Advanced materials for improved PEMFC performance and life

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Abstract

Physical and functional attributes are reviewed for recently developed Nafion® products that satisfy emerging fuel cell requirements—including stronger, more durable membranes, and polymer dispersions of higher quality and consistency for catalyst inks and film formation. Size exclusion chromatography (SEC) analysis has confirmed that dispersion viscosity is related to an "apparent" molar mass, resulting from a molecular aggregate structure. Membranes produced with solution-casting and advanced extrusion technologies exhibit improved water management and mechanical durability features, respectively. Additionally, DuPont has shown that experimentally modified Nafion® polymer exhibits 56% reduction in fluoride ion generation, which is considered a measure of membrane lifetime.
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1. Introduction

1.1. Nafion® PFSA polymer

DuPont introduced Nafion® perfluorinated polymer [1] in the mid-1960s. Nafion® is a copolymer of tetrafluoroethylene or "TFE", and perfluoro(4-methyl-3,6-dioxa-7-octene-1-sulfonyl fluoride) or "vinyl ether", as shown in Fig. 1. Nafion® polymer is a thermoplastic resin that can be melt-formed into typical shapes such as beads, film, and tubing. The perfluorinated composition of the copolymer imparts chemical and thermal stability rarely available with non-fluorinated polymers. The ionic functionality is introduced when the pendant sulfonyl fluoride groups (SO_2F) are chemically converted to sulfonic acid (SO_3H). The copolymer's acid capacity is related to the relative amounts of co-monomers specified during polymerization, and can range from 0.67 to 1.25 meq. g^{-1} (1500–800EW, respectively).

The unique functional properties of Nafion® PFSA polymer have enabled a broad range of applications. Initially, Nafion® membranes were used for spacecraft fuel cells; however, by the early-1980s, membrane electrolysis production of chlorine and sodium hydroxide from sodium chloride emerged as the largest application for Nafion® membranes. Other important industrial applications include production of high purity oxygen and hydrogen, recovery of precious metals, and dehydration/hydration of gas streams. In addition, Nafion® super-acid catalysts are used to produce fine chemicals. Starting in 1995, DuPont began a series of process and product development programs specific to PEM fuel cell applications.

1.2. Nafion® PFSA membranes

The traditional extrusion-cast membrane manufacturing process was developed for "thick" films, typically greater than 125 μm. The extruded polymer film must be converted from the SO_2F to the SO_3K form using an aqueous solution of potassium hydroxide and dimethyl sulfoxide, followed by an acid exchange with nitric acid to the final SO_3H form [2].

Technical advances in fuel cell design and performance have increased demand for thin membranes produced at production rates that will meet the lower conversion cost goals required for fuel cell applications. Furthermore, there is a growing demand for larger production lot sizes, increased roll lengths and improved physical appearance. To meet this need, DuPont developed a solution-casting process for supplying high-volume, low-cost membrane to the fuel cell industry that was planning automated processes for membrane electrode assemblies [3,4].

DuPont's new membrane process uses typical solution-casting technology and equipment, as shown in Fig. 2. A base film [1] is unwound and measured for thickness [2].

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$$-(CF_2-CF_2)_x-(CF_2-CF)_y-$$
$$|$$
$$O-[CF_2-CF-O]_m-CF_2-CF_2-SO_2F$$
$$|$$
$$CF_3$$

TFE   **Vinyl Ether**
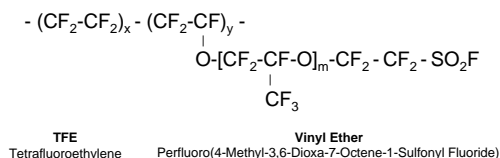Tetrafluoroethylene   Perfluoro(4-Methyl-3,6-Dioxa-7-Octene-1-Sulfonyl Fluoride)

Fig. 1. Nafion® polymer structure before conversion to the sulfonic acid form.

Polymer dispersion is applied [3] to the base film, and both materials enter a dryer section [4]. The composite membrane/backing film is measured for total thickness [5], with the membrane thickness the difference from the initial backing film measurement. The membrane is inspected for defects [6], protected with a coversheet [7], and wound on a master roll [8]. The membrane is produced in a clean room environment [9]. Master rolls are slit into product rolls, which are individually sealed and packaged for shipment.

This process has several key advantages: (1) pre-qualification of large dispersion batches for quality (e.g., free of contamination) and expected performance (e.g., acid capacity); (2) increased overall production rates for H^+ membrane from solution-casting as compared to polymer extrusion followed by chemical treatment; and (3) improved thickness control and uniformity, including the production capability of very thin membranes (e.g., 12.7 μm).

1.3. Nafion® PFSA polymer dispersions

Two patented high-pressure processes, solvent-based [5] and water-based [6], are used to convert Nafion® polymer (sulfonic acid form) into polymer dispersions having solids contents ranging from 5 to 20% by weight. These dispersions are formulated into carbon inks and catalyst coatings, and used either "as supplied" or with modifiers [7], and/or reinforcement materials to fabricate electrode coatings and membranes [8–10].

The manufacture of polymer dispersions has undergone considerable change since first introduced by DuPont, with the recent "second generation" dispersions exhibiting more stable and consistent viscosity, improved acid capacity and reduced metal ion content. These features enable more
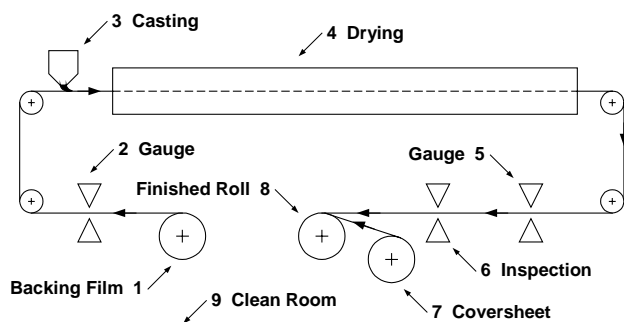
predictable coating formulations, consistent processing, and improved fuel cell performance. A "third generation" dispersion is in the final R&D stages, and will provide broader formulation capabilities for both solvent and polymer content. It will also allow further process simplification for preparing coatings, casting membranes and fabrication of membrane electrode assemblies.
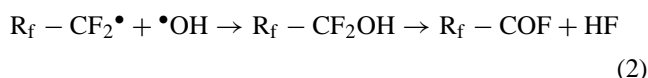
1.4. Polymer chemical stability

The useful lifetime of a membrane is related to the chemical stability of the ionomer. While Nafion® PFSA polymer has demonstrated highly efficient and stable performance in fuel cell applications, evidence of membrane thinning and fluoride ion detection in the product water indicates that the polymer is undergoing chemical attack. The fluoride loss rate is considered an excellent measure of the health and life expectancy of the membrane [11]. Peroxide radical attack on polymer endgroups [12] with residual H-containing terminal bonds is generally believed to be the principal degradation mechanism.

In this degradation mechanism, cross-over oxygen from the cathode side, or air bleed on the anode side, provides the oxygen needed to react with hydrogen from the anode side and produce H_2O_2, which can decompose to give $^\bullet OH$ or $^\bullet OOH$ radicals. These radicals can then attack any H-containing terminal bonds present in the polymer. Peroxide radical attack on H-containing endgroups is generally believed to be the principal degradation mechanism. This form of chemical attack is most aggressive in the presence of peroxide radicals at low relative humidity conditions and temperatures exceeding 90 °C.

Hydroxy or peroxy radicals resulting from the decomposition of hydrogen peroxide in the fuel cell attack the polymer at the endgroup sites and initiate decomposition. The reactive endgroups can be formed during the polymer manufacturing process and may be present in the polymer in small quantities. An example of attack on an endgroup such as CF_2X, where $X = COOH$, is shown below.

Several proposed mechanisms include the following sequential reactions: abstraction of hydrogen from an acid endgroup to give a perfluorocarbon radical, carbon dioxide and water (step 1). The perfluorocarbon radical can react with hydroxy radical to form an intermediate that rearranges to an acid fluoride and one equivalent of hydrogen fluoride (step 2). Hydrolysis of the acid fluoride generates a second equivalent of HF and another acid endgroup (step 3).

$$R_f - CF_2COOH + {}^\bullet OH \rightarrow R_f - CF_2{}^\bullet + CO_2 + H_2O \quad (1)$$

$$R_f - CF_2{}^\bullet + {}^\bullet OH \rightarrow R_f - CF_2OH \rightarrow R_f - COF + HF \quad (2)$$

$$R_f - COF + H_2O \rightarrow R_f - COOH + HF \quad (3)$$

Fig. 2. Solution-casting process for Nafion® membranes.

2. Experimental

2.1. Polymer chemical stability measurements

A sample of Nafion® membrane is treated in a solution of 30% hydrogen peroxide containing 20 ppm iron (Fe^{+2}) salts at 85 °C for 16–20 h. The resulting solution is checked for fluoride ion content using a fluoride specific ion electrode. The same membrane sample is treated two additional times, each treatment using fresh peroxide and iron. The results are recorded as the "total milligrams of fluoride per gram of sample" generated during the three treatment cycles. For membrane operating in fuel cells, the fluoride loss rate is reported as "micromoles fluoride ion per gram of sample per hour".

2.2. Viscosity measurements

Dispersion viscosity is measured using a Brookfield (Middleboro, MA) digital viscometer model LVDVIII+ employing a wide gap concentric cylinder geometry. Using the SC4 series spindles and small sample adapter connected to a temperature controlled water bath (VWR), samples were equilibrated at 25.0 ± 0.1 °C before measurements were taken. For those samples that showed shear-thinning behavior, observed viscosities and shear rates were corrected at the spindle wall using established power law relationships for viscosity, shear rate, and geometry [13]. Dispersion viscosity is reported at $40\,s^{-1}$ shear rate.

2.3. Size exclusion chromatography (SEC)

SEC molecular characterization was performed using a size exclusion chromatograph equipped with a Waters (Bedford MA) 2410 refractive index (RI) detector, Waters 515 HPLC pump, Waters column heater, and Rheodyne injector with 200 μl sample loop. A Precision Detectors (Franklin MA) PD2020 light scattering (LS) detector with static light scattering at 15° and 90° ($\lambda = 800\,nm$) and dynamic light scattering (DLS) at 90° was installed within the 2410 for constant temperature control (40 °C). Samples were eluted through two Polymer Laboratories (Amherst MA) SEC columns (Plgel 10 μm MIXED-B LS) maintained at 50 °C. The LS detector millivolt output relative to ΔR_θ and inter-detector volume were calibrated from an average of six injections (100 μl of ~2 mg ml^{-1}) of a narrow polystyrene standard (Aldrich, product/lot # 330345, MW = 44,000 g mol^{-1}) using dimethyl formamide (DMF) as the mobile phase (0.6 ml min^{-1}).

2.4. Dynamic mechanical analysis (DMA)

The DMA responses were measured using a TA Instruments Model 2980. The test measurements used thick specimens prepared by pressure laminating eight-layers of the 2 mil Nafion® membrane at 1000 psi, 80 °C between DuPont Kapton® polyimide film. Film specimens approximately $15 \times 7 \times 0.4\,mm^3$ were cut from multi-layer membrane laminate for tensile DMA measurements. The test specimen was equilibrated at ambient temperature and humidity, then clamped in the tensile fixture, which is flushed with dry Nitrogen and cooled to −100 °C. The test chamber's relative humidity was not controlled during the DMA tests. Small-amplitude oscillatory stresses were applied at a frequency of 10 Hz, while measurements were made of the storage modulus E' and loss modulus E'' (plus the derived loss tangent, tan delta = E''/E') as a function of temperature. Each DMA test included a number of sequential heating cycles, where the maximum temperature for each cycle progressively extended to a higher maximum temperature.

2.5. Surface tension

The air-liquid (surface) tension for Nafion® polymer dispersions was measured at 23 °C using the Wilhelmy platinum plate method. The platinum plate is pre-cleaned by flame treatment. The sample liquid is placed in a clean glass vessel, free of contaminates that may effect the surface tension of the liquid. The platinum plate (40 mm wide × 0.2 mm thick × 10 mm high) is attached to a force measuring device (Kruss K100 Tensiometer) and bought down into contact with the surface of the liquid being measured, along the 40 mm × 0.2 mm bottom edge. The plate first is submerged below the surface of the liquid to a depth of 2.0 mm to wet the plate, and then pulled back to within 10 μm of the liquid's surface. The force of the liquid pulling down on the plate (the liquid's Wilhelmy force) is measured 60 s after the plate has stopped moving. The surface tension is the Wilhelmy force divided by the wetted length of the plate (its perimeter of 80.4 mm). The cited surface tensions are averages of three measurements, and reported in milliNewton per meter (mN m^{-1}).

2.6. Contact angle

The contact angle data for Nafion® PFSA Membranes was obtained with a Kruss Automated Goniometer DSA10, using an environmental chamber equipped with a dew point sensor to monitor and control conditions. Dew point was set at 12 °C for measurements at 23 °C, which yielded relative humidity of 50% at 23 °C. For each drop of water placed on a sample membrane, contact angles were measured every 5 s for 30 min. The reported "average" contact angle was based on the average of contact angle measurements for five drops of water placed on a particular sample, as a function of time after droplet placement.

2.7. Electrical shorts tolerance

A resistivity test measures the membrane's electrical shorts tolerance caused by penetration of surface fibers

from the gas diffusion layer. The test is performed in a constant humidity, constant temperature room with the samples conditioned at least 24 h before testing. The test apparatus consists of the inner elements of a single fuel cell, namely, the top and bottom electrode plates with lead wires and the top and bottom Pocco graphite flow fields. These elements sit on a rigid base in a constant rate of extension (CRE) test machine and are compressed with a 25.4 mm diameter ball mounted in the center of a 6.35 mm thick rigid steel plate. The ball is pushed by a rod attached to the load cell, so the plate remains parallel to the assembly. The DC resistance of the stack is measured across the electrode plates using an ohmmeter. A square, 50.8 mm × 50.8 mm, of a gas diffusion backing (GDB) material is placed on the bottom flow field with the microporous layer facing up. The membrane is placed over the GDB and a second GDB piece is placed with the microporous layer facing down, over the membrane. The top flow field is then placed on top. The stack is centered over the bottom electrode plate and covered with the top electrode plate with the insulated side up. The CRE machine is closed so that the load cell just begins to measure load. The ohmmeter is attached to the electrode plates and the stack assembly is left to reach equilibrium as the "capacitor" charges. The test begins once the resistance reading is stable. The CRE machine is closed at a rate of 0.635 mm min^{-1}. The resistance is recorded as a function of the applied load and the pressure causing an electrical short is reported. A "failure" occurs when the electrical resistance drops below 1000 Ω.

2.8. Accelerated lifetime

The "time to failure" in hours is measured using a single fuel cell apparatus and proprietary testing protocols. This test is used to compare membranes and MEA designs against each other in a simulated fuel cell environment.

3. Results and discussion

3.1. Polymer chemical stability

Previously, DuPont had determined that fluoropolymer endgroup reactions could be minimized during extrusion processes by pre-treating the polymer with elemental fluorine [14,15] to remove reactive endgroups and impart greater thermal stability. When Nafion® polymer was treated in a similar manner, the number of measurable endgroups was reduced by 61%, thus providing a good candidate for chemical stability testing. Using the peroxide stability test, this treated polymer was compared with a sample of the same polymer before treatment. After >50 h of exposure, there was a 56% decrease in total fluoride ion generated per gram of treated polymer, versus the non-treated polymer, as shown in Fig. 3.
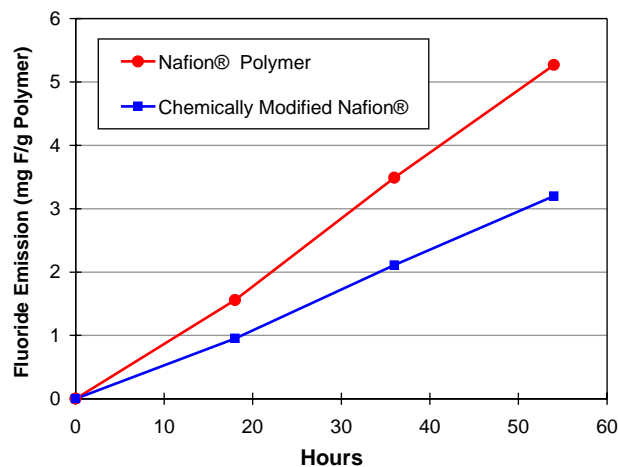

Fig. 3. Fluoride emissions for membranes made using standard and chemically modified Nafion® polymer.

Recently, DuPont has developed proprietary protection strategies that substantially reduce both the number of polymer endgroup sites and their vulnerability to attack. Using ex situ accelerated degradation protocols, Fig. 4 shows that membranes made the modified polymer (type A and type B) exhibited 10 to 25× reduction in fluoride ion emissions when compared to the standard Nafion® N-112 membrane. The reduction in fluoride ion release was consistent with the reduction in the number of reactive polymer endgroups. It confirms that reactive endgroups are the vulnerable sites, and that the polymer can be effectively protected using DuPont's proprietary methods.

It should be noted that the ex situ accelerated degradation tests do not necessarily correlate to fuel cell accelerated degradation results. In one case, when membranes prepared from treated and non-treated polymer were tested in a fuel cell configuration using accelerated operating conditions, both membranes generated similar amounts of fluoride ion. Furthermore, clear relationships between accelerated test
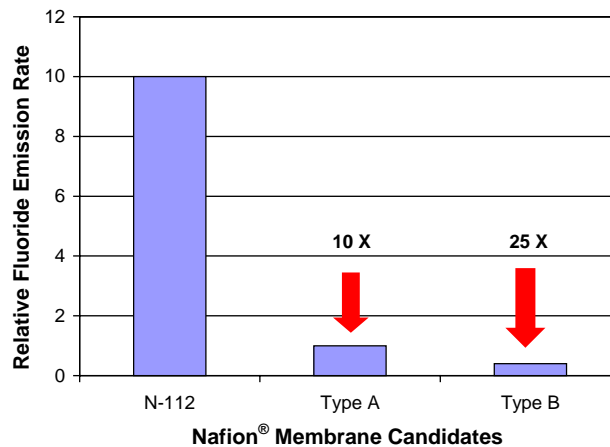

Fig. 4. Reduction in fluoride emissions for developmental Nafion® membranes made using DuPont's proprietary protection strategies.
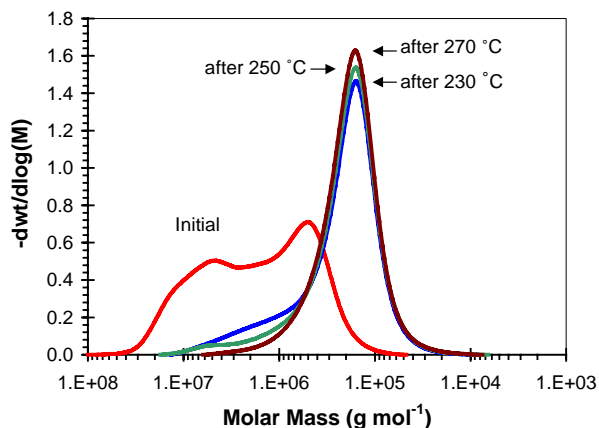
Fig. 5. Change in molar mass distributions after heating dispersions at progressively higher temperatures.

Fig. 6. Surface tension measurements Nafion® polymer dispersions.

protocols and real-time fuel cell operating conditions have yet to be resolved satisfactorily.

DuPont continues to investigate those conditions present during PEM fuel cell operation which initiate F^- formation, including both initial and long-term release rates. The analysis includes identifying PFSA polymer and membrane features susceptible to attack, and subsequent modifications to minimize and/or eliminate polymer stress and degradation. In addition, the scope and range of fuel cell operating conditions are being assessed for their combined effect on fuel cell performance and membrane durability, including polymer structure and endgroups.

3.2. Nafion® PFSA polymer dispersions

Size exclusion chromatography–low angle laser light scattering (SEC–LALLS) has been used to show that observed aqueous dispersion viscosities were related to an "apparent" molar mass, as a result of a process dependent aggregation phenomenon. Typical viscosities are between 4 and 5 cP for the nominal 10% solids aqueous dispersions at the time of manufacture.

As seen in Fig. 5, there was a noticeable high molar mass shoulder due to the aggregate structure in the mass distribution of the "as made" dispersion. On heating the aqueous dispersions to high temperatures, the aggregate structure was irreversibly broken down resulting in narrower
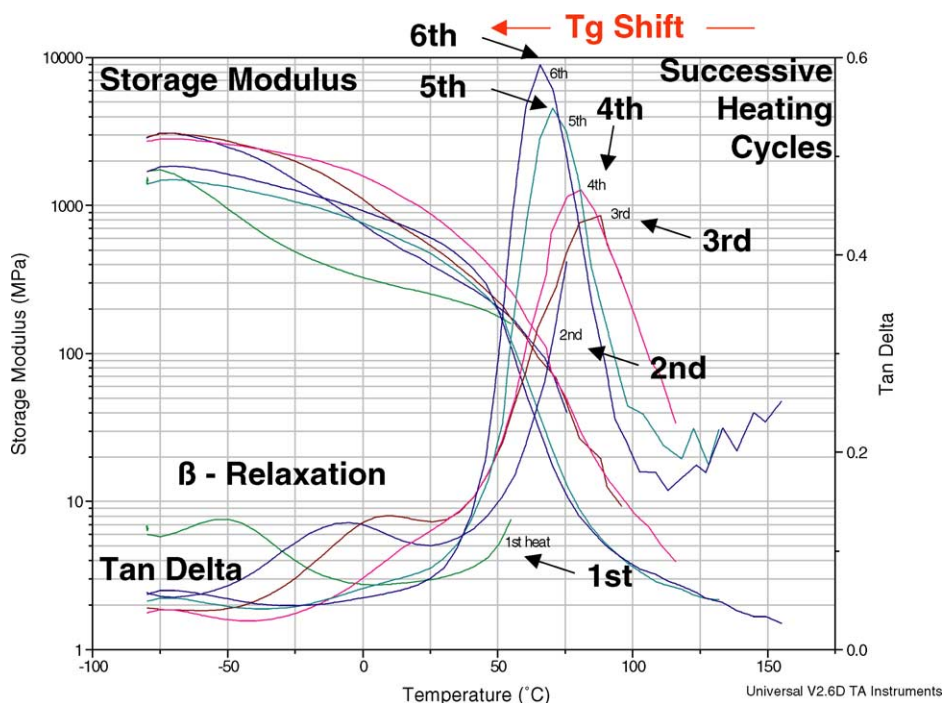

Fig. 7. DMA response data for NR-112 solution-cast membrane.

mono-modal distributions, which were similar for all dispersions. The high temperature heating reduced viscosities to approximately 2 cP. Interestingly, limited two-angle dependant light scattering measurements had indicated a linear relationship between the radius of gyration and molar mass for the aggregate portion of the "as made" distribution. This was consistent with previous research, which concluded that the dispersion particle shape was anisotropic, possibly rod and/or ribbon form.

This evidence suggested a model for Nafion® dispersions where elongated, charge stabilized particles exist on a three-dimensional lattice with the particle centers of mass at the lattice points. Furthermore, for dispersions that had even greater aggregate distributions, viscosity-shear thinning might result as a consequence of particle overlap and lattice deformation in a shear field.

Based on this work and other process developments, DuPont has introduced a new generation of polymer dispersions offering increased acid capacities, reduced metal ion content, and improved color and viscosity stability. The new dispersions are available in 5, 10 and 20% polymer content, two acid capacity levels, and mixed 1-propanol/water and water-only dispersions.

The surface tension of a polymer dispersion is an important consideration for optimization of catalyst coatings and efficiencies, coating adhesion, and membrane formation from dispersion. The surface tensions for the Nafion® polymer dispersions are reported in Fig. 6. The "percent (%)" value next to each data point indicates the dispersion's polymer content, which when added to the wt.% water (indicated on the graph) and wt.% alcohol (inferred) equal 100%. As expected, the aqueous dispersions exhibit the highest surface tensions (50 mN m^{-1}); while increasing alcohol content depresses the surface tension. For example, DE 2021 (containing 20% polymer, 34% water and 46% 1-propanol) has a surface tension of 25 mN m^{-1}. The range of possible surface tensions offers broad formulation capabilities for MEA fabrication.

3.3. Nafion® PFSA solution-cast membranes

The tensile storage modulus exhibits three distinct relaxation modes (α, β, γ) as a function of temperature, and all are sensitive to water content. Kyu and Eisenberg [16] attribute the α-relaxation to the glass relaxation of the hydrophilic phase domains, and the β-relaxation to the glass relaxation for the fluorocarbon phase domains. In Fig. 7, the DMA response for solution-cast membrane shows the dominant α-relaxation (Tg) shifting to lower values with successive heating cycles (and decreasing water content). The Tg starts at 85 °C and decreases to approximately 65 °C during the six successive cycles. This response is similar to that of extrusion-cast membrane. The β-relaxation (−50 to 10 °C) is stronger for solution-cast membrane (starting from humidified samples), but the difference attenuates after heating above 100 °C in dry N$_2$. The γ-relaxation, which occurs
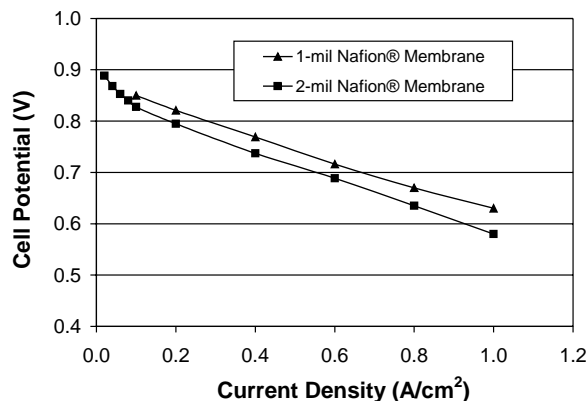

Fig. 8. Single cell MEA performance at 65 °C, 100% RH, 0 psig, H$_2$/Air (80/60%), 0.7 mg$_{Pt}$ cm^{-2} total loading.
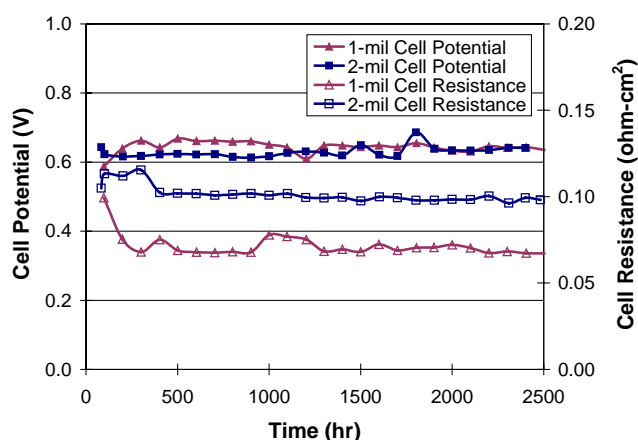

Fig. 9. MEA life test data: cell potential and resistance at 0.8 A cm^{-2} unchanged for 2500 h.

below −80 °C, was not measured. When the membrane sample is re-equilibrated to the initial ambient humidity, the DMA responses return to their original starting values.

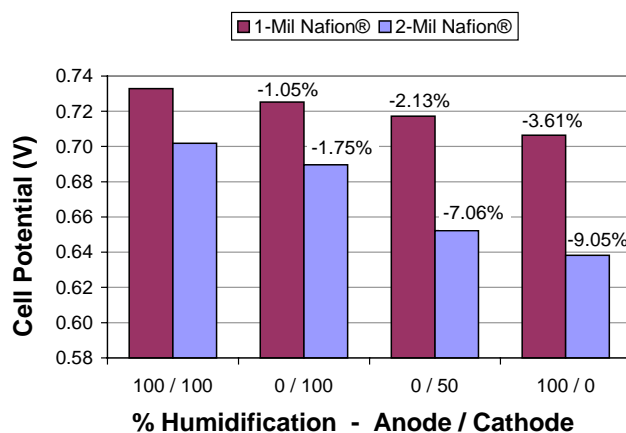Figs. 8 and 9 document single cell performance and life test data for DuPont Fuel Cells three-layer MEAs fabricated

Fig. 10. Humidification effect on MEA performance at 80 °C, 25 psig, H$_2$/Air (50/50%), 0.8 A cm^{-2}, 0.7 mg$_{Pt}$ cm^{-2} total loading.

with catalyst-coated 1 and 2 mil Nafion® membranes, and using commercially available gas diffusion media.

The fuel cell performance gain for 1 mil membrane over 2 mil membrane at high current density operation under reduced humidification is more than the contribution from the cell resistance differential alone. This gain represents enhanced water back-diffusion for the thinner membrane [17]. The 1 mil membrane experiences a lower voltage decline over the range of reduced anode and cathode humidification levels, as shown in Fig. 10. This provides a 10% increase in fuel cell power output for MEAs using the 1 mil membrane versus the 2 mil membrane.

Fabrication requirements, such as lamination, reinforcement, surface coatings, and other membrane related processes rely heavily on interfacial strength, which can be optimized by matching cohesive energies of adjacent layers. This attribute for Nafion® membranes can be estimated by measuring water contact angles. For this evaluation, membrane samples were tested "as made", "annealed" at 130 °C for 30 min in a dry nitrogen purged environment, and "boiled" in D.I. water for 30 min and blotted dry prior to testing.

Fig. 11 illustrates the degree of change in surface characteristics achievable by various membrane treatments; as well as how the surface characteristics change with time for the various treatments. The water contact angle responses for the extruded (N-112) and solution-cast (NR-112) membrane samples were identical for the "annealed" state, but very different for the "as made" and "boiled" states. This behavior may be influenced by the membrane's prior
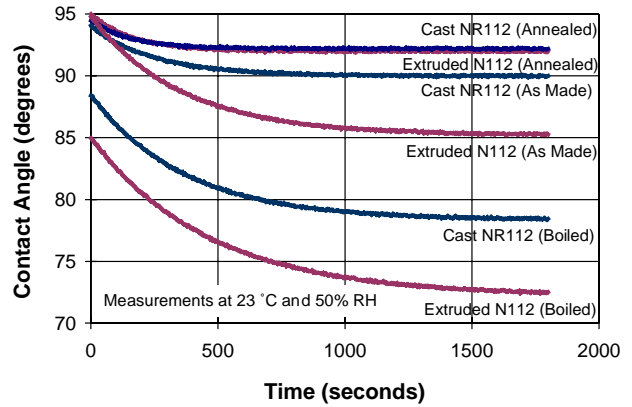

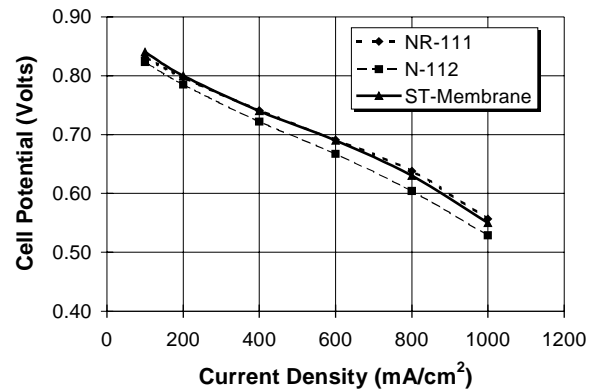Fig. 11. Water contact angle for "as made" and treated 2.0 mil Nafion® membranes.

Fig. 12. Single cell MEA performance at 65 °C, 100% RH, 0 psig, H$_2$/Air (80/60%), 0.7 mg$_{Pt}$ cm^{-2} total loading.
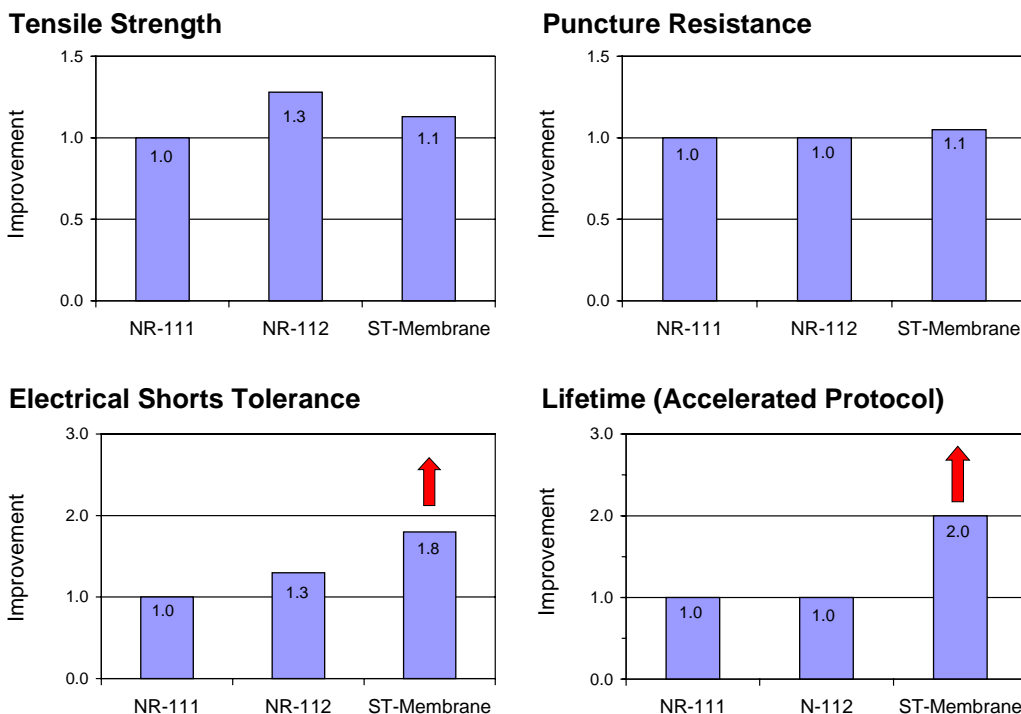

Fig. 13. Improvement comparisons between solution-cast and strengthened membranes.

thermal history (melt extrusion versus solution-cast) and water content, which is higher for the solution-cast (NR) membrane in the "as made" and "boiled" states; but very similar for both membranes in the "annealed" state.

3.4. Nafion® ST membranes

DuPont has developmental programs focused on improving membrane mechanical durability as measured by several physical property and performance indicators. These include mechanical durability, as measured by tensile strength, reduced dimensional change, puncture resistance, electrical short tolerance, and lifetime (voltage over time using accelerated test protocols).

MEAs made with Nafion® ST membrane by DuPont Fuel Cells have demonstrated improved mechanical durability and lifetime, with fuel cell performance similar to Nafion® NR-111 as shown in Fig. 12.

Tensile strength and puncture resistance performance were similar for both solution-cast and ST Membrane. However, compared to NR-111, the ST membrane has 50–80% improvement in electrical shorts tolerance and 2× extended lifetime as measured using DuPont's accelerated test protocol. Fig. 13 summarizes these comparisons.

The reported polymer and membrane improvements are undergoing validation and qualification in several commercial applications. Using the "voice of the customer", DuPont is determining what additional membrane improvements are needed for MEA fabrication and fuel cell applications based on customer evaluations and durability feedback. The improvements will incorporate chemical stability features as they are developed for both the Nafion® polymer and membrane.

4. Conclusions

DuPont Fuel Cell's polymer, dispersion, solution-cast and extrusion-cast membrane technologies provide the fuel cell industry with more efficient and flexible production capabilities, specialized membrane features, and reduced overall MEA fabrication costs. Today, DuPont is operating large-scale, thin membrane production facilities to provide the long-term projected membrane volumes at automotive quality standards and customer performance targets.

Ongoing polymer and membrane improvement programs are focused on providing the required performance, mechanical durability, and chemical stability necessary for successful PEM fuel cell applications. Fundamental research has enabled processing advancements for Nafion® polymer dispersions as well as formulation choices for improved fuel cell membrane fabrication and performance. Developmental ST membrane has shown favorable response based on our current mechanical durability indicators. The pipeline of new products and features is evidence of DuPont Fuel

Cell's commitment and leadership in supplying membranes and components to the fuel cell industry.

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