ratio in Figure 3.13). The total water content in such a Nafion membrane will be similar to that of commercial Nafion, with all of the water in a nonfreezable (and presumably non-evaporative) state. Such membrane fabrication experiments should be coupled to studies to determine the split of freezable/nonfreezable water in pre-stretched recast Nafion, of various draw ratios, as a function of temperature and water vapor activity.

3.7 Electro-osmotic Drag of Water

The last set of experiments for elucidating the properties of water in
pre-stretched recast Nafion was the determination of electro-osmotic water drag (given as the number of water molecules per H\(^+\) that move through the membrane under the influence of an applied electric field). This data was collected in a modified direct liquid methanol fuel cell experiment. The water flux solely associated with proton transport is plotted against current density (which is proportional to the transmembrane proton flux) in Figure 3.16 for commercial Nafion 117 and pre-stretched recast Nafion with a draw ratio of 4. The straight line behavior of the data with a zero intercept indicates that the electro-osmotic drag coefficient of water is independent of current density and can be calculated from the slope of these lines. A plot of this parameter as a function of draw ratio for a series of pre-stretched recast Nafion membranes is shown in Figure 3.17. As expected, the water drag coefficient in pre-stretched Nafion is lower than that in commercial Nafion (10-25% lower) and decreases with increasing draw ratio. This may be the result of an increase in the viscosity of water of hydration, in membrane pores, which promotes more compact proton solvation vehicles and possibly a proton hopping mechanism (as discussed previously). A decrease in the electro-osmotic drag coefficient should, to a certain extent, retard methanol permeability in an operating fuel cell. The measured methanol permeabilities in Figure 3.1, however, can not be linked directly to the reduction in the electro-osmotic drag coefficient.

3.8 Methanol Partitioning in Pre-stretched Recast Nafion

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
Figure 3.16. Electro-osmotic water flux as a function of current density for Nafion 117 and pre-stretched recast Nafion (draw ratio of 4) at temperature of 60 °C.
Figure 3.17. Electro-osmotic water drag coefficient of Nafion 117, unstretched recast Nafion (draw ratio = 1), and pre-stretched recast Nafion of different draw ratios.
of these experiments are shown in Figure 3.18 (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 mol/g 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 [55-57] (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 Figure 3.18 mirrors the methanol permeability vs. draw ratio plot in Figure 3.1 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 coefficients in pre-stretched Nafion [58], which were found to be invariant with draw ratio and equal to that in commercial Nafion. The solubility data are also consistent with the 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) [58]. 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.
Figure 3.18. 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).
4. Conclusion

i. Uniaxially pre-stretched Nafion membranes exhibited unusual proton conductivity and methanol permeability behavior (a proton conductivity that was independent of draw ratio and a methanol permeability decreased with the elongation up to a draw ratio of 4), which make them ideal candidates for use in a direct methanol fuel cell.

ii. Direct methanol fuel cell (DMFC) experiments were carried out with MEAs containing 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 compared to unstretched commercial Nafion. For a feed solution of 1.0 M methanol at 60°C with 500 sccm air at ambient pressure (4.0 mg/cm² 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/cm², as compared to the optimum with a commercial Nafion material (Nafion 117) which generated only 58 mW/cm² of power.

iii. The effect of methanol feed concentration (0.5, 1.0, 3.0, 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/cm² anode and cathode catalyst 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 concentration range, the pre-stretched recast Nafion MEA outperformed Nafion 117, with 33-48% higher power densities.

iv. 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/cm² 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 and 252 mW/cm², respectively, as compared to 181 and 203 mW/cm² for an MEA with Nafion 117. DMFC performance with pre-stretched recast Nafion at 4.0 mg/cm² anode/cathode catalyst loading and 80°C was better than that with Nafion 117 at 80°C with 8.0 mg/cm² catalyst. Also, with a catalyst loading of 8.0 mg/cm² 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.

v. The DSC results (water interacting more strongly with membrane sulfonic acid groups) and macroscopic water swelling (no change in the total water uptake) suggested a new nanomorphology for pre-stretched recast Nafion where there is a decrease in the size and an increase in the number of hydrophilic domains, up to a draw ratio of 4. This structure was confirmed by TEM images of pre-stretched recast Nafion cross sections.

vi. The invariance of macroscopic water uptake and proton conductivity with stretched membrane are consistent with one another. The decrease in
freezable water content with draw ratio in pre-stretched recast Nafton is a new and important result of this study, with potentially important and far-reaching implications. The results suggest that protons are transported through pre-stretched recast Nafton via non-freezable (bound) water.

vii. The electro-osmotic drag coefficient of protons in pre-stretched recast Nafton decreased with increasing draw ratio and mirrored the variation of freezable water content with film elongation. Thus, less freezable (and more nonfreezable) water in a pre-stretched Nafton film translates into a high average viscosity for membrane-phase water, which in turn decreases the number of water molecules that are dragged with protons.

viii. The low methanol permeability in pre-stretched Nafton, as compared to that in a commercial Nafton film, was associated with a decrease in the methanol partition coefficient, where the methanol solubility decreased with increasing draw ratio up to a draw ratio of 4.
5. Suggestions for Future Work

i. The proton conductivity of pre-stretched recast Nafion with high draw ratio at temperatures lower than 0°C needs to be investigated due to the fact that there is more nonfreezable water in pre-stretched recast Nafion. It is anticipated that conductivity of pre-stretched recast Nafion at sub-freezing temperatures will be greater than that of commercial Nafion.

ii. Wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS) experiments need to be carefully performed to characterize the structure of pre-stretched recast Nafion films (both dry and wet samples), especially the organization of crystalline and hydrophilic ionic domains.

iii. The mechanical properties (e.g. ultimate tensile strength and storage modulus) of pre-stretched recast Nafion (both dry and wet samples) needs to be measured and correlated with the polymer WAXS data.

iv. The morphology of DMAc-swollen recast Nafion films needs to be probed to examine the origin of methanol permeability differences between a thick film (a thickness of 100-200 µm for draw ratio of 4) and a thin film (a thickness of 60 µm for draw ratio of 4). Scanning electron microscopy and transmission electron microscopy should be applied for such an investigation.

v. Uniaxial stretching of perflurosulfonic acid polymer other than Nafion
should be examined, such as 3M’s low equivalent weight (high ion-exchange capacity) polymer.

vi. There are a greater number of smaller hydrophilic domains in pre-stretched recast Nafion as shown by the TEM results. With such a morphology, there may be better contact between the catalyst and membrane in an MEA. Electrochemical methods, such as cyclic voltammetry and AC impedance should be performed to investigate the MEA structure and properties, including the catalyst utilization and the resistance at membrane/catalyst interface.
6. Bibliography


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