## Investigation of an Alternative Sulfonated Silane in

## **Ceramic Carbon Electrodes for Fuel Cell Applications**

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**Certificate of Approval** 

## Abstract

The fabrication of an ideal electrode material for fuel cell application that can maintain an optimal water content in both low and high relative humidity (RH) conditions has been studied by many research groups. Previous work by Eastcott et. al has shown great promise when using sulfonated ceramic carbon electrodes (CCEs) on the cathode of a PEMFC in low relative humidity (RH) environments though increased water retention. Through the sol-gel method the use of tetraethylorthosilicate (TEOS) and a small amount of 3-(trihydroxysilyl) propane-1-sulfonic acid (TPS) as the ionomer demonstrated increased porosity, better durability, and better fuel cell performance at low RH when compared to the traditional Nafion ionomer material.

In this work the sulfonated CCE material developed by Eastcott and Easton will be replaced with a more ion conductive sulfonated organosilane monomer component. TPS was replaced with 4-(2-(trihydroxysilyl)ethyl) benzenesulfonic acid (TEBS) and mixed with TEOS and compared to the previous TPS/TEOS system as well as the traditional Nafion ionomer electrode. The sulfonated CCEs were characterized using BET surface area analysis, thermogravimetric analysis, SEM, and TEM. The electrodes were then evaluated in both half-cell and full cell environments. Half-cell data showed an increased ECSA with TEBS when compared to the Nafion ionomer, while full cell data determined a decreased performance at both high and low relative humidities through polarization curves when compared to the TPS/TEOS and Nafion ionomers. The results obtained have determined that an optimization of the sulfonated ratio has to be altered in order to gain a performance similar to that of the TPS based ionomer. The total silane loading was then decreased while the TEBS loading was increased and this showed an increase in fuel cell performance more comparable to the TPS/TEOS ionomer system.

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### Chapter 4: Results & Discussion: Optimization of New Sulfonated CCE

## **List of Abbreviations**

- AC Alternating current
- AWR Anode water removal
- BET Brunauer-Emmett-Teller
- BJH Barrett-Joyner-Halenda
- C Capacitance
- CCE Ceramic Carbon Electrode
- CFP Carbon fiber paper
- CL Catalyst Layer
- CNT Carbon nanotube
- CV Cyclic voltammetry
- DC Direct current
- DTG Differential thermalgravimetry
- E Potential
- ECSA Electrochemically active surface area
- EIS Electrochemical impedance spectroscopy
- FT-IR Fourier Transform Infrared spectroscopy
- GCE Glassy carbon electrode

GDE - Gas diffusion electrode

- GDL Gas diffusion layer
- HOR Hydrogen oxidation reaction

I-Current

- MEA Membrane electrode assembly
- ORR Oxygen reduction reaction
- PBI Polybenzimidazole
- PEMFC Proton exchange membrane fuel cell
- R Resistance
- RH Relative humidity
- RHE Reverse hydrogen electrode
- SEM Scanning electron microscopy
- SHE Standard Hydrogen Electrode
- sPEEK sulfonated polyether ether ketone
- TCBS 4-(2-(trichlorosilyl)ethyl)benzenesulfonyl chloride
- TEBS 4-(2-(trihydroxysilyl)ethyl)benzenesulfonic acid
- TEM Transmission electron microscopy
- TEOS Tetraethyl orthosilicate

- TGA Thermogravimetric analysis
- TPS 3-trihydroxy-1-propane sulfonic acid
- Z Impedance
- $\varphi$  Phase angel
- $\omega$  Angular frequency

## **Chapter 1: Introduction**

### **1.1 Background**

Fossil fuels are used for the majority of the world's energy sources, and with automobiles as a major mode of transportation worldwide, fossil fuel consumption is a global issue. In 2013 Canada had over 31 million vehicles registered, and of that 11 million of those registered vehicles were in Ontario<sup>6</sup>. With the increasing number of vehicles being used around the world greenhouse gas emissions are increasing, particularly in major urban areas. This growing problem has led to the implementation of policies in order to decrease carbon emissions by many countries and governments around the world including Australia, China, the European Union, and Canada. Along with this increase in greenhouse gas emissions from vehicles, the growing population has also exacerbated fossil fuel consumption, not only for transportation, but also for industrial uses. In 2014 it was reported that approximately 85% of the energy consumed by the world was from fossil fuels, while only 2.5% was from a renewable energy source which can be seen in Figure 1.1 based on data collected by British Petroleum (BP) <sup>1</sup>. The large consumption of



#### Oil Coal Natural Gas Hydroelectric Nuclear Renewable Energy

Figure 1.1:World energy consumption in Million tonnes oil equivalent (MTOE) data acquired by BP<sup>1</sup>.

our non-renewable fossil fuels has led to an expected peak in oil consumption in 2018 based of the Hubbert theory<sup>7</sup>. This intensifying world issue has pushed for the use of a new sustainable energy source and as of late has been a major priority for numerous governments around the world<sup>8</sup>.

Currently, the use of small renewable energy devices have seen commercial success in products including cellular phones, laptops, and other stationary applications. Automobile companies are also aiding in the transition to more environmentally friendly vehicles which provide substantially reduced CO<sub>2</sub> emissions when compared to the traditional internal combustion engine<sup>9</sup>. Renewable energy technology, such as Lithium-ion battery technology, has allowed for the transition to an increase in renewable energy consumption. However, to drastically reduce our fossil fuel consumption a self-sustaining energy source is needed. One technology that has shown great promise for use in many applications in society is the fuel cell.

A fuel cell is a device that continuously converts chemical energy to electrical energy with heat and water as the byproducts. The traditional fuel and oxidant gases used are hydrogen and oxygen (from air), respectively, which allow the fuel cell to have a great advantage over current renewable energy devices. The use of simple fuels allow the fuel cell to produce energy as long as the fuel is being provided to the system which cannot be done with batteries or charge storage devices. Using hydrogen as a fuel allows other variations of fuel cells to be made for specific applications, but the proton exchange membrane fuel cell (PEMFC) is the most versatile due to its low operating temperature and the only type of fuel cell that is applied to automotive applications<sup>10</sup>.

PEMFCs can offer many advantages when compared to modern engine designs that require fossil fuels, as well as hybrid engines that combine an internal combustion engine with a charge storage device. The use of PEMFCs can allow efficiency values around 60% compared to internal combustion engines with efficiencies around 20%  $^{10-12}$ . The use of hydrogen also results in no CO<sub>2</sub> emissions which can greatly impact the volume of greenhouse gasses if vehicles adopted fuel cell technology. The use of fuel and oxidant gases also results in a silent engine that requires no moving parts and no added costs for repairs<sup>10</sup>.

### **1.2 Proton Exchange Membrane Fuel Cells (PEMFCs)**

The PEMFC is the most common type of fuel cell used industrially with typical power production anywhere between 1 and 100,000 watts<sup>10</sup>. The power is produced by two main reactions, the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) with the following half-cell reactions:

$$H_2 \rightarrow 2 H^+ + 2 e^-$$
 (E°=0.00 V) (1)

$$O_2 + 4 e^- + 4 H^+ \rightarrow 2 H_2 O$$
 (E°=1.23 V) (2)

The HOR occurs at the anode and allows the splitting of hydrogen gas to produce protons and electrons. The electrons produced travel through an external circuit to power a device, while the protons pass through an ion exchange membrane permeable to protons. The protons and electrons recombine at the cathode where oxygen is passed through. In the cathode the oxygen, protons, and electrons produce water and heat. A schematic of a typical PEMFC is displayed in Figure 1.2. A fuel cell with this design should theoretically produce 1.23 V, but due to the

various factors that can affect the two reactions the typical open circuit voltage (OCV) observed is around 1  $V^{10}$ . The simple design can allow the combination of many cells to connect in series to make a fuel cell stack, which increases the voltage to the desired value for a specific application. A typical stack for automobile applications can require approximately 300 cells in series in order to meet the operation demands<sup>13</sup>, and as result there is a great desire to decrease the size and cost of the fuel cell.



Figure 1.2: Detailed schematic of PEM fuel cell membrane electrode assembly adopted from the U.S. Department of Energy<sup>2</sup>.

### **1.2.1** Components of a PEMFC

#### 1.2.1.1 Proton Exchange Membrane

The components of the PEMFC all have their own important functions which allow the HOR and ORR to proceed. One of these components is the proton exchange membrane which allows the transport of protons from the anode to the cathode. Typically the membrane is a perfluorosulfonic acid polymer, with Nafion being the most common. The structure of Nafion can be seen in Figure 1.3 where the typical value of y is 14<sup>14</sup>. The structure of Nafion allows for high thermal stability as well as mechanical strength and chemical resistance through the floronated backbone, while the terminal sulfonic acid group facilitates high proton conductivity. A typical Nafion cluster-network has pore sizes around 4 nm which allows the trapping of water, which is required for proton transport within the membrane<sup>14</sup>. Other membrane materials such as sulfonated hydrocarbons have been studied for fuel cell applications and bring the added benefit of being cheaper materials to use, but were also more permeable to H<sub>2</sub> and O<sub>2</sub> crossover <sup>15-16</sup>. In the case of automotive applications Nafion has shown better performance when compared to other sulfonated polymers making it the ideal membrane material for fuel cell vehicles<sup>17</sup>.



Figure 1.3: Structure of Nafion®.

### **1.2.1.2 Fuel Cell Electrode**

A traditional fuel cell electrode is comprised of two components, the catalyst layer (CL) that contains the carbon support, the metal catalyst, and the ionomer and the diffusion layer (GDL). Figure 1.4 illustrates the incorporation of these components in a fuel cell electrode. These components allow the interaction of protons, electrons, and gases through contact at the catalyst site. In order for the HOR or ORR to take place a three phase boundary has to be present where the ionomer is in contact with the carbon support and gas reactants are able to diffuse to the catalyst site<sup>10, 18</sup>. The GDL allows the diffusion of reactant gas to the electrode, and is typically made up of fibrous carbon that can be coated with polytetrafluoroethylene (PTFE) to prevent water from blocking gas diffusion. The GDL also acts as a substrate for the other electrode components, providing electron transfer to and from the catalyst. The carbon support is typically made up of a high surface area carbon material such as Vulcan carbon. The high surface area allows a larger dispersion of the metal catalyst used, and at the same time allows the transport of electrons to and from the catalyst sites and GDL. A microporous layer (MPL) is added between the GDL and CL and contains a colloidal dispersion of carbon black and PTFE, which not only enhances surface roughness, but also aids in the maintenance of water during fuel cell operation<sup>19</sup>.



Figure 1.4: Schematic of gas diffusion electrode which displays the gas diffusion layer, microporous layer, and catalyst layer adopted by Saleh et. al<sup>3</sup>.

The metal catalyst is one of the most important components of the fuel cell since this is where the reactions take place. Currently, platinum has been proven to be the best catalyst to be used in both the HOR and ORR<sup>10</sup>. The use of platinum accounts for a large portion of the fuel cell cost<sup>10</sup>, but is the only metal that is efficient enough to be used in the slow kinetics of the ORR which is the rate limiting step of the water forming process. A typical electrode will have a loading of 0.4 mg cm<sup>-2</sup> of platinum, but in order to decrease the cost and increase the performance of the fuel cell the utilization of platinum has to increase<sup>10, 20</sup>.

The ionomer is another important component of the CL as it allows the transport of ions from the catalyst sites to the membrane in the anode, and from the membrane to the catalyst sites in the cathode. The ionomer also acts as a binding agent, and allows better contact with the catalyst sites in order to have a three-phase boundary where a proton, electron, and reactant gas are present for the HOR and ORR take place. As a result the performance of the fuel cell increases substantially and aids in the increase of platinum utilization in the CL<sup>18</sup>. The ionomer has to be able to mix well with the membrane to facilitate good adhesion, making Nafion the most common ionomer used in the CL. Nafion brings great benefits that are perfect for the

catalyst layer, but is also costly and as mentioned water is vital for the transport of protons resulting in poor transport in low relative humidity (RH) conditions. The addition of Nafion can also be detrimental to the electrode performance if too much is added especially if the quantity added covers catalyst sites. As a result a loading of 30 wt% Nafion is typically used since it has been proven to be the quantity required to give the best performance<sup>21-22</sup>. The use of other hydrocarbon based ionomer materials such as sulfonated polyether ether ketone (sPEEK) have been considered, but these materials do not allow good adhesion to Nafion membranes and as a result are not currently considered for automotive applications.

The electrode has many components that can be altered or manipulated to change the performance of the fuel cell. The water content present in the fuel cell is essential in the performance, and as such one of the major factors that have limited the commercialization of PEMFCs since high relative humidities are required for an ideal performance. The water retention within the electrode with various ionomer materials including Nafion, sPEEK, and polybenzimidazole (PBI) have been studied and each have their benefits and drawbacks<sup>17, 23</sup>. The use of alternative ionomer materials that can grant increased interaction with the carbon support can allow for increased fuel cell performance, and at the same time allow better water management in both high and low RH environments.

### **1.3 Ceramic Carbon Electrodes**

The use of various sulfonated hydrocarbon polyelectrolytes including sPEEK, sulfonated polyethersulfone, and sulfonated polyetherimide have been studied in an attempt to decrease the cost of the fuel cell and increase the water retention in low RH environments<sup>15</sup>. Compared to Nafion these hydrocarbon based polyaromatics are less expensive, can easily be functionalized to increase proton conductivity, and have high gas permeability which make them suitable candidates for ionomers<sup>15, 24-25</sup>. The downfall of these ionomer materials are their sensitivity to changes in RH, just like with Nafion, and as a result exhobit a decrease in performance. The incorporation of these alternative ionomer materials with the carbon supported catalyst is also an issue, especially if there is limited contact preventing interactions between protons, electrons, and gas reactants and decreasing the three-phase boundaries.

One type of electrode structure that has been studied over recent years is the ceramic carbon electrode (CCE). A CCE is an electrode containing a carbon support bound together with a silica polymer. This type of electrode provides even dispersion of a carbon support, and through the addition of hydrophilic groups such as sulfonic acid, the conductivity of ions and manipulation of water absorption and retention can be possible<sup>26</sup>. Through their synthesis using the sol-gel method, the nature of the CCE can also be altered to give a very porous material which can increase the number of catalyst sites available for three-phase boundaries. CCEs have been studied extensively in the use of a modified surface polymer electrodes to replace carbon paste electrodes by Lev and co-workers. They found that replacing a carbon paste electrode with a CCE shows an increase in the signal to noise ratio, as well as better stability of the electrode over numerous cycles<sup>27</sup>. Ranganathan and Easton have also shown the use of CCEs in electrolysis cells in the CuCl thermochemical cycle to enhance the crossover of anionic species<sup>28</sup>.

Recently Eastcott and Easton have modified the CCE preparation method for the use in fuel cell electrodes. In their work the carbon supported catalyst was mixed with 3- (trihydroxysilyl)-1-propane sulfonic acid (TPS) and tetraethylorthosilicate (TEOS). This colloidal mixture was then spray deposited on a GDL and used as the cathode of a H<sub>2</sub>/O<sub>2</sub> fuel cell, where an increase surface area, as well as consistent fuel cell performance at low RHs was observed<sup>29</sup>. This improvement to the electrode by the addition of an organosilane ionomer shows great promise for automotive applications since it does not demonstrate sensitivity to changes in RH environments, while their preparation through the sol-gel chemistry allows different CCE materials to be prepared for a variety of fuel cell applications.

### **1.4 Sol-Gel Chemistry**

The preparation of CCEs through the sol-gel method allows easy modification of the materials properties based on how they are prepared. The sol-gel method involves two steps; the hydrolysis where a metal alkoxide and water are mixed to produce an alcohol and the hydrolyzed form of the alkoxide precursor. Next is the condensation step where the hydrolyzed and unhydrolyzed precursors react to form an oxide network<sup>30-31</sup>. Figure 1.5 illustrates the two reaction steps that take place to form the Si-O-Si network. This condensation produces small particles or "sol" dispersed in a liquid "gel"<sup>32</sup>.

The type of sol-gel produced is highly dependent on a variety of factors which include the metal alkoxide used, the amount of water added, the pH of the catalyst used for the reaction, the temperature, and the drying method<sup>33</sup>. The final products can be a dense film, dense ceramics, aerogels, or ceramic fibers depending on these parameters. For example, xerogels are formed when the sol-gel mixture is dried at ambient pressure by heating the solution slowly to remove liquid from the pores<sup>32</sup>. On the other hand aerogels are formed by supercritical drying of the colloidal mixture which retains the hydrated structure and therefore porosity<sup>34</sup>. The pH catalyst mixture gives rise to how the polymer is formed upon polymerization of the sol. A high pH (basic catalyst) gives faster hydrolysis the polymer forms more clustered branches, while low pH conditions (acidic catalyst) forms longer molecules that are not highly branched<sup>30</sup>. The control of these various parameters is why sol-gel chemistry is used in numerous applications.



Figure 1.5: Steps of sol-gel reaction.

## **1.5 Modification of sulfonated silane**

The use of sol-gel chemistry is proven to be beneficial in the production of alternative ionomer materials in fuel cell electrodes. As mentioned previously, though the sol-gel method Eastcott and Easton were able to prepare a CCE which showed no decrease in polarization when the RH was decreased. However, this new electrode does have the disadvantage since it has only proven to be particularly effective in the cathode at low RH. The incorporation of TPS as the sulfonated silane in a CCE for fuel cell applications has initiated the idea for the use of alternative ion conducting materials for ionomers, specifically for the use in both high and low RH. It may be possible that by increasing the ionic conductivity, an improvement to in water management may be possible and allow the use of CCEs in high RH as well as low RH.

One possible ion conducting monomer that could show increased performance at multiple RH conditions is 4-(2-(trihydroxysilyl)ethyl)benzenesulfonic acid (TEBS). This monomer has been proven to increase the ionic conductivity for a number of applications both in the ionomer and the membrane. The exploration of using TEBS exclusively as an ionomer material to increase ion conductivity in the electrodes is non-existent, however, the use of TEBS as other components have been studied. De Almeida et al. used TEBS as a dopant in Nafion membranes with various loadings and the proton conductivity was measured. The doping of Nafion membranes with TEBS demonstrated an increase in proton conductivity and water retention in low RH conditions with low TEBS loadings, but as the loading increased conductivities similar to pure Nafion were observed<sup>35</sup>. Easton and Pickup also used TEBS in an attempt to decrease the Nafion content by functionalizing the carbon support with a monolayer of the TEBS monomer. When treated with TEBS, it was determined that a lower Nafion loading was required to observe similar results to traditional fuel cell MEAs<sup>22</sup>.

Replacing TPS with TEBS in the CCE formulation could be beneficial due to slight differences in their structures, which can be observed in Figure 1.6. The shortening of the hydrocarbon chain may add the benefit of preventing pore blockage of the carbon support for gas diffusion, while the addition of the phenyl ring should increase ion conductivity, which is observed by their differences in pKa (TPS = -2.0, TEBS = -2.8)<sup>36</sup> caused by the possibility of resonance in TEBS<sup>12, 22</sup>. The solvent used to disperse the two organosilanes also can affect the porosity of the electrode. Since TEBS is dispersed in dichloromethane a greater penetration of

the carbon support can be possible as opposed to, TPS which is dispersed in water, leading to less penetration due to the difference in surface tension between the two solvents.



Figure 1.6: Structural comparison of 3-(trihydroxysilyl)propane-1-sulfonic acid (TPS) and 4-(2-(trihydroxysilyl)ethyl)benzenesulfonic acid (TEBS).

## **1.6 Electrochemical Evaluation Fuel Cells and fuel cell** materials

The evaluation of fuel cell electrodes can give great insight on the exposed surface area for electrochemical reactions, porosity and facilitation of water in the electrode, as well as the overall performance of the electrode in various conditions. The analysis completed on both CCE and traditional electrodes can then be compared in order to determine the ideal conditions required to get the best performance out of the fuel cell.

### **1.6.1 Cyclic Voltammetry**

Cyclic voltammetry (CV) is one of the most common analysis methods used in the assessment of electrochemical processes. This technique allows the rapid collection of quantitative information in order to get an understanding about the redox species present<sup>37</sup>. This is done by sweeping between two potentials in a triangular waveform and observing the current response from a faradaic process as this is done. From the current response, the concentration can be determined as well as information on the thermodynamics of the redox process, and the kinetics of electron transfer reactions<sup>37</sup>. The collection of data from CV can be done in one of two ways for fuel cell applications. The first method is in a half-cell environment where the working electrode, which contains the species being studied, is placed in an electrolyte with a reference electrode, and an auxiliary or counter electrode. The second is in a full cell where the reactions are observed *in situ*. In the full cell the anode operates with hydrogen, which acts as both the reference and counter electrode, while the cathode gas feed is nitrogen and acts as the working electrode. In this configuration we can study the electrochemical properties of the cathode.

Platinum catalyst in the fuel cell exhibits several peaks observed with CV. Figure 1.7 shows a typical CV obtained with a platinum catalyst. The main characteristic peaks of a platinum CV are caused by the adsorption and desorption of hydrogen on the platinum surface ( $H_A$  and  $H_D$ ), oxidation and reduction of platinum oxide ( $Pt_{Ox}$  and  $Pt_{Rx}$ ), and the quinone/hydroquinone redox couple ( $Q_{Ox}$  and  $Q_{Re}$ ). The adsorption and desorption of hydrogen on the platinum surface on the platinum surface can give an indication of the catalytic sites available for reactions, also known as the electrochemically active surface area (ECSA). This is done by determining the charge under the peaks from the hydrogen desorption current, as seen in Figure 1.7, and through

a well-known relationship between the desorption of hydrogen and platinum (210  $\mu$ C cm<sup>-2</sup>), the ECSA value can be obtained<sup>38</sup>. Typical ECSA values fall between 40 m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup> and 100 m<sup>2</sup> g<sub>Pt</sub><sup>-1 39</sup>.

The determination of ECSA for fuel cell applications is imperative since it not only determines the surface area of platinum, but it also assists in giving an indication of the state of the electrode and any problems that may exist. For example, the observation of hydrogen crossover can be observed by the slight shift of the voltammogram above the center mark (0 V) in an operating fuel cell. This can be remedied, but if CV is not initially used, it may be difficult to recognize while operating the fuel cell at optimal conditions<sup>40</sup>.



Figure 1.7: Diagram of redox processes observed on platinum catalyst sites when using cyclic voltammetry in  $H_2SO_4$ .

### **1.6.2 Electrochemical Impedance Spectroscopy**

Electrochemical impedance spectroscopy (EIS) is a technique that has been rapidly growing as an electrochemical diagnostic for fuel cell electrodes. EIS records changes in impedance of an electrical system by applying a sinusoidal amplitude AC component to a fixed DC bias potential. By sweeping from high to low frequencies in the AC component, a change in impedance can be observed and recorded. Impedance is essentially the effective resistance to current flow in an AC system, and can arise from both purely resistive (ohmic) and capacitive components of the system and changes in either resistance or capacitance will display a change in the impedance output<sup>41</sup>.

To further understand the concept, the relationship between capacitance, resistance, and impedance must first be understood. For the resistive component the relationship can be described by Ohm's law:

$$\mathbf{E} = \mathbf{I} \, \mathbf{R} \tag{3}$$

Where E is the potential in volts (V), I is the current in amperes (A) and R is the resistance in ohms  $(\Omega)^{41-42}$ . However, in an electrochemical system the transfer of charge is present and as a result capacitance must also be considered. The presence of capacitors and inductors can impede the flow of electrons in AC and can be described trough the following relationship:

$$\mathbf{E} = \mathbf{I} \mathbf{Z} \tag{4}$$

Where Z is the impedance of electrons caused by the presence of a capacitor or inducer. With the addition of an AC component, the amplitude and frequency signal is represented by:

$$\mathbf{E} = \mathbf{E}_{\max} \sin\left(\omega t\right) \tag{5}$$

where  $E_{max}$  is the peak amplitude in volts (V),  $\omega$  is the angular frequency ( $\omega = 2 \pi$  f where f is in Hertz (Hz)) and t is time in seconds (s). When considering a current response from the applied voltage at the same frequency they will not be in phase, and thus separated by a phase angle,  $\varphi$ , which can be expressed by<sup>41</sup>:

$$I = I_{max} \sin(\omega t + \varphi)$$
(6)

where  $I_{max}$  is the peak current response and  $\phi$  is the negative phase angle separating the current and potential waves. In the case of a pure resistor across an alternating voltage, the phase angle is zero since ohms law always applies making<sup>41</sup>:

$$Z_{\rm res} = R \tag{7}$$

In the case of a capacitor, the impedance is represented by  $4^{1-42}$ :

$$Z_{\rm cap} = -\frac{j}{\omega C}$$
(8)

where j is  $\sqrt{-1}$  and C is the capacitance in Farads (F). Since both the resistor and capacitor contribute to the total impedance, when placed in parallel to each other the impedance is represented by:

$$Z_{\text{tot}} = Z_{\text{res}} + Z_{\text{cap}} \tag{9}$$

$$Z = R + j \frac{1}{\omega C}$$
(10)

$$Z = Z' + j Z'' \tag{11}$$

where Z' is the impedance from the resistive contribution, or real impedance, and Z" is the capacitive contribution, or the imaginary impedance.

EIS can also be understood by considering the electrode/electrolyte interface and can then be described using a circuit diagram known as Randles equivalent circuit seen in Figure 1.8<sup>41</sup>. In a simple circuit, at high frequencies the path of least resistance will be through the capacitor since there will be minimal time for charging and discharging. This causes the circuit to act as a simple DC circuit, leaving only the resistance present. As the frequency is decreased the charging and discharging of the capacitor starts to take place, and the path of least resistance is then through the resistor, which can allow the observation of the capacitive component of the impedance.



Figure 1.8: Diagram of simple circuit used to explain how electrochemical impedance spectroscopy is used on a typical electrode/electrolyte interface.
A fuel cell electrode is porous, thus this electrode/electrolyte interface is present in three dimensional space, where Randals equivalent circuit can no longer be used due to its simplicity. In the case of a porous electrode a complex version of Randals circuit is used known as a transmission line model. This model, which is displayed in Figure 1.9, has been considered by many groups to explain the behavior of electrode material<sup>4, 43</sup>. In this model two parallel resistive rails are present, R<sub>electronic</sub> and R<sub>ionic</sub>. R<sub>electronic</sub> is used to describe the resistance associated with the transport of electrons through the carbon support, while R<sub>ionic</sub> describes the resistance associated with the transport of ions through the ionomer. Similar to the simple circuit, the capacitors represent the catalyst sites, and carbon surface exposed to the electrolyte connecting each rail<sup>43</sup>. The total resistance (R<sub>Σ</sub>) is comprised of the sum of R<sub>ionic</sub> and R<sub>electronic</sub>, but as carbon is an excellent conductor R<sub>electronic</sub> is normally considered to be negligible when compared to R<sub>ionic</sub>. Since R<sub>electronic</sub><<**R**<sub>ionc</sub>, this leaves R<sub>Σ</sub> to be essentially equivalent to R<sub>ionic</sub> in most cases<sup>3</sup>. The resistance associated to the membrane (R<sub>mem</sub>) is a completely resistive component, allowing the resistance to be considered real and not part of the change in impedance<sup>43</sup>.



Figure 1.9: Diagram of transmission line model to explain electrochemical impedance spectroscopy in porous electrodes adopted from Pickup's group<sup>4</sup>.

A Nyquist plot is used to illustrate the change in impedance and displays the real impedance (Z') on the X-axis, and the imaginary impedance (Z") on the Y-axis. A typical Nyquist plot obtained from data collected through EIS is illustrated in Figure 1.10. In the high frequency region, a 45° slope is initially formed, known as the Warburg region, which indicates mass transfer resistance to the electrode surface<sup>41</sup>. As the frequency is decreased, the capacitive components caused by charge transport are going to be more significant and an increase in Z" will be observed. This deviation from linearity gives an indication of the resistance associated with the entire electrode ( $R_{\Sigma}$ ) and is determined by the intersection of the two slopes seen in Figure 1.8. When this point is projected to the X-axis the value obtained is  $R_{\Sigma}/3$ , but with the assumption that R<sub>electronic</sub><<R<sub>ionic</sub> this value is assumed to be R<sub>ionic</sub>/3<sup>4</sup>.



Figure 1.10: Example of a Nyquist plot used to observe changes in impedance.

The manipulation of the imaginary impedance can easily be done to give the following expression of capacitance:

$$Z'' = -\frac{j}{\omega C}$$
(12)

$$C = -\frac{j}{\omega Z''}$$
(13)

which can now allow the data to be exhibited in terms of capacitance vs. real impedance, and aids to clarify the effectiveness of the ionomer. An example of a capacitance plot is displayed in Figure 1.11a. The capacitance (Y-axis) represents the ability for both electrons and ions to get to a catalyst site by the height of the plot before it plateaus at the maximum or limiting capacitance<sup>4</sup>. The point where this plot plateaus is also equal to the inflection point of the Warburg region seen in the Nyquist plot, making this plot very informative. This type of plot can sometimes be ineffective in separating the resistive components, especially if the capacitance between electrodes is vastly different. The normalization of the capacitance plot is often implemented to allow a better comparison of changes in  $R_{\Sigma}$  between electrodes and give a better understanding of the ion transport resistance in the ionomer. Such a plot is visible in Figure 1.11b. This plot looks at the distance from the Y-axis to indicate changes in impedance caused specifically by  $R_{ionic}$  in this case<sup>3</sup>.



Figure 1.11: Manipulation of Nyquist plot to give both a) capacitance plot and b) normalized capacitance plot.

# **1.6.3 Polarization Curves**

The evaluation of a full fuel cell's performance is often performed by observing the change in current density as a function of potential, called a polarization curve. Theoretically the shape of this curve should be a horizontal line at 1.23V, but due to various processes at the catalyst surface that are altered by the change in potential, a sigmoidal curve is observed<sup>44</sup>. When the cathode is used as the working electrode the polarization curve starts at high voltages and drastically decreases. As the current density increases, the curve shows a linear relationship to a point where the voltage shows another drastic decrease at high current densities.

Three main losses contribute to this deviation from the theoretical line, the first being activation or kinetic losses. These losses are observed at high voltage/low current densities, and are caused by the slow kinetics of the ORR in comparison to the HOR<sup>44</sup>. Typically when Pt is used as the catalyst this portion of the curve does not change, but changes to oxygen diffusion may cause this region to show variation<sup>17, 45</sup>. Ohmic losses, seen in the second region, are caused by resistance to the flow of ions through the ionomer<sup>44</sup>. Excellent ion transport in the ionomer will show large increases of current density with small changes in voltage. This region can also give an indication of the water content within the electrode. If not enough water is present in the electrode; small increases in current density will be observed with a small decrease in voltage<sup>29</sup>. Losses caused by mass transport are typically observed in the third region of the polarization curve. These losses are associated with the decrease of reactant transport to catalyst sites, frequently observed at high current densities when an accumulation of water results in electrode flooding<sup>44</sup>. This loss is also observed when the surface concentration of the reactant is zero due to the increased rate of the ORR<sup>44</sup>. This limitation can often be eliminated with increased gas flow rates to assist with water removal from the electrode. A typical polarization curve can be seen in Figure 1.12 with each region highlighted.



Figure 1.12: Polarization plot displaying regions where the three main limitations occur.

# 1.7 Objective

The objective of this project is to prepare sulfonated CCEs using TPS and TEBS and compare how PEMFC performance is effected when a more ionically conductive sulfonated silane is used. The CCEs will both be studied using the same ratio of sulfonated to unsulfonated silane that was used by Eastcott et. al. The sulfonated CCE materials will be tested on the cathode side of a full fuel cell with a standard 20% Pt/C catalyst and Nafion as the ionomer on the anode. During this process, the RH at the cathode will be decreased in order to observe the difference in water retention between the two sulfonated silanes. Polarization data will be evaluated along with data collected using CV and EIS to obtain a complete understanding of how water management is affected when alternate sulfonated precursors are used.

# **Chapter 2: Materials & Methods**

# 2.1 CCE Synthesis

# 2.1.1 Monolith preparation

The preparation of CCE materials was completed by following a similar synthesis developed by Eastcott and Easton<sup>46</sup>. The CCE materials were prepared via the sol gel process at room temperature with varying silane concentrations. 20% platinum on Vulcan XC72 carbon black (Premetek) was weighed in a clean, dry 50 mL glass beaker. Deionized water was then added to the beaker to prevent ignition of platinum upon the addition of methanol. The colloidal mixture was stirred mechanically and the addition of methanol (Fisher, 3-5 mL) was made. The CCE samples were made using a combination of 4-(2-(trichlorosilyl)ethyl)benzenesulfonyl chloride, referred to hereafter as TCBS (Gelest, 50% in dichloromethane) and tetraethylorthosilicate, referred to hereafter as TEOS (Sigma). Upon hydration TCBS is converted to 4-(2-(trihydroxysilyl)ethyl)benzenesulfonic acid, referred to hereafter as TEBS. The silanes (TEBS/TEOS) were added drop-wise to the colloidal mixture after which 6 molar NH<sub>4</sub>OH(Sigma, 10.4 µL) was added. The weight percent for TEBS/TEOS composite samples range from 5 wt% to 20 wt% TEBS with a total silane composition between ca. 30 wt% and 40 wt%. CCE electrodes using 3-(trihydroxysilyl)-1-propane sulfonic acid referred hereafter as TPS (Gelest, 30-35 wt% in  $H_2O$ ) and TEOS were made in similar fashion except with a total silane composition of 40 wt%.

#### 2.1.2 Electrode Fabrication

#### 2.1.2.1 Microporous Layer

Prior to CCE deposition on the gas diffusion layer (GDL), a microporous layer (MPL) was deposited on wet-proofed carbon fibre paper (Toray TPGH-090, 10 wt% wet-proofing). The microporous layer was added to increase surface roughness of the GDL and aid in water management in the cathode. The MPL was prepared in-house using a literature procedure<sup>5, 19, 46</sup>. The MPL consisted of Vulcan XC72 carbon black and Teflon binder to have a carbon loading of 2 mg cm<sup>-2</sup> and 35 wt% Teflon loading. The mixture was stirred for one hour, then sonicated for 1 hour and finally left to stir overnight before spraying on carbon fibre paper. After the MPL was spray deposited the newly made carbon fibre paper and MPL sheet was set to dry at room temperature overnight, before being set to dry at 110 °C for 30 minutes, followed by 280 °C for 30 minutes, and finally sintered at 380 °C for 30 minutes.

#### 2.1.2.2 CCE Fuel Cell Catalysts Layer

In order to analyse the electrode material in a fuel cell the method developed by Eastcott was used for testing<sup>5</sup>. A similar process as above was used for CCE preparation where 20% Pt on Vulcan XC72 carbon black (Premetek) was mixed with deionized water, methanol and the silane material were added to give the desired TEOS-to-TEBS weight ratio with a target total silane content of ca. 30 wt% 40 wt%. 6 molar NH<sub>4</sub>OH was then added to the mixture and set to stir for ca. 72 hours where the partially gelled solution was spray deposited on the GDL consisting of the carbon fibre paper (CFP) with an MPL. Then new fuel cell electrode was left to dry at room temperature for 1 hour and then placed in an oven at 90 °C overnight. A platinum

loading between 0.39 mg cm<sup>-2</sup> and 0.5 mg cm<sup>-2</sup> was achieved using this method. Figure 2.1 shows a schematic of the CCE electrode preparation process.



Figure 2.1: Schematic of CCE electrode synthesis and spray deposition preparation for fuel cell testing<sup>5</sup>

## 2.1.2.3 Nafion based gas diffusion electrode preparation

Nafion based catalyst layers (CL) were prepared for testing standard materials to compare to CCE materials. MPLs were not required for Nafion-based CL's to adhere to wet-proofed carbon fibre paper. To produce Nafion based CL's a similar method to CCE fuel cell catalyst layer preparation was used. In this case 20% Pt on Vulcan XC72 carbon black (Premetek) was mixed with deionized water and isopropyl alcohol in a 50:50 ratio, after which the appropriate volume of 5 wt% Nafion (Aldrich, 5 wt% in aliphatic alcohols and water) was added to give a Nafion loading of 30 wt%. The mixture was then sonicated for 1 hour and set to stir overnight before spraying on wet-proofed carbon fibre paper (Toray TPGH-090, 10 wt% wet-proofing). The standard GDE was placed in an oven at 90 °C to dry overnight. A platinum loading of 0.41 mg cm<sup>-2</sup> was attained. The Nafion based electrode will hereafter be referred to as PE20.

# 2.1.3 MEA preparation

Membrane electrode assemblies (MEA) were prepared by cutting a 5 cm<sup>2</sup> square of the Nafion based electrode which was used as the anode for all full cell tests. A 5 cm<sup>2</sup> square of the CCE was also cut and used as the cathode. The two electrodes were placed facing each other with a Nafion NRE 212 PEM (Ion Power) in the middle. The MEA was placed between two sheets of aluminum foil and then between two aluminum plates and hot-pressed at 150 kg cm<sup>-2</sup> at 130 °C for 180 seconds using a Carver laboratory press. The MEA was removed and holes were punched in the membrane to fit the fuel cell assembly (Fuel Cell Technologies).

## 2.1.4 Full Cell Assembly

The full cell was assembled by using the prepared MEA's in a 5 cm<sup>2</sup> fuel cell (Fuel Cell Technologies) placed between with the appropriate silicone gaskets. Gaskets were measured to be 2/3 the thickness of the MEA. The gaskets were placed between the bipolar graphite plates to prevent contact of the plates and which would cause an electrical short. The cell was then compressed using a torque setting of 5.6 N·m.

# **2.2 Electrode Assessment**

# 2.2.1 Half-Cell Measurement Preparation

Half-cell measurements using CCE monoliths were collected by preparing an ink which consisted of ca. 25mg of the CCE material (20% Pt/C with the organosilane ionomer), deionized water, and isopropyl alcohol in a 50:50 mixture to allow a total volume of 500  $\mu$ L. The mixture was then sonicated for approximately 1 hour, or until a homogeneous ink was observed. 2  $\mu$ L of the ink was then deposited on a glassy carbon electrode (0.071 cm<sup>2</sup>) and allowed to dry. Platinum loadings of 0.15 mg cm<sup>-2</sup> were achieved. Nafion containing inks were prepared in an identical fashion except for the addition of 5 wt% Nafion solution. Experiments were performed in the three electrode cell shown in in Figure 2.2. The cell contains catalyst-coated glassy carbon electrode which was used as the working electrode, a silver/silver chloride (Ag/AgCl) reference electrode, and a platinum wire counter electrode.



Figure 2.2:Half-cell apparatus showing working electrode (W.E), reference electrode (R.E), and counter electrode (C.E).

## 2.2.2 Cyclic Voltammetry

Cyclic voltammetry (CV) measurements were conducted using a Solartron 1470 potentiostat controlled using Mutlistat Software (Scribner Associates). For full cell measurements an in-house fuel cell test station was used to conduct CV measurements at a specific temperature and gas flow rate. CV's for full cell measurements were collected at a cell temperature of 30 °C, while half-cell measurements were collected at room temperature in order to determine the electrochemically active surface area (ECSA) of platinum in the electrode.

Half-cell measurements used a three electrode configuration where the electrodes were placed in 0.5 M  $H_2SO_4$  solution which was purged with  $N_2$  for 10 minutes to remove any oxygen. Measurements were obtained by cycling between 1.4 and -0.003 V (vs RHE) at 50 mV s<sup>-1</sup> for 20 cycles, followed by 3 cycles at 20 mV s<sup>-1</sup> which were then used for data analysis.

With full cell CV measurements, H<sub>2</sub> was fed in the anode which served as both the reference and counter electrode with a flow rate of 100 mL s<sup>-1</sup> and N<sub>2</sub> was fed though the cathode at 200 mL s<sup>-1</sup> to act as the working electrode. The gases were allowed to reach a temperature of 30 °C by being passed though humidifier bottles set to the desired temperature. The cell and gas temperatures were allowed to stabilize for 10 minutes prior to the collection of any data. Measurement potentials ranged between 0.08 V to 1.4 V (vs. NHE) for 20 cycles at 100 mV s<sup>-1</sup>, followed by 3 cycles at 50 mV s<sup>-1</sup> which was then used for analysis.

#### 2.2.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) was conducted using an in-house fuel cell test station connected to a Solartron 1260 frequency response analyzer coupled with a Solatron 1470 potentiostat both controlled by CorrWare Software (Scribner Associates). Impedance measurements were collected in order to observe changes in capacitive and resistive components of the electrode material. Half-cell data was collected using a three electrode configuration at room temperature, while full cell data was collected with a cell temperature of 30 °C. Gas feeds for full cell measurements had H<sub>2</sub> fed in the anode to act as both the reference and counter electrode at a flow rate of 100 mL s<sup>-1</sup>, and N<sub>2</sub> fed though the cathode at 200 mL s<sup>-1</sup> to act as the working electrode. EIS data was collected at a DC bias potential of 0.425 V (vs. NHE) between AC frequencies of 0.1 Hz and 100 kHz in order to observe changes at the double layer region of the platinum CV. All measurements were collected succeeding CV measurements. The electrode material used a finite transmission line model developed by Pickup's group to in order to evaluate EIS information<sup>3, 43, 47</sup>.

## **2.2.4 Full Cell Performance Measurements**

Measurements were collected using a Fuel Cell Technologies single cell test station equipped with an Agilent N3300A DC electronic load bank which is displayed in Figure 2.3. This station allowed the control of gas flow rates, gas back pressure, humidifier temperatures and potential load. Data was acquired at a cell temperature of 80 °C at 10 psig (170 kPa) using humidified reactant gases which were passed through a humidifier bottle before reaching the fuel cell. O<sub>2</sub> gas or air, depending on the test being conducted, were passed through the cathode at a flow rate of 200 mL s<sup>-1</sup> and 1000 mL s<sup>-1</sup> respectively, and H<sub>2</sub> gas was passed through the anode at a flow rate of 100 mL s<sup>-1</sup>. Gases and temperatures were controlled using the Fuel Cell Technologies test station which was controlled using LabView Software. The relative humidity (RH) levels of the flowing gasses were controlled by varying the humidifier temperature with respect to the cell temperature. H<sub>2</sub> gas was passed through the anode and was heated at 80 °C to allow 100% RH in the anode while O<sub>2</sub> and air were passed through the cathode humidifiers which were heated to temperatures between 80 °C and 45 °C in order to obtain relative humidities between 100% and 20%.



Figure 2.3: Fuel Cell Technologies Ltd, test station used for full cell measurements.

# 2.3 Physical Characterization

## 2.3.1 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) images of CCE materials at 250x, 500x, and 5000x magnification were collected using a JOEL JSM 6400 SEM.

# 2.3.2 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) images were of CCE materials were collected at the University of Waterloo with a Zeiss Libra 200 MC microscope.

# 2.3.3 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) was collected using a PerkinElmer Spectrum 100 FTIR system. Organosilane gels were mixed with KBr and pressed to observe the presence of sulfonic acid vibrations in both TPS and TEBS organosilane networks. The presence of the phenyl ring in TEBS was also investigated to confirm the addition of TEBS to the organosilane.

# 2.3.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) information was collected using a TA Instruments Q600 SDT thermal analyzer. Samples were heated from room temperature to 1000 °C at a rate of 20 °C min<sup>-1</sup> under flowing air or argon in order to determine the weight percent of varying components in the CCE.

# 2.3.5 BET Surface Area and BJH Pore Size Distribution

Brunauer-Emmett-Teller (BET) surface area measurements and Barrett-Joyner-Halenda (BJH) pore size distribution information using a Quantachrome NOVA 1200e Surface Area and Pore Size Analyzer. BET data was collected by the multi-point BET method while BJH pore size distribution data was collected using the desorption isotherm. All data was processed using NovaWin Software.

# **Chapter 3: Results & Discussion: Substitution of Original Sulfonated Silane**

The replacement of TPS for TEBS will be conducted to observe how the replacement of a more ionically conductive ionomer will affect the behavior of the electrode. An identical ionomer-to-carbon ratio used by Eastcott and Easton will be used for CCE CL containing TEBS. CCE inks containing 5 at% TEBS and 5 wt% TPS with the remainder being TEOS, were prepared both as monolith materials and spray deposited on wet-proofed carbon fiber paper (CFP) containing a MPL as described in section 2.1 and 2.3. The CCEs were compared to inks and GDEs containing 20% Pt/C with a Nafion ionomer which will be termed as PE20 hereafter. Physical characterization of the materials were conducted using TEM and SEM to observe the surface characteristics of the materials, while FT-IR was used to observe the presence of TEBS and TPS in the CCEs. BET surface area and BJH pore size analysis were completed to determine the surface area and pore size of the materials to give a better understanding of the electrodes morphology.

Electrochemical characterization methods were also used to observe how the change in ion conductivity effects the electrode behavior using CV and EIS. The performance of the electrodes were then evaluated using polarization at various RHs and then compared to observe how the change in ionomer effects the performance.

# **3.1 Physical Characterization**

# 3.1.1 Transition Electron Microscopy & Scanning Electron Microscopy

Figures 3.1-3.3 show the SEM image of the spray deposited TPS-based, TEBS-based, and Nafion-based materials at 250x, 500x, and 5000x magnification. At 250x magnification, all electrodes demonstrated uniform coverage with visible cracks typically observed when spray deposition is used. The TPS-based material displayed a very smooth surface indicating a good surface coverage of the organosilane/catalyst mixture. The TEBS-based material displayed large cracking with glass like spots indicating a more brittle material. At 1500x and 5000x all samples appear to have similar porosity with small pores uniformly distributed.



Figure 3.1: SEM image of the Nafion-based electrode spray deposited on CFP at 1) 250x, b) 1500x, and c) 5000x magnification.



Figure 3.2: SEM image of TPS/TEOS electrode spray deposited on CFP at 1) 250x, b) 1500x, and c) 5000x magnification.



Figure 3.3: SEM image of TEBS/TEOS electrode spray deposited on CFP at 1) 250x, b) 1500x, and c) 5000x magnification.

TEM images were collected on all electrode materials in order to get a visual image at a nanometer scale. The 20% Pt/C catalyst material is seen in Figure 3.4 and had many small dark spots present due to the absorption of electrons by platinum and the slightly gray spherical shapes from the carbon support. This image demonstrates that the platinum particles are highly dispersed through the electrode giving a large platinum surface area. The particle size of platinum was also measured to be approximately 2 nm which agrees with values seen in literature<sup>48-49</sup>. Both CCE monolith materials in Figures 3.4 had similar features as the starting material (20% Pt/C), however, the absorption of electrons by the platinum particles demonstrated

a decrease and the carbon support shows a lack of contrast. This indicates that the absorption of electrons by platinum and carbon are reduced due to a thin film coating surrounding the CCE.



Figure 3.4: TEM image of 20% Pt/C, TPS/TEOS, and TEBS/TEOS monolith materials.

# **3.1.2 Infrared Spectroscopy**

Infrared spectroscopy on gelled composites (absence of 20% Pt/C catalyst) was conducted to confirm the presence of sulfonic acid groups in the CCE, as well as the presence of phenyl groups in TEBS to help illustrate the difference in the two CCEs. Figure 3.5 illustrates stretching and bending vibrations for the organosilane gels containing TPS/TEOS and TEBS/TEOS. A broad peak between 1000 cm<sup>-1</sup> and 1250 cm<sup>-1</sup> was observed which includes the stretching of Si-O-Si in the organosilane network which typically appear near 1100 cm<sup>-1</sup>, but due to the presence of the hydrocarbon side chain and terminal sulfonic acid group this peak cannot be resolved<sup>50-51</sup>. The presence of water absorption was observed by a broad peak at 3400 due to stretching and bending vibrations of H<sub>2</sub>O. Bending vibrations of sulfonic acid groups are also seen at 566 cm<sup>-1</sup> in both CCEs, but the bending vibration of the phenyl ring were also seen at 698 cm<sup>-1</sup> indicating the incorporation of TEBS in the silane network. Further confirmation to TEBS in the silane network is seen at 1500 cm<sup>-1</sup> due to C=C stretching in the phenyl group, and 1420 cm<sup>-1</sup> due to the bending vibration of C-H in the phenyl ring<sup>52-53</sup>.



Figure 3.5: FT-IR spectra of gelled TPS/TEOS and TEOS/TEOS organosilanes

## 3.1.3 Thermogravimetric Analysis

The TGA and DTG plots were used in order to determine compositional information on the electrode materials. Figure 3.6 illustrates the TG and DTG curves obtained for the 20% Pt/C and the two sulfonated CCE materials in air. In all samples a large mass loss associated with the combustion of carbon to  $CO_2$  was observed since the electrode materials are carbon based. The catalyst material (20% Pt/C) demonstrated this combustion at ca. 400 °C and had a final weight percent of 20 wt% after 500 °C from the remaining platinum in the catalyst material. The CCE materials also show this large mass loss, but is seen at a slightly higher temperature compared to the standard material. This is due to the integration of the ceramic material with the carbon preventing it from combusting at lower temperatures, or bonding of the organosilane to the carbon surface, causing an increase in the combustion temperature. The TPS-based material exhibited a small mass loss around 200°C which is associated with the loss of sulfonic acid groups<sup>54</sup>. This loss is ca. 3 wt% of the sample which is close to the value observed by Eastcott et.al<sup>55</sup>. This is also seen in the TEBS-based material with a 3% loss between 200°C and 400°C caused by the degradation on the ethylphenyl sulfonic acid group. The final mass for both CCE materials is also higher and is caused by the residual SiO<sub>2</sub>/SiO<sub>1.5</sub> network as well as the platinum from the Pt/C catalyst. The final mass also indicates a total silane loading of ca. 45% with the reaming composition being Pt/C.

The DTG plots for the TEBS-based and TPS-based material had combustion peaks that were at a higher temperature than the initial 20% Pt/C material, supporting the indication of a more thermally stable electrode. The TEBS-based material also observed a slightly higher combustion temperature for carbon than the TPS sample indicating a difference in their interaction with carbon. This increase in the combustion temperature could be attributed to the bonding of the TEBS group to the carbon surface which can increase the carbon combustion temperature.



Figure 3.6: Comparison of a) TGA and b) DTG plots in the presence of air at 20 °C min-1 for 20% Pt/C, TPS-based, and TEBS-based materials. For these plots, not all points are indicated.

# 3.1.4 BET Surface Area & BJH Pore Radius

The BET surface area was obtained for the prepared monolith CCE materials and were compared to 20% Pt/C and the Vulcan Carbon Black support which is shown in Table 3.1. The carbon supported catalyst was expected to have a lower BET surface area than the carbon support due to the dispersion of platinum on the surface. This decrease in surface area is caused by the higher density of platinum compared to carbon and also the blocking of micropores by the platinum particles, leaving a more mesoporous structure exposed for gas adsorption. The TPS-based material demonstrated a larger surface area compared to the carbon supported catalyst, which can be attributed to the formation of smaller pores in the silica material. This surface area is lower than what was reported for similar CCEs by Eastcott et. al<sup>55</sup>, but does show that the

surface area can be modified with the addition of sulfonated organosilane materials. The CCE material prepared with TEBS as the sulfonated material observed a 56% increase in surface area. This increase in surface area is perhaps caused by an increased ionomer porosity, which is added to the already porous carbon black material. The BJH pore radius also displayed very little change in the average pore radius between the carbon support, 20% Pt/C, and TPS-based CCE material. The slight increase in the pore radius when using TEBS demonstrates that there is change in morphology when using TEBS as the sulfonated silane.. There is a slight increase in pore radius in the TEBS-based material, however, the limitation of the analyzer prevents the measurement of micropores which may be abundant in this sample.

Table 3.1: BET surface area and BJH pore radius comparing CCEs to carbon support and 20% Pt/C. Replicates were not collected due to issues with the pore size analyzer.

Sample	Surface Area $(m^2 g^{-1})$	BJH Pore Radius (Å)
Vulcan Carbon XC-72R	234	16.9
20% Pt/C	190	16.8
TPS/TEOS	220	17.0
TEBS/TEOS	338	18.8

# **3.2 Electrochemical Characterization**

# **3.2.1 Half-Cell Measurement of Monolith Materials**

Half-cell measurements for CCE monolith materials were collected in the absence of Nafion and compared to a Nafion-based material. The CCE monolith inks and Nafion-based ink were prepared using the method described in section 2.2.1. Deposition of the CCE ink was difficult and attempted multiple times in order to get good adhesion prior to data acquisition. The collected CVs were then compared to the Nafion-based material. Due to the preparation and deposition of the CCE ink, it was difficult to obtain identical electrode surfaces for each sample which caused the results collected to have an approximate error of 5%. However, the data displayed does represent the typical results obtained when using these materials.

#### **3.2.1.1** Cyclic Voltammetry

Figure 3.7 compares the cyclic voltammograms of the CCE materials with the Nafionbased ink to illustrate how the change in ionomer affects the exposed catalyst surface area. The CCE samples both displayed similar peaks characteristic to platinum, but both had larger redox currents associated with the faradaic processes. The main characteristics of interest were the hydrogen adsorption and desorption peaks which give information on catalyst surface area. The TPS-based material exhibited these characteristics very well, but did not resolve the desorption of hydrogen from different platinum facets. However, this is seen in both the TEBS-based and Nafion-based materials. This increase in current with the substitution of an organosilane ionomer indicates more platinum catalyst sites are being exposed, and in the case of the TEBS-based material there is either an increase in conductivity, or better ionomer incorporation. The TPSbased material also depicted a slight shift to more positive potentials with the H<sub>2</sub> desorption peak indicating slightly higher electrode resistance.

The electrochemically active surface area (ECSA) was also calculated and compared between the CCE materials and the Nafion-based material in order to get a better understanding of the difference in exposed catalyst surface area. The ECSA values can be seen below in Figure 3.8. Literature values for the ECSA of platinum catalysts on carbon supports are anywhere between 40 m<sup>2</sup>  $g_{Pt}^{-1}$  and 100 m<sup>2</sup>  $g_{Pt}^{-1}$  depending on Nafion content, platinum loading, and gas diffusion later used<sup>39, 56-57</sup>. The ECSA for the Nafion-based material was 48 m<sup>2</sup>  $g_{Pt}^{-1}$  which is comparable to the lower end of values in literature<sup>39</sup>. The TPS-based material displayed an increase that was close to the high end of the literature values, which was not observed through half-cell measurements by Eastcott et. al.<sup>55</sup>, but could be due to a better ink deposition on the glassy carbon electrode. The TEBS sample displayed an ECSA that was almost double the ECSA value of the standard material and indicates the addition of TEBS may expose more platinum sites.



Figure 3.7: Cyclic voltammograms in a half-cell comparing the Nafion-based, TPS-based, and TEBS-based materials in 0.5M  $H_2SO_4$  at 20 mV s<sup>-1</sup>.



Figure 3.8: Comparison of ECSA values for the Nafion-based, TPS-based, and TEBS-based materials

#### **3.2.1.2 Electrochemical Impedance Spectroscopy**

Electrochemical impedance spectroscopy (EIS) was performed on the CCE materials and compared to the Nafion-based material. EIS was conducted to study the effect of proton conductivity with the use of various ionomer materials. EIS was implemented immediately after CV experiments were concluded and can be seen in Figure 3.9. The Nyquist plot, displayed in Figure 3.9a, illustrates a clear difference between the addition of TPS and TEBS as sulfonated silanes in the CCE. In the high frequency region, expanded in Figure 3.10, the TPS-based material exhibited a longer Warburg length when compared to the Nafion-based material, indicating a high  $R_{\Sigma}$  within the electrode. This does not agree with the half-cell results observed by Eastcott el.al<sup>55</sup>, however this could also be due to the difficulty of depositing the ink on the glassy carbon electrode. The TEBS-based material had a very similar Warburg length to Nafion indicating a low  $R_{\Sigma}$  value. This could be due to the difference in ion conductivity causing  $R_{ionic}$  to be higher with TPS. It can also be noted that since the CCE is composed mainly of carbon,  $R_{electronic}$  will make a much smaller contribution to  $R_{\Sigma}$  in the organosilane ionomer and as a result the resistance observed is caused by  $R_{ionic}$ .

The capacitance data, illustrated in Figure 3.9b, can also be determined from the EIS data through the manipulation of the imaginary impedance, and can give an idea of the porosity of the material. In the case of the TPS-based material, the capacitance is noticeably larger than that of the Nafion-based and TEBS-based materials. The TEBS-based material demonstrated a slightly higher capacitance when compared to the Nafion-based material indicating similar three-phase boundaries. When comparing the CCE materials the TPS-based material evidently had a larger capacitance indicating a more porous material than the TEBS-based material. This implies that the TEBS-based material has a similar morphology to the Nafion-based material.

The normalized capacitance plot can be used to get a better visualization of the difference in  $R_{\Sigma}$  present in the electrode by eliminating the capacitance. As discussed with the Nyquist plot, the TPS-based material had a much larger  $R_{\Sigma}$  associated with the electrode when compared to the Nafion-based material, even though the capacitance for the TPS-based material is much higher. The TEBS-based material also shows a slightly higher  $R_{\Sigma}$  compared to the Nafion-based material also shows a slightly higher  $R_{\Sigma}$  compared to the Nafion-based material also shows a slightly higher  $R_{\Sigma}$  compared to the organosilane network. This value is not large enough to indicate a substantial difference in  $R_{\Sigma}$  between TEBS and Nafion. This indicates that the use of TPS has better surface coverage allowing access to more catalyst sites, but  $R_{ionic}$  is higher when compared to TEBS due to the difference in ionic conductivity.



Figure 3.9: EIS half-cell data comparing the Nafion-based, TPS-based, and TEBS-based electrodes as a a) Nyquist Plot, b) Capacitance Plot, and c) Normalized Capacitance Plot in 0.5M  $H_2SO_4$ . For these plots, not all points are indicated.



Figure 3.10: High frequency region of Nyquist plot displaying the change in Warburg region for the Nafion-based, TPS-based, and TEBS-based electrodes.

## 3.2.2 Full Cell Evaluation

Full cell measurements were collected by the preparation of CCE electrodes described in section 2.3. Nafion-based electrodes were also fabricated using the method described in section 2.4. The use of spray deposition for electrode fabrication will allow better contact for the CCE by allowing the partly gelled electrode to be incorporated with the MPL. For the collection of data of the standard MEA, Nafion-based electrodes were used on both the anode and cathode, whereas CCE containing MEAs consisted of a Nafion-based electrode on the anode and the CCE on the cathode. CV, EIS, and polarization at varying RH levels were collected and compared for all MEAs. Due to spray deposition method used to prepare the porous GDE, it was difficult to obtain an identical electrode surface for each sample which caused the results collected to have an approximate error of 5%. However, the data does represent the typical results obtained when using these materials.

#### 3.2.2.1 Cyclic Voltammetry

The calculation of ECSA for the CCEs was collected using cyclic voltammetry (CV), and compared to the Nafion-based electrode, which are illustrated in Figure 3.11. The CVs all demonstrated similar platinum characteristics indicating the presence of catalyst sites in the electrodes. The ECSA was calculated for all three electrodes and can be observed in Figure 3.12. The peak current of the H<sub>2</sub> desorption process in the CVs gives the impression that the TEBS-based electrode would have an ECSA value that is between the values of the TPS-based and Nafion-based electrodes. When calculating the ECSA, the charge under the H<sub>2</sub> desorption peak determined that the TEBS-based and Nafion-based electrodes had similar ECSA values, which were around 60 m<sup>2</sup>g<sup>-1</sup><sub>Pl</sub>, while TPS-based electrode had a value almost 25% greater. This is the

not the same observation made in the half-cell analysis and indicates a large difference in the three-phase boundaries between TPS and TEBS. This discrepancy is due to the electrode deposition method between the two experiments, and shows that spray deposition for CCE materials gives better contact to the electrode. As for the TEBS-based electrode, the lower ECSA value indicates a decreased porosity when compared to the TPS-based electrode, agreeing with the data observed in the half-cell. The Nafion-based electrode, however, displayed resolved peaks from the desorption of H from different Pt facets<sup>38</sup>. These peaks were not present in the

TEBS-based electrode indicating a lower ion conductivity even though this feature it is seen in the half-cell. The presence of the quinone/hydroquinone redox couple is also present in both CCE samples at approximatly 0.6 V demonstrating a greater exposure of carbon through the increased porosity.



Figure 3.11: Cyclic voltammograms in a half-cell comparing the Nafion-based, TPS-based, and TEBS-based electrodes with a  $H_2$  anode feed and  $N_2$  cathode feed at 30 °C and 50 mV s<sup>-1</sup>.



Figure 3.12: Comparison of ECSA values the Nafion-based, TPS-based, and TEBS-based electrodes.

#### 3.2.2.2 Electrochemical Impedance Spectroscopy

EIS for all samples in a full cell environment were collected following CV data acquisition and displayed results that differ from the half-cell data that was collected. Figure 3.13a compares the Nyquist plots collected for the three electrodes. The Nafion-based electrode exhibited an imaginary impedance that is almost 3 times the value of both CCE samples. An expansion of the high frequency is shown in Figure 3.14, which show there is a clear difference in Warburg lengths for the three samples. As seen in a half cell environment, the TPS-based electrode displayed the largest Warburg length which agrees with the high  $R_{\Sigma}$  value observed in the half-cell indicating a lower ion conductivity compared to Nafion and TEBS. The TEBSbased electrode demonstrated the lowest Warburg length and also agrees with the half-cell data indicating efficient ion transport resulting in a lower  $R_{\Sigma}$ . The Nafion-based electrode displayed a larger Warburg length compared to TEBS which is likely due to a higher R<sub>electronic</sub> since Nafion has a higher ion conductivity than TEBS, but this contribution still makes  $R_{\Sigma}$  lower than the TPS-based electrode.

Figure 3.13b illustrates the EIS data as capacitance plots. The TPS-based electrode had the highest capacitance, even though there is a high  $R_{\Sigma}$  value. The high capacitance agrees with the half-cell data and indicates that there is an increased porosity which increases the amount of three-phase boundaries, but as a result  $R_{\Sigma}$  is increased indicating a higher  $R_{ionic}$  value when compared to TEBS. The TEBS-based electrode demonstrated a capacitance that is almost double that of the Nafion-based electrode, but was still lower than the TPS-based electrode. This indicates that TEBS has increased ion conductivity compared to TPS, but the amount of threephase boundaries are not as prominent which also agrees with the half-cell data.

The normalized capacitance plot seen in Figure 3.13c further supports this claim by eliminating the capacitive component of the data. The distance of the plot from the Y-axis prior to the plateau is indicative of the Warburg length and shows a distance for the TPS-based electrode that is comparable to the Nafion-based electrode, while the TEBS-based electrode had the smallest slope. This large distance for TPS supports the Nyquist data and demonstrates that there is a much larger resistive component in order to get ions to the three-phase boundaries, whereas the increased ion conductivity of TEBS results in a decreased resistance. This proves that the ionic conductivity of TEBS is greater than TPS, but the ability of TEBS to incorporate in the catalyst material is not as adequate at TPS.



Figure 3.13: EIS full cell data comparing the Nafion-based, TPS-based, and TEBS-based electrodes as a a) Nyquist Plot, b) Capacitance Plot, and c) Normalized Capacitance Plot at  $30^{\circ}$ C with a H<sub>2</sub> anode feed and N<sub>2</sub> cathode feed. For these plots, not all points are indicated.



Figure 3.14: High frequency region of Nyquist plot displaying the change in Warburg region for the Nafion-based, TPS-based, and TEBS-based. For these plots, not all points are indicated.
## 3.2.3 Relative Humidity Performance

#### 3.2.3.1 Nafion-based Electrode

The fuel cell performance at 80 °C was determined by polarization at various relative humidity (RH) levels for both CCEs, and were compared to the Nafion-based electrode. Figure 3.15 illustrates the collected polarization curves between 100% and 20% RH for the Nafion-based electrode in the presence of pure oxygen and air. In oxygen it was observed that as the RH level was decreased, there was also a decrease in cell performance. Between 100% and 80% RH the decrease in polarization was not as great when compared to lower RHs. The decrease in polarization between 40% and 20% RH was also not as pronounced, and is probably due to the stabilization of water content at low RH values. Due to the accumulation of water in the electrode, mass transport losses were also observed at 100% where there is a sudden drop in the curve after 0.6 V. As the RH was decreased, losses due to mass transport at high current densities started to diminish and were no longer present at 60% RH, but losses due to ohmic resistance



Figure 3.15: Polarization curves in the presence of  $H_2/O_2$  and  $H_2/Air$  with a cell temperature of 80°C in various RH conditions for the Nafion-based electrode. For these plots, not all points are indicated.

were still prominent and were the main source in the performance decline due to the decreased water content causing a decrease ion transport throughout the electrode.

In the presence of air a flow rate that was 5 times greater was used in order to achieve the same concentration of oxygen. This results in the same trend being observed, but with lower current densities at all RHs. The polarization at 100% RH and 80% RH displayed similar ohmic resistance until both demonstrated a deviation due to mass transport limitations. Upon decreasing the RH the ohmic resistance was observed to increase due to the higher flow rate required to achieve the same oxygen concentration. The high flow rate prevents the accumulation of water in the cathode which was also seen to dry out the electrode faster at lower RH levels. Limitations due to mass transport were also seen at 100% RH in the presence of air, but occur at lower current densities when compared to pure oxygen because of the diluted oxygen concentration at the catalyst surface even though the same stoichiometry is used<sup>44, 58-59</sup>. In literature the diffusion of oxygen in the presence of nitrogen has been shown to increase the mass transport limitations when compared to other inert gases such as helium<sup>58</sup>. As a result higher flow rates can give a similar stoichiometry of oxygen, but may also decrease gas phase diffusion caused by the presence of slightly larger nitrogen molecules<sup>58-59</sup>.

#### **3.2.3.2 TPS-based Electrode**

The polarization of the TPS-based electrode can be seen in Figure 3.16 in the presence of both oxygen and air. In the presence of oxygen the obtained polarization agrees well with the results reported by Eastcott et. al. where the ohmic losses did not show an increase with a decrease in RH, which indicates sufficient ion transport even in dry conditions and demonstrates a hygroscopic material. At 100% RH there was no indication of current being produced seen by

the low current density at high potentials due to flooding of the electrode, typically seen when excess water is present in the electrode preventing gas diffusion. It was noted by Eastcott that due to the hygroscopic nature of the TPS organosilane, a high water content would result in an overwhelming accumulation of water in the electrode demonstrating extreme mass transport limitations<sup>29</sup>. As the RH level was decreased the limitation to current density caused by mass transport begins to decrease as seen by the increase in the limiting current density. At 20% RH mass transport limitations were still present, but were decreased substantially from 100% RH.

In the presence of air there was an expected decrease in the current density as previously determined. The limitations due to mass transport were also present and flooding of the cell was not as pronounced at 20% RH, but mass transport losses were still observed due to high reaction rates at high current densities. The losses due to ohmic resistance were not present in air indicating a sufficient water content for diffusion of ions.



Figure 3.16: Polarization curves in the presence of  $H_2/O_2$  and  $H_2/Air$  with a cell temperature of 80°C in various RH conditions for TPS-based electrode. For these plots, not all points are indicated

#### 3.2.3.3 TEBS-based Electrode

Figure 3.17 shows the polarization curves in the presence of oxygen and air for the TEBS-based electrode at various RHs. Compared to the other two electrodes at 100% RH in the presence of oxygen, there was a noticeable decrease in the activation region indicating slow reaction kinetics for the ORR. This decrease continued to 40% RH where it stayed relatively similar to the curve at 20% RH. The presence of ohmic losses were also obvious at all RH values when compared to the Nafion-based and TPS-based electrodes. These losses indicate decreased ion transport through the electrode, but when compared to the Nafion-based electrode, the losses between each step in RH is not as extensive. This indicates a low water content resulting in resistance to transport ions through the electrodes. Mass transport limitations were present at low current densities and RHs, and then began to decrease with RH which was also observed with the TPS-based electrode. Mass transport limitations in the polarization curves were noticeable from 100% to 40% RH and were overcome by 20% RH, indicating that water is present in the electrode which contradicts what is observed in the ohmic region. This is indication that the activation losses have a greater contribution to the decrease in polarization when compared to the other limitations in the polarization curve. The limiting current values began to surpass the values obtained with the TPS-based electrode at 40% RH and were comparable to values obtained with the Nafion-based electrode by 20% RH.

In the presence of air the expected drop in current density was observed with the same trends. A larger drop in polarization was noticed after 80% RH, but is be due to fluctuations in the curve caused by mass transport losses. The limitations caused by mass transport were also noticeable at 100% RH, but below 80% RH mass transport limitations were not observed to the same extent as in oxygen.



Figure 3.17: Polarization curves in the presence of  $H_2/O_2$  and  $H_2/Air$  with a cell temperature of 80°C in various RH conditions for the TEBS-based electrode. For these plots, not all points are indicated.

#### **3.2.3.4 Electrochemical Impedance Spectroscopy**

EIS was conducted to get an understanding of how water was being managed with the change in RH for each electrode. The EIS data was compared between each electrode and is displayed in Figure 3.18. The Nyquist plots between each electrode illustrated similar trends with an increase in Warburg length as the RH was decreased, but was not seen as extensive in both CCE samples. The comparison of capacitance depicts the largest capacitance at all RHs with the TPS-based electrode. The TEBS-based electrode also demonstrated a capacitance that was higher

than the Nafion-based electrode, which was then reduced to a value that was comparable to the Nafion-based electrode at 20% RH. This indicates a larger decrease in water content with TEBS than with TPS further demonstrating the hygroscopic nature between the two organosilane ionomers. The normalized capacitance also indicates an increase in resistance as RH is decreased, which was gradual from 100% to 20% RH for both Nafion-based and TPS-based electrodes, but for the TEBS-based electrode the decrease was more abrupt between 40% and 20% RH.



Figure 3.18: Comparison of EIS data with a change in RH for the Nafion-based, TPS-based, and TEBS-based electrodes at gas temperature of 80 °C with a  $H_2$  anode feed and  $N_2$  cathode feed. For these plots, not all points are indicated.

Figure 3.19 illustrates a comparison of the limiting capacitance,  $R_{\Sigma}$ , and the membrane resistance as the RH is decreased. A decrease in capacitance was observed with both CCEs while the Nafion-based electrode stayed relatively the same. The limiting capacitance in Figure 3.22a illustrated a larger decrease with the TEBS-based electrode when compared to the other two electrodes, most likely due to the lower hygroscopicity of the electrode which was also observed as an increase in ohmic resistance in the polarization curves. The comparison of  $R_{\Sigma}$  in Figure 3.22b showed an increase in both CCE electrodes with a decrease of RH, caused by hindered ion transport in the catalyst layer. This increase in resistance was more noticeable with the TEBSbased electrode, especially below 60% RH which suggests a much lower water content in the electrode. This indicates that there is a larger Rionic contribution with TEBS when compared to the other electrodes. TPS-based electrode also demonstrates this, and when the Nafion-electrode is considered the difference in values are not as large. However, the membrane resistance for both CCE's initially demonstrated resistance values that were lower than the Nafion-based electrode. The electrode containing TPS shows a generally lower membrane resistance than the Nafion-based electrode. This trend was also observed by Eastcott et. al and is caused by the diffusion of liquid water from the highly hydrated cathode back to the drier anode, a phenomena that is commonly referred to as anode water removal (AWR)<sup>29</sup>. However, this was not observed to the same extent since the anode material was prepared in-house, and not commercially as was used by Eastcott et. al. This was not observed with TEBS, in fact the membrane resistance increased to values more than double that observed in both TPS-based CLs and Nafion-based electrodes at 20% RH. The large difference in membrane resistance for the TEBS-based electrode suggests insufficient water retention at low RHs resulting in a drier membrane that is less effective for the transport of proton to the cathode.



Figure 3.19: Comparison of a) limiting capacitance, b) total electrode resistance, and c) membrane resistance for the Nafion-based, TPS-based, and TEBS-based electrodes at various RH and cell temperature of 80 °C with a H<sub>2</sub> anode feed and N<sub>2</sub> cathode feed.

## 3.2.3.5 Comparison of Water Retention

Between each MEA there was a noticeable difference in performance as the water content was varied and the contribution of ohmic losses and mass transport also varied with water content. A comparison of each MEA in fully hydrated conditions at 100% RH can be seen in Figure 3.20. At 100% RH it was evident that the TPS-based electrode immediately demonstrated losses from mass transport which was caused by flooding of the electrode with liquid water from to the high porosity of the electrode. The TEBS-based electrode also demonstrated electrode flooding, but at current densities higher than TPS/TEOS further suggesting less liquid water present in the electrode. The electrode containing Nafion shows the best polarization at high RH suggesting a less porous material with good water management.



Figure 3.20: Polarization and power density comparison of the Nafion-based, TPS-based, and TEBS-based electrodes to illustrate how high RH effects performance with a cell temperature at 80  $^{\circ}$ C, H<sub>2</sub> anode feed, and O<sub>2</sub>/air cathode feed. For these plots, not all points are indicated.

In the driest conditions at 20% RH seen in Figure 3.21, the TPS-based electrode outperformed both the TEBS-based and Nafion-based electrodes. Mass transport limitations were still visible for the TPS-based electrode, indicating liquid water was still present in the electrode even at a low RH. This demonstrates the hygroscopic nature of the electrode which was also observed in air. TEBS and Nafion-based electrodes did not demonstrate mass transport limitations implying a low liquid water content within the electrode when compared to the TPSbased electrode. In addition, the contribution to polarization losses caused by ohmic resistance was greater in both the TEBS and Nafion-based electrodes indicating a decreased water content



Figure 3.21: Polarization and power density comparison of the Nafion-based, TPS-based, and TEBS-based electrodes to illustrate how low RH effects performance with a cell temperature at 80 °C,  $H_2$  anode feed, and  $O_2$ /air cathode feed. For these plots, not all points are indicated.

which would be required for sufficient ion transport, and demonstrating low hygroscopicity of the ionomers when compared to the TPS-based material.

Figure 3.22 illustrates the conditions for each electrode at their optimal performance. Through this comparison it was evident that each ionomer performed best in various conditions. The Nafion-based electrode demonstrated the best performance at 80% RH indicating the lowest hygroscopicity of all the electrodes. The TPS-based electrodes demonstrated its best performance at low RHs illustrating a high porosity and excellent hygroscopicity when compared to the other



Figure 3.22: Polarization and power density comparison between the Nafion-based, TPS-based, and TEBS-based electrodes in their optimal conditions with a cell temperature at 80 °C,  $H_2$  anode feed, and  $O_2$ /air cathode feed. For these plots, not all points are indicated.

electrodes. The best performance for the TEBS-based electrode was at 40% RH which indicates that it is not as hygroscopic as TPS, but more hygroscopic than Nafion. However, the activation losses with the TEBS-based electrode was much larger in comparison to the other electrodes indicating decreased ORR kinetics, since both the TPS and Nafion-based electrodes have similar activation losses. The mass transport limitations were also not as pronounced at 40% RH leading to a larger limiting current, but due to greater kinetic losses, lower potentials were needed to achieve this current density.

Comparing each electrode at 40% RH in Figure 3.23 demonstrate that the activation losses also increase with Nafion and are comparable to the TEBS-based electrode at lower RH. This increase in activation losses demonstrates decreased oxygen kinetics caused by decreased oxygen permeability<sup>15, 18, 60</sup>. However, due to the higher hygroscopicity of TEBS when compared to Nafion, there is sufficient water present in the electrode for ion transport at 40% RH. This also indicates that the activation losses with the TEBS-based electrode have a larger contribution to the decrease in polarization than the other limitations in the electrode.



Figure 3.23: Polarization and power density comparison of the Nafion-based, TPS-based, and TEBS-based electrodes at 40% RH with a cell temperature at 80 °C,  $H_2$  anode feed, and  $O_2/air$  cathode feed. For these plots, not all points are indicated.

The decrease in performance in all regions (kinetic, ionic, and mass transport) when using the TEBS was unexpected since the theoretical benefits of adding a phenyl ring alluded to a more capacitive electrode, which should have similar or more enhanced electrode performance. Half-cell measurements also pointed to a more ionically conductive material with a lower electrode resistance. A comparison of each region can perhaps give more information to reasons why using TEBS as the sulfonated silane in the organosilane network resulted in a decreased performance.

Figure 3.24 displays the observed potential 40 mA cm<sup>-2</sup> in the presence of pure oxygen and air for the three electrodes tested. Observing how the potential changes at a fixed low current density can aid in the comparison of losses in the kinetic region and how the RH effects these losses in each electrode. When the electrodes were compared it was evident that the TEBS-based electrode exhibited a greater kinetic losses, which increased as the RH decreased. This was similar to what was observed with the Nafion-based electrode, except for the fact that the TEBSbased electrode requires a greater potential to drive the ORR forward. The increase in the required potential indicates that oxygen reduction is hindered in some way when using TEBS while this is not observed when using TPS, and is not as excessive when using Nafion. Observations in literature indicate diffusion of oxygen is faster in hydrophilic domains, while solubility is higher in the hydrophobic domains of the ionomer<sup>15, 18</sup>. When comparing the sulfonated organosilane materials it is evident that TEBS has a more hydrophobic structure because of the phenyl ring, and this can affect the oxygen diffusion and thus the oxygen reduction kinetics. With that being said, based off data observed in literature the higher hydrophobicity of TEBS will increase the solubility of oxygen in the ionomer when compared to TPS, but as a result decrease the oxygen diffusion to catalyst sites<sup>15, 18, 61</sup>. Additionally, a low water content can also decrease the permeability of oxygen. Through EIS it was determined the TEBS-based electrode had the lowest water content observed by the large  $R_{\Sigma}$  value. This low water content could be another reason to the large activation loss observed with the TEBS-based electrode. This increase in activation losses is also present for the Nafion-based electrode, but the water content was observed to be greater than TEBS through EIS which would allow sufficient permeability of oxygen. In the case of TPS, similar permeability to Nafion was observed

between 80% and 60% RH, but due to the hygroscopic nature a higher water content is present at lower RH allowing better permeability than Nafion.



Figure 3.24: Comparison of the potential at 40 mA/cm<sup>2</sup> at various RH conditions for the Nafionbased, TPS-based, and TEBS-based electrodes with a cell temperature at 80 °C, H<sub>2</sub> anode feed, and O<sub>2</sub>/air cathode feed.

Observing the current density at 0.5V assists in illustrating the changes observed in the ohmic resistance as the RH is changed. Figure 3.25 shows this for the three electrodes and it can be seen that the TEBS-based electrode had a similar trend to Nafion. The low current density at high RH is due to the flooding of the CCE electrodes which was also observed in the polarization curves. As the water content decreased, the ohmic resistance began to show a greater contribution and was depicted as a decrease in polarization below 60% RH with TEBS. This indicates that at low RH the TEBS-based electrode cannot retain water as well as the TPS-based electrode which demonstrates high current densities at low RH at 0.5 V. This comparison proves how effective TPS is at retaining water and using it for hydration at low RH when compared to the other two electrodes.

In the presence of air the same trends as in oxygen were observed for all three electrodes, except for the TPS-based electrode which showed a small decrease in current density. This is

attributed to the high flow rates required with air which results in the removal of water from the electrode.



Figure 3.25: Comparison of the current density at 0.5 V at various RH conditions for the Nafionbased, TPS-based, and TEBS-based electrodes with a cell temperature at 80 °C, H<sub>2</sub> anode feed, and O<sub>2</sub>/air cathode feed.

Figure 3.26 compares the peak power density for each MEA in order to determine how well water is facilitated in the electrode with a change of water content. Changes in power density also aid to indicate how mass transport limitations are effected by the RH, which for a hygroscopic material should decrease with RH from the decrease in water content. In the presence of pure oxygen, the peak power density observed for the TPS-based electrode showed an increase in power density as the RH was decreased, indicating a decrease of liquid water in the electrode which will result in decreased mass transport limitations. The TEBS-based electrode illustrated an increase in power density up to 40% RH, where the power density then started to decrease. This was also observed in the comparison of current density at 0.5 V, and indicates that ohmic limitations are contributing more to the loss in power. The trend observed with Nafion was slightly different where the peak power density had a relatively consistent

power density up to 60% RH, and then had a very subtle decrease at lower RHs. It was also observed that at high RH the peak power density for the Nafion-based electrode was higher than that of both CCEs, but at low RH Nafion had the lowest power density. This supports the claim of cathode flooding in the CCEs since Nafion is seen to have the lowest power at low RH when compared to both CCEs.



Figure 3.26: Comparison of the peak power density at various RH conditions for the Nafion-based, TPS-based, and TEBS-based electrodes with a cell temperature at 80  $^{\circ}$ C, H<sub>2</sub> anode feed, and O<sub>2</sub>/air cathode feed.

In the presence of air the same trends as in oxygen were observed, but a power density that was lower overall. The Nafion-based electrode demonstrated a more noticeable decrease in peak power density after 80% RH when compared to both CCEs. From this data it is evident that Nafion is not as hygroscopic as both organosilane ionomers in the CCEs since water is not retained as effectively at high flow rates and at a lower oxygen concentration, especially after 80% RH. This also indicates that the CCE materials are more prone to flooding at high RH due to the increased hygroscopicity when compared to Nafion. This trend was also observed with the current density at fixed potential comparison which supports the decreased current densities at high RH caused by flooding.

The replacement of TPS for TEBS has shown that the addition of a phenyl ring, and shortening of the carbon chain has drastically decreased the performance in a fuel cell. The large increase in activation losses imply that there is a decrease in the oxygen reduction kinetics. The decrease in the oxygen reduction kinetics has been discussed by Peron et. al and was attributed to the increase in the hydrophobic region of the sulfonated side chain<sup>17</sup>. Holdcroft's group has also discussed the permeability of oxygen within the catalyst layer, and have suggested that the decrease of water content in an ionomer can change its morphology, leading to changes in the oxygen permeability<sup>18</sup>. That being said, if the total hydrophilicity of the organosilane can be increased this may increase the water retention within the electrode which may also increase the ORR kinetics.

Another possibility for the lower hydrophilicity for water retention could have to do with the orientation of the TEBS monomer. Bonding of the TEBS monomer on the carbon support may orient the monomer into a carbon pore and cause it to be inaccessible to use in the sulfonic acid network. In this case the interaction is detrimental since the sulfonic acid groups may not be in an orientation to allow ion transport. The interaction of the monomer and carbon support may also cause the inaccessibility of sulfonic acid groups by penetration of small pores within carbon prior to polymerization, which was also discussed by Peron and Holdcroft<sup>15</sup>.

The high electrode resistance observed with the TEBS-based electrode could indicate insufficient ion transport caused a decreased percolation pathway which may not allow ions to transport efficiently. On the other hand, the total silane loading may be too high causing the assumption that  $R_{electronic} << R_{ionic}$  to not be true. A high silane loading can increase  $R_{electronic}$  if

there is a decrease in electronic conductivity by coverage of catalyst sites which has been seen to occur with high loadings of sPEEK in the catalyst layer<sup>21</sup>.

In the next chapter, the role of the total silane loading and sulfonic acid content will be studied to address the issues on oxygen permeability, decreased water content, and increased electrode resistance. The silane and TEBS content in the organosilane has to be optimized in order to study their roles in the ORR kinetics and water content in the electrode. The ionomer-to-carbon ratio used for the TEBS/TEOS has been proven to be ineffective in retaining enough water for a comparable performance. By increasing the TEBS content in the electrode an increase in the performance may be possible. The increase in TEBS content may allow more water to be retained, as well as possibly change the morphology of the electrode which has an effect on the morphology which in turn may increase the oxygen permeability to give a better performance<sup>18, 61</sup>. The increased TEBS content may also increase the proton conduction. A similar result was also observed by Easton and Holdcroft when using sPEEK in low wt%, where an increase in sPEEK wt% resulted in better proton conduction indicating a sufficient water content in the electrode<sup>21</sup>. Higher TEBS loadings may increase the wettability of the electrode and also allow better performance, perhaps also at low RHs.

The total silane loading will also be decreased in an attempt to decrease  $R_{\Sigma}$  by allowing more access to catalyst sites, especially if a 40 wt% loading is too high for this organosilane system. The decrease in total silane loadings may also allow better incorporation in the carbon catalyst and possibly increase the number of three-phase boundaries making it more comparable to TPS/TEOS. These modifications will lead to the optimization of the TEBS-based electrode in the next chapter.

# Chapter 4: Results & Discussion: Optimization of New Sulfonated CCE

The TEBS-based electrode was optimized by decreasing the total silane loading in an attempt to decrease the electrode resistance. The total silane loading was decreased from 40 wt% to 30 wt% total silane. The goal here was to decrease the electrode resistance to values comparable to that of the TPS-based and Nafion-based electrodes. The new TEBS-based electrode was fabricated using the same method as discussed above and is expected to have a 5 at% TEBS loading with the remainder of silane being TEOS (95 at%). The TEBS loading was also increased from 5 at% to a maximum of 20 at% TEBS in an attempt to increase the ion conductivity which may also increase water retention and oxygen diffusion. The new TEBS loadings used were 10 at%, 15 at%, and 20 at% TEBS with the remaining silane percentage being TEOS.

The new CCEs were physically characterized using FT-IR, TGA, and BET analysis since both TEM and SEM didn't show a significant difference between the initial electrodes. Electrochemical analysis of the new electrodes were also completed using CV and EIS in the full cell to evaluate the electrodes prior to performance testing. Half-cell measurements were not conducted due to the difficulty of depositing the CCE monolith ink on the glassy carbon electrode, and the improved data when spray deposition was used. Performance evaluation of the new TEBS-based electrodes were performed and displayed as polarization curves at various RH conditions to observe how the TEBS loading affects performance. EIS at various RH was also performed on each electrode to observe the water content at various conditions. The data collected was then compared to the data collected from the 5 at% TEBS/TEOS electrode at 40 wt% total silane as well as data acquired from the TPS-based and Nafion-based electrodes.

## 4.1 Physical Characterization

## 4.1.1 Infrared Spectroscopy

Infrared spectroscopy on gelled composites (no 20 wt% Pt/C catalyst) with various TEBS loadings was conducted to confirm the presence of sulfonic acid groups as well as the presence of the phenyl ring structure in TEBS. Figure 4.1 illustrates the presence of a broad band between 1000 cm<sup>-1</sup> and 1250 cm<sup>-1</sup> which includes the Si-O-Si stretching vibrations typically seen at ca. 1100 cm<sup>-1</sup> for each sample. The broad peak at 3400 cm<sup>-1</sup> in all samples is associated with the stretching and bending vibrations from adsorbed water in the sample surface. As determined previously, the bending vibrations of sulfonic acid groups were also observed at 566cm<sup>-1</sup> while the bending vibration of the phenyl ring were seen at 698cm<sup>-1</sup>, 1500cm<sup>-1</sup>, and 1420 cm<sup>-1 52-53</sup>. The presence of these peaks, which are also present at a higher silane loading in Figure 3.5, confirm the presence of TEBS in the silane network.



Figure 4.1: FT-IR spectra of gelled TEBS/TEOS organosilanes with varying TEBS loadings.

## 4.1.2 Thermogravimetric Analysis

TGA and DTG data was obtained for all TEBS-based monolith materials new TEBS loadings, displayed in Figure 4.2. The data collected was compared to the original TEBS-based monolith with 40 wt% total silane to determine the new total silane loading. It was evident that the final weight percent of all new TEBS-based materials had final weight percentages that were ca. 10 wt% lower than the original. This confirms that the new total silane loading is ca. 30% with varying TEBS loadings. Through the weight loss between 120 °C and 500 °C, it was determined that the loss of SO<sub>3</sub>H corresponds to the desired TEBS loading for each sample. It was also observed that both the 5 at% TEBS and 15 at% TEBS samples had similar carbon combustion temperatures to the initial sample, while the other two monoliths showed a decrease



Figure 4.2: Comparison of a) TGA and b) DTG plots for TEBS/TEOS CCEs with varying TEBS loadings at 30 wt% total silane compared to TEBS/TEOS CCE at 40 wt% total silane. For these plots, not all points are indicated.

in the onset of carbon combustion. This does not show a typical trend and therefore can be ruled out as a result from the preparation of the sample.

## 4.1.3 BET Surface Area and BJH Pore Radius

The BET surface area for the samples with 30 wt% total silanes and varying loadings of TEBS was collected and compared to the original sample at 40 wt% total silane and 5 at% TEBS. Table 4.1 shows a general trend of an increase in surface with an increase in TEBS loading, except for the 10 at% TEBS sample which had a surface area similar to the initial TEBS-based monolith at 40 wt% total silane. This suggests a change in the porosity for the new TEBS loadings which may indicate a morphology similar to that of the TPS-based electrode. BJH pore radius also determined a slight increase in the pore radius with TEBS loading implying a shift to larger pore diameters, which is not indicative of increased porosity. However, due to the limitation to the access of micropores by the BET analyzer the porosity can be more microporous which cannot be separated out though this analysis.

Table 4.1: BET surface area and BJH pore radius comparing TEBS at various loadings. Replicates were not collected due to issues with the pore size analyzer.

Sample Composition (TEBS/TEOS)	Multi-Point BET Surface Area $(m^2 \ g^{-1})$	BJH Pore Radius (Å)
20% Pt/C	190	16.8
40 wt% - TEBS <sub>5</sub> :TEOS <sub>95</sub>	338	18.8
30 wt% - TEBS <sub>5</sub> :TEOS <sub>95</sub>	231	18.9
30 wt% - TEBS <sub>10</sub> :TEOS <sub>90</sub>	352	17.1
30 wt% - TEBS <sub>15</sub> :TEOS <sub>85</sub>	280	19.1
30 wt% - TEBS <sub>20</sub> :TEOS <sub>80</sub>	291	19.1

## 4.2 Electrochemical Characterization

Electrochemical evaluation of the CCE electrodes with varying TEBS loading were analyzed in a full cell environment. MEAs were prepared in an identical fashion as previously described in section 2.1.3. The CCEs with varying TEBS loading were placed on the cathode while standard Nafion-based electrodes were used on the anode. CV and EIS was performed to evaluate the electrodes prior to performance testing with a H<sub>2</sub> anode feed and N<sub>2</sub> cathode feed at a cell temperature of 30 °C. Polarization curves with a H<sub>2</sub> anode feed and O<sub>2</sub>/air cathode feeds at varying RHs were collected and compared to each TEBS loading with a cell temperature of 80 °C. The TEBS loadings that demonstrated the most improvement in performance were then compared to the performance of the TPS-based and Nafion-based electrodes.

## **4.2.1 Cyclic Voltammetry**

CVs of the CCEs with varying TEBS loading were collected and compared to the initial TEBS-based electrode containing 40 wt% total silane (Figure 4.3). The characteristic peaks for platinum were all present for all TEBS loadings, but compared to the higher silane loading, all the new electrodes displayed smaller peaks sizes. The desorption of hydrogen from platinum also displayed similar peak currents for all TEBS loadings when the total silane loading was decreased. The resolution of hydrogen desorption from different platinum crystal structures was also improved for the samples with lower silane loadings. This suggests that there may be increased ion and electron conductivity, or a better incorporation of the organosilane with the Pt/C when compared to higher silane loadings. The presence of the quinone/hydroquione redox couple was also visible which is from defects of the carbon surface possibly created upon

gelation of the sol-gel. A small peak is also present at approximately 0.75 V in the 10 at% TEBS and 20 at% TEBS electrodes. This peak occurs at a potential close to the onset of Pt-oxide oxidation and the formation of quinone, and perhaps is caused by an interaction between the phenyl ring in TEBS and the platinum surface<sup>62</sup>. Another possibility could be an interaction between the Nafion membrane incorporated in the electrode and TEBS<sup>63</sup>, but since this peak does not show an increase with TEBS loading it was not investigated any further.

The ECSA for all TEBS loadings with 30 wt% total silane was calculated and displayed as a bar graph in Figure 4.4. A low standard deviation in ECSA values was observed and did not demonstrate a substantial difference in value between electrodes indicating similar platinum exposure. This also implies that the morphology does not change drastically with TEBS loading.



Figure 4.3: Cyclic voltammograms in a half-cell comparing TEBS at various loadings and 30% total silane to TEBS at 5% TEBS and 40% total silane in 0.5M  $H_2SO_4$  at 20mV/s<sup>-1</sup>



Figure 4.4: Comparison of ECSA values for TEBS/TEOS CCEs with varying TEBS loadings.

## 4.2.2 Electrochemical Impedance Spectroscopy

EIS was performed on each MEA at the end of the CV collection. Figure 4.5 shows the comparison between impedance as the TEBS loading was increases and also between total silane loadings. The Nyquist plot demonstrated a variance in Warburg lengths between 30 wt% and 40 wt% total silanes. When expanded to the high frequency region in Figure 4.6, a drastic increase in  $R_{\Sigma}$  was observed (Figure 4.7) as an extension of the Warburg length when the total silane loading was decreased. This indicates that both  $R_{ionic}$  and  $R_{electronic}$  are increasing, but the contribution from each component cannot be separated. Upon increasing the TEBS loading to 10 at%, the  $R_{\Sigma}$  value exhibited a substantial decrease to a value lower than the original sample at 40 wt% silane. This indicates that  $R_{ionic}$  has a greater contribution to the increase in  $R_{\Sigma}$  since it is expected that  $R_{ionic}$  will decrease upon increasing the number of sulfonic acid groups.

Upon further increasing the TEBS loading, a small increase in  $R_{\Sigma}$  was also observed which is due to the increase in  $R_{electronic}$  from the organosilane ionomer further supporting the suggestion that  $R_{ionic}$  has a greater contribution to the increase in  $R_{\Sigma}$ . The limiting capacitance also demonstrated a decrease with a decrease in the total wt% of silane. This indicates that there is a decrease in porosity upon decreasing the total silane loading and as a result less catalyst sites are exposed for reactions. However, as the TEBS loading was increased a small increase in capacitance was also observed. This implies there is a change in morphology upon increasing the TEBS loadings, but when compared to the 40 wt% silane the porosity is still lower. The



Figure 4.5: EIS half-cell data comparing TEBS loadings at 30 wt% total silane to 5 at% TEBS with 40 wt% total silane as a a) Nyquist plot, b) Capacitance plot, and c) Normalized capacitance plot at 30 °C with a  $H_2$  anode feed and  $N_2$  cathode feed. For these plots, not all points are indicated.

normalized capacitance also aids in illustrating the increase in  $R_{\Sigma}$  upon decreasing the wt% of silane indicating that  $R_{ionic}$  has a larger influence on the  $R_{\Sigma}$  than  $R_{electronic}$ .



Figure 4.6: High frequency region of Nyquist plot displaying the change in Warburg regions for TEBS at various TEBS loadings and 30 wt% total silane and 5 at% TEBS with 40 wt% total silane. For these plots, not all points are indicated.



Figure 4.7: Comparison of  $R_{\Sigma}$  values between 5 at% TEBS at 40 wt% silane, and various TEBS loadings at 30 wt% total silane.

## **4.2.3 Relative Humidity Performance**

The polarization curves for electrodes at 30 wt% total silane and varying TEBS loadings between 5 at% and 20 at% were collected. MEAs were prepared using the identical procedure discussed previously in section 2.1.3. Each electrode was tested at 80 °C and the RH at the cathode was varied between 100% and 20% RH. H<sub>2</sub> gas was fed in the anode, and oxygen or air was fed in the cathode to observe changes in oxygen diffusion with a diluted oxygen concentration. The collected data was then compared to observe how the TEBS loading would affect the performance. The electrodes that demonstrated the best improvement from the original sample at 40 wt% total silane and 5at% TEBS was then compared to the TPS-based and Nafionbased electrodes.

#### 4.2.3.1 5 at% TEBS Loading

The polarization curves for the CCE containing 5 at% TEBS and 30 wt% total silane at varying RH conditions is displayed in Figure 4.8. In the presence of oxygen it was observed that as the RH was decreased, the performance of the fuel cell also decreased. Similar to the sample with 40 wt% total silane, there were significant losses in the activation and ohmic regions of the curve. The losses associated with the activation region remained relatively the same from 100% RH down to 60% RH, where the losses associated with the kinetics of the ORR then showed a decrease at 40% RH. This is due to the insufficient hydration of the membrane and electrode, which result in the decreased diffusion of oxygen as discussed previously<sup>16, 18</sup>. The insufficient hydration of the membrane can also cause the decreased transport of ions within the electrode which manifest in the ohmic region<sup>16</sup>. As the RH was decreased the ohmic losses demonstrated a dramatic decrease in polarization between 60% and 40%, and continued to

decrease down to 20% RH. The losses due to mass transport limitations suggest the opposite to what is being observed in the other two regions of the curve. At 100% RH the dramatic decrease at low current densities indicate flooding of the electrode with liquid water. Flooding of the electrode was also observed down to 60% RH, where it was then overcome and was no longer a contribution to the decrease in polarization. This trend was also observed with the same TEBS loading at 40 wt% total silane. Through further inspection of the polarization curves at both 30 wt% and 40 wt% total silanes and 5 at% TEBS, ion transport did not appear to be hindered substantially between 100% and 60% RH suggesting that a sufficient water content was present within the electrode at high RH conditions. This indicates that the kinetic losses from oxygen diffusion in the ionomer has a greater effect on the decrease in performance than the other limitations in the electrode.



Figure 4.8: Polarization curves at 80 °C and varying RH for 5 at% TEBS/TEOS electrode with  $H_2$  anode feed and O<sub>2</sub>/air cathode feed. For these plots, not all points are indicated.

In the presence of air similar results were obtained when comparing to the same TEBS loading at 40 wt% total silane. There was an overall decrease in current density, which was expected, but it was also observed that the activation losses were large in all RH conditions. The region associated with ohmic resistance did not show a great decrease in ion transport until the step between 40% and 60% RH.

#### 4.2.3.2 10 at% TEBS Loading

The polarization curve for the TEBS-based electrode at 30 wt% total silane and 10 at% TEBS is displayed in Figure 4.9. When compared to the 5 at% TEBS loading, the polarization curves illustrated an improvement in performance at all RHs in the presence of pure oxygen. The losses in the activation region demonstrated an increase from 100% to 40% RH when compared to the previous loading. At 20% RH the open circuit voltage (OCV) exhibited a dramatic decrease when compared to the OCV at higher other RH conditions. This MEA was remade and the polarization data was repeated and the same decrease in OCV was observed which leads to the belief that it is perhaps due to poor ionomer contact under low water contents. This drop in OCV indicates that pinholes are present in the MEA and hydration of the electrode were not able make this MEA useable. 10 at% TEBS proves to be unable to retain water at low RH, but the increasing current density at low potentials demonstrate that this was not detrimental to the overall performance. The ohmic losses from ion transport did not show a significant decrease with RH as was observed with 5 at% TEBS. Mass transport limitations were displayed at all RH conditions and was the dominating limitation at 100% RH indicating severe flooding of the electrode. Flooding of the electrode was observed down to 20% RH, where the dramatic drop in voltage appeared to be reaching the limiting current density. This small increase in potential at

high current densities is visible when the surface concentration approaches zero and is caused by a fast reaction rate at high current densities<sup>44, 59</sup>.

In the presence of air an increase in the activation losses was not observed. This suggests that an increase in sulfonic acid content assists in the retention of water in the membrane which would help increase oxygen diffusion in the ionomer. The polarization curves between 100% and 80% RH illustrated an increase which is due to the slight decrease in water content from high flow rates. This slight decrease in water would result in the minor decrease in the mass transport limitation, which appears to be the limitation causing the low current density at high RH. The ion transport resistance observed in the ohmic region showed a gradual increase which is caused by a decrease in water content, but is not as extensive as the 5 at% TEBS electrode.



Figure 4.9: Polarization curves at 80 °C and varying RH for 10 at% TEBS/TEOS electrode with  $H_2$  anode feed and  $O_2$ /air cathode feed. For these plots, not all points are indicated.

## 4.2.3.3 15 at% TEBS Loading

Figure 4.10 illustrates the polarization curves for the TEBS-based electrode with a 15 at% TEBS loading at 30 wt% total silane. In the presence of oxygen the activation region had a higher current density at 100% RH when compared to lower TEBS loadings. This region then demonstrated a decrease as RH was decreased, but at 20% RH the activation losses did not show a large increase when compared to the polarization curves at lower TEBS loadings. The increase in the activation region indicates that the increase of sulfonation is actually beneficial to the ORR which is due to the increase in the water content. The ohmic losses also appeared to be relatively constant between 100% and 60% RH, and then displayed a decrease at 40% RH. The decrease in water content between 60% and 40% may not be high enough to have sufficient ion transport throughout the electrode, but compared to the lower TEBS loadings the ion transport was not hindered as much. The effect of a decreased water content can also be observed as a decrease in the mass transport limitation as the RH was decreased. Between 100% and 60% RH the dramatic drop in potential caused by electrode flooding as visible. The flooding was then overcome at 40% RH and was not observed at 20% RH. This helps to demonstrate that there was a decrease in the water content in the cell, which supports the increase in ion transport resistance observed in the ohmic region of the curve.

In the presence of air a similar trend to oxygen was observed, except between 100% and 80% RH where the polarization curves increased. This is also due to flooding experienced at 100% RH which causes the mass transport limitations to have a very strong influence on the polarization curve. As the RH was decreased, some liquid water was removed because of the high flow rates used which allows increased performance of the cell. The ohmic losses in the presence of air were also visible and show a gradual increase, but is not as extensive when

compared to lower TEBS loadings. Mass transport limitations were also overcome by 40% RH which was also observed in pure oxygen.



Figure 4.10: Polarization curves at 80 °C and varying RH for 15 at% TEBS/TEOS electrode with  $H_2$  anode feed and  $O_2$ /air cathode feed. For these plots, not all points are indicated.

## 4.2.3.4 20 at% TEBS Loading

With a 20 at% TEBS loading in pure oxygen the polarization curves showed an in increase in performance down to 40% RH (Figure 4.11). The activation losses did not indicate a significant increase when compared to the 15 at% TEBS loading. This indicates that ORR kinetics have improved by increasing TEBS loading, but the losses in the activation region demonstrate a small decrease with RH which was also seen at 15 at% TEBS. The losses in the ohmic region due to ion transport resistance also appeared to stay consistent down to 40% RH, where a decrease was observed due to a low water content and the decreased hygroscopicity of TEBS in comparison to TPS. The increase in TEBS loading did allow more sulfonic acid groups to be present for the retention of water at lower RH conditions, supporting the change in morphology observed in the BET data. The large increase in ohmic losses between 40% and 20%
RH show that the use of TEBS requires a higher water content than TPS to have efficient ion transport within the electrode. Mass transport limitations were also observed in all RH conditions, but were the major limitation from 100% to 60% RH as seen with lower TEBS loadings. Between 40% and 20% RH, the mass transport limitations did not seem to indicate flooding of the electrode since there was not a dramatic drop in potential, but does indicate that a decrease in surface concentration is present which was observed with 10 at% TEBS<sup>44</sup>. This suggests that at 40% RH there is an ideal water content in the electrode for reactant diffusion to catalyst sites, and does not hinder ion transport in the electrode.



Figure 4.11: Polarization curves at 80  $^{\circ}$ C and varying RH for 20 at% TEBS/TEOS electrode with H<sub>2</sub> anode feed and O<sub>2</sub>/air cathode feed. For these plots, not all points are indicated.

Changing the oxidant gas to air exhibits a decrease in polarization in all RH conditions which was expected. The activation losses also demonstrated a decrease when the RH was reduced from 80% to 40% RH, but is then consistent between 40% and 20% RH. The ohmic losses also displayed a decrease at in all RH conditions indicating a decrease in water retention

when switched to air. This was also observed at lower TEBS loadings which show a gradual increase in ohmic resistance as the RH was decreased. This was noticed with the use of air when the flow rate of the gas is increased to achieve the same concentration of oxygen. As a result the liquid water that could be used to help facilitate ion transport is removed, making the electrode dryer than with pure oxygen at the same RH. Flooding of the cell caused with liquid water also shows a decrease which results in the increase of oxidant gas diffusion. Flooding appeared between 100% and 60% RH in oxygen, but in the presence of air was only observed between 100% and 80% RH. This is also due to the increased flow of reactant gas allowing the removal of liquid water from the electrode, also allowing the visualization of the mass transport limitation due to a decreased surface concentration at high current densities.

#### **4.2.3.5** Electrochemical Impedance Spectroscopy

EIS was performed at the completion of the performance test, where the cell was then rehydrated for analysis in various RH conditions. Figure 4.12 displays the EIS data as the RH was decreased for each TEBS loading, and are compared to observe how the TEBS loading affects the water content and ion transport in the electrode. The Nyquist plots displayed similar trends between all electrodes where there was an increase in the Warburg length as the RH was decreased. This indicates that there is a decrease in ion transport with RH which is expected since this is also observed at a higher silane loading with both TPS-based and TEBS-based electrodes. At 5 at% TEBS the shape of the Nyquist plots were not identical to the plots at higher TEBS loadings. This implies that the electrode is extremely resistive and supports the initial data collected where the resistance was mainly due to insufficient sulfonation, causing R<sub>ionic</sub> to be the main contribution to increased resistance at low RH. With the increase in TEBS loading, the increase in the Warburg length appeared to be more gradual. At 10 at% TEBS the Warburg length had a slight increase between 80% and 60% RH, but then had a large increases as the RH was decreased. However, at 20 at% TEBS the Warburg length was seen to increase at approximately the same rate with the decrease in RH. This is due to the increased water retention which is expected with increased sulfonic acid content in the electrode.

A comparison in the capacitance plots also demonstrated a noticeable difference between 5% at TEBS and higher TEBS loadings. At 5 at% TEBS there was a large decrease that occurred between 80% and 60% RH, where the capacitance plots then remain at the same height and slope indicating high resistance to get ions to the catalyst sites. However, as the TEBS loading was increased the height of the capacitance plots appeared to be the same for all electrodes. The plots also appeared to have the same height as the RH was decreased. As the TEBS loading was increased, a decrease in the capacitance height was also observed between 80% and 60% RH. This was not seen at 20 at% TEBS where a decrease was observed with each decrease in RH. At 20% RH the height of the capacitance plot appeared to be the same, but at 20 at% TEBS the slope appeared to be lower indicating a higher resistance. The normalized capacitance also helps to illustrate that the resistance gradually increased with the decrease in RH for all TEBS loadings, except at 5 at% TEBS indicating an increase in Relectrionic which is also seen in Figure 4.12.



Figure 4.12: Comparison of EIS data in various RH conditions for TEBS/TEOS CCE with varying TEBS loadings at 80  $^{\circ}$ C with a H<sub>2</sub> anode feed and N<sub>2</sub> cathode feed. For these plots, not all points are indicated.

A better comparison of the effect TEBS loading has on the resistance and capacitance is seen in Figure 4.13 where both are compared as the RH is decreased. For all TEBS loadings there was a similar trend observed, where a decrease in the limiting capacitance can be seen as the RH is decreased. The limiting capacitance at 5 at% TEBS had the lowest values at all RH compared to the higher TEBS loadings. This helps to indicate that the amount of three-phase boundaries are lower when compared to the higher TEBS loading will also increase the porosity. When the TEBS loading was increased there was an increase in limiting capacitance, which then decreased when the TEBS loading got to 20 at%. This shows that there is no drastic change in morphology when the TEBS loading gets to 20 at%, and also shows that increasing past 15 at% TEBS may begin to block catalyst sites and hinder electron transport<sup>21, 35</sup>.

 $R_{\Sigma}$  within the electrode demonstrated a large increase for 5 at% TEBS as the RH was decreased. The other TEBS loadings had much lower resistance values that were more comparable, indicating that ion transport at 5 at% TEBS is inefficient causing R<sub>ionic</sub> to increase faster than R<sub>electronic</sub> which was also observed in the initial EIS data at 30 °C. This also indicates that there is relatively no water retention at 5 at% TEBS, perhaps due to the decreased number of sulfonic acid groups when the total silane loading was decreased from 40 wt% to 30 wt%. The membrane resistance as also higher with 5 at% TEBS when compared to the higher loadings which also supports the belief that the water retention is lower with this composition. All TEBS loadings demonstrated a slight increase in membrane resistance when decreasing the RH, but 15 at% and 20 at% TEBS show similar resistance which is lower than the others at 20% RH.



Figure 4.13: Comparison of a) limiting capacitance, b) total electrode resistance, and c) membrane resistance for TEBS/TEOS CCEs with various TEBS loadings at various RH and cell temperature of 80 °C with H<sub>2</sub> anode feed and N<sub>2</sub> cathode feed.

## 4.2.4 Performance Comparison of Various TEBS Loadings

A comparison of the potential at 40 mA cm<sup>-2</sup> as the TEBS loading was increased is illustrated in Figure 4.14. In the presence of oxygen the potentials obtained above 5 at% TEBS show a large increase, which then decreased with RH. The electrode containing 15 at% TEBS showed a relatively consistent value when compared to the other TEBS loadings. The overall increase in potential from 5 at% TEBS demonstrates that higher TEBS loadings have a positive effect on the ORR kinetics, by increasing the diffusion of oxygen in the organosilane ionomer. This can be attributed to the increased water content in the electrode which has been known to effect the oxygen diffusion and solubility in literature<sup>15, 18</sup>.

In the presence of air there the decrease in potential was not large when compared to the collected data in the presence of oxygen. The trend observed was similar to that in oxygen, where an increase in potential was observed at TEBS loadings above 5 at%. This indicates that the diffusion of oxygen is not greatly affected when the oxygen concentration is diluted. This result supports the thought that the kinetics of the ORR was hindered inadvertently because of the low TEBS loading. This also shows that by increasing the TEBS loading, an increase in oxygen permeability is possible which can help increase the fuel cell performance with a TEBS-based electrode.



Figure 4.14: Comparison of the potential at a fixed current density with the change in RH for TEBS/TEOS CCEs with various TEBS loadings.

Observing the change in current density at 0.5 V with various TEBS loadings (Figure 4.15) illustrates a similar trend to the TPS-based electrode at TEBS loadings greater than 5 at%. Between 10 at% and 20 at% TEBS, the current density at 0.5 V displayed an increase with the

decrease in RH which implies a decrease in ion transport, but is due to flooding of the cell. This seems to be the most probably reason since it is seen in the polarization curves that mass transport is the main limitation for the fuel cell performance. It was also observed that mass transport losses were overcome after 40% RH, but ion transport was also observed to decrease and was observed in the ohmic region of the polarization curve. This was also seen in the polarization curves where a decrease in current density was observed below 40% RH. This observation indicates that the increase in TEBS loading has changed the morphology to one that is more similar to the TPS-based electrode.

In the presence of air a similar trend to oxygen was observed, however, at all TEBS loadings above 5 at% a decrease in current density below 60% RH was observed. This indicates that ohmic resistance is higher which is caused by decreased ion transport. This is caused by the high reactant flow rate which was discussed earlier, resulting in an increase of water removal from the electrode and cause drying of the electrode to occur faster.



Figure 4.15: Comparison of the current density at a fixed potential with the change in RH for TEBS/TEOS CCEs with various TEBS loadings.

The peak power density as the RH was decreased is illustrated in Figure 4.16 and compares TEBS loadings. The trend observed in pure oxygen was similar to that seen in the current density at 40 mA cm<sup>-2</sup> comparison, and demonstrates how RH effects the mass transport of the fuel cell performance. As determined earlier in the polarization curves, the performance of the fuel cell increased with the decrease of the mass transport limitation down to 40% RH in most electrodes. There does not seem to be a drastic change in the power density as the TEBS loading is increased above 5 at%, which indicates that there is a similar platinum surface between each electrode which was also seen and discussed in the CVs.

In the presence of air the higher flow rate seemed to have had a negative effect on the power density below 60% RH, where there was a decrease with all TEBS loadings. This was also observed when comparing the changes in the ohmic region which is associated with the removal of water from the electrode.



Figure 4.16: Comparison of the peak power output with the change in RH for TEBS/TEOS CCEs with various TEBS loadings.

A comparison of the fuel cell performance at 40% RH for the various TEBS loading is displayed in Figure 4.17. The polarization curves were compared to the 5 at% TEBS sample at 40 wt% total silane in order to observe how the performance was effected by both total silane loading and TEBS loading. As expected, in the presence of oxygen the performance of the fuel cell increased with TEBS loading where 5 at% TEBS had the worst performance and 20 at% TEBS had the best performance. The activation losses exhibited a decrease with the TEBS loading demonstrating that TEBS loading has an effect on the oxygen permeability in the ionomer. This decrease in activation losses are also indicative of an increased water content in the MEA. The ohmic resistance also decreased with an increase of TEBS loading and helps to support this by demonstrating that an increase in sulfonic acid groups can allow for an increase in water retention on the electrode. However, the mass transport limitations were present for the 20 at% TEBS electrode, but did show a decrease in current density caused by a decreased surface concentration. This is ideal since it shows sufficient water is in the electrode at RH conditions lower than that required for optimal conditions when using Nafion, and further indicating TEBS is a more hygroscopic material when compared to Nafion. When compared to the TPS-based electrode the optimal RH was higher which also demonstrates that TEBS is a less hygroscopic material than TPS.

In the presence of air an increase in performance was observed with 30 wt% total silane and TEBS loadings greater than 5 at%. At TEBS loadings higher than 5 at%, the performance also had identical performance despite the increase in TEBS loadings. This indicates that as the TEBS loading increases above 10 at% there is no further increase in the solubility and diffusion



Figure 4.17: Comparison of polarization curves at 40% RH for various TEBS loadings. For these plots, not all points are indicated.

of oxygen. However, the slight difference in water content between 10 at% and 20 at% TEBS show a small decrease in the ohmic losses, which results in slightly better performance.

#### **4.2.4.1** Performance Comparison to TPS and Nafion-based Electrodes

When taking into account the increase of both water content and oxygen permeability, the samples with 15 at% and 20 at% TEBS show the most improved performance when compared to 5 at% TEBS at 40 at% total silane. As was performed before, comparing the performance of each electrode in both their wettest and driest conditions can give an indication of how well the material can retain water. Figure 4.18 shows the comparison of both the polarization and power density of the 15 at% and 20 at% TEBS-based, TPS-based, and Nafion-based electrodes at 100% RH. In the presence of oxygen, both TEBS-based electrodes had a much better performance at 100% RH when compared to the initial electrode at 40 wt% silane. Their performance was more comparable the Nafion-based electrode and also demonstrated that as the TEBS loading increased, so does the mass transport limitations. This shows that the electrode is retaining more

water upon increased sulfonation and also suggests that the morphology is becoming similar to the TPS-based electrode. The ion transport, however, had similar resistance to the Nafion-based electrode indicating that there is less water present when compared to the TPS-based electrode since extreme flooding is not observed.



Figure 4.18: Comparison of polarization and power density curves at 100% RH for 15 at% and 20 at% TEBS-based, TPS-based and Nafion-based electrodes at 80 °C with a H<sub>2</sub> anode feed and O<sub>2</sub>/air cathode feed. For these plots, not all points are indicated.

In the presence of air the opposite trend was observed with the TEBS-based electrode. The 20 at% TEBS electrode had similar ion transport to Nafion, while the 15 at% TEBS electrode had similar ion transport to the TPS-based electrode. This implies that at 15 at% TEBS there is more mass transport limitations than 20 at% TEBS in air, while in oxygen the opposite is observed. This inconsistency is attributed to the fluctuations in the polarization curve caused by flooding of the electrode. From the data it is clear that the morphology is more similar to that of the TPS-based electrode than the Nafion-based electrode and demonstrates a more porous electrode.

A comparison of the electrodes in the driest conditions can be seen in Figure 4.19 where they are all compared at 20% RH. Both TEBS-based electrodes similar ohmic losses were observed, which are higher than the TPS-based electrode, but lower than the Nafion-based electrode in the presence of oxygen. This further demonstrates that TEBS is less hygroscopic when compared to TPS, but more hygroscopic than Nafion. The lower ohmic losses observed in the 20 at% TEBS electrode suggest better ion transport when compared to 15 at% TEBS due to a higher water content, but mass transport limitations indicate no flooding in both. In fact the 20 at% TEBS electrode seems to show mass transport limitations from the decrease of surface concentration instead of from flooding.

In the presence of air the two TEBS-based electrodes also had polarization curves that lied between the TPS-based and Nafion-based electrodes. The 15 at% TEBS electrode had better ion transport than the 20 at% TEBS sample which also suggests a change in the morphology when the TEBS loading is increased past 20 at%.



Figure 4.19: Comparison of polarization and power density curves at 20% RH for 15 at% and 20 at% TEBS-based, TPS-based and Nafion-based electrodes at 80 °C with a H<sub>2</sub> anode feed and O<sub>2</sub>/air cathode feed. For these plots, not all points are indicated.

A comparison of optimal performance for both TEBS-based, TPS-based, and Nafionbased electrodes is seen in Figure 4.20. It was previously determined that Nafion required the highest RH in order to give the best performance, while the CCEs provided better performance at lower RHs. When comparing the electrodes it was apparent that the increased performance of the new TEBS-based electrodes produced comparable results to the other electrodes, whereas the 5 at% TEBS at 40 wt% total silane had a performance much lower than both TPS and Nafionbased electrodes. The activation losses for each electrodes best performance appeared to be similar between all the electrodes, indicating that the oxygen permeability in the ionomer has increased and is now comparable. The ohmic losses with 15 at% TEBS were slightly higher when compared to the other electrodes illustrated by the lower polarization curve. This indicates that at 15 at% TEBS there is a slightly lower water content and ion transport is slightly more limited. At 20 at% TEBS there was sufficient water in the electrode for ion transport and the losses associated in this region are similar to that of the TPS-based and Nafion-based electrodes.



Figure 4.20: Comparison of polarization and power density curves for 15 at% and 20 at% TEBSbased, TPS-based and Nafion-based electrodes in their respective optimal RH conditions at 80 °C with a  $H_2$  anode feed and  $O_2$ /air cathode feed. For these plots, not all points are indicated.

The mass transport limitations at 15 at% TEBS appeared to be lower when compared to the other electrodes and 20 at% TEBS shows this limitation, but at higher current densities than TPS/TEOS. This comparison also demonstrates that TPS is more hygroscopic even when the TEBS loading is increased to 20 at% since flooding is not observed in the TEBS electrode at optimal conditions.

In the presence of air there is a slight increase in ohmic resistance observed for both TEBS electrodes when compared to TPS-based and Nafion-based electrodes. This indicates that there may be a slightly lower water content in these two electrodes in their optimal conditions. The mass transport losses are also observed in all the electrodes with similar limiting current densities for both TEBS loadings that are higher when compared to TPS/TEOS and Nafion ionomers.

Observing the performance of each electrode at 40% RH in Figure 4.21 demonstrated that both TEBS-based electrodes outperform the Nafion-based electrode, whereas the TEBS-based electrode at 40 wt% was showing a similar performance to Nafion at 40% RH. This increase in performance demonstrates better water retention for the TEBS-based electrode when the TEBS loading is increased in order to get more sulfonic acid groups present. At 20 at% TEBS the performance was also similar to the TPS-based electrode indicating that this may be the loading required to get a similar water retention to TPS, however the lower performance at 40% RH for 20 at% TEBS further proves that the material is not as hygroscopic as TPS.



Figure 4.21: Comparison of polarization and power density curves at 40% RH for 15 at% and 20 at% TEBS-based, TPS-based and Nafion-based electrodes at 80 °C with a H<sub>2</sub> anode feed and O<sub>2</sub>/air cathode feed. For these plots, not all points are indicated.

A closer look at how the activation losses compare between TEBS, TPS, and Nafionbased electrodes as the RH was decreased can be seen in Figure 4.22. Compared to the TPSbased electrode both TEBS-based electrodes demonstrated a decrease in potential with RH, whereas the TPS-based electrode had an overall increase in potential with decreased RH. The trend observed with the TEBS-based electrode is similar to the trend observed with the Nafionbased electrode, but at higher potentials. This slight decrease in potential with RH shows that the TEBS loading is now sufficient for efficient oxygen permeability oxygen when compared to Nafion-based electrode, but not as efficient as the TPS-based electrode due to the lower water content in TEBS at low RH. As discussed in literature this may be due to the difference in morphology resulting in a lower water content with TEBS when compared to TPS which cannot be observed in the SEM images<sup>18</sup>. The argument of a higher water content can also be used since it has been observed through numerous experiments that TPS is more hygroscopic than TEBS which may also account for increased solubility and diffusion of oxygen<sup>18</sup>. In the presence of air the same trends were observed, except at 100% RH where Nafion had the highest potential. This is mainly due to the flooding observed in both CCEs at high RH conditions which cause the current densities to be really low at high potentials, and as a result poor performance is observed.



Figure 4.22: Comparison of the potential at 40 mA cm<sup>-2</sup> in various RH conditions for 15 at% and 20 at% TEBS-based, TPS-based, and Nafion-based electrodes at 80 °C with a H<sub>2</sub> anode feed and O<sub>2</sub>/air cathode feed.

The current density at 0.5 V, which shows how well water is retained as the RH is decreased, demonstrated similar trends for all CCEs and a relatively consistent current density for the Nafion-based electrode, which can be seen in Figure 4.23. In all CCEs the increase in current density as RH decreases indicates that there is flooding of the electrode due to mass transport limitations resulting in poor fuel cell performance. This can be said since flooding with a TPS-based electrode is observed down to 20% RH and was also observed by Eastcott and Easton<sup>29</sup>. However, at 15 at% TEBS a decrease in current density was observed below 40% RH which indicates the mass transport limitations are overcome, and ohmic resistance is starting to make a larger contribution to the decrease in performance. In the presence of air the TPS-based electrode also showed a decrease in current density at 0.5 V caused by the slight decrease in water content from the high flow rates, which is also observed for the other CCE electrodes.



Figure 4.23: Comparison of the current density at 0.5 V in various RH conditions for 15 at% and 20 at% TEBS-based, TPS-based, and Nafion-based electrodes at 80 °C with a H<sub>2</sub> anode feed and  $O_2/air$  cathode feed.

The peak power density for all CCEs show similar values at all RH conditions, which were all higher than the Nafion-based electrode below 60% RH. This comparison can be seen in Figure 4.24 and shows how flooding effects the overall performance of the electrode. In all CCEs mass transport limitations are seen to hinder the performance of the cell at high RH conditions. This supports the fact that a high RH is detrimental for the fuel cell if CCE materials are used at the cathode. The high water content causes major blockage of the porous structure, and inhibits the diffusion of reactants to the catalyst sites. As the accumulation of water was decreased through decreasing the RH, the CCE materials are hygroscopic enough to retain water for efficient transport of ions and transport of reactant gases to the catalyst sites. As for Nafion there was a relatively consistent power output that was much better than the CCEs at high RHs, since Nafion is not as porous as the CCEs, allowing the flooding to not be as severe. This was not as beneficial at lower RHs since Nafion was not able to retain water as effectively and resulted in a lower power density when compared to both CCEs. This also helps to explain the



Figure 4.24: Comparison of the peak power density in various RH conditions for 15 at% and 20 at% TEBS-based, TPS-based, and Nafion-based electrodes at 80 °C with a H<sub>2</sub> anode feed and  $O_2$ /air cathode feed.

hygroscopic nature of the CCEs which have been discussed as one of the major benefits to using the organosilanes as the ionomer in the electrode.

### 4.2.4.2 Electrochemical Impedance Spectroscopy Comparison to TPS and Nafion-based Electrodes

The comparison of the resistance data collected through EIS for 15 at% and 20 at% TEBS at 30 wt% total silane were compared to the data from the TPS and Nafion-based electrodes in Figure 4.25. The limiting capacitance in Figure 4.25a still shows that the TPS-based electrode had the largest capacitance when compared to the other electrodes indicated a greater porosity. Both new TEBS-based electrodes also had limiting capacitance values that were greater than that observed with Nafion demonstrating more three phase boundaries. This difference in limiting capacitance shows that the increase in TEBS loading still results in a more porous electrode when compared to Nafion even though the total silane loading was decreased, however the sulfonic acid content has to be increased in order to achieve this increased capacitance.

The comparison between  $R_{\Sigma}$  values, seen in Figure 4.25b, allowed the comparison of electrode resistance and gave more information on the source of this resistance. In the case of TPS an increase in resistance was observed below 60% RH which was expected since it was also observed by Eastcott and Easton and attributed to AWR<sup>29</sup>. This is most likely due to an increase in R<sub>ionic</sub> since a diffusion of water from the electrode to the membrane is known to occur. This was also seen in both CCEs, but the 15 at% TEBS loading had a lower resistance indicating a lower increase in R<sub>ionic</sub> when compared to TPS due to the higher ion conductivity of TEBS. This also implies that there is a lower water concentration gradient and AWR is not being observed at the same extent as is seen with TPS. The higher resistance observed with a 20 at% TEBS loading

indicates that the latter may not be the case, and that there is a larger  $R_{electronic}$  contribution since increasing the TEBS loading also led to an increase in  $R_{\Sigma}$  in the initial EIS data in section 4.2.2. The electrode resistance observed in Nafion does not show a great increase when compared to the CCEs which indicates AWR is not as extensive as with CCE cathodes, and as a result both  $R_{ionic}$  and  $R_{electronic}$  are both lower.



Figure 4.25: Comparison of a) limiting capacitance, b) total electrode resistance, and c) membrane resistance for 15 at% and 20 at% TEBS-based, TPS-based and Nafion-based electrodes in various RH conditions with cell temperature of 80 °C, H<sub>2</sub> anode feed, and N<sub>2</sub> cathode feed.

The resistance associated with the membrane is a better indicator in the direction the water is moving in the electrode. The comparison of the membrane resistance for each electrode is seen in Figure 4.25c where the CCEs had a generally lower membrane resistance when compared to the Nafion-based electrode. The low resistance at lower RH implies that there is enough water present in the membrane to allow ion transport from the anode to the cathode when the CCEs are used. This confirms that AWR is being observed and the diffusion of water from the cathode to the anode is occurring, especially when TPS is. When both TEBS-based electrodes are compared to TPS, a slightly higher resistance is observed. This demonstrates that TPS is a more hygroscopic material that can retain water at lower RHs and diffuse it to the membrane to allow ion transport, and this is not the case with TEBS even though it has better ion conductivity than TPS.

From the results obsvered it can be concluded that TEBS is not as hygroscopic as TPS and thus is less effective at very low cathode RH. However, TEBS is more hygroscopic than Nafion and can retain water down to approximetly 40% RH. The actual TEBS loading does play a role in the materials hygrospicity and allows the permeability of oxygen to increase, but only to a certain extent. As was seen with sPEEK-based CLs the increased sulfonation aids in the increase of proton conducitvity from 5 at% to 20 at% TEBS, but increasing the sulfonation too much can start to increase the electronic resistance<sup>21</sup>. The increased performance of the fuel cell with a lower TEBS loading may also confirm the thought of 40 wt% total silane with the TEBS/TEOS system may be too resistive and as such lower total silane loadings have to be used.

# Chapter 5: Conclusions & Future Directions

## 5.1 Conclusions

For this project the sulfonated silane in a CCE for fuel cell applications that was previously studied by Eastcott and Easton, was replaced with a more ionically conductive sulfonated silane. Monolith CCEs were fabricated using 3-(trihydroxysilyl)-1-propane sulfonic acid (TPS) and tetraethylortosilicate (TEOS) in a 5 at% TPS to 95 at% TEOS ratio with a total silane loading of 40 wt%, similar to that used by Eastcott and Easton. TPS was then replaced by 4-(2-(trichlorosilyl)ethyl)benzenesulfonyl chloride which upon hydration converts to 4-(2-(trihydroxysilyl)ethyl) benzenesulfonic acid (TEBS) using the same wt% silane loading and at% as TPS. The electrodes were characterized by SEM and TEM to observe their surface characteristics. It was determined using SEM that at low magnifications the TPS had more of a smooth surface when compared to the other electrodes, while the TEBS showed more cracks and glass like imperfections on the surface. TEM showed the coverage of the CCEs with a thin film.

Electrochemical evaluation on the CCEs were conducted and compared to the standard 20% Pt/C containing Nafion in a half cell. The CV data collected showed that the TEBS electrode had the largest ECSA, while EIS demonstrated that TEBS had a similar  $R_{\Sigma}$  value as PE20 indicating similar ion transport in the electrode. The TPS/TEOS electrode resulted a longer Warburg length in comparison to the other electrodes which resulted in a larger  $R_{\Sigma}$  leading to the belief that ion transport is slower with TPS because of the lower ion conductivity. EIS also helped to show that TPS/TEOS was more porous than the other electrodes as observed by larger electrode capacitance, but the differences in microstructures could not be observed with BET surface area analysis due to the mesoporous limitation of the analyzer.

The electrochemical evaluation of the catalyst layers in the full cell showed that TPS had better electrochemically active surface coverage than TEBS while the half-cell measurements showed the opposite result. This discrepancy was associated with the different methods of deposition where half-cell measurements used monolith inks that were air dried in large blocks before deposition on the glassy carbon electrode. The full cell electrode fabrication involved spray deposition of thin layers of partially gelled CCE materials that were subsequently allowed to dry on the electrode surface. EIS data collected in the full cell agreed with the half-cell measurements and aided in showing that TEBS was less porous than TPS though a higher capacitance, however, this capacitance was higher than the Nafion containing electrode demonstrating that it has a higher porosity than the standard electrode. The resistance data also agreed with the half-cell measurements showing that TPS had lower ion conductivity resulting in a higher  $R_{\Sigma}$  value.

Performance tests at various RHs was performed and compared between each electrode. Polarization curves showed that at high RH Nafion performed the best while both CCEs were prone to flooding. This was also observed by Eastcott et. al. when TPS/TEOS was used and also indicates that TEBS has a higher hygroscopicity than Nafion, but not to the same extent as TPS/TEOS<sup>29</sup>. When compared in dry conditions TEBS/TEOS showed poor performance with high activation losses indicating poor oxygen reduction kinetics. The decreased kinetics was caused by poor water retention as a result of insufficient sulfonation. The reduced sulfonation caused reduced gas permeability and also reduced ion transport needed for fast oxygen reduction kinetics and was also and is supported though the increase in  $R_{\Sigma}$  especially at low RH.<sup>18, 61</sup>. Observing the polarization curves at 40% RH gave the indication that TEBS/TEOS has a morphology more similar to Nafion since the activation losses increased with a decrease in RH for both these electrodes. The resistance data collected through EIS also confirmed that TEBS has limited water retention at low RH and the AWR seen with TPS/TEOS is not as extensive.

The decreased water retention upon increasing the ionic conductivity of the sulfonated silane in the initial CCE demonstrated that another change in morphology in may provide better ion transport, increased water retention, increased oxygen permeability, and simultaneously decrease the electrode resistance. In an attempt to decrease the  $R_{\Sigma}$  within the electrode the total silane loading was decreased from 40 wt% to 30 wt%, and in an attempt to increase the water content and retention for oxygen permeability and ion transport, the TEBS loading was increased between 5 at% and 20 at%. Through BET analysis a small change in surface area was observed when the TEBS loading was increased showing a change in porosity. The decrease in total weight percent at 5 at% TEBS showed a dramatic increase in  $R_{\Sigma}$ , but upon increasing the TEBS loading to 10 at% the value decreased substantially. This was shown to be caused by a large  $R_{ionic}$  value at 5 at% TEBS due to the lower sulfonic acid content in the electrode. A small increase in  $R_{\Sigma}$  was then observed upon further increasing the TEBS loading and this was attributed to an increase in  $R_{electronic}$  indicating TEBS is more electronically resistive than TPS especially when TEOS is added.

In full cell experiments the increased TEBS loading showed an improved performance with an increase in TEBS loading, indicating increased water retention and provided better oxygen permeability. When compared to TPS/TEOS and Nafion flooding was still an issue that caused high mass transport limitations, and also showed TEBS to have an ideal RH at 40%. When each electrode was compared at 40% RH, TPS/TEOS and 20 at% TEBS showed similar performance with similar limiting current densities. However, at lower RHs TPS/TEOS still outperformed TEBS/TEOS and PE20. The change in  $R_{\Sigma}$  with RH collected through EIS showed TEBS/TEOS has comparable values to TPS/TEOS, but due to the higher R<sub>electronic</sub> component at high TEBS loadings there is a higher  $R_{\Sigma}$  at low RH for 20 at% TEBS. The increase in TEBS loading did show a decrease in membrane resistance at 15 at% and 20 at% TEBS demonstrating the presence of AWR at high RH when compared to TPS. However, at low RH 15 at% TEBS had a slightly higher membrane resistance than TPS indicating lower hygroscopicity.

The results obtained have demonstrated that the replacement of the sulfonated silane used in CCE fabrication can alter the performance of the fuel cell. The direct replacement of TPS for TEBS did not show enhanced performance, but upon optimization of the silane ratios the behavior of the two begin to show comparable results. The work has also shown that the alteration of one component in a CCE ionomer (in this case ion conductivity) can have a dramatic influence on the performance, and as such, many factors have to be taken into account in order to use alternative sulfonated organosilanes in a CCE network. It should also be noted that the increased performance when using higher loadings of TEBS was done with a lower total silane loading than what was used by Eastcott and co-workers. To confirm that the total silane loading used is ideal a higher total silane loading with both 15 at% and 20 at% TEBS should be used, but due to time constraints this was not completed in this work.

## **5.2 Future Directions**

Durability measurements with CCE containing with TEBS should be completed and compared with that done with TPS/TEOS by Eastcott and Easton. The increased durability of the electrode under long term conditions outperformed electrodes that used Nafion as the ionomer. If durability tests done with TEBS/TEOS show similar or better durability then work including both sulfonated organosilane materials can also be done. This may include using the TPS/TEOS system on the cathode and TEBS/TEOS on the anode for tests in dry conditions. Using CCEs on both ends of a fuel cell will not only decrease the cost since less Nafion is used, but may also allow the fuel cell to be used exclusively in dry conditions which is not done currently. Accelerated degradation testing is also another method that can be implemented to observe the degradation pathways that not only the carbon material and platinum material can undergo, but also monitor the overall degradation of the organosilane monomer over time. A similar method used by Saleh et. al. can give a better understanding of the contributions the ionomer makes to the observed increase of the electrode resistance<sup>3, 47</sup>.

The determination of permeability for the TEBS/TEOS system was not studied extensively. The use of air did give some information on how the transport of oxygen is facilitated though the ionomer, however, this was only used to observe the overall change in polarization between the two oxidant gasses. Future work on this topic can include the in depth analysis of oxygen permeability with the TEBS/TEOS system, and compare it to the work that has currently been done by Eastcott et. al.<sup>58-59</sup>. The use of various carrier gasses can further separate the difference in diffusion and solubility between each ionomer material and confirm that a low TEBS loading can cause a decrease in the ORR kinetics, which ultimately result in a decreased performance.

The use of TEBS as the sulfonated silane in the organosilane network may not be the only way to increase the performance of the CCE. The structure of TEBS may cause more interactions with the carbon surface than expected, and because of this the orientation of the TEBS monomer may be a factor that has to be taken into account when increasing the performance of the fuel cell. This can be overcome by orienting the sulfonated silane in such a way that it prevents this interaction. Work done by Easton and Pickup showed that grafting the carbon support with a TEBS monolayer required less Nafion to achieve the same performance when compared to unfunctionalized supports<sup>22</sup>. Selvarani et.al. was also able to show that the grafting of carbon supports with phenyl sulfonic acid groups increases the three-phase boundaries, and in turn the overall performance of the fuel cell<sup>64</sup>. Future work can include this functionalization along with the use of the TEBS/TEOS organosilane to increase the three-phase boundaries as well as the water retention. This orientation can also be used with TPS/TEOS and possible require less of the organosilane to be needed in the electrode.

The use of modified versions of both TPS and TEBS could be another way to further improve the behavior and performance of the CCEs. The use of the propyl chain demonstrated that low quantities of the sulfonated ionomer are needed, while the shortening of the chain and addition of the phenyl ring required higher quantities. Since TPS and TEBS are commercially available, new monomer materials would have to first be synthesized in order to be used. One monomer that could be considered in the future is 4-(trihydroxysilyl)butane-1-sulfonic acid which is similar to TPS, except a butyl chain is present. This monomer could demonstrate how the chain length effects the behavior of the CCE and could also give more insight to the differences in performance between TPS and TEBS. The same idea could be applied to TEBS where a propyl chain could be used and may require a quantity similar to that of TPS for ideal electrode behavior. The modification of the chain could also be done in order to get more insight of how ion conductivity effects the performance, where the TPS hydrocarbon chain could be fluorinated to increase the ion conductivity by changing the electron density and make the structure more similar to Nafion. A modification like this could give more understanding on how the introduction of the phenyl ring effects the electrode, and also how the hydrophobicity/hydrophilicity effects the performance of a CCE.

Another modification that can be made to the sulfonated CCE can be the replacement of Vulcan carbon to carbon nanotubes (CNT) which are more resistant to degradation, and can also easily be functionalized with sulfonic acid groups<sup>54, 65</sup>. The removal of the platinum catalyst is another modification that is being explored in the attempt to use the sulfonated CCEs in supercapacitors because if the high surface area. Currently the only data that has been collected has shown that the incorporation of the TPS/TEOS system can increase the charging layer in the CV. The replacement of TPS for TEBS can also be done to this electrode which may allow increased ion transport to the carbon surface and further enhance the charging ability of supercapcitors.

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