Accelerated Mechanical Degradation of Anion Exchange Membranes via Hydration Cycling

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Ion exchange membranes are a promising class of materials for use in fuel cells, barrier layers, and water splitting devices. While the majority of research related to anion exchange membranes is on improving the chemical stability and increasing ionic conductivity, the mechanical performance under relevant operating conditions is vital to device lifetime. While chemical degradation remains a significant issue for membrane stability in anion exchange membranes (AEMs), mechanical stability is also an integral factor in fuel cell lifetime. The polymer needs to be processed into thin, durable membranes and withstand the stresses inside a fuel cell at operating conditions. Microcracks formed from repeated hydration and dehydration cycles in a fuel cell are the most common form of mechanical failure. Several attempts have been made to correlate mechanical failure with a common mechanical property, such as elongation at break or Young’s modulus and yield strength. Cycling the humidity correlated well with a reduction in the strain at failure even though the yield stress and yield strain remained largely unchanged.

Most of the available literature on mechanical properties of ion conducting polymer membranes is limited to stress-strain curves in various states of hydration. Tensile strength and Young’s modulus decrease as the polymer absorbs water. The elongation at break increases due to plasticizing effect of the absorbed water. Also noted by Marestin et al. is the lack of a comprehensive study of mechanical properties including the combined effect of water content and temperature. Custom environmental chambers built around a mechanical tester are common for detailed exploration of properties at different humidities, and the testing is usually performed at a constant temperature and relative humidity; time dependence is not considered. Bauer et al. investigated the dynamic mechanical response to Nafion 117 under different temperature and relative humidity conditions, concluding water acts as a plasticizer at lower temperatures, but stiffens the membrane at higher temperatures. Creep measurements are another way to measure mechanical performance and Majsztir et al. report tensile creep and creep recovery for an extruded Nafion N1110 film with a custom environmental chamber.

Mechanical properties of films relate to conductivity. In an alkaline exchange quaternary ammonia polysulfone membrane, a sharp increase in water uptake with increasing ion exchange capacity (IEC) correlated directly with a sharp decrease in Young’s modulus. In poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) blends, a 10.5 PVA:PAA ratio best balanced the need for ionic conductivity and mechanical strength for solid polymer electrolyte applications.

The membrane undergoes many cycles of small stresses in a fuel cell, which can lead to mechanical failure. The stresses can be mechanical, thermal, chemical, or hygral. A single cycle is not enough to induce significant damage, but the cumulative effect of many cycles leads to microcracks and membrane failure. The rheological characterization of materials exhibiting non-linear deformation is an example of these kinds of stresses. Hygral stress relates to the stress on a material caused by the absorption and desorption of water. Nafion NR111 was put under a cyclic mechanical stress, and a stress of only 1/10 of the tensile strength of the uncycled membrane was needed to break the membrane. The authors also concluded the stress induced by the water-uptake cycling was the primary driver for the overall mechanical decay of the membrane. The stress change from either cooling or drying Nafion NR111 was shown to be on the order of 0.2 to 2 MPa. General Motors tests for mechanical durability of the membrane electrode assembly (MEA) by exposing the membrane to an alternating two minute cycle of 0%RH and 90°C dew point gas at 80°C. Gas crossover (hydrogen) is measured and the membrane must survive at least 20,000 cycles without gas crossover to pass.

We build off of the demonstration of a single wet to dry stress measurement and the industrial cyclical tests to introduce a water stress metric. The new measurements are based on cycling the membrane between high saturation and dry air conditions at elevated temperature, and compare this new metric with traditional mechanical testing metrics. Our goal is to accurately measure the stress water puts on the membrane as water absorbs and desorbs into and out of the membrane and how this stress changes over many cycles.

Experimental

Materials.—Four ion exchange membranes were compared (Figure 1). Nafion 115 is a commercial proton exchange membrane produced by DuPont that is widely studied in the fuel cell literature. Nafion 115 was obtained from Ion Power, Inc. The film was prepared via a standard method of boiling in 0.5 M sulfuric acid for an hour, deionized water for an hour, 3 wt% hydrogen peroxide for an hour, and finally deionized water again for an hour. The membrane was then placed in an oven at 80°C for over 12 hours to dry. PE-b-PVBTMA is a polyethylene-b-polyvinyl benzyl trimethylammonium diblock copolymer with a 70:30 PE:PVBTMA block ratio and molecular weight of 64,800 g/mol. The polymer was cast from xylene at 80°C with a film coater into 300 cm² films 12 ± 3 μm thick. These films were very flexible and exhibited low dimensional swelling. Kraton Polymers Inc. (Houston, TX) kindly provided a symmetric pentablock copolymer comprised of poly(4-tert-buty styrene)-b-poly(2-methylbutylene)-b-poly(4-tert-buty styrene)-b-poly(2-methylbutylene)-poly(4-tert-buty styrene) which was further

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processed to have 43% of the mid-block functionalized with benzyl trimethylammonium. The molecular weight of the base pentablock is approximately 15-10-28-10-15 kg/mol.25 The synthesis and characterization is reported elsewhere.26 The brominated polymer in powder form was cast from tetrahydrofuran (THF) using a film coater. The brominated film was then placed in a 25 wt% trimethylamine solution for at least 48 hr to achieve quaternization of the brominated end group. The final film had a thickness of ∼60 μm. ATMPP is an amminated tetramethyl polyphenylene received from Sandia National Labs.27 ATMPP is widely studied and shows promise as a platform for an anion exchange membrane in a working fuel cell.28–32

**Rheometry.**—Rheological measurements were done on an ARES-G2 rheometer (TA Instruments) using a modified Sentmanat Extensional Rheometer (SER).33 Details on the SER fixture are available elsewhere.26 Samples were cut into rectangles measuring between 2–4 mm wide and ∼20 mm long. Thicknesses ranged from 10–100 microns. Tests were run at various temperatures and relative humidities using a custom oven, which was described previously.33 Extensional rates were based on testing conditions modified from ASTM D882, Tensile Properties of Thin Plastic Sheeting.35 According to the standard, the speed of the testing and the grip separation are dependent on the percent elongation at break. The speed of the testing is calculated from the initial strain rate multiplied by the initial grip separation. With the SER drums, the speed of drum rotation can be altered, but the separation distance between the drums is fixed. Using the same formula as the ASTM standard and a fixed grip separation of 12.7 mm (distance between the center point of the two SER drums), a rate of grip separation can be calculated. This grip separation rate is then converted to an engineering strain rate using the geometry of the drums, yielding an engineering strain rate of 0.33 s⁻¹ for materials whose elongation to break was greater than 100%. For elongation between 20% and 100%, the rate of 0.0167 s⁻¹ was used, and for elongation less than 20% the rate used was 0.0033 s⁻¹. At least five replicates were averaged for the final data. Error bars are one standard deviation.

Extensional tests on the SER measure stress as a function of engineering strain.26,33 To compare SER data with typical tensile measurements, an Engineering Stress was calculated using the fixed starting area of the sample. Extensional Stress is the property that factors in the exponential decrease in sample area. The stress at break and Young’s modulus were calculated from the Engineering Stress. Young’s modulus was taken as the slope at low strains in the linear, elastic region. The stress at break was taken as the stress at the break point. Elongation is calculated by multiplying the final engineering strain by 100. At least five tests were run for each sample.

**Conductivity.**—Ionic conductivity was measured by electrochemical impedance spectroscopy using a four-electrode in-plane conductivity cell. Impedance spectra were obtained over a frequency range of 0.3 to 10⁶ Hz using a multi-channel potentiostat (BioLogic VMP3). A TestEquity sample chamber controlled temperature and humidity during data acquisition. Membrane resistance was defined as the low frequency intercept of the Nyquist impedance plot and conductivity, σ, was calculated using the film dimensions where R is the membrane resistance, l is the length between electrodes, and t and w are the thickness and width of the membrane sample, respectively (Equation 1).

\[
\sigma = \frac{1}{R \cdot t \cdot w}
\]  

Reported conductivity data are the average of at least three separate membrane samples and multiple impedance spectra at each steady-state temperature; error bars are one standard deviation.

**Water uptake.**—Water uptake (WU) was characterized using a dynamic vapor sorption apparatus (SMS DVS Advantage 1, Allentown, PA). A membrane sample, about 4 mm², was placed on a glass weigh
plate and the change in mass was measured gravimetrically under different humidity conditions. The WU of the membrane was calculated based on equation (Equation 2).

\[ \text{WU} = \frac{m_{\text{RH}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100 \]  

where \( m_{\text{RH}} \) is the mass of the sample at the given relative humidity and \( m_{\text{dry}} \) is the mass of the dry sample. The mass of the dry membrane was taken as the measured mass at the end of the initial 4-h drying period. Given the WU at saturated conditions and the known ion exchange capacity \( (\text{IEC}) \) of the membrane, the hydration level, \( \lambda \), which is the number of waters per cation functional group, can be calculated using equation (Equation 3). The molecular weight of water \( (m_{\text{H}_2\text{O}}) \) is needed to complete the equation.

\[ \lambda = \frac{\text{WU}}{m_{\text{H}_2\text{O}} \cdot \text{IEC}} \]  

**Water stress.**—The water stress measurement is a method of characterizing the mechanical response of ion exchange membranes under cyclic hydration conditions. The membrane was loaded on the film/fiber tool on the TA Instruments ARES-G2 rheometer. The membrane was loaded and rested for 60 minutes at 80°C and 90%RH in order to reach a steady-state mass uptake. The hold time was based on dynamic vapor sorption experiments performed at 60°C, 95%RH. The membrane was then stretched to put a small tension on the film while remaining within the elastic region (plastic deformation does not occur). The elastic region was defined from tensile tests at 60°C, 90%RH. Using the environmentally controlled oven, the membrane was subjected to alternating cycles of 95%RH and 0%RH at 80°C. Short cycle times of 10 min were used to accelerate degradation, while 60 min cycles allowed the membrane to reach steady-state water absorption and desorption for each cycle. Samples were about 3 mm wide and the initial gap was set to 10 mm. Three replicates were done for each reported measurement. The water stress was calculated by subtracting the difference between the measured stress from the wet cycle and the dry cycle (Figure 2). As the membrane dried, the film contracted and this contraction force was measured by the rheometer’s axial force transducer. Once the humid atmosphere was reintroduced, the film absorbed water and relaxed, thus decreasing the axial force.

**Results and Discussion**

Conductivity, water uptake, and tensile testing data were reported previously for some of these membranes\(^{26,28,33} \) and pertinent data are reproduced for comparison with the water stress measurements.

**Conductivity and water uptake.**—At 60°C and 95%RH the QP43 and ATMPP membranes have an order of magnitude greater conductivity than the PE-b-PVBTMA with about half the water uptake (Table I). Properties reported in Table I were either measured for this work or reported in the references by some of the same authors. All the AEMs still trail Nafion 115 in conductivity, although in general PEMs or reported in the references by some of the same authors. All the

![Figure 2](image-url)  
A typical transient normal stress response from a water stress experiment on ATMPP.

![Figure 3](image-url)  
Stress at break for Nafion 115 (benchmark), PE-b-PVBTMA, QP43, and ATMPP at 60°C for both dry and saturated relative humidity conditions.

**Tensile testing.**—The three main mechanical properties taken from a stress-strain curve vary in relevance to the operating conditions in an electrochemical device. The membrane needs to be strong enough to handle when dry or wet and withstand stresses associated with being loaded in a membrane electrode assembly. All four membranes exhibit a stress at break greater than 10 MPa with the exception of the QP43 in the high hydration condition (Figure 3). A stress at break of 10 MPa or greater can be handled without damaging the film.

A dry elongation greater than 100% is a conservative metric for a robust film. For a film in a working electrochemical device however, the membrane should at least handle mechanical strain greater than the dimensional change due to water uptake. Combining the dry elongation and the dimensional change due to water uptake into a single metric is useful to compare the mechanical and hygral forces acting on the membrane. We propose that the dimensional change ratio (mechanical elongation over swelling due to hydration) should be greater

| Ion Exchange | Water uptake (%) | Dimensional swelling (at 25°C (vol%)) | Conductivity (mS/cm) | Reference |
|--------------|------------------|--------------------------------------|----------------------|-----------|
| Nafion 115   | 0.9              | 17.1 ± 0.1                           | 21 ± 1               | 137 ± 17 (H\(^+\)) | 23, 24    |
| PE-b-PVBTMA  | 1.2              | 32.3 ± 0.2                           | 14 ± 4               | 2 ± 0.5 (Br\(^-\))  | 26        |
| QP43         | 0.8              | 16.4 ± 0.7                           | 34 ± 3               | 2 ± 0.5 (Br\(^-\))  | 28        |
| ATMPP        | 2.5              | 13.7 ± 0.3                           | 43 ± 3               | 20 ± 2 (Br\(^-\))   |           |
than 10 for a stable membrane (Table II). Nafion 115 and the PE diblock are both comfortably over this threshold (∼20), but ATMPP and QP43 are both near 1. The polyaromatic backbone of ATMPP is chemically different than the polyaliphatic block polymers (QP43 and PE-b-PVBTMA), which may contribute to the small dimensional change ratio. Additionally, aromatic, non-ionic blocks in the QP43 membrane could similarly contribute to the small dimensional change ratio, while the smaller, non-ionic polyethylene block leads to significantly higher elongations and higher dimensional change ratio in the PE-b-PVBTMA membrane under both dry and wet conditions (Figure 4).

In an electrochemical device, a membrane will mainly be subject to oscillations in force, temperature, and relative humidity. While individual oscillations are not strong enough to destroy the membrane, a membrane should withstand these small forces without short or long term damage. The Young’s modulus is the best metric to define the elasticity of the membrane and ideally the value should be ∼75–450 MPa. Below 75 MPa, the membrane can behave more like a fluid and above 450 MPa, the membrane becomes too stiff. The difference between modulus values at dry and hydrated conditions should also be minimized. Nafion 115 meets these requirements, but the anion exchange membranes do not (Figure 5). The PE diblock and QP43 membranes both become very soft under hydrated conditions at 60 °C (<15 MPa). The ATMPP membrane shows less variation, but is too stiff dry and softens considerably when hydrated.

Water stress.—The tensile testing at static temperature and relative humidity conditions are useful to compare different membranes, but tensile testing does not represent the smaller, cyclical stresses imposed on a membrane in a working device. The water stress protocol, introduced here, attempts to quantify the hygral stresses a membrane encounters in a working device.

The water stress tests were run at an elevated temperature of 80 °C to accelerate degradation. ATMPP exhibits a significantly higher water stress than either the PE diblock, QP43, or Nafion 115, correlating with the higher Young’s modulus from the tensile testing (Figure 6). ATMPP and QP43 lose ∼40% of the peak water stress over 20 cycles while the PE diblock and Nafion 115 lose less than 10%. Nafion 115 and PE-b-PVBTMA show an initial increase in water stress (<30%) over the first several cycles before leveling off or trending lower. An ideal membrane would have a low water stress (<2 MPa) that does not change with cycling. The membrane should maintain its ability to absorb and desorb water completely reversibly over a large number of cycles, thus losing a negligible amount of its maximum water stress.

The test was extended out to 100 cycles covering over 33 hours to better gauge longer term membrane performance (Figure 7). While Nafion 115 maintained a low water stress and lost less than 5% of its maximum stress, the ATMPP exhibited a higher water stress and loss ∼65% of its maximum water stress. QP43 also lost ∼60% of its maximum water stress, but maintained a lower overall water stress in the range of Nafion 115. The PE diblock maintained a low overall stress (∼1 MPa), but lost ∼30% of its maximum water stress. Large error bars on the ATMPP data are most likely due to slow water absorption kinetics. Specifically, water absorption/desorption is on a longer time scale than the 10 minute cycle frequency. The short time frame is in comparison to the dynamic vapor sorption (DVS) experiments which can run for 2 hours at a given humidity to reach steady-state conditions.
mass uptake. In our accelerated testing protocol, the membrane cannot fully absorb and desorb water in the course of a single hydration or dehydration cycle.

Due to the longer times needed to reach steady-state mass change for hydration and dehydration, the cycle times were extended to 60 minutes to allow for full water absorption and desorption. The total test time of 33 hours was maintained and only the ATMPP and QP43 materials were tested. Both QP43 membranes lose nearly 40% from their peak water stress, but the QP43 remains in a much lower water stress range (1–2 MPa) (Figure 8).

Both of the 33 hour tests were compared to investigate how the cycle time affected the water stress. The 60 min cycle water stress averaged ~50% higher in QP43 and ~80% higher in ATMPP than the 10 min cycles (Figure 9, Figure 10). Cycling more often over the same period of time resulted in lower water stress values and led to higher degradation in both membranes (Figure 11). Cycling more frequently may lead to temperature and relative humidity instabilities in the environmental oven, however, the total testing time could be extended until membrane failure. For quicker screening of membranes, the 10 minute cycling over just 20 cycles (7 hours) differentiated between the four chemistries.
Conclusions

We have demonstrated a new protocol to quantify the mechanical properties of chemically different ionomers. Traditional tensile testing was performed under controlled environmental conditions and benchmarks of $\geq 10$ MPa stress at break, $\geq 100\%$ elongation at break, and Young’s modulus between 75–400 MPa are proposed. A minimum strength is needed to withstand processing and handling. However, the membrane is not under extensional tension in a working device, so a higher strength is not needed. The membrane should be able to elongate mechanically at least 10 times more than it swells with water, so an elongation at break greater than 100% is proposed. A membrane must have elasticity to withstand many small hygral and mechanical cycles. A low Young’s modulus ($< 75$ MPa) indicates the polymer may flow when hydrated, while a Young’s modulus above 400 MPa indicates the polymer may be too stiff to accommodate the mechanical cycling as the polymer absorbs and desorbs water. Nafion 115 meets all of these criteria as expected, but the AEMs studied all far short in at least one metric. The PE-b-PVBTMA membrane is too elastic when hydrated. The QP43 membrane is too weak and elastic when hydrated and has low elongation when dry. The ATMPP membrane is too stiff when dry. The QP43 membrane is more mechanically similar to the PE-b-PVBTMA membrane, but has conductivity (20 mS/cm) and water uptake values ($\sim 15\%$) similar to the ATMPP, a much more stiff membrane.

The new water stress metric was able to differentiate between the various chemistries. The stiff ATMPP and the more elastic QP43 membranes softened during the course of the long and short term humidity cycling which could mean they will perform poorly over time in a working fuel cell subject to similar humidity cycles. Nafion 115 performed very well, justifying its widespread study and use. The PE-b-PVBTMA membrane showed promise in its ability to absorb and desorb water reversibly as its performance most closely resembles that of Nafion 115. More long term testing is warranted. ATMPP has a Young’s modulus greater than 400 MPa at 60°C and dry conditions, while the other three have a Young’s modulus less than 250 MPa at the same conditions. While QP43 and PE-b-PVBTMA have similar elasticity profiles in the dry and wet conditions, they perform differently in the water stress cycling tests. Young’s modulus was not able to differentiate these polymers so another metric may be more useful in predicting membrane performance through hygral cycling.

The ratio of the mechanical elongation at dry conditions over the in-place dimensional swelling was also indicative of water stress performance. Nafion 115 and PE-b-PVBTMA have ratios $\sim 20$, while ATMP and QP43 have ratios near 1. The high T$_{g}$ components in QP43 and ATMPP contribute to a low elongation at dry conditions, suggesting that polymers containing more low T$_{g}$ components be used in AEM development. The block ratios in the QP43 pentablock could be altered to include a higher fraction of the hydrogenated isoprene and a lesser fraction of the t-butyl styrene for optimal mechanical properties without sacrificing ionic conductivity.

The combination of the static tensile tests and the water stress accelerated testing protocol provide insight on the performance of membranes under mechanical and hygral stresses. A simple metric comparing the mechanical elongation in a dry condition with the in-plane swelling percentage in liquid water can be used to predict how membranes will perform under hygral cycling. In designing anion exchange membranes, we show that elastic components are more favorable than stiff for mechanical robustness under hydration cycling. While improving chemical stability and ionic conductivity will continue to be important issues to address, mechanical performance under device operating conditions is critical to development of robust ion exchange membranes.

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