Final Report

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Project Objective: The overall goal of this project is to collect and integrate critical structure-property information in order to develop methods that lead to significant improvements in the durability and performance of PEMFC membrane materials.

Background: The University of Southern Mississippi-DOE project is focused on the fundamental improvement of PEMFC membrane materials with respect to chemical, mechanical and morphological durability as well as the development of new inorganically-modified membranes. Project personnel include the principal investigators (R.B. Moore and K.A. Mauritz), 2 postdoctoral associates and 4 PhD graduate students.

Dielectric Spectroscopy (DS) studies of Nafion® Membrane Degradation

DS studies of unfilled Nafion membranes

Solution cast Nafion® 212 films were cleaned by refluxing in 8M HNO₃ for 2h, rinsing three times with deionized water and then boiling in deionized water for 1h. Accelerated chemical degradation was conducted using Fenton's reagent (FeSO₄/H₂O₂) at room temperature for pre-specified times. Samples were then dried at 70° C for 12h under vacuum and then kept in a vacuum oven at room temperature until tested.

Before being placed between the electrodes in the dielectric spectrometer the films were preconditioned in a moisture chamber with controlled 6.4% relative humidity (RH) for 4d. Upon removing specimens from the chamber they were immediately loaded into the spectrometer, this

process taking less than 2 min. Quick sample transference is critical because slight variations in atmospheric RH and loading times significantly alters the β (high temperature) relaxation of the AR (as received) sample. To enhance sample reproducibility, the moisture content of the AR samples was further conditioned in the instrument by drying each specimen until the β relaxation had an f_{max} (frequency at dielectric loss = ϵ'' peak maximum) value of approximately 5100 Hz. Degraded films did not require this later *in situ* conditioning step. Rather, the Fenton-degraded samples were simply dried under vacuum at room temperature. Due to their fragile nature and temperature sensitivity, the additional cleaning and drying at 70°C was not used on the degraded samples.

A ϵ'' vs. f and T (temperature) response surface of a cleaned as-received Nafion® sample is seen in Figure 1.

212/AR CL/SPE-4/AFR06/0995

Figure 1 (left). 3D ϵ'' - f - T surface for cleaned as received Nafion® 212 acid films.

There is a ridge on this surface that is the locus of points that are peaks, located at respective values of f_{max} , over the range of tested temperatures. This ridge is the β relaxation which has been associated with a glass transition. The peak emerges at approximately -80°C although its high frequency tail is already visible at temperatures as low as -100°C

C. This peak shifts to higher f_{max} in usual non-Arrhenius fashion according to the Vögel-Fulcher-Tammann-Hesse (VFTH) equation¹ from approximately -80 to 60°C. However, at ~70°C the peak deviates from VFTH behavior by shifting to *lower* frequencies with increasing T and this opposite trend continues until 200°C.

A cut through this surface, i.e., graph ϵ'' vs. f for fixed T, allows more detailed examination of this relaxation, an example being in Figure 2 for T = 10°C. The data is best fitted using three Havriliak-Negami (HN) relaxation terms and a dc conductivity term to account for the upswing in ϵ'' at low f .^{2,3}

$$\epsilon^*(\omega) = \epsilon' - i\epsilon'' = -i \left(\frac{\sigma_0}{\epsilon_0 \omega} \right)^N + \sum_{k=1}^3 \left[\frac{\Delta \epsilon_k}{1 + (i\omega \tau_{HN})^{\alpha_k}} \right] + \epsilon_{\infty k} \quad (1)$$

Figure 2. ϵ'' vs. $\log f$ for cleaned, as-received Nafion® at 10° C. The data is well-fitted with three HN terms and a dc conductivity term at low f .

The presence of two-relaxations, with a major and minor peak in the region of the glass transition (β relaxation), is similar to behavior described by Yeo and Eisenberg who also determined that the two peaks shift to higher temperatures with de-sorption of water.^{4,5} The sensitivity of relaxations to residual water was studied in our group and mentioned in earlier reports. The temperature behavior of the relaxation time $\tau_{\max} = (2\pi f_{\max})^{-1}$ for the major, rightmost peak for both specimens confirms that the β relaxation obeys the VFTH equation until approximately 70° C, but not at higher temperatures.

Figure 3 shows ϵ'' vs. $\log f$ curves, also at 10° C, for films degraded in Fenton's reagent for 75h along with non-degraded films for a control. Degradation shifts $f_{\max}$ to lower values in such a way that $\tau_{\max}$ increases by decades, reflecting significantly slower chain motions. This appears counterintuitive as it is expected that chain segmental motion would increase due to the generation of shorter, degraded chain lengths.⁶

Figure 3. ϵ'' vs. $\log_{10} f$ plots, at 10° C for Nafion® 212 acid films degraded in Fenton's reagent for 75h as well as the curve for a non-degraded as-received sample. Two separate data sets for each sample are presented to illustrate reproducibility of relaxation peak position.

One explanation is linked to the idea that SO_3H groups coordinate with Fe^{+2} ions that enter the membrane from the Fenton electrolyte during the degradation process. These interactions might prevent smaller chains from leaching out of the 75h degraded samples because the samples were tested after degradation without further cleaning with HNO_3 . To clarify whether Fe^{+2} ions coordinate with SO_3^- groups, samples degraded for 60h were cleaned and dried as described in the experimental section. These 60h degraded and cleaned samples were seen to have the same spectroscopic signature as those that were degraded for 60h and not cleaned as well as the as received samples. Thus, after 60h of degradation, any coordination of Fe^{+2} ions with sulfonic acid groups does not appear to affect dielectric spectra in a way associated with molecular weight fragments that are present or not. To further understand the situation, both cleaned as-received and degraded films were fully converted to the organic, less hydrophilic TBA^+ form. There are no spectroscopic differences between TBA^+ -exchanged degraded films and those of TBA^+ converted as-received cleaned films. This suggests that interactions between side chains are not involved in this phenomenon. Studies showed that water absorption/desorption properties are drastically altered between as-received and degraded 75h films. Specifically, water uptake significantly changes between 60 and 75h of degradation. τ_{max} for the β relaxation was not affected by moisture as was the case for the cleaned as-received samples. This might imply that a catastrophic molecular degradation occurs between 60 and 75h of degradation.

Another explanation for the increase in τ_{max} involves an upward shift in average molecular weight caused by low molecular weight fragments that were leached out of the

membrane into the external Fenton's electrolyte during the degradation experiment. Longer chains will have longer relaxation times. We prefer this explanation.

Figure 4 shows $\log \tau_{max}$ vs. T plots for untreated and 75h degraded samples. $\log \tau_{max}$ vs. $1/T$ plots are nonlinear which implies that this is not a relaxation that can be described in terms of conventional activated rate theory.

Figure 4. $\log \tau_{max}$ vs. T plots for Nafion® 212 acid films degraded in Fenton's reagent for 75h and an untreated control. Two specimens from the same film are plotted in each case to demonstrate very good reproducibility.

The degraded sample curves are significantly vertically shifted from those of the cleaned as-received control, again demonstrating that the former have slower, more

restricted chain motions.

The Vögel-Fulcher-Tammann-Hesse (VFTH) equation is given by equation 2.

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{k_B(T - T_V)}\right) \quad (2)$$

k_B is the Boltzmann constant and τ_0 , E_a , and T_V are parameters obtained by fitting the equation to experimental data. τ_0 is a hypothetical relaxation time at infinite temperature. E_a , having units of energy, is not associated with an activated process. T_V , the Vogel temperature, is the temperature at which chain segments become frozen in a hypothetical situation in which a polymer is cooled at quasi-static rate from the rubbery state.

Curve-fitted VFTH equation parameters for these samples are in Table 1. While τ_{max} increases by three orders of magnitude, T_V increases with degradation which suggests more restrictive chain mobility. This increase in T_V is in harmony with an upward shift in polymer molecular weight due to low molecular weight fragments leaching out of the membrane during the degradation experiment. Shorter chains have greater free volume per mass because of the higher density of chain ends which act as packing defects.

Table 1. τ_{max} at 10° C obtained from fitting the H-N equation to data, and Vögel temperature obtained by fitting the VFTH equation to τ_{max} vs. temperature data for samples degraded for 75h as well as for an un-degraded control.

Sample	Relaxation time (s)	T_V (K)	In the H-N equation the fitted α and β parameters determine the distribution of relaxation times, $G(\tau)$, such that α characterizes the distribution breadth and β the degree of curve asymmetry. ^{2,3} $G(\tau)$ is given by the following equation: ^{2,3}
212 AR Cl-spec1	1.72×10^{-6}	153	
212 AR Cl-spec2	1.42×10^{-6}	135	
212 75hrs Deg-spec1	1.26×10^{-3}	192	
212 75hrs Deg-spec2	1.85×10^{-3}	172	

$$G(\tau) = \frac{\left(\frac{\tau}{\tau_{0,1}}\right)^{\beta, \alpha_1} \sin(\beta, \Theta_1)}{\pi \tau \left[\left(\frac{\tau}{\tau_{0,1}}\right)^{2\alpha_1} + 2 \left(\frac{\tau}{\tau_{0,1}}\right)^{\alpha_1} \cos(\pi \alpha_1) + 1 \right]^{\frac{\beta_1}{2}}} \quad (3)$$

where

$$\Theta_1 = \arctan \left(\frac{\sin(\pi \alpha_1)}{\left(\frac{\tau}{\tau_{0,1}}\right)^{\alpha_1} + \cos(\pi \alpha_1)} \right)$$

$G(\tau)$ vs. τ curves for 75h degraded vs. non-degraded samples are shown in Figure 5. Degradation not only broadens the relaxation distribution and shifts it to longer times (indicating slower chain motions) but a bimodal curve is transformed to a trimodal curve. This might be interpreted in terms of molecular weight distribution broadening with chain degradation.

Figure 5. $G(\tau)$ at 10°C for Nafion[®] 212 acid films degraded in Fenton's reagent for 75 h as well as for an untreated sample. Overall shift to the right reflects slower motions.

In polymer blends, relaxation peak broadening is usually attributed to concentration fluctuation or intrinsic mobility differences between blend

components.⁷ Within the context of Nafion[®], at some degradation stage one can consider a 'blend' of chains of lengths so diverse as to create microstructural heterogeneity, in part because the solubility of chains depends on molecular weight and the effect is more pronounced for shorter chains. Thus, given the validity of this view, there will be a distribution in chain dynamics, i.e., distribution of relaxation times.

Dielectric Spectroscopy (DS) studies of Nafion[®]/Silicate Nanocomposite Membrane Degradation

As described in earlier reports, the motivation for imparting metal oxide nanoparticles via membrane-in situ sol-gel reactions is to increase membrane hydrophilicity at higher temperatures as well as enhance mechanical durability in terms of RH cycling. In particular, hyperbranched metal oxide particles containing numerous hydrophilic OH groups along their arms that extend into the ionomer can structure hydrogen bonded water pathways along which protons can easily hop and will be intimately incorporated in the matrix.

Nafion[®]/silicate nanocomposites were prepared by swelling 112 acid films in methanol/water (3:1 vol/vol) for 1d, adding tetraethylorthosilicate (TEOS)/methanol (3:1 vol/vol) and stirring for different times up to 20 min. Films were then removed from the mixture, immersed into MeOH for 1-2 sec to remove possible surface precipitates and then dried under vacuum at 100°C for 1d to further drive sol-gel reactions. Different silicate percents were adjusted based on the time between adding TEOS/MeOH and removing samples from the mixture. Two samples with 6 and 34% silica were then degraded in Fenton's reagent for 30h. After degradation, samples were washed with 2M HCl by refluxing for 2h and then refluxing in DI H₂O for 1h to remove remaining FeSO₄. Films were then dried under vacuum at room temperature for 1d, stored in a humidity chamber at $\approx 0.2\%$ RH for at least 4d prior to DS testing. Each experiment consisted of, first, frequency sweep iterations at $T = 70^\circ\text{C}$ for 3.6h and then temperature cycles from -130 to 200°C in 10°C increments.

Shifts in macromolecular dynamics in membranes degraded in Fenton's reagent, and untreated HNO_3 acid cleaned samples, were studied. Figure 6 shows characteristic molecular motions along crests on the response surface for Nafion[®] 112 H^+ , as received, and an HNO_3 -cleaned sample. Two main molecular motions are observed: the β relaxation with onset at 0°C and α relaxation (involving ion-hopping) with onset at $\approx 80^\circ\text{C}$. The alteration of the β relaxation by silicate incorporation and degradation of these hybrid membranes were investigated.

Figure 6. ϵ'' vs. f and T response surface for Nafion[®] 112 acid films, as received and HNO_3 cleaned.

Figure 7 shows ϵ'' vs. f at 60°C for films with different silicate loading. The β relaxation peak did not change much with silica content which might suggest that the silicate component resides mainly in the hydrophilic domains as seen in SAXS studies. An extra peak on the high f wing is observed for the 20 min - reacted sample (highest silica loading of 34%). At low f , ϵ'' is related to the dc conductivity, σ_{dc} , according to $\epsilon'' \approx \sigma_{dc} / \epsilon_v \omega$ where $\omega = 2\pi f$ and ϵ_v is the vacuum permittivity.

Figure 7. ϵ'' vs. f at 60°C for films with different silica loadings as per indicated reaction time.

ε'' at low f decreases with increased silica % which can be explained in terms of decreasing σ_{dc} due to trapping $-\text{SO}_3\text{H}$ groups within silica cages and/or increased proton migration tortuosity.

For the 20 min-reacted sample with 34% silica, the effect of degradation on the β relaxation is seen in Figure 8. Peak data were fitted to the Havriliak-Negami equation after subtraction of the dc contribution. The dc-subtracted spectra are shown in the insert. Degradation does not affect the β peak position (f_{max}) of 34% silica samples. In fact, the degraded unfilled sample showed the greatest shift to longer τ_{max} reflecting slower motions (Figure 8). Coordination of SO_3H groups with Fe^{+2} ions as well as the leaching out of degraded low molecular weight chains might be implicated. The peak position for the degraded 34% silica sample is very close to that of the un-degraded unfilled control.

It is important to separate the effect on T_g -related motions of Fe^{+2} ions that enter the membrane during degradation, from the effect of molecular weight degradation. This was accomplished by washing degraded specimens with HCl to affect ion exchange and dialyzing Fe^{+2} and co-ions into the external bath.

Figure 8. Effect of degradation on the β relaxation for the 20 min-reacted sample with 34% silica. Insert shows the H-N equation fitted spectra with subtraction of dc conductivity.

The $\log_{10} \tau_{max}$ vs. $1/T$ curves are non-Arrhenius (Figure 9) and the degraded samples have longer relaxation times at a given temperature.

Figure 9. $\log \tau_{max}$ vs. $1/T$ for untreated and 34% silicate-containing films and degraded samples.

At constant T , chain motions for both undegraded unfilled and degraded 34% silicate containing membranes are similar but slower for the degraded unfilled membrane. Perhaps, for degraded Nafion[®]/(34% silica), generated $\bullet OH$ radicals are diverted into another process

not involving the chain such as abstraction of H atoms from Si-OH groups by $\bullet OH$ radicals, leaving Si-O $\bullet$ ions or radicals. Chain motions for the filled degraded and undegraded samples are rather similar. Clearly, this type of filler affects degradation.

$G(\tau)$ for the β relaxation at 60°C for these cases (Figure 10) shows that macromolecular motions of the unfilled degraded sample are the slowest because $G(\tau)$ shifts to greater τ relative to the unfilled undegraded sample while motions within the degraded sample with 34% silica is similar to those of the undegraded unfilled sample.

Figure 10. $G(\tau)$ vs. τ at 60°C for unfilled and Nafion[®]/(34% silicate) films and degraded samples.

Nafion®/Silicate Nanocomposite Membranes: Effect of a Sol-gel Catalyst on Particle Size/distribution

A new procedure for the sol-gel process is being conducted using *dibutyltin dilaurate* catalyst. This procedure was used with polydimethylsiloxane films and resulted in very well dispersed silica domains with particles sizes in the range 30-50 nm.⁴

Using that catalyst, we were able to prepare Nafion®/silicate nanocomposites with loadings up to 113% (wt/wt) which is completely glass. The procedure includes swelling the membrane in ethanol for 1d, then adding a 1% TEOS:dibutyltin dilaurate (wt/wt) mixture to the reaction pot with slow stirring; membranes were left in the reaction pot for different times to vary silica loading. Finally, membranes were taken out of the pot and their surfaces were rinsed with ethanol for 1~2 sec to remove any TEOS on the surface and then dried carefully. The membranes were left for one day in atmospheric conditions to allow completion of the sol-gel reactions as they absorb moisture directly from the atmosphere to complete the reaction (moisture % lab is 50-60% RH). While the sol-gel reaction continues within the membranes after the indicated immersion times, the diffusion-controlled exchange of reactants and solvent across the membrane/solution interface ceases. The time between immersion in TEOS/dibutyltin dilaurate/ethanol mixture and removal of the membrane from solution will be referred to as diffusion time rather than reaction time.

Changes in the β transition of these composites with different silica content were checked using dynamic mechanical analysis DMA (Figure 11). Samples are presented in codes represent the diffusion time for each sample. It is clear that as immersion time of the sample in the TEOS/cat/ethanol mixture increases, i.e., increased silica content, the β transition shifts to higher temperature. There is almost a 93°C increase in the glass temperature over the extremes of this composition range.

Figure 11. DMA loss tangent vs. T curves for Nafion®/silicate samples prepared using dibutyltin dilaurate catalyst with different diffusion times vs. untreated control sample.

Further ATR-FTIR, proton conductivity and ²⁹Si solid state NMR studies are being conducted to investigate these new types of silicate structures formed within Nafion® and their effect on proton conductivity at high temperature as well as membrane degradation.

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Nafion®/Titania Nanocomposite Materials: Mechanical Durability Studies

Nafion® membranes chemically degrade in fuel cell environments due to attack of •OH radicals formed due to fuel crossover. These membranes have inferior gas barrier and mechanical properties due to poor *dimensional stability with humidity change*. Variation in membrane water content and fuel humidity leads to differential swelling generating internal mechanical stresses which, coupled with attack of peroxide decomposition radicals, eventually leads to failure. In concept, fuel crossover can be reduced if inert particles are placed along gas diffusion pathways, i.e., within the polar clusters of Nafion®. Obstacles posed by these particles force gas molecules along tortuous pathways and reduce crossover, thereby increasing membrane durability. Also, if these particles are interconnected they can form load bearing networks that provide mechanical reinforcement, thus minimizing mechanical and chemical degradation. To this end, we affected membrane-*in situ* growths of nanoscopic metal oxide structures via sol-gel reactions of metal oxide precursors. Here we report results for titania filled Nafion® membranes.

Nafion® 112 membranes were cleaned by boiling in 8M nitric acid for 2h followed by boiling in deionized water twice for 2h to leach out residuals. The membranes were then dried at 100° C under vacuum for 24h. titanium iso-propoxide was used as the sol-gel precursor monomer and 2, 4-pentanedione was added as a catalyst to slow the reaction. A ratio of 0.4 for 2, 4-pentanedione-to-alkoxide monomer was maintained. The membrane was swollen in a methanol-water mixture for 24h, then temporarily removed for ~30s during which time the precursor monomer and 2, 4-pentanedione were added and stirred to form a homogeneous reaction solution. Then, the membrane was re-immersed for 15 min and after removal from the reaction mixture, followed by methanol wash, it was dried at 100° C for 16h. After drying, the membrane was refluxed in 8M HNO₃ for 4h followed by refluxing in deionized water twice for 1h each. The membranes were then dried at 100° C under vacuum for 24h. A control Nafion® sample was subjected to similar processing conditions, save for the reaction procedure.

Membrane Characterization

Inorganic uptake, water uptake and equivalent weight (EW)

The difference between dried membrane weights following the sol-gel treatment and subsequent nitric acid/water cleaning is considered as the titania weight uptake which for the composite membrane was gravimetrically measured to be 20%. The Nafion® control sample lost 3% of its initial weight assumedly because low molecular weight fragments leached out of the membrane in alcohol solution during membrane swelling.

Vacuum dried samples, after weighing for initial weight were immersed in deionized water for 24h. The samples were taken out of water and blotted dry and weighed to determine

water uptake. For EW measurements, vacuum dried membranes, after weighing for initial weights, were added to a flask containing deionized water and soaked for 24h. To neutralize the acidic groups, a known excess of 0.01N standard NaOH solution was added to the flasks and stirred for 3h. Excess NaOH was measured by titrating against 0.01N standard acetic acid solution using phenolphthalein indicator. Equivalent weights were calculated by dividing the number of moles of sodium hydroxide consumed by the sample into its dry weight. Average values of water uptake and EW of Nafion[®] and Nafion[®]/titania over three samples each are in Table 2. Water uptake and EW of the Nafion[®]/titania composite membrane were calculated with respect to the Nafion[®] fraction (0.8) in the membrane. By this measure, water uptake of the composite membrane was 40% lower than that of the unfilled membrane. For unfilled Nafion[®] the water uptake is distributed throughout the entire volume but for the composite membrane the titania structures occupy a considerable amount of space and reinforce the polymer (limiting swelling), thereby reducing percent by weight. Titania structures inserted into the polar clusters also simply block entry of water molecules in these domains.

Table 2. Equilibrium water uptake and EW for Nafion[®] and Nafion[®]/titania membranes.

	Nafion [®] /titania	Nafion [®]
Water uptake (weight %)	13.6 ± 2.1	22.3 ± 2.0
Equivalent Weight (g/mol)	1143 ± 20	1152 ± 37

FTIR-ATR chemical structure analysis

The position of bands characteristic of titanate structures are discussed in references 3-5 at the end of this section.

The C-F stretching band at 1200 cm⁻¹ was used as an internal standard to scale the absorbance of both spectra the same. The uniform-scaled spectra for Nafion[®]/titania and unmodified Nafion[®] are shown in Figure 12. When the membrane is introduced into the sol-gel reaction monomer solution, titanium iso-propoxide reacts very rapidly. In the near surface region of the membrane, the speed of this reaction relative to monomer diffusion can cause a U-shaped titania gradient with high composition near the surface, as discovered in earlier studies of similar materials so that a spectrum of the near-surface region may not be that of the interior.[1, 2] Also, the absorbance of all polymer bands can be expected to be diminished by virtue of having lower concentration as the inorganic component occupies part of the volume. This dilution effect, in fact, is seen across the spectral range in Figure 12.

Beginning at the high wavenumber region, there is the band for S-O asymmetric stretching in SO₃⁻ groups. The maxima for the modified and unmodified samples coincide but it is also significant that the band width has not changed with inorganic modification. The unaltered band width can be interpreted as being due to an unchanged distribution of molecular environment around sulfonate groups despite the inorganic incorporation. To the right of the SO₃⁻ peak is a strong CF₂-CF₂ band whose position is essentially invariant with inorganic modification. Continuing to the right, there is the symmetric stretch of the SO₃⁻ group, whose peak wavenumber and profile do not change with inorganic modification. The wavenumber invariance of both sulfonate peak vibrations might indicate that the titanate phase does not interact with these groups as S-O bond polarization does not seem to change as it might through inductive effects. This is in harmony with the unchanging EW with titanate uptake, as discussed above.

The doublet at around 980-960 cm⁻¹ is due to the two ether groups in the long side chains. The lower wavenumber component absorbance becomes of lesser absorbance relative to the high

wavenumber component. This could indicate interactions of titanate structures with the two oxygens, both of which have hydrogen bonding capability.

Ti-O-Ti stretching vibrations are seen in a band at $\sim 700\text{ cm}^{-1}$. This band is evidence of successful condensation reactions required for particle formation and the low peak height-to-peak width ratio indicates a broad distribution in the environment (varying degrees of Ti atom coordination about bonded TiO_4 tetrahedra) about these vibrating groups. There is a $\text{CF}_2\text{-CF}_2$ band in this location, the absorbance which, of course, must account for part of the strength of the Ti-O-Ti band in the un-subtracted spectrum. The Ti-O-Ti band is not to be confused with the $\text{CF}_2\text{-CF}_2$ band because the composite band is of greater, rather than less, than the absorbance associated with the $\text{CF}_2\text{-CF}_2$ band. There is a band at $\sim 600\text{ cm}^{-1}$ which is in the region of Ti-O stretching in $\text{Ti}(\text{OPr})_4$ molecules which shows that there remain un-hydrolyzed monomers, as well.

The inset in this figure shows absorbance in the region of O-H stretching for both the control and titania-modified Nafion[®]. Unmodified Nafion[®] shows a broad band that is likely due to water that, due to the wide band width, exists in a large number of hydrogen bonding states. The Nafion[®]/titania sample also has a broad band in this region that can be ascribed to water molecules that hydrate accessible uncondensed TiOH groups as well as Ti(O-H) stretching vibrations.

In summary, while there seems to be no significant interactions between the SO_3^- groups and the inserted titanate structure, the ether groups, which are closer to the main chain, are affected. The FTIR analysis indicates successful titania network formation with significant uncondensed non-interacting Ti-OH groups.

Figure 12. FTIR-ATR spectra of Nafion[®] and Nafion[®]/titania composite membranes.

Mechanical durability analysis

Mechanical properties of membranes at 80°C and 100% relative humidity (RH) were tested using an MTS Alliance RT/10 tensile setup equipped with a 100N load cell. A custom design environmental chamber and sparger were built to control chamber temperature and RH. 18 mm wide samples were used for all tensile experiments.

Both modified and control membranes were clamped inside the environmental chamber that was held at 80°C . After mounting, the samples were conditioned for 2h with a 100% RH nitrogen stream supplied at a flow rate 300cc/min. After such conditioning, the membrane swells due to water uptake and to hold the sample to its extended swollen length, the crosshead position was slowly adjusted until a tension of 0.1N was detected. The crosshead position was then locked and the 100% humidified nitrogen stream switched to dry N_2 at the same flow rate (300cc/min). The temperature of the dry N_2 stream was the same as that of the humidified N_2 stream and the chamber temperature was maintained at 80°C . This change of circulating gas stream causes the membrane to lose water such that the sample attempts to regain its un-swollen length except that the clamps are locked at

the swollen length position and the sample consequently exerts a contractile force. These resistive forces were monitored for 2h after the humidity drop. Figure 13 shows stresses developed for two Nafion[®] and two Nafion[®]/titania membranes measured for 2h after the humidity drop.

Stress-time profiles for the two control Nafion[®] samples reach peak values at around 58 and 71 min, and then drop. Peak stress values for the two samples were 1.56 MPa and 1.89 MPa, respectively. The stresses in the two samples do not peak at the same time as the rate of water loss by the samples could be different due to water condensation in the chamber or minor material differences. Nonetheless, the profiles for both samples are similar and both yield after reaching a critical stress. Due to low modulus and lack of cross-linking or reinforcement in this unfilled membrane, it is unable to withstand the contractile stress developed and yields perhaps through chain slippage through entanglements that limit the stress from increasing.

Figure 13. Contractile stress response to humidity change from 100% down to 0% at 80° C for H⁺Nafion[®] (dotted line) and Nafion[®]/titania (solid line) membranes.

In strong comparison, the composite membrane resists the dimensional constraint. For both composite samples, at ~ 70 min the stress reaches peak values of 8.4 and 8.6 MPa and remains fairly constant during the experimental timeframe. It can be concluded that the *in situ* grown titanium oxide quasi-networks provide good membrane reinforcement and prevent it from yielding due to humidity change. If chain slippage is involved in failure then it can be imagined that the inorganic inclusions anchor the chains, thereby restricting their motion through entanglements. This could be beneficial for fuel cell membranes in the situation of clamped MEAs at the intersection of lands and grooves of gas distribution plates that experience periodic stresses due to humidity changes. Without such reinforcement, the unmodified membrane will experience structural and mechanical hysteresis such that swelling fatigue may eventually cause local yielding which can lead to cracking and ultimate failure.

Tensile stress-strain curves for four samples each of Nafion[®] and Nafion[®]/titania membranes at 80° C and 100% RH are shown in Figures 14 a and b. The samples after conditioning for 2h with a 100% relative humidity nitrogen stream were stretched at a rate of 5 mm/min.

The stress rise does not start at the origin as the curves are displaced along the strain axis. The reason for this is that as the sample expands due to water uptake during conditioning force is not registered until the sample reaches its natural length. The curve displacement is diagnostic of sample dimensional stability. After this, the curve has a profile typical of a ductile material and a modulus can be determined from the displaced initial region of the curve. The maximum strain up to the point when the stress begins to rise corresponds to the increase in sample length with respect to the initial dry length, i.e., swelling. The initial part of the curve for all samples is shown in Figures 15 a and b, as well.

Figure 14. Tensile-stress strain curves at 80°C and 100% RH of a (A) Nafion® and (B) Nafion®/titania composite membranes.

Figure 15. Initial strain region of stress-strain curves at 80°C and 100% RH for (A) Nafion® and (B) Nafion®/titania membranes.

The Nafion®/titania membrane has better dimensional stability than that of unfilled Nafion® because the percent length increase for the former is 5 ± 1 % while that of the latter is 10 ± 3 %. The average modulus is 120 ± 7 MPa for the composite but considerably lower at 36 ± 7 MPa for the unmodified Nafion® membrane. Table 3 summarizes the mechanical properties.

Table 3. Mechanical properties of Nafion[®] and Nafion[®]/titania membranes at 80° C and 100% RH.

	Initial Modulus	Length increase due to humidity change	Strain at break	Stress at break
	MPa	%	mm/mm	MPa
Nafion [®] /Titania	120.4 ± 7.1	5.7 ± 1.0	3.1 ± 0.2	24.1 ± 1.68
Nafion [®]	36.2 ± 7.2	10.0 ± 3.2	4.1 ± 0.4	20.8 ± 3.2

Incorporation of such sol-gel-derived structures not only enhances membrane modulus but imparts better dimensional stability against humidity change which could be beneficial in enhancing the physical durability of membranes in fuel cells.

Scanning Electron Microscopy (SEM)

Damage surface morphology of the clamped Nafion[®] and Nafion[®]/titania membranes subjected to the RH drop of from 100% down to 0% at 80° C, were inspected using SEM and the material damage incurred is shown in Figure 16.

Figure 16. SEM micrograph of Nafion[®] (bottom) and Nafion[®]/titania (top) membrane after contractile stress buildup vs. time at constant strain experiments with drop in RH.

The unfilled Nafion[®] membrane shows significant signs of yielding when subjected to the RH drop and subsequent contractile stress. The entire width of the membrane shows cavities and stretching/orientation indicating failure propagation. On the contrary, the Nafion[®]/titania

membrane does not show such cooperative failure. There are isolated cavities but the mechanical integrity is greatly improved relative to the unmodified membrane. These morphological results and interpretations are highly supported by the contractile stress vs. time curves in Figure 13 that show a significantly greater resistance offered by the composite.

Electrical impedance measurements of conductivity

Membrane proton conductivity was measured using a 4 point probe configuration (Bekkttech). For consistent membrane water content, the cell with sample was immersed in deionized water. Z'' vs. Z' was measured over the frequency range 500 Hz to 1 MHz using an impedance analyzer. The Z' intercept was the resistance to compute conductivity.

The impedance behavior of Nafion® and Nafion®/titania membranes at room temperature is shown in Figure 17 and respective conductivities were computed to be 0.078 S.cm^{-1} and 0.033 S.cm^{-1} . Titania conductivity is less than half that of Nafion® which may be due to lower water uptake as well as more tortuous proton pathways.

Figure 17. Impedance spectra of Nafion® and Nafion®/titania membranes at room temperature in water.

It is reasonable to think that side chains become trapped during growth of the inorganic quasi-networks. The SO_3H groups at the ends of the side chains catalyze the sol-gel reaction of the titanium isopropoxide monomer so that branched titanate structures could rapidly form cages

around the acid groups and shield them from being proton hopping sites. However, this is apparently not the case as the EW does not change although sections of the chain closer to the backbone may be engulfed by titanate structures. These facts are borne out by our FTIR spectroscopic studies of these materials that showed that, while the doublet C-O-C band was influenced by titania insertion, the two bands for the SO_3H group were not.

Membrane durability studied by open circuit voltage (OCV) decay test

To test durability and fuel crossover, MEAs were tested under OCV conditions at 90°C and 30% RH. Platinum loading in the electrode was estimated to be $0.41 \pm 0.1 \text{ mg.cm}^{-2}$. Ultra pure hydrogen (0.2cc/min) and ultra pure oxygen (0.3cc/min) were used as fuels. The test was performed for 20h and anode and cathode effluent was independently collected in cold traps. Before the test, the cold traps and exhaust pipes were thoroughly washed to ensure no fluoride contaminant. Fluoride emission rate (FER) from the effluent was measured using an fluoride ion selective electrode. Before FER measurements the electrode was calibrated for a 0.1-5 ppm range using fluoride standard solutions. The OCV decay curve is shown in Figure 18.

Figure 18. OCV voltage curves for Nafion® and Nafion®/titania membranes at 90°C and 30% RH.

The starting OCV for Nafion®/titania is 3.6% higher than that of Nafion® which is interpreted as better gas barrier properties. Incorporation of the titania network reduced fuel crossover and thereby minimized voltage loss. This is further supported by the rate of OCV decay. In 20h the OCV for Nafion® decreased by 0.091 V at a rate of 4.5 mV/h whereas for Nafion®/titania it decreased by 0.025 V at a rate of 1.2 mV/h. The voltage decay rate for Nafion® is 3.5 times higher than that of the Nafion®/titania membrane.

Fluoride emission rate (FER)

More specifically, the fluoride content of effluent collected during the OCV study for both anode and cathode is shown in Figure 19.

Figure 19. FER of Nafion® and Nafion®/titania membranes for anode and cathode.

It can be seen that FER for the Nafion®/titania MEA is at least an order of magnitude less than that of Nafion®. This test indicates a reduced rate of membrane chemical degradation,

which is again attributed to better gas barrier properties. Reduction in fuel crossover may have lowered the rate of hydrogen peroxide formation which could reduce the rate of membrane chemical degradation. By reducing fuel crossover one can not only reduce voltage loss and increase cell efficiency but can also retard membrane degradation.

Fuel cell performance

Polarization curves of the Nafion[®]/titania and Nafion[®] control membrane in the fuel cell before and after the OCV test are shown in Figure 20.

Figure 20. Polarization curves for Nafion[®] and Nafion[®]/titania membranes before and after OCV at 80°C, 75 % RH.

The performance of the titania-incorporated Nafion[®] membrane is extremely poor compared to that of the pure Nafion[®] membrane. Based on low water uptake and low proton conductivity, this poor performance is not unexpected. However, the performance of Nafion[®]/titania is *unchanged* after the OCV test compared to

a huge drop in performance of the Nafion[®] membrane. The unmodified Nafion[®] membrane, due to poor dimensional stability and poor mechanical properties, yields under stresses developed due to humidity and temperature changes. Weak regions may serve as paths for gas diffusion. Periodic swelling/de-swelling stresses induced during fuel cell operation will lead to further membrane weakening and increase fuel crossover. Fuel crossover produces H₂O₂ which on decomposition forms reactive hydroxyl radicals which degrade the polymer. Thus, mechanically weak regions, after experiencing microscopic material hysteresis owing to periodic stresses, and attack from hydroxyl radicals, may eventually form pinholes.

For the Nafion[®]/titania membrane the inorganic reinforcement significantly improves dimensional stability and increases initial elastic modulus which resists physical stresses. Also, the network imparts better fuel gas barrier properties reducing chemical degradation due to crossover.

Linear sweep voltammetry (LSV)

LSV was performed to check for H₂ crossover and electronic shorting in the MEA. H₂ and N₂, saturated at room temperature, were passed through anode and cathode sides, respectively, at a flow rate of 0.2 slpm. The working electrode (cathode) was swept from 0 to 0.8 V (vs. SHE) at 4 mV.s⁻¹ and the current due to oxidation of crossover hydrogen was recorded. The hydrogen crossover curves for Nafion[®] and Nafion[®]/titania membranes before and after the OCV test are shown in Figure 21.

Before the OCV test, the crossover current for Nafion[®]/titania is higher than that of unmodified Nafion[®] which indicates that addition of the inorganic quasi-networks has not improved hydrogen barrier performance. However, the relative increase in hydrogen crossover is more for the unfilled Nafion[®] membrane after OCV testing. This result reinforces the conclusion that unmodified Nafion[®] degrades faster than Nafion[®]/titania.

Figure 21. Hydrogen crossover current for Nafion® and Nafion®/titania membranes before and after OCV testing.

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Methanol Solubility Study of New Generation Nafion®

In accordance with the post-processing treatments milestone, we have conducted Small Angle X-Ray Scattering (SAXS) on Nafion® NRE 212CS films with various thermal annealing histories. As stated in previous reports, we have devised an annealing procedure that will stabilize dispersion cast Nafion® films in boiling methanol. We notice mechanical stability in boiling methanol occurring after the following annealing treatments: 15 min at 175°C for H⁺ and 15 minutes at 275°C for Na⁺.

SAXS analysis was conducted at Argonne National Labs using the Advanced Photon Source. The beam line setup consisted of a sample to detector distance of 2930 mm, beam wavelength of 0.83 Å (energy of 15 keV). Figure 22 represents the log-log scattering profile of NRE212CS H⁺ annealed for 15 min at various temperatures. Based on our previous reports, we know mechanical stability occurred at 175°C after 15 min, but we needed to determine the cause of stability. From Figure 22, a shift in the crystalline scattering peak ($q \approx 0.05 \text{ Å}^{-1}$) to smaller q values is observed at the methanol stability temperature of 175° C. The shift toward lower q values is indicative of a larger scattering distance between electron dense domains. An increase in the magnitude of the crystalline scattering peak is also observed, which may represent an increase in the amount of crystallinity present in the film. The ionomer peak ($q \approx 0.2 \text{ Å}^{-1}$) remains constant throughout the range of annealing times. The strong morphology-property correlation of the crystalline peak suggests that either crystallinity or chain entanglement after 15 min at 175°C may be the cause for increased methanol stability.

Figure 22. SAXS profile of NRE 212CS H^+ annealed for 15 min between 100-200° C.

SAXS analysis was also conducted on the Na^+ counterion form of NRE 212CS. We previously reported that the Na^+ form of the film disintegrated in boiling methanol within seconds but reached mechanical stability after annealing at 275°C for 15 min. Figure 23 displays the SAXS profile of NRE 212CS Na^+ annealed for 15 min from 100 to 300 °C.

Figure 23. SAXS profile of NRE 212CS Na^+ annealed for 15 min between 100-300° C.

In Figure 23, we see a large crystalline scattering peak of the untreated, as-received Na^+ form of NRE 212CS. After annealing the film for only 15 min above 275° C, we see a dramatic decrease in the intensity of the peak, due to the melting of the majority of crystallites in the film. It is interesting to notice that the degree of crystallinity dramatically decreases at the exact moment that the film becomes stable in boiling methanol. Due to the inherent lack of crystallinity shown in the SAXS profiles, we can conclude that the methanol stability is increased due to onset of ion-

hopping at temperatures above the α relaxation, which facilitates the development of chain entanglements.

SAXS Analysis of Extruded Nafion® 117CS Membranes

Nafion® 117CS was neutralized with the following counterions prior to SAXS analysis: H^+ , Na^+ , Cs^+ , tetramethylammonium (TMA^+), and tetrabutylammonium (TBA^+). This series of counterions were chosen to represent a broad range of ionic interactions within the electrostatic network of Nafion®. Each set of samples in the counterion forms were annealed at various temperatures and times. The temperatures ranged from 100° C to 275° C depending on the counterion type, while all samples were annealed at the following times; 10, 30, 60, 90, 120, 240, 480, 720, and 1440 min. The objective of the in-depth study of annealing Nafion® was to determine the effects of temperature and time on the crystalline and ionic morphology of the perfluorosulfonate ionomer.

Figure 24 displays the effect of annealing time at various temperatures of 117CS in the Na^+ counterion form. The Na^+ counterion was selected based on its high strength ionic interactions, which provide a strong electrostatic network throughout the perfluorosulfonate ionomer. Figure 24a shows Na^+ -form 117CS annealed at 150° C between 10 and 1440 min. The peak at $q \approx 0.045 \text{ \AA}^{-1}$ has been attributed to scattering from the crystalline domain of the polymer. Minimal changes in the crystalline peak intensity were noticed with annealing temperatures below 175° C. Figure 24b displays the scattering profile of Na^+ -form 117CS after annealing for various times at 175° C. The crystalline peak shape is consistent through all nine annealing times, but a shift of the peak maximum from $q \approx 0.045 \text{ \AA}^{-1}$ to $q \approx 0.042 \text{ \AA}^{-1}$ is noticed. A shift to lower q values for the crystalline scattering peak indicates a larger scattering distance between electron dense regions. Figures 24c and d show the effects of annealing Na^+ form 117CS for various times at both 200° C and 225° C, respectively. In agreement with the trend at 175° C, the crystalline scattering peak maximum shifts to $q \approx 0.037 \text{ \AA}^{-1}$ at 200° C and finally down to $q \approx 0.026 \text{ \AA}^{-1}$ at 225° C. A slight increase in scattering intensity of the crystalline peak is also noticed when compared to the as-received Na^+ -form 117CS sample. Figures 24 e and f display the effects of annealing Na^+ form 117CS at 250° C and 275° C for various times. The interesting feature in these two figures is the dramatic decrease in the intensity of the crystalline scattering peak. In agreement with the SAXS analysis of Na^+ form NRE 212CS, the crystalline scattering peak decreases dramatically in intensity once the annealing temperature reached 275° C and was attributed to the melting of the crystallizable polytetrafluoroethylene backbone segments in Nafion®.

It appears that a crystalline peak is present around $q \approx 0.045 \text{ \AA}^{-1}$ for the Na^+ -form samples annealed at 250° C. The faint crystalline peak is believed to be due to the large crystallites that are unable to melt around 250° C. As seen in the scattering profiles of Na^+ -form 117CS annealed at 275° C, the crystalline peak is absent throughout all of the annealing times and is attributed to the melting of all polytetrafluoroethylene units in the Nafion® membrane.

Figure 24 (a-f). SAXS profiles of Na⁺-form Nafion® 117CS annealed between 10 and 1440 minutes at 150, 175, 200, 225, 250, and 275°C

As opposed to the Na⁺ counterion, the tetramethylammonium (TMA⁺) counterion is much larger in hydrodynamic volume but exhibits a similar strength within the electrostatic network. By neutralizing the Nafion® samples with the TMA⁺ counterion, we examined the effects of an organic ionic species on both the crystalline and ionic domains after annealing at various times and temperatures. Figure 25 displays the effect of annealing time at various temperatures of 117CS in the TMA⁺ counterion form.

Figure 25 (a-f). SAXS profiles of TMA⁺-form Nafion® 117CS annealed between 10 and 1440 minutes at 150, 175, 200, 225, 250, and 275°C

Figure 25a shows the effects of annealing TMA⁺-form 117CS at 150° C between 10 and 1440 min. Similar to the Na⁺-form samples in Figure 24a, the TMA⁺-form samples in Figure 25a display a crystalline peak at low q values, but there is also a peak around $q \approx 0.200 \text{ \AA}^{-1}$, which is attributed to the ionomer region of the membrane. By increasing the annealing temperature to 175° C, as shown in Figure 25b, the crystalline peak shifts from $q \approx 0.037 \text{ \AA}^{-1}$ to $q \approx 0.034 \text{ \AA}^{-1}$, and the ionomer peak remains constant. Figure 25c displays a shift in the crystalline peak to $q \approx 0.03 \text{ \AA}^{-1}$ with increasing annealing temperature to 200° C. It is also interesting to notice a dramatic sharpening of the ionomer peak in Figure 25c as the annealing temperature increases. It

has been shown previously in our research group that heating counterion-exchanged Nafion[®] above a critical temperature and cooling to a desired temperature has a dramatic effect on the reorganization of the ionomer morphology. As shown by Figures 25 c-f, the maximum ionomer peak sharpening (225° C) corresponds well with the highest thermo-mechanical transition using DMA (240°C). Beyond an annealing temperature of 250° C, the ionomer peak begins decreasing in intensity and broadening as shown in Figures 25 e and f. On the other hand, the crystalline peak dramatically decreases in intensity and finally diminishes due to melting around 275°C. The melting of the Nafion[®] crystallites is similar for both the Na⁺-form samples in Figure 24 and the TMA⁺-form samples in Figure 25.

Effect of Solvent and Film Casting Temperature during Solution-Processing of H⁺ form Nafion[®] Membranes

In our previous work, we showed that it is possible to significantly alter the fuel cell performance of MEAs by using Nafion[®] solutions neutralized with mixed organic/inorganic counterions during the casting step. In order to understand these differences, we need to have a more in depth understanding of what really occurs at the molecular level and if there are some significant changes in morphology that can explain these phenomena. The solution-processing technique is a powerful tool to produce membranes with a wide range of properties. The proton form of Nafion[®] membranes can be solution processed using various solvents at different casting temperatures. The work that follows describes the preparation of H⁺-form Nafion[®] solutions in different solvents, the fabrication of these membranes, the characterization of their solubility in ethanol and water, and morphological analysis using small and wide angle X-ray scattering.

Casting Technique to Produce Solution-Processed H⁺-form Nafion[®] Membranes

A matrix of various solvents and casting temperatures are shown in Table 1 and these are used throughout this study to optimize the solution-processing technique of H⁺ Nafion[®] films.

Table 4. Matrix of solvents and casting temperatures chosen for preparing the solution-processed H⁺-form Nafion[®] membranes

Solvent	Boiling Point (°C)	Casting temperatures (°C)				
DMSO	189	180	150	125		
Ethylene Glycol	197.3	180	150	125		
DMF	153		150	125	80	
1-Butanol	118			110	80	50
Ethanol	78				75	50

Figure 26 clearly shows how solvent and casting temperature affects the solubility of H⁺ solution-processed membranes. For each solvent used, the percent solubility of all the solution-processed membranes decreased with increasing casting temperature.

Figure 26. Percent solubility of solution-processed H⁺-form Nafion[®] using various solvents and casting temperatures

WAXS and SAXS Analysis of Solution-Processed H⁺-form Nafion[®]

Figures 27 and 28 demonstrate the effect of casting H⁺ Nafion[®] at 180° C in a polar aprotic solvent such as DMSO versus a polar protic solvent, ethylene glycol (EG).

Figure 27. SAXS profile of solution-processed H⁺-form Nafion[®] cast at 180°C on glass

Figure 28. WAXS profile of solution-processed H⁺-form Nafion[®] cast at 180°C on glass

Figure 27 shows that the ionomer peaks, at $q \approx 0.2 \text{ \AA}^{-1}$, are identical; however, there is a slight shift towards lower q values for the crystalline scattering peaks suggesting that DMSO helps in increasing the average distance between crystallites compared to EG. The WAXS patterns in Figure 28 show that ethylene glycol is responsible for a much narrower and slightly more intense crystalline peak at $q \approx 1.2 \text{ \AA}^{-1}$ suggesting induced higher crystallinity.

Figure 29 (top). SAXS profile of solution-processed H⁺-form Nafion[®] cast at 150°C on glass.
Figure 30 (bottom). WAXS profile of solution-processed H⁺-form Nafion[®] cast at 150°C on glass.

When the membranes are cast at 150°C, there is a noticeable difference between the membrane cast with DMF and the two other membranes cast with DMSO or EG. The SAXS plot in Figure 29 suggests that the average distance between crystallites is greater when DMF is used based on the shift to lower q values for the crystalline scattering peak. Figure 28 also shows a shift to higher q values for the ionomer peak, indicating that the average distance between ionic aggregates gets smaller from DMSO to EG and finally DMF. The WAXD data shown in Figure 30 suggest a more defined or sharper crystalline peak when using DMSO, but a different organization of the crystalline regions compared with the membranes cast with DMF or EG at that same temperature. The sharpening of the crystalline peak was observed with DMSO and EG at higher temperatures.

Figure 31 (top). SAXS profile of solution-processed H⁺-form Nafion[®] cast at 125°C and 110°C on glass

Figure 32 (bottom). WAXS profile of solution-processed H⁺-form Nafion[®] cast at 125°C and 110°C on glass

Figures 31 and 32 represent the SAXS and WAXS data, respectively, of the H⁺-form membranes cast at 110 and 125°C. Figure 30 suggests that using a polar protic solvent, such as EG, leads to a shift of the crystallite peak to lower q values compared with an aprotic solvent such as DMF or DMSO. It appears that the distance between crystallites is much smaller, along with a broader distribution of the average distance between crystallites when DMSO or DMF is used to cast proton form membranes at 125°C. The ionomer peak size distribution and average distance between ionic domains are also impacted by the type of casting solvent, as shown in Figure 31.

Figure 33 (top). SAXS profile of solution-processed H⁺-form Nafion[®] cast at 80° C and 75° C on glass

Figure 34 (top). WAXS profile of solution-processed H⁺-form Nafion[®] cast at 80° C and 75° C on glass

Figure 35. SAXS profile of solution-processed H⁺-form Nafion[®] cast at 50°C on glass

Figure 36. WAXS profile of solution-processed H⁺-form Nafion[®] cast at 50°C on glass

Figures 33–36 represent the SAXS and WAXS data of the solution-processed H⁺ Nafion[®] membranes cast at 75/80°C and 50°C, respectively. In both cases, the SAXS patterns show a very broad distribution of the average distance between crystallites and a very weak and non-defined ionomer peak. The WAXS curves in Figures 33 and 35 do not show much difference between the effects of either casting solvent or temperature. As it was already show earlier, these membranes can be re-dissolved in a mixture of ethanol and water very easily. Consequently, these membranes may not be very suitable for fuel cell applications and more specifically for direct methanol fuel cell membranes.

In-Plane Proton Conductivity Testing

Proton conductivity measurements were performed on Nafion[®] membranes using AC impedance spectroscopy and a Bekttech four-point conductivity cell. Figure 37 shows proton conductivity of Nafion[®] NR 117CS as a function of time under two given relative humidity conditions.

Figure 37. Nafion® NR117CS at 80°C, 30% and 95% RH – Conductivity as a function of time

We observe a very different behavior of the membrane depending on the humidity conditions in which the sample is placed. The sample tested at 30% RH shows a low but relatively constant value for conductivity over time. However, the data collected for the same membrane at 95% RH shows a steady decrease of the conductivity during that 150 hr run. We are currently investigating the origins of what we observed at high relative humidity. Several questions need to be answered. Have we reached an equilibrium condition to perform this measurement at high relative humidity? Does the water act as a plasticizer for Nafion® when the temperature at which the measurement is performed is close to the α relaxation temperature of Nafion®? Is there a morphological rearrangement that occurs within the membrane that leads to that decrease in proton conductivity? Is it just experimental error due to the humidity chamber and measurement equipment? Can it be an electrical and or electronic “deactivation” that occurs at the surface due to the successive AC impedance cycles? All these questions have to be investigated and answered, and we are working with Bekttech to address the important issues.

NR117 CS versus NRE 212 CS at 80°C

Figure 38. Nafion® NR117CS, NRE 212CS at 80°C with AC impedance technique versus NRE 212CS Bekktech data with DC resistance technique – Conductivity as a function of relative humidity

Figure 38 shows Nafion® data performed using AC impedance against data collected by Bekktech using the DC resistance technique. The data collected on the NR117CS and NRE 212CS are relatively reproducible using the AC technique despite that we can observe a deviation at low humidity for the thinner membrane. It is important to note that the data we collected are slightly higher than the data collected by Bekktech, specifically at higher relative humidity. We are investigating what can explain this difference. One of the causes could be sample preparation. Bekktech tested Nafion® membranes as received while we tested Nafion® membranes that we cleaned and reacidified in aqueous nitric acid. In order to alleviate these differences, we are currently working closely with Bekktech to find a way to define reliable procedures that would lead to consistent data between different sources.

Alternative Membrane Systems

Recent research involves the synthesis of novel high-temperature, hydrocarbon materials suitable for Proton Exchange Membrane applications in PEMFC's. Understanding the importance of high temperature stability, we have designed our novel copolymer to have a highly aromatic backbone, synthesized via the copolymerization of fluorenone and bisphenolic monomers. We will promote adequate water transport across the membrane by including flexible, sulfonated sidechains via the reaction of 1,3-propane sultone to a functionalized form of the copolymer. Due to polarity differences between the sulfonated ionic sidechains and the aromatic backbone structures, aggregation of ionic species is expected. The resulting phase separation will constitute the proper microstructure necessary for fluid transport of proton species across the membrane and to the cathode catalyst layer. Hydrophilic sidechains will afford a continuous phase wherein proton conductivity will occur, while the hydrophobic matrix will be

stable against degradation. The proposed novel copolymer is presented in Figure 39. In this research, the copolymerization and subsequent purification routes have been investigated.

Figure 39. Synthetic scheme for novel copolymerization and sidechain attachment

Synthesis of Fluorenone Copolymer

2,7-dibromo-9-fluorenone was reacted with 4,4'-(Hexafluoroisopropylidene) diphenol ("Bisphenol AF") in the presence of potassium carbonate and N,N-Dimethylacetamide (DMAc), with toluene as an azeotropic solvent assisting in removal of water. Step-wise copolymerization was conducted in two steps: dehydration and nucleophilic aromatic substitution. Dehydration was conducted under nitrogen for 4 hours at 145°C using a Dean-Stark Trap. Nucleophilic aromatic substitution was achieved by increasing the temperature to 155°C for approximately 96 hours. The reaction scheme for the copolymerization is shown in Figure 40.

Figure 40. Novel copolymerization of 2,7-Dibromo-9-fluorenone and Bisphenol AF

In an attempt to increase reactivity, and therefore improve the synthetic yield, 2,7-Dichloro-9-fluorenone was used in place of the dibrominated monomer. Similar reaction products were obtained. Additionally, the synthetic formulation was performed at various wt% solids in order to determine the optimal conditions for polymerization.

Synthesis of an Anthraquinone Copolymer

The novel copolymerization of 1,5-Dichloroanthraquinone and Bisphenol AF was performed in a method similar to that of the fluorenone copolymerizations. A general synthetic scheme is shown in Figure 41.

Figure 41. Novel copolymerization of 1,5-Dichloroanthraquinone and Bisphenol AF

Purification

Upon completion of each copolymerization, the reaction mixture was allowed to cool to ambient temperature and subsequently diluted with 3mL DMAc. The diluted copolymerization product was precipitated into a solution of 100mL Methanol and 1mL Hydrochloric Acid (conc.). The precipitate was vacuum filtered and repeatedly washed with 100mL of Methanol followed by 100mL of DI Water. Following washing, the product was dissolved in 50mL Chloroform and filtered to remove inorganic salts. The final product was precipitated from Chloroform into Methanol and dried in a vacuum oven at 80°C.

Characterization

Initial characterization has been performed, including preliminary NMR analysis and solution-processing studies.

NMR Analysis. Purified copolymers were dissolved in deuterated chloroform and characterized via ^1H and ^{13}C NMR spectroscopies. Results have been largely inconsistent and signal the need for optimization of purification procedures prior to further characterization via NMR spectroscopy.

Solution-Processing Studies. Purified copolymers have been dissolved in various high-temperature boiling point solvents (e.g., DMAc, DMF, NMP) and cast onto glass plates at various elevated temperatures. Figure 42 shows an improvement in film formation when solution-processed from DMF (b.p. = 153° C) as opposed to chloroform (b.p. = 61° C).

Figure 42. Optical micrographs of fluorenone copolymer film formation under various solution-processing conditions: a) from chloroform at 20° C; b) from DMF at 145° C

Films cast from low-temperature boiling point solvents (e.g. Chloroform) were 'mud-cracked' and discontinuous, while films cast from high-temperature boiling point solvents proved continuous and transparent. Regardless of solution-processing procedure, however, films were not mechanically sound, indicating that the copolymers may be of relatively low molecular weight. Therefore, optimization of molecular weight is required prior to further solution-processing studies.

Patents: None

Publications/Presentations:

Publications

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Presentations

1. K.A. Mauritz: "Organic-Inorganic Nanocomposite Fuel Cell Membranes." ACS Symposium on Organic/Inorganic Hybrid Materials II, Ventura Beach, CA, 2-5 Mar 08 Invited.
2. K.A. Mauritz, "Model studies of the characterization of the durability of Nafion® membranes and Nafion/inorganic oxide nanocomposite membranes." Materials Research Society Meet., San Francisco, 5 Mar 08. Invited.
3. K.A. Mauritz, "Characterization of the durability of Nafion membranes and Nafion/inorganic oxide nanocomposite membranes." Illinois Institute of Technology, 7 May 08. Invited.
4. K.A. Mauritz, "Characterization of PEMFC Durability," DOE 2008 Annual Merit Review and Peer Evaluation. Arlington, VA, 11 Jun 08. Poster.
5. Hassan, M.K.; Mauritz, K.A. "Broadband Dielectric Spectroscopic Studies of Nafion® Silicate Nanocomposite Membranes" Amer. Chem. Soc. Spring Meet 10 Apr 2008; *PMSE Prepr.* 2008, 98, 891.
6. Hassan, M.K.; Mauritz, K.A. "Nafion® Silicate Hybrid Membranes Via Dibutyltin Dilaurate-Catalyzed in Situ Sol-Gel Processes" Amer. Chem. Soc. Spring Meet 9 Apr 08; *PMSE Prepr.* 2008, 98, 740.
7. Hassan, M.K.; Rhoades, D.W.; Osborn, S.J.; Moore, R.B.; Mauritz, K.A. "Chain Dynamics of Nafion® Films Neutralized with Tetrabutyl Ammonium Counterions as Investigated by Broadband Dielectric Spectroscopy" ACS Spring Meet 10 Apr 2008; *Amer. Chem. Soc., Div. Fuel Chem. Prepr.* 2008, 53, 533.

8. K.A. Mauritz "Characterization of Degradation of Nafion Fuel Cell Membranes by Dielectric Spectroscopy and Nafion/[Inorganic Oxide] Nanocomposite Membranes." Simon Fraser University, Vancouver, BC, 11 Dec 08
9. K.A. Mauritz, "Dielectric Spectroscopy as a Probe of Molecular Motions in, and Chemical Degradation of Nafion and Hydrocarbon Fuel Cell Membranes." Asilomar Conference on Advances in Materials for Proton Exchange Membrane Fuel Cell Systems, Pacific Grove, CA, 18-21 Feb 07.
10. Mauritz, K.A.; Mohammad, H. "Broadband Dielectric Spectroscopy Characterization of Chemical Degradation in Nafion®/Silicate Nanocomposite Membranes." AIChE Meet., Houston, 26 Apr 07. Invited.
11. Mauritz, K.A.; Mohammad, H. "Characterization of the Durability of Nafion Membranes and Nafion/Inorganic Oxide Nanocomposite Membranes." AIChE Meet., Houston, 26 Apr 07. Invited
12. Moore, R.B.; Mauritz, K.A. "Analysis of the Physical and Chemical Stability of Cast Nafion® Membranes with Respect to Methanol Solubility and Radical Attack." AIChE Meet., Houston, TX, 26 Apr 07.
13. S.J. Osborn, 2007 Spring AIChE Meeting, Houston, TX. "Analysis of the Physical and Chemical Stability of Cast Nafion® Membranes with Respect to Methanol Solubility and Radical Attack", Apr 26, 2007.
14. K.A. Mauritz, "Characterization of the Degradation of Nafion Fuel Cell Membranes by Dielectric Spectroscopy and Nafion/[Inorganic Oxide] Nanocomposite Membranes." Chemical Sciences Division Seminar, Oak Ridge National Labs, 4 Jun 07.
15. K.A. Mauritz, "Characterization of the Degradation of Nafion Fuel Cell Membranes by Dielectric Spectroscopy and Nafion/[Inorganic Oxide] Nanocomposite Membranes." Plenary Speaker, 2007 National Graduate Polymer Research Conference, U. Tennessee, 6 Jun 07
16. R.B. Moore, Proton Exchange Membrane Fuel Cell Systems 2007 Asilomar, CA "Consideration of Chain Dynamics and Processing Parameters in the Properties and Performance of Perfluorosulfonate Ionomers in PEMFC Applications", 19 Feb 07.
17. Patil, Y., Mauritz, K.A. "Inorganic Modification of Nafion® for elevated temperature fuel cell operation." Am. Chem. Soc. Fall Natl. Meet, 2007, Boston.
18. R.B. Moore, Fluoropolymer 2006, Charleston, SC. "Morphological and Molecular Dynamics in Perfluorosulfonate Ionomer Membrane Systems", Oct 18, 2006.
19. R.B. Moore, "Probing the Molecular and Morphological Origins of Relaxations in Perfluorosulfonate Ionomers", Drexel University, Department of Chemical and Biological Engineering, Philadelphia, PA, September 29, 2006.
20. R.B. Moore, "Manipulating the Glass Transition of Nafion®: Membrane Properties and PEMFC Performance," Plenary Lecture at the 2006 Fall ACS Meeting, Div. Fuel Chem., San Francisco, CA, September 11, 2006.
21. Mauritz, K.A., with M.K. Hassan, D. W. Rhoades, S.J. Osborn, and R. B. Moore. "Broadband Dielectric Studies of Nafion® Degradation". 232nd Amer. Chem. Soc. Natl. Meet., Div. Fuel Cell Chem., Proton Exchange Membranes for Fuel Cells Symposium in Honor of Prof. James McGrath. 2006.
22. Mauritz, K.A. "Characterization of the Durability of Nafion Membranes and Nafion/Inorganic Oxide Nanocomposite Membranes". Dept. Chem. Engr., Colorado School of Mines, Golden CO, 13 Oct 06.
23. Rhoades, D.W.; Mauritz, K. A.; Peusch, D. "Dielectric Spectroscopic Analysis of Amine Modified Nafion® Precursor Films". 232nd Amer. Chem. Soc. Natl. Meet., PMSE Div., General Papers/New Concepts in Polymeric Materials; Characterization, Sep. 10-14, 2006.
24. Mauritz, K.A., with R.B. Moore, M. Hassan, S. 2006 DOE Hydrogen Program: High Temperature Membrane Working Group, Washington, D.C., 16-19 May 2006.

25. Mauritz, K.A., with R.B. Moore. "Characterization of PEMFC Durability," FreedomCar and Fuels Partnership Technical Meet, Detroit, Aug 16, 2006.
26. RB Moore/K.A. Mauritz. Improved Membrane Materials for PEM Fuel Cell Applications, 2007 DOE Hydrogen Program Review, Arlington, VA, 16 May 07.

Task Schedule

Task ID	Project Milestone	Task Completion Date				Project Status
		Initially Planned	Revised Planned	Actual	Percent Complete	
1	Acquisition of Equipment	10/31/06	9/30/06		100%	Complete
2	Development of Characterization Methods	2/28/07	11/30/07		100%	Complete
3	Modifications of Nafion Membranes and MEAs	9/30/07	3/31/08		100%	Complete
3.1	Membrane Fabrication Procedures	1/31/07	3/31/08		100%	Complete
3.2	Post-Processing Treatments	12/31/06	3/31/08		100%	Complete
3.3	MEA Fabrication Procedures	2/28/07	3/31/08		100%	Complete
3.4	Inorganic Modification of Membranes	6/30/07	3/31/08		100%	Complete
4	Membrane Durability Studies	10/31/07	3/31/08		100%	Complete
5	Alternative Membrane Systems	9/30/07	5/31/08		100%	Complete

Milestone expected to achieve in 2007 – M2

Milestone expected to achieve in 2008 – M6

Project Spending and Estimate of Future Spending

Quarter	From	To	Estimated Federal Share of Outlays	Actual Federal Share of Outlays	Estimated Recipient Share of Outlays	Actual Recipient Share of Outlays	Cumulative
1Q06	1/1/06	3/31/06					
2Q06	4/1/06	6/30/06					
3Q06	7/1/06	9/30/06	228,066.69	228,066.69	62,285.84	62,285.84	290,352.53
4Q06	10/1/06	12/31/06	182,336.17	182,336.17	20,406.65	5,610.51	478,299.21
1Q07	1/1/07	3/31/07	5,349.33	5,349.33	62,061.37	76,857.51	560,506.05
2Q07	4/1/07	6/30/07	49,825.01	49,825.01			610,331.06
3Q07	7/31/07	9/30/07	969.92	969.92			611,300.98
4Q07	10/1/07	12/31/07	6,551.11	6,551.11			617,852.09
1Q08	1/1/08	3/31/08					617,852.09
2Q08	4/1/08	5/31/08	21,901.77	21,901.77			
Totals			495,000	495,000	144,753.86	144,753.86	639,753.86

* Update quarterly – Previous quarters should show actual expenditures and should coincide with the SF269 numbers; future quarters should show estimates. Estimates need to be provided for the entire project. If spending for a given quarter is different than estimated, then the remaining quarter's estimates should be updated to account for the difference. Total DOE and Cost Share Estimate amounts should be the same as the Award amount.

General Notes: 1) DOE Laboratory partner spending should not be included in the above table. 2) The information in this table should be consistent with the information provided in section 10 of the quarterly financial status reports (SF269 or SF269A).