Preparation And Characterisation Of Stabilized Nafion/phosphotungstic Acid Composite Membranes For Proton Exchange Membrane Fuel Cell (pemfc) Automobile Engines

2008

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PREPARATION AND CHARACTERISATION OF STABILIZED NAFION®/PHOSPHOTUNGSTIC ACID COMPOSITE MEMBRANES FOR PROTON EXCHANGE MEMBRANE FUEL CELL (PEMFC) AUTOMOBILE ENGINES

by

ROHIT AGARWAL
B.Tech Institute of Technology BHU, 2006

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Mechanical, Materials and Aerospace Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Fall Term
2008

Major Professor: James M Fenton
ABSTRACT

Membrane durability is one of the limiting factors for proton exchange membrane fuel cell (PEMFC) commercialisation by limiting the lifetime of the membrane via electrochemical/mechanical/thermal degradation. Lower internal humidity in the membrane at high temperature (>100 °C) and low relative humidity (25-50 %RH) operating conditions leads to increased resistance, lowering of performance and higher degradation rate. One of the promising candidates is composite proton exchange membranes (CPEMs) which have heteropoly acid (HPA) e.g. Phosphotungstic acid (PTA) doped throughout the Nafion® matrix. HPA is primarily responsible for carrying intrinsic water which reduces the external water dependence. The role of relative humidity during membrane casting was studied using surface analysis tools such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Thermo-gravimetric analysis (TGA), and Scanning electron microscopy (SEM) / Energy dispersive spectrometer (EDS). Membrane casting at lower relative humidity (30% approx.) results in finer size, and better PTA incorporation in the composite membrane.

The effect of increase in PTA concentration in the Nafion matrix was studied with regards to conductivity, performance and durability. In-plane conductivity measurements were performed at 80 °C and 120 °C. During theses measurements, relative humidity was varied from 20% to 100% RH. Membrane conductivity invariably increases on increasing the relative humidity or operating temperature of the cell. Membrane conductivity increases with increasing PTA content from 3% to 25% PTA but never reaches the conductivity of membrane with 0% PTA. Possible explanation might be the role of cesium in PTA stabilisation process. Cesium forms a complex compound with PTA inside host matrix, rendering the PTA incapable of
holding water. In plane conductivity measurements only measure surface conductivity, hence another reason might be the existence of a PTA skin on the membrane surface which is not truly representative of the whole membrane. XRD revealed that the structure of the composite membrane changes significantly on addition of PTA. Membrane with 3% PTA has structure similar to Nafion® and does not exhibit the characteristic 25° and 35° 2Θ peaks while membrane with 15% PTA and 25% PTA have strong characteristic PTA peaks. Also the membrane structure with 25% PTA matches well with that of PTA.6H2O. By applying the Scherer formula, PTA particle size was calculated from Full width half maximum (FWHM) studies at 17° 2Θ peak of the membranes. Particles coalesce on increasing the PTA concentration in the membrane leading to larger particles but still all particles were in nanometer range. Also the FWHM of membranes decreased at 17° 2Θ peak on increasing the PTA concentration, leading to higher crystallinity in the membrane. Structure analysis by FTIR indicated increase in PTA signature intensity dips, as the PTA concentration in membrane increases from 0-25%. Also by FTIR studies, it was found that some PTA is lost during the processing step as shown by comparison of as cast and protonated spectra. Possible reasoning might be that some amount of PTA does not gets cesium stabilized which gets leached away during processing. TGA studies were performed which showed no signs of early thermal degradation (temperature >300 °C), hence the assumption that all membranes are thermally robust for intended fuel cell applications. The membranes with different amounts of PTA were then catalyst coated and tested for 100-hour at open circuit voltage (OCV), 30% RH and 90 °C. By increasing the PTA in the host Nafion® matrix, the percent change in fuel crossover decreases, percent change in ECA increases, cathode fluoride emission rate decreases, and percent change in OCV decreases after the 100 hour test. Possible reasons for decreasing percentage of fuel crossover might be the increased internal
humidity of the membrane due to increasing PTA incorporation. It is reported that during higher relative humidity operation, there is decrease in fuel crossover rate. Increasing ECA percentage loss might be due to the fact that HPA in the membrane can get adsorbed on the catalyst sites, rendering the sites inactive for redox reaction. Decrease in cathode fluorine emission rate (FER) might be due to the fact that there is more water available internally in the membrane as compared to Nafion®. It is reported that at higher relative humidity, FER decreases. ECA and crossover both contribute to the OCV losses. Higher component of OCV is crossover loss, which results in mixed potentials. Hence decreasing percentage of crossover might be the reason behind the decreasing OCV loss. Initial performance of fuel cell increases with increasing PTA concentration, but after the 100 hour test, higher PTA membrane exhibited highest performance loss. Increasing initial fuel cell performance can be due to the lowering of resistance due to PTA addition. Increasing ECA losses might be responsible for the increasing performance losses on adding more PTA to host membrane.
Dedicated to

My late uncle Mr. C. L. Agarwal,

My father Mr. A.K. Agarwal

&

My mother Mrs. Sarita Agarwal
ACKNOWLEDGMENTS

First and foremost, I would like to thank my advisor, Dr. James M Fenton for his help and support throughout this work. It really was a great learning experience and an overall growth of personality. I would also like to thank Dr. Darlene Slattery for her encouraging words as she always tried to bring out the best out of me. I would like to thank Dr. Xinyu Huang, Dr. Nahid Mohajeri and Dr. Neelkanth G. Dhere for serving on my final examination committee and for their invaluable suggestions. The Department of Energy and United Technologies supported this research. I would like to thank Dr. Russ H. Kunz, L. Bonville and their colleagues at the University of Connecticut for testing some of our samples and providing valuable troubleshooting information. A special word of thanks goes to Kirk Scammon from AMPAC’s Materials Characterization Facility. I enjoyed the joyful company of Dr Naheed Mohajeri while working in the lab and her insight on academic issues. I would like to acknowledge the help of following colleagues during this project: Bo Li, Stephen Rhoden, Marianne Rodgers, Pyongho Choi, Benjamin Pearman and others at the Florida Solar Energy Center. Dr Ali Raissi, Dr Vijay Ramani, Dr Nicoletta Sorloica Hickman and Dr Vishal Mittal gave essential inputs at various stages of my research. I thank Saurabh Verma, Karthikeyan Ramasamy and all my friends at UCF for their timely help and support. Words cannot truly express my deepest gratitude and appreciation to my parents, brothers and family members, especially my late uncle who always gave me his love and emotional support.
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<th>Definition</th>
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<tr>
<td>µm</td>
<td>micrometer ($10^{-6}$ meter)</td>
</tr>
<tr>
<td>ACRONYM</td>
<td>Definition of Acronym</td>
</tr>
<tr>
<td>CCM</td>
<td>Catalyst Coated Membrane</td>
</tr>
<tr>
<td>Cs</td>
<td>Cesium</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethyl Formamide</td>
</tr>
<tr>
<td>ECA</td>
<td>Electrochemical Active Area</td>
</tr>
<tr>
<td>EPMA</td>
<td>Electron Probe Micro Analysis</td>
</tr>
<tr>
<td>FC</td>
<td>Fuel Cell</td>
</tr>
<tr>
<td>FER</td>
<td>Fluoride Emission Rate</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas Diffusion Layer</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>Hydrogen Peroxide</td>
</tr>
<tr>
<td>HPA</td>
<td>Heteropoly Acid</td>
</tr>
<tr>
<td>N112</td>
<td>Nafion® 112</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer ($10^{-9}$ meter)</td>
</tr>
<tr>
<td>NTPA</td>
<td>Nafion®/tetratek®/phosphotungstic acid</td>
</tr>
<tr>
<td>°C</td>
<td>degree celsius</td>
</tr>
<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen Reduction Reaction</td>
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<tr>
<td>PEM</td>
<td>Proton Exchange Membrane</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton Exchange Membrane Fuel Cell</td>
</tr>
<tr>
<td>PFSA</td>
<td>Perfluorosulfonic Acid</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<td>--------------</td>
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<tr>
<td>PSSA</td>
<td>Polystyrenesulphonic Acid</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TC</td>
<td>Thermocouple</td>
</tr>
<tr>
<td>XEDS</td>
<td>X-ray Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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1.0 INTRODUCTION

There is a growing scientific and public consensus that increasing levels of greenhouse gas emissions are changing the earth’s climate and automobiles play an important role in enhancing the green house effect. There is no prediction as to what will happen to worldwide oil prices or global oil demand. Oil recently hovered around $143 /barrel price range and $4/gallon gas at the pump. Any prediction in the price of oil in the future is difficult. The introduction of fuel cells into the transportation sector will increase fuel efficiency, decrease foreign oil dependency, and become an important strategy/technology to mitigate climate change\textsuperscript{1-5}. Fuel cells are electrochemical reactors that convert the chemical energy of the fuel into electrical energy. The electrolyte sandwiched between electrodes, the anode and the cathode, comprise the basic structure of a fuel cell. In a typical fuel cell operation, fuel is oxidized at the anode releasing electrons, which are consumed at the cathode during the oxygen reduction reaction after traveling through the external circuit. Fuel cells are categorized and named according to their electrolyte. Table 1 lists the different types of fuel cells, the electrolyte used, and their operating temperature\textsuperscript{2}, which can vary from 60-1000 °C. The ionic conductivity of these electrolytes is highly temperature dependent. Further details on the different types of fuel cell and their operation can be found in references\textsuperscript{1, 2}.
Table 1. Fuel cell classification based on electrode used and the operating temperature.

<table>
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<tr>
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<th>Electrolyte</th>
<th>Operating Temperature</th>
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<td>Polymer Electrolyte Membrane Fuel Cell</td>
<td>Polymer Membrane</td>
<td>80 °C</td>
</tr>
<tr>
<td>Alkaline Fuel Cell</td>
<td>Potassium Hydroxide</td>
<td>65-220 °C</td>
</tr>
<tr>
<td>Phosphoric Acid Fuel Cell</td>
<td>Phosphoric Acid</td>
<td>180-205 °C</td>
</tr>
<tr>
<td>Molten Carbonate Fuel Cell</td>
<td>Molten Carbonate</td>
<td>650 °C</td>
</tr>
<tr>
<td>Solid Oxide Fuel Cell</td>
<td>Ceramic</td>
<td>600-1000 °C</td>
</tr>
</tbody>
</table>

1.1 Polymer Electrolyte Membrane Fuel cell

The polymer membrane acts as electrolyte in a Polymer Electrolyte Membrane Fuel Cell (PEMFC). Since the charge carrier in the membrane is a proton, the fuel cell is also known as a proton exchange membrane fuel cell. Though it holds significant promise in transforming the transportation sector, it also holds considerable potential in portable (like batteries for mobile electronics, laptops, etc) and stationary applications (power backup, generator, etc.). If hydrogen is used as a fuel, the PEMFC can also be called a “zero emission engine” as it produces water as the only product. Successful commercialization of the PEMFC will help solve climate change and oil dependency.

1.1.1 PEMFC Components

At the anode, hydrogen (H₂) diffuses through tortuous pathways where it adsorbs on the platinum (Pt) catalyst, which acts as an electrode in a PEMFC. The Pt catalyzes the dissociation of the H₂ molecule into two hydrogen atoms (H) bonded to two neighboring Pt atoms. Then each H atom releases an electron to form a hydrogen ion (H⁺). An ionomic material, typically a
proton-conducting polymer binds the electrode. Current flows in the circuit as these H\(^+\) ions are conducted through the membrane to the cathode while the electrons pass from the anode through the outer circuit and then to the cathode. The oxygen (O\(_2\)) molecule is reduced at the cathode. Although thin, a polymer electrolyte membrane (PEM) is an effective gas separator. The PEM, along with the electrodes, constitute a membrane electrode assembly (MEA). As shown in Figure 1, the MEA is in direct contact with gas diffusion layers (GDLs) or backing layers on both sides\(^2\). Bipolar plates encompass the GDLs and the whole configuration is called a unit PEMFC. Many such unit cells make up a stack. GDLs are usually made of a porous carbon paper or carbon cloth, and are often wet-proofed with Teflon\(^{®}\) to ensure that the pores in the carbon cloth (or carbon paper) do not become clogged with water. Wet proofing while removing water, prevents rapid gas diffusion necessary for a high rate of reaction to occur at the electrodes.
Figure 1. Schematic diagram of PEMFC components along with the typical thickness and half cell reactions occurring at respective electrodes.
1.1.2 Current Density-Voltage Curve

The ideal performance of a fuel cell is dictated only by the thermodynamics of the electrochemical reactions that occur (a function of the reactants and products). Reactions in a typical PEMFC operating on H₂ and air are listed below, in Equations 1-1, 1-2, and 1-3.

Anode: \[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \quad E_{\text{o,Anode}} = 0.0\text{V}_{\text{RHE}} \quad (1-1) \]

Cathode: \[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad E_{\text{o,Cathode}} = 1.23\text{V}_{\text{RHE}} \quad (1-2) \]

Cell: \[ 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \quad E_{\text{o,Cell}} = 1.23\text{V}_{\text{RHE}} \quad (1-3) \]

The maximum electrical work \( W_{\text{el}} \) obtainable in a PEMFC operating at constant temperature and pressure is given by the change in Gibbs free energy \( \Delta G \) of the electrochemical reaction (Equation 1-4).

\[ W_{\text{el}} = \Delta G = -nF*E \quad (1-4) \]

Where \( n \) is the number of electrons taking part in the reaction, \( F \) is Faraday’s constant (96,487 C/mole) and \( E \) is the ideal cell potential. The reversible (i.e. maximum) standard potential \( E_0 \) for the \( \text{H}_2/\text{O}_2 \) cell reaction is 1.229 volts per mole of hydrogen (at 25 °C, atmospheric pressure, unit activity for the species, and liquid water as the product) as determined by the change in Gibbs free energy. The current density vs. voltage curve is referred to as the polarization curve. Deviations between the ideal equilibrium potential and the polarization curve provide a measure of fuel cell efficiency.

For producing electrical energy from fuel, chemical (fuel) energy is first converted to thermal, which is then converted to mechanical energy, which can then be further converted to electrical energy. For the thermal to mechanical conversion, a heat engine is used. The maximum
efficiency of such an engine is limited by the ratio of the absolute temperatures at which heat is rejected and absorbed, respectively. Fuel cells convert chemical energy directly into electrical energy and hence are not limited by Carnot Efficiency (Equation 1-5).

\[ \eta_{\text{ideal}} = \frac{\Delta G}{\Delta H} \quad (1-5) \]

Reactant utilization and gas composition have significant impacts on fuel cell efficiency. In an ideal (reversible) fuel cell there should be no voltage dependence of current according to Faraday’s law. The actual cell potential is less than its ideal potential because of several types of irreversible losses, often referred to as polarization, overpotential or overvoltage, though only the ohmic losses actually behave as a resistance. Activation losses, ohmic and mass transport related losses constitute the overpotential. Further information on typical PEMFC operation can be found in the literature.

1.2 Ionomers and Composite Membranes

Recently, there has been a lot of focus on developing composite electrolytes to be suitable for use in high temperature PEMFC operation, elevated temperatures (above 100°C) and either pressurized operation at high relative humidity or atmospheric pressure at low relative humidity (25-50% RH). The advantages of such an operation would be efficient heat rejection, enhanced electrochemical reactions at both electrodes, and simplified water management (only single phase of water, present as a vapor). Some added advantages are simplified adjoining cooling systems as the temperature gradient between the fuel cell stack and coolant is increased, CO tolerance is increased hence low quality reformed hydrogen can be used as a fuel instead of ultra zero grade or ultra pure grade hydrogen, and, most importantly, waste heat generated can be used as a practical energy source in virtue of its higher temperature operation.
For Proton Exchange Membrane Fuel Cell Automobiles to be affordable the Department of Energy (DOE) goals for membrane conductivity targets over a wide range of temperatures and relative humidity must be met by 2010. At room temperature, conductivity should be 75 mS/cm at 80% RH. At 80 °C and 53-95% RH, conductivity should be greater than or equal to 125 mS/cm and at 120 °C. Conductivity should be greater than 100 mS/cm for 20-50% RH. Nafion®'s conductivity at room temperature and 80% RH is ~20mS/cm, at 80 °C and 90% RH conductivity is ~ 80mS/cm, and at 120 °C and 50% RH conductivity is ~ 30mS/cm. Hence today a huge gap exists between conductivity targets and the present state-of-the-art Nafion® membranes. One of the technical challenges for fuel cell operation at elevated temperature and atmospheric pressure, and therefore low humidity conditions, is the high resistance of the Nafion® membrane. When Nafion® is used below 100 °C with 100% relative humidity; the proton conductivity of Nafion® is suitable for most fuel cell applications. In hydrated Nafion® membranes, water dissociates protons from the sulfonic acid groups of Nafion® and swells the ionic clusters, enhancing proton mobility and thus proton conductivity7-9. However, when the operating temperature rises above 100 °C while the system is kept at one atmosphere pressure, the membrane becomes a poor conductor due to insufficient hydration. At low relative humidity, there is not enough water inside the membrane to help proton conduction. As a consequence, protons are tethered to the sulfonic acid group firmly, and conductivity is poor. To maintain 100% RH above 100 °C, the system must be pressurized5. However, the parasitic loss caused by the compressor lowers the overall system efficiency, and high pressure also complicates system design. Hence Nafion® is not suitable for atmospheric pressure (1 atmospheric pressure) and elevated temperature (100 °C) operation.
Incorporating heteropoly acid into Nafion® like ionomers gives composite membranes, which are suitable for high-temperature and low relative humidity PEMFC operation. At elevated temperature, the acid can dissociate the protons from the sulfonic acid group of Nafion®, help retain water inside the membrane, and increase the proton concentration. Several acids have been used to improve proton conductivity, including liquid acids such as phosphoric acid and sulfuric acid, and solids such as SiO₂, TiO₂, zeolite, heteropoly acids, and zirconium hydrogen phosphate. Savinell and his co-workers used phosphoric acid or sulfuric acid doped Nafion® or polybenzimidazole PBI membranes for high temperature operation. The phosphoric acid doped PBI showed good conductivity at 150-200 °C. Lee measured the conductivity of similar membranes such as Nafion®-SiO₂ at elevated temperature under pressurized and well humidified conditions, and found no improvement over Nafion®. Solid heteropoly acids such as phospho-tungstic acid (PTA) have been used for high-temperature operation. Although good conductivity has been shown at elevated temperatures, their application has been limited to vapor-phase operation due only to concerns of the solubility of the heteropoly acid in water. An in-situ sol-gel approach using metal alkoxide precursor was found to have superior stabilization over a range of membrane compositions. PTA is a strong acid and it has as many as 29 associated crystalline water molecules depending on the relative humidity.

A microscopic proton conduction mechanism model proposed by Gierke and Hsu is largely accepted for proton exchange membranes. Protons conduct through the Nafion® like membranes by two different mechanisms in the ion cluster network model. One is the vehicular mechanism or physical migration of hydrated proton by means of water acting like a vehicle. The second is the Grotthus mechanism where the proton associates with the hydrogen-bonded
network of water molecules and a proton at the other end of the network dissociates, this is often referred to as a “hopping mechanism”. The cluster network model for ionomers such as Nafion® divides the ionomer microstructure into a hydrophobic domain consisting of the fluorinated backbone and a hydrophilic domain comprising the sulfonic acid moiety and the absorbed water. A network of short and narrow channels interconnects these clusters. The size of the cluster is strongly dependent on the system water content.

Nafion® and PTA form a Lewis acid pair. The weaker acid should behave as a proton acceptor to increase the proton dissociation of the stronger acid. The hygroscopic nature of PTA increases the remaining water in the membrane to increase conductivity. Conductivity increases because of the Grotthuss mechanism, as now there is a larger concentration of acid sites. A polymer membrane with good proton conductivity at elevated temperature, atmospheric pressure, and low relative humidity is required. When the fuel cell is operated at low relative humidity and high temperature, the Grotthuss mechanism is dominant. This mechanism can occur in a waterless environment when compared to physical migration, which requires large amounts of water.

The challenge is to produce a more durable, reliable and cheaper material that can satisfy the requirements noted above. Some sacrifice in material lifetime and mechanical properties may be acceptable, providing that conductivity and performance thresholds are met and cost factors are commercially realistic. One of the important contenders for high temperature PEMFC operation is Nafion® as a host matrix with heteropolyacids dispersed throughout in the form of nanometer size particles that retain a certain degree of water to help the mobility of protons within the matrix during high temperature operation. This type of membrane is also called a composite proton exchange membrane. Nafion® has a Teflon® like backbone as shown in Figure 2. Heteropolyacids typically exist in hydrated phases, with the degree of hydration varying from
29 to 6 molecules of water (waters of hydration) per heteropoly acid molecule. The exact number of waters of hydration depends upon the temperature and relative humidity of the environment\textsuperscript{7,8}. As shown in Figure 3, the composite proton exchange membranes (CPEMs) are less dependent on water present in the membrane system as opposed to pure Nafion\textsuperscript{®} membrane as composite membranes have now an additional pathway for the proton to transfer via the heteropoly acid\textsuperscript{7}.

\[
\begin{array}{c}
\text{(CF}_2\text{CF}_2)_x \quad \text{(CF CF}_2)_y \quad \text{O} \\
\text{O} \\
\text{(CF}_2\text{CF})_n \quad \text{O} \quad \text{(CF}_2\text{CF}_2) \quad \text{SO}_3\text{H}^+ \\
\text{CF}_3
\end{array}
\]

Figure 2. Structure of Nafion\textsuperscript{®} where x determines the equivalent weight of the ionomer. General equivalent weight of Nafion\textsuperscript{®} is 1100.

This leads to the buildup of “vehicle” molecules on one side of the medium. Hence a concentration gradient is generated, driving vehicular counter diffusion in the opposite direction. This results in the net transfer of protons through the medium. The rate of proton transfer via this mechanism is a strong function of the rate of vehicular diffusion.
Figure 3. Schematic structure of (a) Proton Exchange membranes (PEMs) and (b) Composite Proton Exchange membranes.

On the other hand, the Grotthuss mechanism involves stationary water molecules (no translation motion of the vehicle molecules), with the proton itself hopping from molecule to molecule\textsuperscript{15}. In hydrated membranes, the large water content in the system effectively shields the charge associated with the sulfonic acid anion, leading to a more favorable hydrogen bond network\textsuperscript{16, 17}. Also, there is close proximity of the clusters to one another that facilitates low activation energies for protonic hopping. Moreover, the high concentration of vehicle molecules in the system, promotes water diffusion. If the HPA additives (e.g. PTA) are uniformly dispersed in the host ionomer, the composite membrane now has shrunken clusters of sulfonic acid moieties with a low level of hydration interdispersed among HPA additive agglomerates. Conductivity of the
HPA molecules at low humidities is lower than that of pure Nafion®; no improvement in conductivity of composite membrane over pure Nafion® can be expected if a classical behavior of a phase separated blend is exhibited by the composite. However, if the additive particle size is sufficiently small (a few nm small), the existing waters of hydration of the additive can form an effective bridge between shrunken clusters, thereby providing a pathway for proton hopping from one cluster to another. Hence reducing the activation energy required for proton hopping and, in effect, the hopping resistance at high temperatures and low relative humidities, resulting in reduced membrane resistance. If the particle sizes are large, the dispersion of the additive will be poor and only a minimal number of clusters will be bridged. Based upon the above reasoning, it would be advantageous to reduce HPA particle size and have more uniformly dispersed HPA in the host membrane.

1.3 Degradation

Durability, apart from performance and conductivity requirements is one of the significant barriers to PEMFC commercialization and hence the subject of recent interest. To recover the cost of investment, some of the desired lifetimes of PEMFC are about 40,000 hours for stationary applications, 5,000 hours for cars, and 20,000 hours for buses. Degradation is a complex issue, as it is not based on just one component of the PEMFC, but due to contribution of all components.

1.3.1 Sealant Material
Sealant materials do not play a significant role in performance and conductivity measurements, but can affect degradation if the degraded products of the seals contaminate other components of the fuel cell. Seals are integral for integrity of the cell during operation.

1.3.2 Bipolar Plates

Bipolar plates are responsible for facilitating water and heat management as well as carrying current away from the cell. Hence bipolar plates should be a good conductor of heat and electrons. Bipolar plates work under high chemical and electrochemical corrosive environments. Non-porous graphite carbon\(^{18}\) and polymer graphite composites\(^{19}\) are some of the limited choices available, and introducing machined channels in them adds to the cost of PEMFC. Protective coatings around metallic bipolar plates only reduce, not eliminate, corrosion, but increase the interfacial resistivity. Metal ions dissolved from bipolar plates leads to a shortening of membrane life.

1.3.3 Gas Diffusion Layer (GDL)

GDLs are often wet-proofed with Teflon\(^{®}\) to ensure that the pores in the carbon cloth (or carbon paper) do not become clogged with water, which would prevent rapid gas diffusion necessary for a good rate of reaction to occur at the electrodes. A very thin layer provides poor electrical contact between the catalyst layer and the current collecting plate. Also, the thinner GDLs do not possess the mechanical strength to combat the mechanical degradation and compression forces in a fuel cell hence allowing the collapse of the pores in the GDL into the MEA. According to Lee and Mérida\(^{20}\), the compressive strain increases with the applied pressure and even more strongly with temperature. Hence optimum thickness of GDL is a crucial parameter to be considered. Degradation of polytetrafluoroethylene (PTFE) used as hydrophobic coating has been reported by Schulze et.al.\(^{21}\). GDL hydrophobicity changes during long hours of
operation, which disturbs the delicate balance of water and reactant transport, might show up as a significant decrease in performance or appreciable rise in resistance.

1.3.4 Catalyst Layer

Platinum remains the best choice of catalyst available, but it is very expensive. When CO is present in the fuel stream from reforming, the platinum is alloyed with other materials such as ruthenium to reduce poisoning of the fuel cell and retain performance. It also makes economic sense to bring down the catalyst loading in electrodes hence Pt supported on carbon having high surface area is used. Carbon supports are stable at low cell voltages, but during cell startup, or, shutdown and idle time, the cathode voltage can be >0.9V and can result in carbon corrosion. Surface oxide formation also diminishes the hydrophobicity and can influence the water transport in the fuel cell. Electrochemical active area loss can generally be attributed to recrystallization and dissolution of Pt particles also called the Ostwald ripening process. Carbon supported catalyst can recrystallize by crystallite or atomic migration across the support substrate. The size of Pt-based catalyst particles used in a PEMFC is on the nanometer scale, usually in the range of 2–6 nm. Nanoparticles have a strong tendency to agglomerate due to their high specific surface energy, consequently decreasing the performance of the PEMFC. Electrode durability is important because it balances the transport phenomenon responsible for the three-phase boundary reaction. The ionomer used in the membrane is generally impregnated in the electrode structure as well. Without the addition of some Nafion, the majority of the catalyst sites are inactive. However, as more Nafion is added, the porosity of the composite decreases and limits mass transfer. Ionomer in the catalyst layer degrades faster than that in membrane hence assisting the movement of Pt particles as well as providing a
pathway for delamination of the electrode from the electrolyte. The dissolved catalyst can diffuse to the ionomer phase where they can precipitate and become electrochemically inactive\textsuperscript{22, 25}. Operating relative humidity also affects the catalyst degradation. When relative humidity is increased from 25% to 100%, there is reported to be higher ECA loss due to higher Pt particle growth resulting from lowering of activation energy.

1.4 Electrolyte

In the past decade, power density requirements have come closer to being met hence the recent focus on cost and durability. Membrane stability is considered to be a significant barrier for PEMFC commercialization. New Department of Energy (DOE) guidelines require that successful membranes should have conductivity in the range of 100mS/cm, minimal gas permeability i.e. $<10^{-12}$ mol H\textsubscript{2} cm\textsuperscript{-1} s\textsuperscript{-1} kPa\textsuperscript{-1} and $<10^{-11}$ mol O\textsubscript{2} cm\textsuperscript{-1} s\textsuperscript{-1} kPa\textsuperscript{-1}. Electronic resistance is generally not an issue until and unless manufacturing failure occurs. Initial PEM candidates were made by condensation of phenolsulphonic acid and formaldehyde at General Electric (GE). They were extremely brittle and hydrolyzed easily\textsuperscript{31, 32}. Second generation membranes were made from partially sulphonated polystyrene. However the lifetime of second-generation membranes was limited to 200 hours (hr) at 60 °C. They were highly susceptible to oxidative degradation of C-H bonds due to the high cathode potential and hydrogen peroxide formed during PEMFC operation. Use of antioxidants helped little as they were consumed with time, and cross-linking density increases resulted in brittle membranes leading to mechanical failure. Resolution of the above problem occurred with the invention of partially fluorinated polyelectrolyte polymers like poly α, β, β, trifluorostyrene sulphonic acid\textsuperscript{33}. Due to fluorine atoms attached to carbon atoms, its thermal and chemical stability increased but it had poor physical properties. In the mid 1960s DuPont® developed a new membrane with structure based
on aliphatic perfluorocarbon sulphonic acid. It has a structure similar to that of Teflon® with ether linkages, followed by CF₂ groups before the terminal sulphonic acid. Introduction of CF₂ groups made the membrane stable to oxidative attack at high cathode potentials and to hydrogen peroxide attack coming from anode side. Dow Chemical Company and Asahi Chemical Company came up with higher ratios of SO₃H group to CF₂, lowering the equivalent weight and hence increasing the conductivity. By 1968, the morphology and characteristics of the Nafion® membrane with increasing equivalent weight (1100-1500) has been studied by General Electric²⁹. Thinner membranes lead to higher crossover, but reduced mechanical stability. Nafion® remains the most widely used membrane with major emphasis given on increasing its conductivity, performance and durability. Addition of HPA and / or reinforced layers to Nafion® are some of the significant routes to achieving the three objectives of optimum conductivity, performance and durability.

1.5 Electrolyte Durability: Cause and Effect

There are three main categories for membrane lifetime issues; (i) thermal (ii) mechanical and (iii) chemical/ electrochemical. Success in understanding the durability of the membrane lies in decoupling these three effects and having a thorough understanding of their individual roles in degradation of the electrolyte.

Thermal Degradation

Relatively stable nature of C-F bond and shielding effect of electronegative fluorine atoms gives Nafion® its thermally stable nature. A study conducted by Surowiec and Bogoczek³⁰ using thermal gravimetric analysis (TGA), differential thermal analysis, and infrared
spectroscopy, concluded that Nafion® loses sulfonic acid groups above 280 °C and only water below 280 °C. Nafion® is not affected till 150 °C after which almost all water is lost and irreversible dry out occurs. Loss in the perfluorinated matrix occurs at temperatures >400 °C. For high temperature PEMFC operation, the thermal stability of Nafion® is adequate. If the membrane is exposed to high temperature during MEA processing/fabricating step, irreversible dry out decreases the water uptake hence the conductivity and performance will be sacrificed. Extensive morphological relaxation takes place above the glass transition temperature of the membrane (T_g) hence improper exposure to high temperature leads to modified/undesired membrane properties. Dry Nafion® has a T_g between 130 and 160 °C, while hydrated Nafion® has a T_g between 80 and 100 °C.

**Mechanical Degradation**

Mechanical properties of Nafion® such as tensile strength, tear strength and puncture resistance are adequate, but use of very thin membranes (25 microns) requires properly designed quality control measures for MEA fabrication and cell assembly. Introduction of pinholes, foreign materials, excessive stress and uneven pressure on the membrane during MEA manufacturing can initiate propagating cracks. Non-uniform contact pressure, high differential initial gas pressure over the membrane, and fatigue from stresses occurring during temperature and humidity cycling are potential causes for membrane failure. Baldwin *et al.* stated that mechanical failures are the main cause of fluoride loss, which is a direct measure of membrane life for perfluorocarbon membranes. Inadequate humidification makes the membrane brittle and fragile and penetration of the catalyst particles from electrode into the membrane can cause local high stress areas. These stress points can also be caused by misalignment of the catalyst transfer decal. Fuel starvation causes oxygen to be produced at the anode, leading to localized heat
evolution resulting in holes, and stress points in the membrane. This also leads to a drop in cell potential as oxygen and hydrogen crossover increases.

**Chemical/Electrochemical Degradation**

Chemical degradation is the most significant of the three modes of electrolyte degradation and one of the prominent causes of membrane failure. It occurs at a slow rate over thousands of hours hence the added disadvantage of time consuming test experiments. There is insufficient data in the literature as to where do the chemical degradation starts and even the mechanism at best is nascent. There is a technique called Fenton’s test which yields end products similar to that of running a PEMFC over thousands of hours, but life predicted by that method does not resemble the exact operational life of PEMFC as there are different parameters such as change in relative humidity or fuel starvation while running a PEMFC, which cannot be mimicked by Fenton’s test. There is another technique to determine membrane life also known as an Accelerated Degradation Test (ADT) which involves running a PEMFC under certain conditions like 30% RH, 90 °C temperature, open circuit voltage which can then be related back to exact life of the membrane. It is reported that peroxide radicals are produced in low levels during a typical PEMFC operation, which are major cause of physical and chemical breakdown of the membrane.

**Electrolyte decay mechanism**

The first credible life testing data was obtained from the Gemini space program for NASA. The data was used for low temperature PEMFC operation with H2/O2 and had life of 500-1000 hours. It came as a surprise because similar membranes were used previously for
electrodialysis without much damage to the integrity of the membrane, a clear indication of the harsh environment in a PEMFC operation and subsequent need to study the environment more closely. The peroxide attack at the alpha hydrogen was found to be the prime cause of membrane degradation. The electrolyte experiences a harsh oxidizing environment at the cathode side and a reducing environment at the anode side in addition to attack by the peroxy and hydroperoxy radicals formed during PEMFC operation. Nafion® and other perfluorinated membranes were a big step forward in dealing with the problem and were stable for thousands of hours of efficient operation. Effluent water analysis from the Nafion® membrane after life testing was found to contain fluorine ion, low molecular weight perfluorocarbon sulphonic acid and carbon dioxide. Stucki et al.\textsuperscript{37} reported that water electrolyzers using Nafion® membranes had highly reactive oxygen species (OH• and OH\textsubscript{2}•) responsible for the decay. LaConti et al. stated that membrane degradation\textsuperscript{35} and loss in ion exchange capacity (IEC) was primarily happening at the anode i.e. near the hydrogen side. Using surface analysis, he found that the sulphur concentration was lowest at the anode and increased until it reached the cathode. Based on the above SEM/EDX analysis, consistent for hundreds of stacks, the following degradation mechanism (Equations 1-6 through 1-10) was proposed. Molecular oxygen diffuses from the cathode side to the anode side where it reacts with atomic hydrogen, after which it gets chemisorbed on the Pt surface of the anode catalyst layer to give free radicals, namely peroxide and hydroperoxide. Reduction of the formed free radicals is inhibited by the hydrogen covered Pt electrode and hence they diffuse to the PEM. Presence of impurity cations accelerates the above process.

\begin{equation}
(1) \text{H}_2 \rightarrow 2\text{H}^\bullet
\end{equation}
\begin{equation}
(2) \text{H}^\bullet + \text{O}_2 \rightarrow \text{HO}_2^\bullet
\end{equation}
\begin{equation}
(3) \text{HO}_2^\bullet + \text{H}^\bullet \rightarrow \text{H}_2\text{O}
\end{equation}
(4) $H_2O_2 + M^{2+} \rightarrow M_3^{3+} + OH\bullet + OH^-$  

(5) $OH\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet$  

Wang and Capuano\textsuperscript{40} grafted styrenic groups onto fluorocarbon backbone, and finally sulphonated the grafted membrane. By soaking membrane in 30\% $H_2O_2$, they found similar sulphonate group loss as proposed above. Büchi \textit{et al.}\textsuperscript{41} and Scherer\textsuperscript{39} agreed with the formation of hydroperoxy radical, and further alleged (for sulphonated linear polystyrene) that $HO_2\bullet$ reacted with the tertiary carbon of the membrane. Pozio \textit{et al.}\textsuperscript{42} found that fuel cells with stainless steel plates had higher fluoride emission rate studied in effluent water than that with graphite plates and was attributed to a Fenton’s reagent type mechanism. Pozio \textit{et al.}\textsuperscript{42} suggested that the peroxide may have formed due to incomplete oxygen reduction on the catalyst surface.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$  \hspace{1cm} (1-11)

Guo \textit{et al.} and Watanabe\textsuperscript{52-54} agreed with the above mechanism and suggested that the intermediate reacted with trace metal ions to give peroxide radicals. Yu \textit{et al.}\textsuperscript{46} reported higher sulfur loss near the cathode side of the membrane. This was attributed to the above intermediate mechanism.

The above two mechanisms of degradation were based on evidence of sulphur profiling across the whole thickness. Hubner and Roduner\textsuperscript{43} studied photolysis of $H_2O_2$ and used model studies to develop the radical attack mechanism. $OH\bullet$ radical was identified on the cathode side, using a spin trap method combined with electron paramagnetic resonance (EPR) spectroscopy. Panchenko \textit{et al.}\textsuperscript{44} observed degradation \textit{in situ} by placing a fuel cell inside the microwave resonator of an EPR spectrometer. Immobilized organic radicals were found at the cathode and free radical intermediates of the oxidation reaction at the anode. ESR spectroscopy determined that when Nafion\textsuperscript{®} membranes were exposed to the Fenton reagent; the initially formed radical
was HOO•. The formation of radicals from accumulated H$_2$O$_2$ can be accelerated by high current density (low voltage difference), which increases electrochemical reaction rates. Curtin et al. proposed a mechanism$^{47}$ for the radicals formed at the anode side, which attack the H-containing end groups. It begins with abstraction of hydrogen and the perfluorocarbon radical thus formed reacts with a hydroxyl atom to produce HF and acid fluoride, which is finally hydrolyzed. According to this proposed mechanism, the fluoride emission rate calculated from the product water is indicative of the chemical degradation rate in a PEMFC.

**Mechanism for peroxide and radical formation**

H$_2$O$_2$, which is supposed to be the species that is formed within the MEA, is hard to get rid of and is primarily responsible for membrane decay by oxidation via various radicals. H$_2$O$_2$ is primarily$^{48}$ formed during the oxygen reduction reaction also known as ORR. In acidic solution, possible ORR mechanisms are given below

\[
\begin{align*}
O_2 + 4H^+ + 4e^- & \rightarrow 2H_2O; \ E_o = 1.23V \quad (1-12) \\
O_2 + 2H^+ + 2e^- & \rightarrow H_2O_2; \ E_o = 0.67V \quad (1-13)
\end{align*}
\]

In a typical PEMFC, with Pt as catalyst, generally ORR occurs via Equation 1-12 but the reaction listed in Equation 1-13 also occurs as a parallel reaction or reaction intermediate giving rise to H$_2$O$_2$ in PEMFC. There are several pathways for H$_2$O$_2$ formation$^{49}$ and they have been detailed in the literature. Rotating ring disc electrodes have been used to study the ORR experimentally in which ORR occurs at the central electrode$^{50, 51}$. Ring current gives a measure of H$_2$O$_2$ yield and is diffusion limited oxidative current. On decreasing the disk potential, H$_2$O$_2$ yield increases, and reaches maxima at the anode potential range in PEMFC operation, which corresponds to the potential of H$_2$ adsorption. The cathode typically operates at potentials >0.6,
hence the proof that H₂O₂ is typically formed at the anode and the oxygen present is because of crossover effects. H₂O₂ formed at the anode can cross into the membrane and attack the ether links or branching chains of polymers. H-containing terminal bonds in the membrane are prone to attack by radicals especially under low relative humidity and high temperature (>90 °C). LaConti et al. 35 determined that the equivalent weight of the polymer during degradation process of Nafion® did not change, and there is a fixed ratio of fluorine, carbon and sulfur containing products released. Dupont manufactured membranes with higher life and lower fluoride emission rates in which the number of reactive end groups was reduced by alternative synthesis route. Wang and Capuana 40 found using infrared spectroscopy that membrane degradation in PEMFC is due to loss of S=O bonds, and found similar loss in spectra when the membrane was soaked in 30% H₂O₂. Furthermore, Panchecko 44 observed that a spin trap at the cathode attaches to radical defects formed from membrane degradation. H₂O₂ formed at the anode, which crosses to the membrane can combine with trace levels of transition metal ions M²⁺ to give OH• radical as shown below.

\[ \text{H}_2\text{O}_2 + \text{M}^{2+} \rightarrow \text{M}^{3+} + \cdot\text{OH} + \text{OH}^- \]  (1-14)

The above-formed •OH radical can further lead to formation of •OH₂ radical.

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH} \]  (1-15)

\[ \cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \cdot\text{HO}_2 \]  (1-16)

The above reaction is known 55 to occur in Fenton’s test. Fenton’s reagent is used as an accelerated test medium for PEMs. Degradation products from polystyrene sulfonic acid (PSSA) or perfluorocarbon sulfonic acid (PFSA) membranes were found to be similar in the Fenton medium and in PEMFC product water, using nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry. Another accelerated test involves running the PEMFC at open circuit
voltage (OCV) in a fuel cell. On open circuit voltage, crossover oxygen can react with hydrogen at the anode or crossover hydrogen can react with oxygen at the cathode. In conditions other than open circuit voltage, \( \text{H}_2 \) and \( \text{O}_2 \) are consumed at the three-phase boundary thus lowering the rate of crossover. The increased gas crossover, which occurs during the open circuit voltage, accelerates degradation. In addition, water generated from the fuel cell reaction also decreases the formation of peroxide radicals. Thus open circuit voltage especially with low humidity conditions, can be an accelerated test compared to normal fuel cell conditions.

1.6 Quality Control / Degradation Prevention

Possible prevention methods include avoiding/reducing metal contamination from all possible sources (end plates, reactant gas flows, etc.) by increasing quality control cycles, decreasing gas permeability, using radical inhibitors or peroxide-decomposition catalysts deposited within membranes to decrease the severity of radical attacks, or use of a sacrificial material to prevent direct attack on the membrane, etc. Although the Fenton test is considered a benchmark for PEM durability evaluation, it has some limitations, for deterioration of the membrane in such a test involves no electrode process and has nothing to do with operating potential, relative humidity, fuel and oxidant starvation, etc. An alternative approach would be to run a long-term fuel cell test and conduct postmortem analysis to study the changes in membrane properties. However, this method needs at a minimum hundreds of hours to obtain detectable degradation. Testing fuel cells for such lengthy periods of times is expensive and generally impractical hence membrane degradation phenomenon is still a mystery and hinders effective prevention methods to be developed. Baldwin et al.\textsuperscript{56} reported that fluoride loss rate from the fuel cell and electrolyzers are an excellent measure of the life of the cell in the absence of premature mechanical failures. They came up with the relationship based on millions of hours of testing. Fluoride emission rate
(FER), rate at which the membrane loses fluorine in a set time was measured by fuel cell effluent water analysis and was used to quantify the membrane degradation rate. One significant step in preventing the decay process in the electrolyte would be optimizing the membrane water content (increasing the water content lowers the concentration of $\text{H}_2\text{O}_2$), which can be increased by use of HPA inside the PFSA membrane. HPA has inherent water attached, the amount of which depends on the temperature, relative humidity of membrane, etc; effectively bridges the hydrophilic clusters; and decreases the activation energy for proton hopping. Figure 4 shows the various causes or conditions of component degradation during PEMFC operation and also the effects it has on components or degradation mechanisms (for PFSA membranes) of components and measurable properties used to quantify the degradation rate.
Figure 4. Degradation causes/conditions, along with effects and measurable properties for change in states of various components of PEMFC
2.0 EXPERIMENTAL TECHNIQUE

This section presents the experimental details of the research methods employed. This includes the material description, cell configurations, operating conditions, and the experimental methods used.

2.1 Fuel Cell Component:

2.1.1 Membrane

Commercially available Nafion® 112 (Ion Power, DE) and FSEC1 membranes were used for conducting various conductivity tests, performance and degradation studies. FSEC1 is Tetrake® (a CF₂-CF₂ based material) sandwiched between two layers of solution consisting of Nafion®/PTA/DMF/EtOH. This membrane was cast on a glass using a humidity box and casting support as shown in Figure 5, giving a membrane approximately 1 mil or 25 microns thick.

![Figure 5](image_url)

Figure 5. (a) The glass support with balance leads (b) A humidity control box for casting membranes at particular RH%.
The cast membrane is then vacuum treated at 100 °C to remove excess DMF and then subsequently cesium treated for a day to exchange ions with protons. This renders PTA insoluble in water. Further heat treatment and protonation give the desired membranes to be tested for conductivity studies. When the membrane electrode assembly (MEA) is prepared, the membrane is catalyst coated after casting.

2.1.2 Catalyst

Catalyst ink was prepared by mixing the catalyst with as-received 5% Nafion® 1100 solution (Solution Technologies, Mendenhall, PA). The Nafion® loading in the electrode was 35 wt%. The catalyst used was 46 wt% Pt/C (Tanaka Kikinzoku Kogyo K. K., Japan). Methanol was used as the solvent in the catalyst ink. The catalyst ink was homogenized (Ultra-Turrax® T8, IKA Works, Germany) for ~6 hours to ensure good dispersion.

2.1.3 Electrode and CCM/MEA Fabrication

The electrodes were fabricated by spraying the catalyst ink obtained by homogenizing onto the membrane. The calculation for the desired Pt/C loading in CCM thus obtained drives the number of cycles the automated spray gun makes on the membrane. Generally for 0.4 mg/cm² loading, it makes 4 rectangular rounds with each round consisting of two intertwined rounds each about 1 cm above the other. The finished product thus obtained is called CCM or MEA. The catalyst loading on membrane can be crosschecked by measuring the weight of the membrane before and after coating. These measurements have to be made very carefully as there are chances of tape surrounding it peeling off certain parts of MEA.

2.1.4 Cell Hardware and Assembly
The cell hardware and assembly consists of two graphite plates (anode and cathode) with single serpentine flow fields of area $25 \text{ cm}^2$ and ports for inlet and outlet reactant gases. The cell is heated using 60 W heating pads. The CCM and the gas diffusion layers (GDL) are placed between Teflon® gaskets, which are then placed between the flow fields. The active area of the CCM is $25 \text{ cm}^2$. In a standard cell, a pinch of 12mil was used (defined as the difference between the sum of thickness of the CCM and GDLs and the total thickness of the gaskets). The hardware was assembled by applying a uniform torque of 40 in.lb to each of the 8 bolts.

### 2.2 Conductivity Measurement

The BekkTech conductivity cell is shown in Figure 6. The Teflon® support (square Teflon® piece) was placed under the clamp of the BekkTech conductivity cell. This prevents unnecessary bending of the platinum wires during assembly. Current was measured at the platinum wires as shown in Figure 7 with voltage measured across the inner electrodes. All four screws holding the top membrane clamp have been removed.

![Figure 6](image1.png)

**Figure 6.** (a) BekkTech Conductivity Cell with Teflon® support beneath the membrane/platinum wire probe configuration. The membrane has been inserted properly in the Main Body with top clamp off to the side. (b) Sample assembly under Pt Wires.
The top membrane clamp was then removed from the bottom membrane clamp. Tweezers were used to gently lift the platinum wires up from the bottom clamp. The membrane sample was inserted under the platinum wires perpendicular to the voltage measurement probes in the main body. It was ensured that there was adequate overlap between the ends of the membrane and platinum gauze at either end of the sample.

![Figure 7. Schematic of conductivity cell depicting the voltage and current measurement in a four-probe conductivity cell.](image)

Tweezers were used to place the top membrane clamp onto the top surface of the membrane sample. The membrane clamp was secured using the four fasteners.

A Type T internal thermocouple was inserted into the bottom membrane clamp beneath the membrane. The thermocouple was positioned such that the junction was directly below the membrane. The junction is typically ~0.5 mm to 1 mm from the end of the thermocouple. Once placed, fittings were “snugged” around the thermocouple. Each sample was tested for approximately six days first at 80 °C, and then 120 °C. A membrane sample was assembled into the conductivity cell/cell hardware fixture and tested at 80 °C and 120 °C without removal from
the cell hardware. Figure 8 shows a typical conductivity plot of conductivity vs. time at a particular at a fixed temperature (80 °C), relative humidity (70% RH), flow rate and pressure. Hydrogen gas was used for all conductivity tests. Only nitrogen and hydrogen were connected to the test station. Fuel flow rates and temperatures were set based on the desired test membrane temperature and test relative humidity. When testing at membrane temperatures > 100 °C, the system was operated at pressures above atmosphere to achieve 100% RH. System pressure was raised by restricting gas flow out of the system via a regulator placed after the exhaust gases passed through a condenser. The pressure was adjusted by dialing the regulator valve until the desired pressure is read off the gauge. A system pressure of 230 kPa was used for testing at a membrane temperature of 120 °C.

![Four Electrode Conductivity N112 80 C, 70% RH](image)

Figure 8. Sample conductivity plot at fixed temperature (80 °C), relative humidity (70% RH).

After initial jumps, conductivity value starts stabilizing after an hour.
2.3 Degradation Studies

2.3.1 Cell Operating Conditions

All the tests for MEAs were carried out at atmospheric pressure i.e. 1 atmosphere. The operating conditions were 90 °C cell temperature and 30% inlet relative humidity (RH) for both the anode and cathode reactant gases. The gas flow rates were 200 cm$^3$/min. All the tests were conducted at open circuit voltage (OCV) condition, hence drawing no current.

2.3.2 Effluent Water Analysis

The anode and cathode exhaust gases were passed through Teflon® tubes and the condensate water was collected in high-density polyethylene bottles. At the operating condition of 90°C and 30%RH the condensation rate of water is 2 cm$^3$/h based on the condenser temperature of 25 °C. To ensure complete condensation of water, the exhaust was passed through long Teflon® tubing before the condenser (polyethylene bottles). All water samples collected were analyzed for fluoride content. A fluoride ion selective electrode (Thermo Electron, Orion 96-09) was used for the fluoride analysis. The electrode was connected to the ion selective electrode meter (Orion 290A+, Thermo Electron) to read the concentration directly. To adjust the ionic strength 50 cm$^3$ of total ionic strength adjustment buffer (TISAB II, Fisher Scientific) solution was added to 50 cm$^3$ of the sample. In case of effluent volume <50 cm$^3$, de-ionized H$_2$O was added to the sample to obtain 50 cm$^3$. The dilution was taken into account in the FER calculation. At a particular operating condition, effluent water was collected for a certain period of time and the FER was calculated from the concentration of fluoride in the effluent water and the condensation rate of water. The FER was calculated separately from the anode and cathode condensate and summed.
for the total FER. In figures where only a single value of FER is reported for a particular operating condition, it represents the total FER. In figures where the FER is plotted against time, the data point at a particular time represents the FER based on effluent water collection at that time from the time at which the previous water sample was collected. The lines used to connect the data points are just for clarity.

2.4 X-ray Diffraction Studies (XRD)

The x-ray diffraction patterns of PTA, Nafion® and composite membranes were obtained using a Rigaku D/MAX XRD (Cu Kα radiation, 1.54 Å) located at the Materials Characterization Facility at the University of Central Florida, Orlando. In each case, the sample was placed on a holder and subject to X-ray radiation at various 2θ angles between 10° and 90°.

2.5 Scanning Electron Microscope (SEM)

Hitachi S3500N SEM was used to obtain data regarding the surface topography of the membranes. The voltage used was 10kV, with a magnification of 250x. The surface was carbon coated before putting in the SEM.

2.6 Thermo-Gravimetric Analysis (TG/DTA)

Thermogravimetric Analysis (TGA) (TA instruments; model no. 2950, Newcastle, DE) was used to run samples from 30 °C to 450 °C using a heating step of 10 °C/min. Percentage weight loss was plotted against temperature. Sample weights of approximately 4 mg were used. The studies were performed in a nitrogen atmosphere.
2.7 Fourier Transform Infrared Spectroscopy (FTIR)

IR spectra of membranes were obtained using a vector 22 FTIR spectrometer (Bruker Analytic GmbH, Bremen, Germany). Percentage transmission vs wavelength inverse was measured to characterise the membranes in terms of their structure.

2.8 Linear Sweep Voltammetry (LSV)

Linear sweep voltammetry was performed at room temperature using a potentiostat (Princeton Applied Research, Oak Ridge TN, Model No 273A) to monitor fuel crossover and to check for electronic shorts of the membrane electrode assembly. Humidified H₂ was used as anode gas and humidified N₂ as cathode gas. A flow rate of 200 cm³/min was used for both the gases. A potential range of 0-400mV was used as higher voltages cause platinum oxidation. The scan rate was 4 mV/s and the fuel cell cathode (working electrode) was driven so that any hydrogen that crossed through the membrane was measured in the form of an oxidation current. Current initially increases with increasing voltage from 0 mV, but reaches a stable value around 300mV as all the hydrogen that crosses over is instantaneously oxidised resulting in a limiting current. If the limiting current is not constant in the potential sweep range of 0-400mV, the increasing current indicates an internal electronic short. Figure 9 shows the typical LSVs with normal and shorted behaviour.

2.9 Cyclic Voltammetry (CV)

CV experiments were performed to evaluate the electrochemical active area of the electrode (ECA) and to make sure that the electrodes are active before performance testing.
Figure 9. Typical LSVs showing limiting current trends with and without the internal shorting. Resistance for shorted MEA keeps on increasing instead of being stable.

Typically, electrochemical activity of the cathode is of more interest due to sluggish oxygen reduction reaction kinetics. Cyclic voltammetry was performed at room temperature using a potentiostat (Princeton Applied Research, Oak Ridge TN, Model No 273A). Humidified H₂ was used as anode gas and humidified N₂ as cathode gas. A flow rate of 200 cm³ / min was used for both the gases. A potential range of 0-800mV was used. The scan rate employed was 40 mV/s. The sweep rate is higher in a CV experiment than LSV experiment to augment the peak size. The polarisation imposed on the anode or counter electrode is assumed to be small relative to the cathode or working electrode. The only difference between the CV and LSV experiment is the reverse scan to monitor the reduction phenomenon. Hence the experiment measures the redox
hydrogen electrochemical activity on the cathode catalyst surface. A typical cyclic voltammetry curve along with the calculation used to obtain the ECA is shown in Figure 10.

Figure 10. Typical CV curve for MEA used in fuel cell. Electrochemical active surface area is calculated using the area under the hydrogen adsorption / desorption peaks. Formula used is given as: 

$$ECA = \frac{\text{Area under the peak}}{\text{[scan rate in V/s]} \times (210 \text{C/cm}^2 \text{-Pt}) \times \text{Total Pt loading in mg}}$$
2.10 Performance Curve Measurements

Before measuring the performance curve, linear sweep voltammetry and Cyclic Voltammetry (CV) were employed to measure fuel crossover and Electrochemical Active Area of the respective membrane. Crossover measures the hydrogen crossover from anode to cathode and is known as fuel crossover. For this study, the maximum thickness of the membrane used was 2mil. Hence crossover should not be more than 4 mA/cm². ECA is calculated using Corrware software provided by Scribner Associates. Before measuring performance, the cell was humidified for at least 3.5 hours. This step is performed to introduce water into the membrane to improve its ionic conductivity and reactant permeability. Then the cell was operated in break-in-mode (0.55 V under H₂/Air) to allow it reach a steady state while operating in a benign fashion. For all degradation studies, performances were measured at 80°C under Air-Oxygen-Air.

2.11 Open Circuit Voltage (OCV)

OCV was performed at room temperature using a 850C Scribner Associates fuel cell test station to monitor the voltage obtained when no current was drawn from the fuel cell. Humidified H₂ was used as anode gas and humidified N₂ as cathode gas. As flow rate of 200 cm³/min was used for both the gases. During the whole 100 hour durability test, a drop in voltage was recorded every 10 seconds and plotted against time. It is well established that operating the fuel cell at OCV degrades the cell much faster than at any other current density.
3.0 RESULTS AND DISCUSSIONS

3.1 Effect of Casting RH

While casting membranes for intended high temperature PEMFC operation as described in the experimental methodology section, the membranes were seen to have a difference in appearance.

The membranes cast at higher relative humidity invariably gave a more cloudy appearance than the membrane cast at lower relative humidity. To further investigate the differences, a series of membranes were cast with varying relative humidity namely, 30%, 40%, 50% and finally 60% RH to see differences in surface morphologies and also whether there were any other differences.

Figure 11. Physical appearance of (a) membrane cast at 40% RH and (b) membrane cast at 60% RH
The differences in appearance of membranes cast at 40% and 60% RH are shown in Figure 11. XRD was performed to observe changes in crystalline nature of the host Nafion® matrix. Nafion® has a characteristic peak of 17° 2θ, largely attributed to the PTFE-like backbone. Nafion® has a largely amorphous nature while PTA is highly crystalline characterized by high activity peaks in the range of 5-60° 2θ, with peaks at 25 and 35° 2θ. As shown in Figure 12, the composite membrane nature turns more crystalline and it loses the characteristic 17° 2θ peak as casting relative humidity decreases. The XRD pattern for membranes cast at 60% RH represents little PTA incorporation and a high Nafion® peak at 17° 2θ whereas the membrane cast at 50% RH has a lower 17° 2θ peak and matches well with XRD pattern for PTA.6H2O. Membranes cast at 40% RH matched well with the PTA pattern with no water. Also the Full Width Half Maximum value for the 60% RH membrane was 0.523°, for the 50% RH membrane the value was 0.905°, and for the 40% RH membrane, the value was 2.901°. Hence the crystallinity of the membrane increases on reducing the casting relative humidity. This confirms that changing a small parameter like casting relative humidity is related to the changing nature of the composite membrane crystalline structure. The next step would be to study the FTIR spectra of the above membranes and see if any concrete difference occurs.
Figure 12. XRD pattern of NTPAs with 15% PTA at different relative humidity. The peak at 17°
2Θ is a characteristic of pure Nafion®. Peak at 35°2Θ is a characteristic PTA peak. As seen,
Nafion® nature decreases steadily on increasing the PTA loading and the PTA peak becomes
prominent.
Figure 13. Full Width Half Maximum and particle size variation with increasing relative humidity while casting the membrane as measured by the $17^\circ\,2\Theta$ peak. The particles coalesce together on increasing the relative humidity and the membranes have lower crystallinity.

The FTIR spectra were obtained to study possible interaction changes between the HPA and the sulphonic groups in Nafion® matrix. The characteristic PTA keggin structure has a minima at 1080, 985, 890, and 800 cm$^{-1}$. A distinctive split in the W=O$_i$ band at 980 cm$^{-1}$ as reported by Yadav$^{63}$ and Asthana was visible in all the composite membranes. As shown in Figure 14, the minima at 890 cm$^{-1}$ corresponding to the W-O$_{cornershared}$ bond is not visible in the Nafion® membrane as well as that of the 60% RH cast membrane, indicating that PTA might not be added
to the high RH membrane as intended. The mimima at 810 cm\(^{-1}\) that corresponds to the W-O\(_{\text{edgeshared}}\) bond and 1080 cm\(^{-1}\) corresponding to the symmetric stretching of SO\(_3\) group\(^{64}\) were also not found in membranes cast at high relative humidity.

![Figure 14. Room temperature IR spectra of protonated NTPAs with varying casting relative humidity.](image)

Thermographs of various composite membranes cast at varying relative humidity are given in Figure 15. Decomposition onset in these membranes started at around the same temperature, i.e.,
300 °C. Hence little difference was found in terms of thermal degradation properties in above membranes. All membranes were however thermally suitable to be used in a PEM fuel cell operation above 120 °C.

![Graph showing TGA analysis of composite membranes cast at varying relative humidity.](image)

Figure 15. TGA analysis of composite membranes cast at varying relative humidity. Different relative humidity are marked in the above graph

Scanning Electron Microscopy was performed on 40% RH and 60% RH membranes using an electron beam of 10 kV and a magnification of 250x. Samples were coated with carbon to prevent charging. Coated samples were left in vacuum for a day to ensure all gases came out prior to SEM operation. As seen in Figure 16, particle size was found to be on the order of a few microns in both cases with bigger agglomerated particles in the case of the 60% RH membrane.
Figure 16. SEM micrographs showing particle size in (a) membrane cast at 40% RH and (b) membrane cast at 60% RH.
Figure 17. EDAX micrograph of (a) Membrane cast at 40% RH and (b) Membrane cast at 60% RH.

This SEM data was not consistent with the particle size profiles of the membranes found by XRD analysis. Also there is a possibility that the particles are in nanometer range and not seen at the stated magnification and resolution. The particles seen may be dust particles or other foreign entities. Hence no conclusion was made based on the SEM analysis. Energy dispersive spectroscopy was employed to gather the tungsten peaks along with other element peaks. As is evident from Figure 17, there is higher concentration of tungsten and consequently PTA in
membranes cast at higher relative humidity. But due to the inconsistent data, no firm conclusions were based on SEM/EDS analysis. The XRD results hint that the particles gets larger and also there might be higher tungsten concentration at the surface for a membrane cast at 60% RH rather than that cast at 40% RH.

3.2 Effect of Increasing PTA Level in Naftion® Matrix

Incorporation of HPA like PTA is reported to increase the conductivity of the composite membrane in comparison to the ones without the HPA. Performance at high temperature operations is also reportedly enhanced significantly. However, no such data is available for the durability of the membrane. As detailed in the literature review section, comparison of durability data is not an easy task and often confusing as there is no established standard. Recently DOE and US Fuel Cell Council are trying to establish the same. There is also a decoupling problem as to how to quantify various modes of degradation independently, e.g., chemical, mechanical and thermal degradation mechanisms all play mutually assistive roles in degrading the membrane.

3.2.1 In plane conductivity measurements

The relationship between ionic conductivity and temperature can be expressed by the Arrhenius relation $\kappa = A \exp \left(-\frac{E}{RT}\right)$ where $\kappa$, $A$, $E$, $R$ and $T$ denote the ionic conductivity, frequency factor; activation energy for ionic conduction, gas constant, and temperature, respectively. $\kappa$ was measured at 80 °C and 120 °C for all membranes.
Figure 18. Four probe conductivity measurement data taken at different relative humidity, plotted as a function of time for N112 at 120 °C.

Nomenclature NTPA is used for the Nafion®/Tetratek®/Phosphotungstic acid composite membranes in the ensuing parts. Phosphotungstic acid is abbreviated as PTA.

Bekktech is a LLC, which specializes in In-plane membrane conductivity measurements and has provided the four probe conductivity apparatus for the Department of Energy (DOE) project.

Figure 18 shows in-plane conductivity (κ) data taken as a function of time. The variation of relative humidity is on the primary y-axis and conductivity in mS/cm is on the secondary y-axis. Before taking conductivity data as a function of relative humidity, the relative humidity was maintained at 70% for about 3 hours. After the initial hold at 70% the whole scan from 70% to 20% back to 100% RH would take 7.5 hours. It is important to hold the membrane long enough
at a particular relative humidity to obtain a stable conductivity reading. In some experiments it required more than an hour for the apparatus to attain relative humidity stability depending on the membrane, temperature and relative humidity used. Thicker membranes (>50μm) in general took longer time to stabilize than thinner membranes (~25μm). As shown in the figure, conductivity is recorded at the point when the relative humidity stabilizes as marked by cross symbols in both curves. Conductivity is calculated based on the dry dimensions of the membrane and swelling of the membrane was not considered in the calculation. For Nafion® like membranes the experimental error was less than 12%.

Figure 19.  Forward and backward scans of conductivity as a function of relative humidity for N112 at 120 °C. The two scans are within 8% of each other.

Figure 19 shows the typical hysteresis curve exhibited by a 50μm thick Nafion® membrane (N112 in this case) when going from 70% RH to 20% RH and back to 100% RH. The hysteresis curve is obtained not due to the fact that the humidifier has not stabilized at a
particular relative humidity and time as described in Figure 8; rather is due to the relatively slow uptake of water into the membrane or the slow removal of water from the membrane. The difference in conductivity on a hysteresis curve at a particular relative humidity is within 8%. Hence the average surface conductivity (κ) is in between the backward (70% RH- 20% RH) and forward (20%-100% RH) scan data at a particular relative humidity with +/- 4% difference from either curve. For clarity, in further discussions, only the forward scan i.e. relative humidity scan from 20% to 100% will be presented. The backward scan obtained in all experiments discussed in forthcoming results was always greater in value (within 8%) than the forward scan.

![Graph showing membrane conductivity plotted as a function of relative humidity for 80 °C and 120 °C. The Department of Energy Conductivity Goals at 80 °C and 120 °C along with conductivity values of Nafion® are also presented.](image)

Figure 20. FSEC1 membrane conductivity plotted as a function of relative humidity for 80 °C and 120 °C. The Department of Energy Conductivity Goals at 80 °C and 120 °C along with conductivity values of Nafion® are also presented.
In Figure 20, the membrane conductivity of FSEC1 is plotted as a function of relative humidity for 80 °C and 120 °C. The Department of Energy Conductivity Goals for conductivity at 80 °C and 120 °C along with a few conductivity values of Nafion® (80 °C and 90% RH and 120 °C and 50% RH) are also presented. The Teflon® support in the FSEC1 membranes provides mechanical strength and longer mechanical life of the membrane. Although the conductivity of the FSEC1 membrane (~25 μm) is about the same as the Nafion® 112 membrane (~50 μm) the thinner FSEC1 membrane should exhibit half the voltage loss across the membrane. So apart from adding PTA to NTPA and getting higher conductivity, one would expect higher performance and stability.

![Graph showing conductivity comparison for N112 and NTPA-0% PTA at 80 °C and 120 °C with forward scan only.](image)

Figure 21. Conductivity comparison for N112 and NTPA-0% PTA at 80 °C and 120 °C with forward scan only.

Figure 21 shows the comparison between conductivity of N112 and NTPA with 0% PTA at 80 °C and 120 °C. Bekktech provided the measurements for the N112 membranes. At 80 °C,
the conductivity of N112 for 20% RH is 4.15 mS/cm, whereas that for NTPA with 0% PTA for 20% RH is 6.9 ms/cm and the difference in conductivity gets larger for higher relative humidities. At 120 °C, the conductivity of N112 for 20% RH is 4.80 mS/cm, whereas that for NTPA with 0% PTA for 20% RH is 8.00 ms/cm, and the difference in conductivity gets larger for higher relative humidity. The conductivity of NTPA with 0% PTA was higher than that of N112 at both temperatures and over the whole forward relative humidity scan range. N112 is an extruded membrane, whereas, all NTPA membranes were cast. Also, NTPA is structurally different, as it has a Teflon® support, which N112 does not possess. Addition of Teflon® support reduces the conducting Nafion® content of the membrane and replaces it with a non-conducting fluorinated hydrocarbon (-CF₂-) based material. Studies¹³ have shown that as cast Nafion® 1100 equivalent membranes have a lower conductivity than the extruded N112 membrane of the same equivalent weight. The shape of the conductivity curves obtained for the different membranes at a particular temperatures are the same with each curve being parallel to the other curves. The thickness of the membrane is very important for fuel cell applications, because lower thickness results in less resistance for the proton to travel. Lower resistance results in less loss in operating voltage, resulting in higher performance obtained at any current density. A lower membrane thickness also increases the gas crossover through the membrane. Hence an optimization is desired in membrane thickness.
Figure 22. Conductivity comparison of N112 and FSEC1, measured at Bekktech and that of FSEC1 measured at FSEC. As seen, the data is reproducible within experimental error.

Figure 22 shows a comparison of the conductivity of FSEC1 membranes containing 15% PTA as a function of relative humidity measured both by Bekktech, in Colorado, and by myself at FSEC, in Florida, for both 80 °C and 120 °C. The Bekktech measurements and my measurements superimpose over each other for both temperatures. The conductivity of N112 as measured at Bekktech also matches well over most of the relative humidity range. At 100 RH%, there is a large difference in conductivity between the two membranes. At 80 °C, for FSEC1, the conductivity is 136mS/cm whereas for N112, it is 110mS/cm. At 120 °C, for FSEC1, the conductivity is 231mS/cm whereas for N112, it is 172mS/cm. Possible reasoning might be high availability of water at 100% RH results in effective separation of proton from sulphonic groups, resulting in effective Lewis group acids. Also vehicular mechanism of proton transfer is
enhanced, due to high presence of vehicle (water) molecules. Since FSEC1 is half the thickness of N112, it will have half the resistivity and hence half the voltage loss across the membrane. The Nafion® content has been reduced to less than 50% in FSEC1 due to the Teflon® support and the thinner thickness. Adding PTA (15%), which has a higher conductivity than Nafion 1100 equivalent weight ionomer, should increase the conductivity further, but this is not the case.

Figure 23. Conductivity comparison for different NTPA membranes with different loadings of PTA at 80 °C. NTPA – 15% is the same membrane as FSEC1.
Figure 24. Conductivity comparison for different NTPA membranes with different loadings of PTA at 120 °C. NTPA – 15% is the same membrane as FSEC1.

Figure 23 and Figure 24 show conductivity of NTPA membranes as a function of relative humidity for various concentrations of PTA at 80 °C and 120 °C, respectively. At 80 °C, the conductivity of NTPA with 0% PTA at 20% RH is 6.90 mS/cm. The conductivity decreases on addition of 3% PTA, but increases thereafter on addition of more PTA. The same trend follows at 120 °C. Possible reasoning for the behavior exhibited in Figure 23 and Figure 24 may be the relative distances between the PTA particles in the Nafion® matrix. At 3% PTA concentration, the distances between the particles are too long for effective proton transport by Grotthuss mechanism, hence making PTA act like a non-ionic conductor, void or porosity. Whereas on increasing the PTA concentration, the relative distance decreases hence, making a continuous path for protons to move along the PTA. The higher conductivity of the 0% NTPA is surprising.
in that PTA particles are more conductive than Nafion®. The particles must either be acting as insulators, or they alter the structure of the Nafion® so that the Nafion® is less conductive. The particle size of the PTA is another important consideration as they should be very small and well distributed within the Nafion® matrix to have effective bridging between the hydrophilic regions. X-ray Diffraction (XRD) should be an effective tool to estimate the particle size. As one evaporates the solvent, while casting there is a possibility that the particles accumulate on the surface and do not have a uniform distribution throughout the membrane. Convective flow of air with various relative humidity over the membrane can effect the evaporation rate of the solvent and hence the particle size and distribution throughout the membrane. Chemical processing of the membranes with cesium and sulphuric acid treatment may remove water associated with PTA, which helps in the conductivity of the membrane. Complete replacement of the protons on the PTA with cesium, while making the PTA more stable, may lower the conductivity of the PTA and that of the Nafion®.

When dealing with the conductivity of composite membranes, one has to be very cautious, as there are different parameters involved, which can affect the final calculation. For instance at 80 °C and 30% RH, the conductivity of NTPA with 0% PTA is 13.81mS/cm, which should decrease if PTA particles are assumed to be inert and not affecting the conductivity of the composite membrane. NTPA with 3% PTA as described in experimental method section was prepared by adding 3% PTA by volume to the Nafion® solution having Teflon support. Hence assuming that no PTA is lost during various processing steps and all PTA shows up in the final membrane, there should be approx 3% loss. PTA has a conductivity of 0.17 S/cm at room temperature.
Consider a particle with an electrical conductivity $\sigma_f$ in a matrix with an electrical conductivity $\sigma_m$. The composite electrical conductivity along the particle axis can be estimated using rule of mixture (ROM) with sufficient accuracy. Therefore, the electrical conductivity, $\sigma_c$ of a discontinuous particle–reinforced unidirectional composite can be estimated using the above effective conductivity and rule of mixture,

$$\sigma_c = (\sigma_f)^*v_f + (\sigma_m)^*(1- v_f)$$

(1-17)

Where $v_f$ is the particle volume fraction. We can use above equation to calculate $\sigma_f$, as the value of $\sigma_c$ is known experimentally and assuming $\sigma_m$ to be the conductivity of NTPA with 0% PTA along with known volume fractions of PTA in each NTPA. Figure 25 shows the conductivity variation with relative humidity of PTA at 80 °C. The conductivity of PTA at 25 °C and 80% RH is 170mS/cm$^6$. Hence addition of PTA should add to the conductivity of NTPA membranes, which is not the case at low relative humidity i.e. until 60% RH, the conductivity of PTA remains negative and only at higher relative humidity it contributes to conductivity of NTPA. Hence instead of aiding in the conductivity, PTA is actually hurting the conductivity of NTPA at low relative humidity. The basic tenet of adding PTA to Nafion® matrix was to obtain a higher conductivity at low relative humidity due to the increase in concentration of acid sites mainly accounted to Groththus mechanism in addition to its other added advantages as outlined in introduction. At high relative humidity, vehicular mechanism of conduction becomes prominent and might be the reason for increase in conductivity as more water molecules are present for physical migration of proton. Figure 26 shows the conductivity variation with relative humidity of PTA at 120 °C.
Figure 25. Back calculation of PTA k using NTPA with 0% PTA as base case at 80 C.

Figure 26. Back calculation of PTA k using NTPA with 0% PTA as base case at 120 C.
Conductivity follows the same pattern as NTPAs at 80 °C. Although in both cases, jump in conductivity from 90-100% RH is the most for NTPA with 15 % PTA instead of NTPA with 25% PTA. Conductivity of NTPA with 15% PTA jumps from being negative to a large positive number whereas that for NTPA with 25% PTA increases in steps from 70-100% RH. During the cesium (Cs) treatment of the membrane, PTA forms a compound (Cs-PTA), which is no longer hygroscopic and requires large hydration levels to act as effective HPA, which PTA does at high RH%.

XRD Data

Making composite membranes with small PTA particles is critical in obtaining high conductivity membranes. If the particles are of nanometer (nm) size they can bridge the hydrophilic channels and help in proton hopping at low relative humidity through the Grotthuss mechanism. With addition of more PTA, the crystalline nature of the membrane should increase as indicated by the decrease in Full Width Half Maximum (FWHM). FWHM of a peak is defined as the expression of the extent of a function, given by the difference between the two extreme values of the independent variable at which the dependent variable is equal to half of its maximum value. Moore and Martin \(^{58}\) and Gierke \(^{59}\) reported that Nafion® exhibits a diffraction peak around 17.5° 2\(\Theta\). PTA is a highly crystalline substance and exhibits pronounced activity in the range of 5-60° 2\(\Theta\) especially at 25 and 35° 2\(\Theta\).

The XRD intensities on the y-axis were shifted to be put on the same curve and do not represent the absolute values. Figure 27 shows the diffraction patterns for Nafion® 112 extruded membrane and that of NTPA – 25% PTA membrane. The Nafion® 112 has a distinctive 17° 2\(\Theta\) peak followed by the amorphous bump at around 40° 2\(\Theta\). NTPA – 25% PTA has the
characteristic PTA peak at 25° 2θ and has reduced peak at 17° 2θ relating to the Nafion® feature. Hence the pattern for NTPA - 25% PTA is the sum of the Nafion® 112 and the PTA patterns.

Figure 28 shows the XRD profile for increasing concentrations of PTA in the Nafion® matrix. X-Ray Diffraction (XRD) was used to provide information regarding the morphological properties and the degree of crystallinity of the membranes. In all the NTPA membranes, the Nafion® diffraction peak is present at 17.5° 2θ. NTPA with 0% PTA exhibits a strong Teflon® peak at 17° 2θ whereas on increasing the PTA concentration, this peak becomes less intense and the PTA characteristic becomes more prominent.

Figure 27. XRD pattern of Nafion® 112 and NTPA – 25% PTA membranes. The peak at 17° 2θ is a characteristic of pure Nafion®. Peak at 25° 2θ is characteristic PTA peak. NTPA – 25% PTA diffraction pattern fits well with that of PTA.6H2O.
The 17°2θ peak gets narrower as PTA is added. PTA.6H2O fits the XRD pattern for NTPA with 25% PTA, hence it is likely that the protonated membrane has 6 waters of hydration attached with PTA.

Figure 28. XRD pattern of NTPAs with increasing PTA loading from 0–25% PTA. The peak at 17°2θ is a characteristic of pure Nafion®. Peak at 25°2θ is characteristic PTA peak. As seen, Nafion® nature decreases steadily on increasing the PTA loading and the PTA peaks become prominent.
The Full Width Half Maximum (FWHM) of this peak as a function of PTA loading is shown in Fig. 29. Compared with NTPA-0% PTA, the FWHM values of NTPA with PTA composite membranes was smaller as the concentration of PTA was increased. FWHMs equaled to 3.42° for NTPA with 0% PTA, 3.22° for NTPA with 3% PTA, 1.92° for NTPA with 15% PTA, 0.89° for NTPA with 25% PTA. Smaller FWHM values indicated that increasing the PTA concentration increases the crystallinity with regards to that of NTPA with 0% PTA. It is believed that a high crystallinity corresponds to open ion-channels, and dehydrated, collapsed channels correspond to a decrease in crystallinity. Hence the increasing crystalline nature of the NTPA membranes with increasing PTA concentration, visible by the FWHM values should lead to increased internal hydration. The Nafion® diffraction peak at 2\(\Theta\) = 12-22° was deconvoluted into two peaks by Dimitrova, 2\(\Theta\) = 16° for amorphous region and 17.5° 2\(\Theta\) for crystalline scattering from polyfluorocarbon chains of Nafion®. Dimitrova found that increasing SiO₂ changes the ratio of intensity between the crystalline and amorphous scattering. The same is found on increasing the PTA concentration in Nafion®.

The particle size in the NTPAs varies with increasing PTA concentration and is plotted on the secondary y-axis in Fig. 29. Particle sizes equaled to 2.5 nm for 3% PTA, 4.2 nm for 15% PTA, 9.2 nm for 25% PTA membrane. The PTA particles coalesce together with increasing concentration within the composite membrane. Using the Scherer formula, the particle size calculation was done. Stress free membrane structure was assumed in the calculation.
Fig. 29. Full Width Half Maximum and particle size variation with increasing concentration of PTA in Nafion® as measured by $17^\circ$ 2$\Theta$ peak. The particles coalesce together on increasing the PTA loading and membranes have higher crystallinity.

**FTIR data**

IR spectra for PTA and Nafion® is presented in Figure 30. The characteristic PTA keggin structure has minima at 1080, 985, 890, and 800 cm$^{-1}$ 62. Yadav and Asthana63 reported the distinctive split in W=O$_t$ band at 980 cm$^{-1}$, dip at 890 cm$^{-1}$ corresponding to the W-O$_{cornershared}$
bond, at 810 cm\(^{-1}\) corresponding to the W-O\(_{\text{edgeshared}}\) bond and 1080 cm\(^{-1}\) corresponding to the W-O\(_{\text{center}}\) bond. Key features of PTA and Nafion\(^®\) overlap, making it difficult to confirm the presence of PTA in the membrane. The blocking of 985 cm\(^{-1}\) presence of PTA by the C-O-C bond stretching of Nafion\(^®\) around 980 cm\(^{-1}\) is one such example. Hence the presence of PTA is best confirmed by the dip at 890 cm\(^{-1}\), corresponding to the W-O\(_{\text{cornershared}}\) bond\(^{64}\).

Figure 30. Room temperature IR spectra of Nafion\(^®\) 112 and NTPA – 0% PTA after protonation.

All dips are clearly seen in PTA sample and in the NTPAs with concentration range of 0-25% PTA before protonation as shown in Figure 31. Figure 32 shows the IR spectra before and after protonation for NTPA – 15% PTA. Some amount of PTA is lost on protonation as seen in Figure 32 indicating that the PTA might be washed out of the support. Same behavior was observed for rest of NTPAs. Figure 33 shows the IR spectra for NTPAs after protonation. As
seen in the figure, the characteristic dip at 890 cm$^{-1}$ has increased intensity for increasing amount of PTA, indicating enhanced amount of PTA in protonated membrane.

Figure 31. Room temperature IR spectra of as cast NTPAs with varying concentration of PTA, ranging from 0-25%.
Figure 32. Room temperature IR spectra of as cast NTPA – 3% PTA and protonated NTPA – 3% PTA. As seen, characteristic PTA dip at 890 cm$^{-1}$ is lowered for protonated NTPA
Figure 33 Room temperature IR spectra of protonated NTPAs with varying concentration of PTA, ranging from 0-25%.

**TGA data**

For perfluorocarbon ionomer membrane, shielding effect of fluorine and the thermal stability of the C-F bond prevents any structural changes before 150 °C\(^65\). Above 200 °C, loss of sulphonate groups begin\(^35\). Water, trace amounts of SO\(_2\) and CO\(_2\) are produced between 35 °C and 280 °C.

Wilkie et al\(^65\) proposed a mechanism for thermal degradation of Nafion\(^\circledR\) in its protonic form. It includes cleavage of C-S bonds to form SO\(_2\), an OH\(^-\) radical and a carbon based radical which further degrades, leading to a chain of self propagated reactions. Rikukawa and Sanui\(^66\) proposed the onset of degradation temperature in Nafion\(^\circledR\) at around 280 °C. TGA analysis on composite NTPAs with PTA concentration ranging from 0-25% are shown in Figure 34. Similar
decomposition onset temperature around 280 °C confirms the thermal stability of the NTPA membranes for fuel cell use. Since the PTA does not entirely decompose even at temperatures of 450 °C, a residual mass is seen in the thermographs above 450 °C.

![Thermographs of NTPA with 0% PTA, 3% PTA, 15% PTA, and 25% PTA; in N₂ atmosphere; 10°C / min scan rate.](image)

Figure 34. Thermographs of NTPA with 0% PTA, 3% PTA, 15% PTA, and 25% PTA; in N₂ atmosphere; 10°C / min scan rate.

3.2.2 Degradation studies

All assembled cells, which were tested for beginning of life, were then put to 100 hr degradation test at Open Circuit Voltage (OCV), 90 °C, 30% RH and 200 ccm flow rate conditions. Voltage drop along with Fluoride Emission Rate (FER) was measured for each during the test. Performance, crossover (CO) and electrochemical active area (ECA) were monitored for each
membrane before and after the test. The test station lost cathode gas pressure for approx 10 hours while running the durability test for the 25% PTA concentration membrane.

**Linear Sweep Voltammetry (LSV)**

LSV was measured at the beginning and end of the 100 hour durability test. Before the test LSV results revealed that the H₂ crossover in all MEAs irrespective of the PTA concentration was very small. It indicates structural integrity of the MEAs and also the absence of holes. Also the LSV curves did not had a slope to it indicating absence of internal shorting. Representative LSV before and after the 100 hour test for NTPA - 15% PTA is shown in Figure 35. As seen, the LSV increases considerably after the 100 hour test due to severity of the operating conditions. The LSV value before the test for NTPA – 0% PTA was 2.5mA/cm², NTPA – 3% PTA was 2.8mA/cm², NTPA – 15% PTA was 1.828mA/cm², NTPA – 25% PTA was 2.2mA/cm². After the 100 hour test the LSV value for NTPA – 0% PTA was 4.05mA/cm², NTPA – 3% PTA was 4.34mA/cm², NTPA – 15% PTA was 2.63mA/cm², NTPA – 25% PTA was 3.08mA/cm². The percentage increase in the crossover after the 100 hour durability test is defined as 

\[
\frac{(\text{Final Crossover} - \text{Initial Crossover})}{\text{Initial Crossover}} \times 100
\]

Also, the limiting hydrogen flux was calculated using 

\[
J(H_2) = \frac{i}{nF}, \text{ where } i \text{ is the current density in Amperes/cm}^2, \text{ n is the moles of electrons exchanged per mole of species which equals 2 in the fuel crossover equation, } F \text{ is Faraday’s constant equal to 96,485 coulomb/equivalent.}
\]

Using this calculation, hydrogen flux for NTPA – 0% PTA membrane increased from \(1.3 \times 10^{-8} \text{ mol/s/cm}^2\) to \(2.1 \times 10^{-8} \text{ mol/s/cm}^2\).
Figure 35. Representative linear sweep voltammograms on MEAs fabricated with NTPA – 15% PTA membrane before and after the 100-hour durability test. Scan rate 4mV/s, room temperature, atmospheric pressure, 200-cm³/min H₂ on anode and N₂ on cathode.
Figure 36. LSV percentage change with increasing PTA concentration in NTPAs before and after the 100-hour durability test. The 100 hour test for NTPA with 25% PTA was interrupted for approx 10 hours due to the loss of inert gas pressure overnight.

There is clearly a trend as seen in Figure 36, which indicates that on increasing the PTA concentration in the NTPA, the percentage change in LSV decreases. Increase in tortuosity of the path that fuel faces due to increase in PTA concentration might be the reason for this behavior. Another line of reasoning might be the increase in local relative humidity within the MEA due to PTA, which has additional 6 waters of hydration attached to it and is hygroscopic by nature. It had been pointed out in the literature that increase in relative humidity leads to decrease in the crossover rate \(^{68}\).
Cyclic Voltammetry (CV)

ECA was measured at the beginning and end of the 100 hour durability test. Before the test ECA results revealed that the carbon supported Pt in all MEAs irrespective of the PTA concentration was electrochemically active and there was no electrochemical disconnect between the electrode and the electrolyte. It indicates structural integrity of the electrodes. Also the ECA was calculated using the adsorption peak.

Representative ECA before and after the 100 hour test for NTPA - 25% PTA is shown in Figure 37. As seen, the ECA decreases after the 100 hour test due to severity of the operating conditions. The ECA value before the test for NTPA – 0% PTA was 20.823 m²Pt/gPt, NTPA – 3% PTA was 19.765 m²Pt/gPt, NTPA – 15% PTA was 22.563 m²Pt/gPt, NTPA – 25% PTA was 21.622 m²Pt/gPt. After the 100 hour test the ECA value for NTPA – 0% PTA was 19.365 m²Pt/gPt, NTPA – 3% PTA was 17.393 m²Pt/gPt, NTPA – 15% PTA was 18.501 m²Pt/gPt, and NTPA – 25% PTA was 16.865 m²Pt/gPt. The percentage increase in the ECA after the 100 hour durability test is defined as [(Final ECA – Initial ECA)/ Initial ECA]*100. Also, the limiting current obtained using LSV is represented in CV curves by the stabilised desorption peak currents from 0.4-0.7 mV. During the reverse potential sweep, i.e. potential range of 0.4 to 0.05V vs the counter electrode, proton (H⁺) is reduced to adsorbed H (H_ads).
Figure 37. Representative ECAs for MEAs fabricated with NTPA – 25% PTA membrane before and after the 100-hour durability test. Scan rate 40mV/s, room temperature, atmospheric pressure, 200-cm$^3$/ min $\text{H}_2$ on anode and $\text{N}_2$ on cathode.
Figure 38. ECA percentage change with increasing PTA concentration in NTPAs before and after the 100-hour durability test. The 100 hour test for NTPA with 25% PTA was interrupted for approx 10 hours due to the loss of inert gas pressure overnight.

Figure 38 shows the percentage change in the ECA values before and after the 100-hour durability test. As seen, there is clearly a trend, which indicates that on increasing the PTA concentration in the NTPA, the percentage ECA loss increases. Hence there is more loss in ECA on addition of PTA in the NTPA membranes. As reported\textsuperscript{67}, the adsorption of PTA particles on the electrode surface decreasing the available active sites for redox reaction in the electrolyte. Another line of reasoning might be the increase in local relative humidity within the MEA due to PTA, which has additional 6 waters of hydration attached to it and is hygroscopic by nature. It had been pointed out in literature that increases in relative humidity leads to decrease in ECA\textsuperscript{68}. 
Charge related to the double layer charging was accounted for in the analysis otherwise which can lead to an overestimation in the charge attribution to the electrochemical activity.

3.2.3 Performance Analysis

After initial characterization of membranes, humidifying the cell for at least 3 hr and operating the cell in break-in mode as described in the experimental methodology section, the cell was ready for performance testing. As shown in Figure 39, initial performances of the cell build with different PTA concentrations in the composite membrane were measured and compared. The cathode gas used was air. The temperature of PEMFC was 80 °C. The performance of PEMFC increases by increasing the heteropoly-acid concentration in Nafion®, as shown in Figure 39. Resistance also increases with increase in PTA concentration, which, because conductivity is inversely proportional to resistance, supports the results obtained for in-plane conductivity described earlier in Section 4.2.1 where lower conductivity of membranes with increasing PTA concentration was observed. Figure 39 also shows the posttest performance or end of life performance (EOL) after the 100-hour test. Through plane resistance before the test for 0% PTA MEA varied from 52-85 mΩ cm², for 5% PTA from 19-25 mΩ cm², for 15% PTA from 78-80 mΩ cm², and for 25% PTA from 61-87 mΩ cm² as the current density increases from 0-2000 mA cm². The range of post test resistance data for 0% PTA is 68-90 mΩ cm², 5% is 12-18 mΩ cm², 15% is 59-86 mΩ cm², and 25% is 13-17 mΩ cm². The change in resistance for 5% membrane is the least, and the change in 25% membrane was the most. Amongst pretest data, conductivity is highest for 5% PTA, followed by 0% PTA, 25% PTA and 15% PTA. Amongst posttest data, 5% PTA membrane is highest, followed by 25% PTA, 15% PTA, and finally 0% PTA concentration membrane.
Figure 40 depicts the percentage change in voltage, before and after the 100-hour test. The decrease in performance is highest for 25% PTA concentration, followed by 15%, 5%, with the lowest being 0%. The relationship between pre and posttest performances using oxygen as the cathode gas is plotted in Figure 41. As expected at any given current density, voltage obtained is higher than that by air. Gain is defined as the difference in voltage obtained by running PEMFC with oxygen and air at any given current density. Figure 42 shows the gain curves at all current density.
Figure 39. Beginning of life (BOL) performance and End of experiment performance curves (air) and resistance plots for NTPA MEAs with 0-25% PTA concentration.
Figure 40. Percentage change in voltage after durability testing at 90 °C, 30% RH, and 0-25% PTA concentration.
Figure 41. Beginning of life (BOL) performance and End of experiment performance curves (oxygen) and resistance plots for NTPA MEAs with 0-25% PTA concentration.
Figure 42. Gain data for NTPA MEAs with 0-25% PTA concentration before and after the 100-hour test.
3.2.4 OCV Analysis

The OCV of each MEA was monitored for 100 hours, as shown in Figure 43. The abrupt drop in 25% PTA OCV curve is due to loss of cathode gas pressure for approx 10 hours.

![OCV curves for NTPA membranes during 90 °C, 30% RH, and 0-25% PTA concentration durability tests.](image)

**Figure 43.** OCV curves for NTPA membranes during 90 °C, 30% RH, and 0-25% PTA concentration durability tests.
Figure 44 shows the percentage change in OCV before and after the test. The percentage drop in OCV decreases with increasing PTA concentration except at 25% PTA because of abrupt shutdown during nighttime which is the primary reason for the different slope after 70 hours. The % drop in OCV varies from 15.8% for 0% PTA to 10.5% for NTPA with 15% PTA.

![Figure 44. Percent decrease in OCV during durability tests at 90 °C, 30% RH, and 0-25% PTA.](image)

3.2.5 FER Analysis

High-density polyethylene (HDPE) bottles were used at anode and cathode outlets to collect effluent water. This water was collected twice a day for approx 100 hours. FER for anode and cathode was plotted separately as shown in Figure 45. The highest FERs are observed for
NPTA with 25% PTA concentration 0.44 μmol cm$^{-2}$ h$^{-1}$ (cathode), and 0.4 μmol cm$^{-2}$ h$^{-1}$ (anode), which was still decreasing after 100 hours partly due to the cathode gas shutdown for 10 hours. FER for NTPA with 5% PTA concentration was found to be 0.12 μmol cm$^{-2}$ h$^{-1}$ (anode) and 0.132 μmol cm$^{-2}$ h$^{-1}$ (cathode), which is the lowest. The most stable FER was exhibited by 0% PTA concentration NTPA, which was found to be 0.16 μmol cm$^{-2}$ h$^{-1}$ (anode) and 0.22 μmol cm$^{-2}$ h$^{-1}$ (cathode). Except for NTPA with 15% PTA concentration, the cathode FER is always higher than that of the anode. Hence, there is definitely an added advantage of having HPA in the Nafion® matrix, as it leads to lower FER, as shown by various curves for 5% PTA, and 15% PTA concentration NTPA membranes. The slope of 25% FER is higher than all other NTPA concentrations, which are mainly stabilized. Though nothing concrete can be said about 25% FER, it can be deduced that it will have lower FER than that of 0% PTA NTPA. FER for N112 is much higher and in the range of 0.63 μmol cm$^{-2}$ h$^{-1}$ (cathode) and 0.5 μmol cm$^{-2}$ h$^{-1}$ (anode), though there is a thickness factor involved too, as thickness of N112 is double that of NTPAs. Hence it’s safe to draw the conclusion that all NTPAs have lower FER at the end of 100 hours of testing at above described conditions. Among the different NTPAs, addition of PTA results in lower FER than that without the PTA (0% PTA NTPA). 100 hours might not be enough to get statistical differences of stabilized FER for all NTPA membranes as power shutdown to test station, inert, anode, or cathode gas shutdown during the durability testing is commonly observed in most reported data on durability.
Figure 45. FER of NTPA after durability testing at 90°C, 30% RH, and 0-25% PTA loading.
Physical characteristics of NTPA membranes cast at 30-60 RH% were studied using surface characterization tools such as XRD, FTIR, SEM/EDAX, and TGA. Membranes cast at lower relative humidity exhibited better incorporation of PTA properties. XRD indicated membranes cast at 30% RH show largest loss in amorphous nature of Nafion ($17^\circ\Theta$) and gain in crystalline nature ($35-65^\circ\Theta$). FTIR studies indicate the increasing intensity of keggin structure dips on decreasing the casting relative humidity. Thermographs of various NTPA membranes showed little difference in thermal properties of membranes and all the NTPA membranes were found suitable for high temperature fuel cell applications. Particle size found in all NTPA membranes was in order of nanometers but particle size increases with increasing casting relative humidity. This indicates that lower RH% while casting the membrane results in a finer network of PTA particles throughout the host matrix (Nafion®).

Efforts were made to optimize the PTA loading in NTPA with regards to conductivity, durability and performance of a unit cell. NTPAs with 0%, 3%, 15%, and 25% PTA concentration were fabricated and tested. In plane conductivity measurements were performed at two temperatures 80 °C, and 120 °C. Membrane with no PTA exhibited the highest conductivity ($\kappa$) at both temperatures and all RH% ranges. NTPA with 3% PTA concentration had drastically reduced $\kappa$, which increases with increasing PTA concentration in NTPA, but never reaches that exhibited by 0% NTPA membrane. Possible reasoning might be the reduced water uptake properties of PTA after Cs treatment and reprotonation. Through plane conductivities obtained by current interrupt method while measuring the performance data also indicates that $\kappa$ of 0% NTPA is highest. Morphological studies of different NTPAs were carried out to observe structural changes. XRD studies indicated the higher 25° 2\Theta peak and diminishing 17° 2\Theta peak (Teflon backbone) as we
go higher in PTA concentration. Moreover, increasing sharpness of 25° 2Θ peaks bear testimony to increasing particle size of PTA against the broad peaks for NTPA with 3% PTA concentration. After building cells using various NTPAs, initial crossover, ECA and performance were measured. No trend was visible for initial ECA or Crossover for different NTPAs. However, performance increased with increasing PTA loading in Nafion®. It gets better PTA content increases. The same trend was observed when the cathode gas was switched to oxygen. End of life performance for NTPA with 25% PTA exhibited the largest performance loss and the one with 0% PTA exhibited the least performance loss. 15% NTPA exhibited highest gain before and after the 100-hour test. Percentage decay in OCV decreases as PTA content increases. Cathode FER was always higher except that for 15% NTPA. All NTPAs exhibited lower FER than N112 and among the NTPAs, the one with added PTA had lower FER than 0% PTA NTPA membrane. Hence addition of PTA to Nafion® matrix leads to a decrease in in-plane conductivity, through-plane conductivity, lowering of FER, lower loss in OCV, lower Crossover and lower ECA. It also results in higher initial performance but exhibits the largest drop in performance. Hence there are advantages of adding PTA in Nafion matrix but cesium stabilization of PTA needs to be further investigated and PTA water uptake properties studied carefully before obtaining maximum benefits of PTA addition. Swelling measurements can be carried out as an extension of this study, which could reveal any difference in water uptake properties of NTPAs. Mechanical stress-strain curve could provide possible insights in the mechanical properties and differences among NTPAs. Furthermore, SEM/EDAX along with TEM can resolve the particle size considerations. A degradation test protocol was developed, to minimize differences in degradation rate due to catalyst ink, GDL permeability, etc. and not the membrane alone.
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