Effect of Phosphotungstic Acid in Electrodes on PEMFC Performance at Elevated Temperature and Low Humidity

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ABSTRACT

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The aim of this study was to enhance PEMFC performance at elevated temperatures and reduced relative humidity. Such an improvement will advance the efforts made towards the integration of PEMFC technology with existing transportation systems. Addition of Phosphotungstic acid (PWA) in the Nafion® electrolyte membrane has proven to be a promising approach to address this issue. The same concept has been extended to Nafion® in the electrode layer. Improved fuel cell performance from PWA incorporated membrane and electrodes has been observed by estimating the primary sources of losses contributed by activation losses, ohmic resistance and mass transport limitations of the supplied reactants to the reaction sites.

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CHAPTER 1: INTRODUCTION

Some of the crucial requirements for commercialization of Proton Exchange Membrane Fuel Cells (PEMFCs) are the reduction in cost of operation and manufacture and improvement in the power output of the PEM fuel cell. These limitations can be attributed to several factors, one of which is the operating temperature of the fuel cell [1]. Current technologies employ Nafion® as the proton-conducting membrane [2]. It is also incorporated in the electrode layer to enable proton conductivity, improve catalyst utilization and oxygen permeability [3,4]. However, for Nafion® to have adequate proton conductivity the operating temperature is restricted to 80°C [5-7] and at this temperature, the catalyst is intolerant to CO poisoning [8], which requires ultra-high purification of the fuel fed to the anode, thus increasing the operating costs of the fuel [1]. Also, at 80°C the efficiency of the fuel cell is low due to reduced electrode kinetics [9]. If the fuel cells have to be integrated with existing transportation systems, radiators in these systems have to be large enough to maintain the required temperature of 80°C [9].

On increasing the operating temperature, the power density is increased. Tolerance to CO poisoning is heightened, thus simplifying the reformer based fuel system, making it more cost-effective. However, when Nafion® based fuel cells are operated at temperatures above 100°C, the membrane gets dehydrated, increasing the resistance to proton transfer. According to the transport mechanism [5-7] in the membrane, protons are transported as hydronium ions \([H_3O^+]\). This problem can be addressed by adding a nanocomposite which modifies the properties of the membrane by
creating pathways for shuttling of protons. Proton transfer becomes less dependent on hydration, enabling high temperature operation [10].

Previous work has reported the results of adding heteropolyacids (HPAs) in the membrane matrix [10], among which Phosphotungstic Acid (PWA) was found to be effective in drier environments [10,11]. The possibility of further improvement in high temperature performance by extending this concept to the electrode layer is explored in this study.

The objective of the work is to examine the variation in cell performance caused by the presence of the hybrid composite ionomer in the electrodes and the membrane. This Membrane Electrode Assembly (MEA) is compared with two other MEAs, one with the same composite only in the membrane, and the other is the reference MEA, without the composite in either the membrane or the electrode. Initial investigation was to identify the optimum operating conditions (temperature and humidity) of the hybrid composite MEA. For better understanding of the effect of the composite, MEAs containing different components in the electrode and membrane were prepared and tested at elevated temperatures and low humidity conditions.

Addition of the PWA nanocomposite in the electrode layer resulted in enhanced performance at all operating conditions. Although the highest power output was obtained at a temperature of 80°C and relative humidity of 100%, the effectiveness of the additive was more pronounced at lower RH operating conditions.
CHAPTER 2: LITERATURE REVIEW

The increasing demand for alternative sources of energy has promoted extensive research in fuel cell technology, as they are capable of clean, low noise and efficient generation of power. Among the different types of fuel cells, Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are a viable substitution for Internal Combustion Engines (ICEs) as they fulfill conditions such as high power density, compact size, quick start-up time, and show promise of achieving cost-efficiency [12,13]. Nafion®, a perfluorosulfonic acid ionomer, is the most common choice of polymer in PEMFCs owing to its superior proton conductivity, thermal and mechanical stability [2]. It is also a vital component of the electrode matrix. Ticianelli et al. [3] report a reduction in platinum loading to 10%, which is desirable in terms of cost reduction, by impregnating the electrode with this ionomer. The rationale behind this is that, Nafion® in the electrode layer enables the formation of Triple Phase Boundaries (TPBs) of the three phases; gas, catalyst and ionomer. An increase in the number of such sites, where the three components co-exist is translated as an increase in catalyst activity and transport of ions, resulting in higher cell potential. However, this effect is positive only at low current densities where activation polarization is dominant. At high current densities where polarization is mainly due to mass transfer resistance, the Nafion® present may restrict the flow of gases to the catalyst surface causing a further decrease in potential. Therefore, the amount of Nafion® to be added is optimized [3,4]. Ensuring homogeneity of the ionomer and catalyst distribution in the substrate enhances interfacial compatibility between the electrode and electrolyte layers [14].
Nafion® requires high levels of hydration for transport of protons. Therefore, operating at temperatures above 80°C would dry up the membrane leading to a drop in conductivity [2]. However, operation at current conditions of 80°C poses additional problems. The anode catalyst is susceptible to deactivation in the presence of CO [8,9] which requires high purification of the fuel thus increasing the cost. Also, to replace ICEs in automobiles, the design of the cooling system has to be modified to suit low temperature needs of PEMFC [13].

Several advantages arise at elevated temperatures of operation [15-17]. The kinetics of the redox reactions at the electrodes is enhanced [9]. Achieving water balance in the MEA, which is critical for optimal performance, is also easier [8,18]. The need for saturation of fuel and oxidant is eliminated, making the fuel cell design less complicated [8,13]. To enable the use of Nafion®, at higher temperatures, its properties can be modified based on the understanding of proton transport mechanisms, namely the vehicular mechanism and Grottuss mechanism [2], occurring in the membrane. In the first, the proton attaches itself to a water molecule, which acts as the vehicle and diffuses through the hydrophilic ionic clusters [6] present in the membrane. In the Grottuss mechanism, the water molecules are oriented to form a continuous pathway between the ionic clusters, and the proton migrates by ‘hopping’ from one molecule to the other. In both cases, hydration of the membrane is essential for suitable proton conductivity [7]. To address this issue, it is suggested that doping the membrane with a heteropolyacid enables proton transport at low levels of hydration [18,19]. The molecular structure of HPAs indicates that they exist as hydrates due to presence of waters of crystallization.
According to Ramani et al. [10], these water molecules can form bridges between ionic clusters facilitating proton transport even when Nafion® is not completely hydrated. However, the size of the additive particle has to be in the same range as that of the clusters, which are nanometer sized [6], to create bridges between them. When particle dimension exceeds the cluster size, HPAs are dispersed in the medium as a separate phase without any contribution to proton conductivity [10].

Different types of HPAs such as Phosphotungstic acid (PWA), Silicotungstic Acid (SWA), Phosphomolybdic acid (PMA) and Silicomolybdic acid (SMA) were tested as polymer additives in a previous study [10]. All the mentioned composite membranes showed better thermal stability as verified by TGA analysis. The distribution of PWA composite in the membrane was examined by SEM and found to be uniform, but the size of the PWA clusters was in the range of $10^{-6}$ m and a modification in the casting procedure was recommended to attain reduced particle size. Cyclic Voltammograms (CVs) of the different composite membranes revealed the stability of the additives. The CVs of molybdenum-based membranes were devoid of a distinct double layer region due to the presence of accompanying peaks, recognized as the resultant of molybdenum-polyanion redox reactions. It was inferred that the molybdenum tends to get accumulated in the catalyst layer by separating out from the membrane. The reviewed paper [10] concluded that tungsten based additives are better stabilized as a composite than the molybdenum heteropolyacids and the particle size should be restricted to nanometers.

Mahreni et al. [11] have also demonstrated the stability of Nafion/PWA composite membrane at relatively higher temperature and drier environment. The
membrane fabrication procedure described in their paper was adopted for this experiment. The optimum composition of Nafion®: TEOS: HPA was 85.67:12.85:1.48 (wt %) as substantiated by physico-chemical characterizations and comparison of internal resistances at different additive concentration [11]. Addition of higher SiO₂ quantities (product of TEOS hydrolysis) increased the brittleness of the polymer by forming a separate network of SiO₂ instead of being distributed as individual particles attached to the ionomer [21]. To ensure that the optimum filler quantity that was added was incorporated as nanoparticles among the ionic clusters in the membrane, the sol-gel method was selected in [11]. As per the reference [21], incorporation of membranes with sol-gel derived nanometer size particles reinforces their mechanical and structural properties making them suitable for PEMFCs. In one procedure for fabrication of the “hybrid” membranes, the polymer solution was used as the substrate for the sol-gel reaction of an alkoxide catalyzed by an acid or base. The resulting membrane from casting the solution was verified by physical characterizations to be a uniform dispersion of the nano-composite particles, which adhere to the ionic clusters [21]. The sequence of the reaction as outlined in Mahreni et al. [11] was also along these lines; TEOS was first hydrolyzed in an aqueous solution by the acid catalyst and the silanol (≡SiOH) groups from this reaction formed hydrogen bonds with the H⁺ of Nafion® and simultaneous ionic bonds with the negatively charged PWA ions. This mechanism signified that the additives were bonded at a molecular level in the nanometer scale and are not just mixed as separate phases at the macro level. Thus, leaching of PWA was less likely to occur assuring that this was the suitable method of additive dispersion. The other secondary
practices in their procedure [11], such as recasting the membranes from a solution of DMF and annealing at higher temperatures were found to dictate the structural characteristics of the membrane. Nafion® cast from DMF was known to render the membranes insoluble to polar solvents as opposed to the ones cast from isopropanol solution [22]. Annealing at 140°C enabled cross-linking and improved the mechanical and chemical stability by altering the arrangement of bonds in the ionomer [22]. Thus, the optimum weight ratios of the additives and appropriate casting procedure were selected.

Apart from using HPAs as additives in Nafion®, several HPAs have also been investigated to replace Pt as the cathode catalyst [23] as they have been promoted as good proton conductors with catalytic properties on the redox reactions [17,23,24]. The use of HPAs as catalysts revealed huge activation losses; the maximum current density obtained at 0.2 V was 256-335 mA/cm² [23]. Although the OCP for these MEAs was between 0.646 V to 0.797 V, the current was generated only from 0.45 V, establishing that HPAs cannot be substituted for Pt. As an extension of this result, incorporating HPAs as catalysts in the electrode layer can lead to severe activation losses. In this context, the function of HPA that can be exploited is its high proton conductivity. PWA has higher proton conductivity than a similar HPA, phosphomolybdic acid (PMA) which serves as a more active redox catalyst, but demonstrated to catalyze undesirable redox reactions at the electrodes [10]. Having justified the choice of PWA/TEOS composite to enhance proton conductivity of Nafion® at elevated temperatures and low humidity and based on the knowledge that Nafion® is an essential ingredient in the electrode as well, it is expected that adding HPA/TEOS to the electrode is required boost overall performance.
CHAPTER 3: EXPERIMENTAL SECTION

3.1 Materials for the preparation of the membrane:

Nafion® (5% wt solution from Du Pont, DE 521), Phosphotungstic Acid (PWA, H₃PW₁₂O₄₀·xH₂O, reagent grade obtained from Sigma Aldrich, FW 2880.05), Tetra Ethyl Ortho Silicate (TEOS, Si(OCH₃)₄, obtained from Sigma Aldrich, ≥ 99%, FW 208.33), N,N-Dimethylformamide (DMF, (CH₃)₂NC(O)H A.C.S reagent obtained from Sigma Aldrich, ≥ 99.8%, FW 73.09), Sulfuric Acid (H₂SO₄, A.C.S reagent obtained from Sigma Aldrich, 95-98%, FW 98.08), Hydrogen Peroxide (H₂O₂, obtained from Fisher Scientific, 3% certified, F.W. 34.01)

3.2 Materials for the preparation of the electrodes:

Unless otherwise mentioned, materials used were from the same stock used for membrane preparation. Platinum, nominally 40% on carbon black (obtained commercially from Alfa Aesar), Isopropanol (Fisher Chemicals, certified, FW 60.10), Nafion®, PWA and TEOS.

3.3 Preparation of the MEA:

Three categories of MEAs were assigned to study the effect of the hybrid composite electrodes. They were prepared with the following membrane and electrode components given in Table 1.
Table 1. MEA components

<table>
<thead>
<tr>
<th>MEA-designation for each category</th>
<th>Membrane component(s)</th>
<th>Electrode component(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA-1</td>
<td>Nafion®/TEOS/PWA</td>
<td>Pt/C/Nafion®/TEOS/PWA</td>
</tr>
<tr>
<td>MEA-2</td>
<td>Nafion®/TEOS/PWA</td>
<td>Pt/C/Nafion®</td>
</tr>
<tr>
<td>MEA-3</td>
<td>Nafion®</td>
<td>Pt/C/Nafion®</td>
</tr>
</tbody>
</table>

All Nafion® and Nafion®/TEOS/PWA membranes were cast in-house; membranes for MEA-1 and MEA-2 were prepared as per the procedure described in Mahreni et al [11] as follows. Approximately 11 ml of the as received Nafion® solution was kept at room temperature until the solvent was expelled. 0.5 g of the Nafion® residue obtained was re-dissolved in an appropriate amount of DMF to give 5 wt% of solution. Separately, PWA was dissolved in de-ionized water and TEOS was added in the ratio given in [11], sonicated, and mixed with Nafion® solution again in an ultrasonicator for 6 hrs. After keeping this solution standing for 24 hrs at ambient temperature, it was cast at 80°C for a period of 2 hrs and annealed for 10 hrs at 140°C. The prepared membrane was pre-treated by boiling at 80°C in 3% H$_2$O$_2$ (30 mins) to eliminate organic impurities and then in 0.5M H$_2$SO$_4$ (40 mins) to get rid of metallic impurities [19,25]. The excess acid was washed off by boiling the membrane in de-ionized water. The membrane for MEA-3 was cast using a similar procedure, excluding the preparation and addition of PWA/TEOS. The thickness of the cast membranes was 48 ± 7 µm. The electrodes were deposited onto the membranes from an ink mixture comprising of 40 wt% Pt/C, de-ionized water, isopropanol, and Nafion® or the Nafion® composite with PWA/TEOS in the case of MEA-1. As given in a previous publication [14], 0.5 g of 40 wt% Pt/C was
wetted with 3 ml of de-ionized water and mixed for 1 min in an ultrasonicator to make a paste. 7 ml of isopropanol was added to serve as a dispersing medium. Following this was an addition of 5 wt% Nafion® solution in the quantity of 30 wt% with respect to the amount of carbon in the mixture. The proportion of ingredients as indicated created an ink mixture with viscosity suitable for spraying. The catalyst ink for MEA-1 was a mixture of the solvents and Pt/C catalyst with weight ratio of Nafion®: TEOS : PWA, as 85.67:12.85:1.48 (wt%), in order to maintain the percentage of the three components identical to that of the membrane. Appropriate substances were added to prepare the inks for corresponding MEAs as specified in Table 1. MEAs were fabricated [14] by directly spraying the ink on the cast membrane, using an airbrush (Badger Airbrush: 155-1) and isopropanol from the sprayed ink was evaporated by exposing to an IR lamp. The loadings of the cathode were maintained around 0.4 mgPt/cm² and that of the anode was about 0.2 mgPt/cm² to 0.3 mgPt/cm². The MEA was then hot pressed [25] (simultaneous application of pressure and heat) in a hydraulic press, at 5000 psi and 120°C for 2 mins to ensure proper attachment of the electrodes with the membrane [25]. The prepared MEAs were then assembled in the fuel cell hardware as described below.

3.4 Cell assembly and testing procedure

Each MEA with 5 cm² surface area of electrode was sandwiched between gas diffusion layers, whose basic function is to direct the flow of gases to the electrode surface uniformly. This assembly was placed between Teflon gaskets exposing only the electrodes to ensure that there is no room for leakage of gases. On either sides of the MEA, were graphite bipolar plates with serpentine flow channels, which serve two
purposes: directing the reactant flow over the electrode surfaces and providing electrical contact between the MEA and current collectors. The assembled fuel cell was then connected to the Fuel Cell Test Station 890CL (Scribner Associates Inc.). The humidified fuel and oxidant gases were fed to the fuel cell. The complete operational set-up is presented schematically in Figure 1 and the diagram of the fuel cell set-up is shown in Figure 2.

Figure 1. Schematic representation of gas flow to the fuel cell (adapted from [26]).
The essential electrochemical techniques such as study of polarization losses, voltammetric techniques and Electrochemical Impedance Spectroscopy (EIS) were conducted to evaluate the performance of the MEAs. The experimental set-up and analysis approach for each type of the recorded data are outlined in Chapter 4.
CHAPTER 4: ANALYSIS TECHNIQUES

4.1 Polarization losses

The decrease in output voltage from the theoretical value (determined by Nernst equation (17)) over a range of current densities is due to polarization losses. A detailed description of polarization losses and the evaluation of data are given in Chapter 5 (Assessment of Performance losses in PEMFCs by Polarization Models). Polarization data was obtained using fuel-oxidant combinations of H2-O2 and H2-Air; with flow rates of 0.2 l/min. Operating temperature of the fuel cell ranged from 80°C to 100°C (Table 2) and Relative Humidity (RH) of the inlet gases was varied as 100-75-50% at each cell temperature by adjusting the temperature of the spargers containing water. Relative humidity (RH) at a temperature $T$ is calculated as

$$RH \, (\%) = \frac{P_{H_2O}}{P_{H_2O}^s(T)} \times 100 \tag{1}$$

where $P_{H_2O}$ is the partial vapor pressure of water in the feed stream and $P_{H_2O}^s(T)$ is the saturated vapor pressure and is a function of temperature [27].

The feed gases are saturated at the sparger temperature ($T_{RH}$) prior to entering the cell which is maintained at temperature ($T_{FC}$). The approximate relative humidity achieved by regulating the temperatures of the cell and spargers is indicated in Table 2. On comparing the polarization characteristics of the MEAs at different operating conditions, the effect of added components can be understood.
Table 2. Relative Humidity (RH) of the feed streams for the cell temperature (T_{FC}) and sparger or humidifier temperature (T_{RH}).

<table>
<thead>
<tr>
<th>T_{FC} (°C)</th>
<th>80</th>
<th>80</th>
<th>80</th>
<th>90</th>
<th>90</th>
<th>90</th>
<th>90</th>
<th>100</th>
<th>100</th>
<th>99a</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_{RH} (°C)</td>
<td>63</td>
<td>73</td>
<td>80</td>
<td>68</td>
<td>73</td>
<td>83</td>
<td>90</td>
<td>82</td>
<td>92</td>
<td>99a</td>
</tr>
<tr>
<td>RH (%)</td>
<td>50</td>
<td>75</td>
<td>100</td>
<td>40</td>
<td>50</td>
<td>75</td>
<td>100</td>
<td>50</td>
<td>75</td>
<td>100</td>
</tr>
</tbody>
</table>

a At 100%RH, the maximum temperature that could be set for the humidifiers was 99°C.

Before recording the data, the MEA was humidified by maintaining a potential of 0.65 V for over 3 hrs till the current and resistance reached steady values [28]. The polarization data for the test MEA was recorded by scanning current from 0 A to the current achievable at 0.2 V, at steps of 0.1 A and holding for 30 secs at each current value. The scan was programmed to terminate when the attained potential reached 0.2 V. The plots of potential versus current density from this procedure are shown in Figures 12 to 14 of Chapter 6 (Results and Discussions) along with the inferred results.

4.2 Voltammetric techniques

4.2.1 Background

An electrochemical reaction takes place with the transfer of electrons between the electrodes and species followed by chemical conversion to form products. For the reaction to occur, the energy barrier, typical to any reaction, has to be overcome. This energy is provided by applying a potential; the reaction ensues, electrons are generated and transferred through the external circuit as current [29]. The current produced in an electrochemical reaction is proportional to the electrode surface, the concentration of the reactant at the surface and the rate constant [30]. The rate constant is found to be an
exponential function of the applied voltage. Therefore, changing the applied voltage or the concentration affects the current produced.

Voltammetric techniques use this knowledge in several ways such as to understand the mechanism of the electrochemical process, to detect presence of species, characterizing the electrode surface and to estimate the crossover of the reactants. In these techniques, voltage is applied to the electrode surface and the current response is recorded. Among the methods applicable, Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV) are employed to gauge the performance of the electrode. The drawback with the use of this method for platinum dispersed carbon electrode is that, the double layer charging and redox reactions due to the carbon substrate may conceal the true Pt activity. Also, the maximum switching potential cannot exceed 1 V as carbon oxidation may occur with carbon based electrodes [3].

4.2.2 Experimental set up for LSV and CV

The data was collected for the three MEAs at the same operating conditions employed for polarization analysis i.e. at temperatures 80°C, 90°C and ~100°C, and each temperature at RHs of 50%, 75% and 100%. The instrument used to control the potential was a Solartron Electrochemical Interface (Model no. SI 1287) and was interfaced with the computer using a GPIB. For LSV, the potential was scanned from 0 to 0.8 V at a rate of 2 mV/s, with H₂ at the anode and N₂ at the cathode at 0.2 l/min [31]. The experimental set up for CV was the same as that of LSV, except that instead of a single forward scan, the voltage was cycled several times forward and backward between the two switching potentials [32].
4.2.3 Linear Sweep Voltammetry (LSV) analysis

LSV is exploited to detect the crossover that occurs by permeation of hydrogen or conduction of electrons through the membrane, both of which result in the loss of current. In addition to decrease in the Open Circuit Potential (OCP), the negative effects of crossover include formation of peroxide radicals from the interaction of H₂ and O₂ in the presence of Pt. These species, being highly reactive, facilitate MEA degradation and pinhole formation [33]. LSV is a single scan of the cathode (the working electrode) between two potentials at a chosen scan rate to monitor the current produced. Nitrogen was purged at the cathode while hydrogen was purged at the anode. On applying the load, the hydrogen that had crossed over to the cathode oxidized to produce current. Based on the current produced, the crossover was determined from equation (2),

\[
\dot{N}_{H_2} = \frac{i_X}{nF}
\]  

(2)

where \( \dot{N}_{H_2} \) (moles of H₂/s.cm²) is the hydrogen flux and \( i_X \) (mA/cm²) is the current produced from LSV; \( n \) is the number of electrons for H₂ oxidation and is equal to 2, F is the Faraday’s constant. The scan rate also regulates the current generated by altering the thickness of the diffusion layer that restricts the amount of gas reaching the surface. At faster rates, the thickness of the layer is reduced allowing the species to access the electrode surface more easily. On the other hand, when the rate of change of voltage is very low, the molecules have more time to reach the electrode surface and undergo reaction. LSV is mainly applied in this study to understand the extent of crossover, so lower scan rates are exercised to ensure that all the crossed over species can react. As the
reduction potential is approached, the species are oxidized/reduced producing current. This current is distributed about the reduction potential resulting in flatter peaks as compared to those obtained at higher scan rates [34].

4.2.4 Cyclic Voltammetry (CV) analysis

Cyclic Voltammetry is conducted to determine the Effective Catalyst Surface Area (ECSA) of the electrode. In this method, the potential of the working electrode (i.e. the cathode in this case) is cycled between two fixed values in both the forward and backward direction and a plot of current as a function of voltage (cyclic voltammogram) is obtained [35]. As the potential is changed, certain electrochemical reactions are favored at corresponding voltages as the energy barrier is crossed. The generated current for the occurring reactions is exhibited as peaks in the voltammogram; the position of the peak indicates the oxidative-reductive species while the height and area of the peak indicate the active surface area [33].

In CV, the voltage is scanned at a relatively faster rate in comparison to LSV. Since the voltage is suddenly increased to the reduction potential, the reactant molecules near the electrode surface are instantly reduced. They produce a relatively large value of current, which is reflected as a peak at this potential in the voltammogram [34]. If the scan rates are too high, the actual reduction potential might be skipped, leading to flatter peaks appearing around the standard reduction potential of the molecules.

To determine the activity of the Pt catalyst, in-situ Cyclic Voltammetry is conducted in which the anode is taken as the pseudo-reference electrode and the cathode is the working electrode [36]. Nitrogen is fed to the cathode side and hydrogen to the
anode; Solartron potentiostat interfaced with a computer was used to perform and record the cyclic voltammogram. A typical voltammogram is shown in Figure 3. The potential is swept from 0 to 0.8 V for the forward scan at 50 mV/s scan rate during which hydrogen desorption from platinum takes place as per the reaction,

$$\text{Pt-H}_{\text{ads}} \rightarrow \text{Pt} + \text{H}^+ + e^-$$

During the reverse scan, hydrogen adsorption takes place in the direction opposite of the above reaction. The peak current densities observed between 0.1 V to 0.3 V refer to hydrogen desorption in the forward scan and the adsorption peaks occur between same potentials in the reverse scan. By calculating the area under the peaks (Figure 3), the ECSA can be determined from the following equation (3) [35]

$$\text{ECSA} = \frac{Q_{Pt}}{\Gamma \ast L} \quad (3)$$

where ECSA (cm$^2$/mg Pt) is effective catalyst surface area, $Q_{Pt}$ ($\mu$C/cm$^2$) is the charge density, $\Gamma$ ($\mu$C/cm$^2$ Pt) is the charge necessary for the reduction a single layer of protons adsorbed on Pt is taken as 210 [35] and $L$ (mgPt/cm$^2$) is the Pt loading in the cathode.
Figure 3. Typical cyclic voltammogram depicting the shaded area as the charge associated with hydrogen desorption (adapted from [36]).

4.3 Electrochemical Impedance Spectroscopy (EIS)

4.3.1 Background

Reactions at the electrode in a PEMFC proceed in a series of steps i.e. transfer of reactants to the electrode surface through the built up double layer (mass transfer resistance and capacitance), exchange of electrons between the electrode and charged species (charge transfer resistance), and proton conduction through the membrane and electronic conduction through the external circuit (ohmic resistance). The effect of these individual processes can be isolated by Electrochemical Impedance Spectroscopy, a diagnostic tool, which takes advantage of the step-wise occurrence of the electrochemical reaction [37]. Impedance can be measured both ex-situ and in-situ, of which the latter is
more appropriate to study the fuel cell as a system. In *in-situ* method, anode is taken as both the counter and reference electrode while cathode is the working electrode. The drawback of this method is that the effect of the two electrodes cannot be differentiated. The anode effect is usually taken to be negligible relative to the cathode because the kinetics of H\(_2\) oxidation are better and the diffusion of H\(_2\) to the reaction sites is easier due to its molecule size [35]. Thus, the major contribution to losses occurs at the cathode and this technique can be applied to estimate these losses.

The principle behind this technique is explained as follows. For a particular voltage applied to a fuel cell, the current yield is determined by the total impedance of the system. It is a combination of the resistances associated with the processes occurring in the system, which have unequal rates. To segregate the influence of these differently paced processes, the voltage is perturbed at different frequencies from as high as 1MHz to a minimum of 0.01 Hz. The current produced at high frequencies is due to the fast processes and at low frequencies it is a feature of the slow processes [33]. The current response is used to evaluate the frequency dependent impedance. To ensure that the steady state of the system is not greatly disturbed, the amplitude of the sinusoidal perturbation signal is lower than the thermal voltage [33] and is usually 5 mV to 15 mV [33,37]. This is the potentiostatic mode, in which a Frequency Response Analyzer (FRA) supplies a sinusoidal AC voltage superimposed on DC voltage and the output current reveals the impedance spectrum [37]. In a similar way, if current is perturbed with an AC signal and voltage response is recorded, it is the galvanostatic mode. The spectrum obtained from the measurement separates the contributions of electrolyte resistance,
charge transfer resistance, capacitance of the double layer and the mass transfer resistance [37]. This impedance data is interpreted by developing an equivalent electric circuit that imitates the performance the cell when the same voltage signal is applied.

The various types of hindrances can be modeled as combination of elements in the circuit. A widely accepted circuit model for the membrane-electrode units is given by the Randles equivalent circuit, which is shown in Figure 4. $R_{hf}$ is a measure of the ohmic resistance in the cell which is the aggregate of the membrane and electronic resistance of which the latter is less significant. $R_{ct}$ symbolizes the charge transfer resistance and $C_{dl}$ is analogous to the capacitance of the double layer at the junction of the electrode and electrolyte [33]. The losses due to mass transfer are replaced by $Z_w$, known as the Warburg impedance. $Z_w$ is included when the cell performance is controlled by both kinetic and diffusion processes [37].

The ambiguity in this method is that, for each impedance spectrum several equivalent models can be constructed to give the same result. However, by assessing the type of processes in the fuel cell, a fairly precise circuit can be realized [38].
In this work, the purpose of the composite is to reduce the electrode and electrolyte resistance at low humidity and higher temperature. Therefore, by observing the ohmic resistance variation for the three MEAs at the tested operating conditions, the effectiveness of the composite can be established. To eliminate the diffusion effects which are not as relevant, the data was collected near high applied DC potential [39]. At this potential, dominant charge transfer resistance conceals the effect of diffusion controlled processes, eliminating the low frequency arc that is typical of the impedance spectra at lower applied potentials [40-45]. Thus, the equivalent Randles circuit for the spectra obtained at high DC potential (Figure 5) is devoid of the Warburg impedance. As the applied DC potential is increased, the charge transfer is reduced. To confirm that the circuit matches the fuel cell as closely as possible, the capacitor in Figure 4 is replaced by a Constant Phase Element (CPE) [38] in Figure 5.

![Figure 5. Equivalent circuit representing only charge transfer and ohmic resistances (adapted from [41,45]).](image-url)
The CPE is a more generic representation of impedance with parameters that can account for the non-ideal behavior of the analogous electric units. The impedance of the constant phase elements is given by

\[
Z_{CPE} = \frac{1}{q(i\omega)^{\hat{n}}}
\]

\(\hat{n}\) is between 0 to 1 and depending on its value the physical significance of \(q\) is established. A quick understanding of the relation between \(\hat{n}\) and \(q\) is given in [38]. When the CPE behaves like an ideal capacitor, the value of \(\hat{n}\) equals 1 and \(q\) is replaced by the capacitance, \(C\). For \(0.8 \leq \hat{n} \leq 1\), the CPE has non-ideal capacitive characteristics due to rough morphology of the electrode. At lower \(\hat{n}\) values, the CPE is modeled as a resistor or Warburg element accordingly and the details are enumerated in [38]. In this context \(\hat{n}\) is constrained to values between 0.8 and 1, as CPE is used to represent capacitive behavior of the double layer formed at the electrode/electrolyte interface. In real systems, heterogeneous, non-uniform nature of the electrode surface causes it to deviate from purely capacitive behavior [46]; the capacitor is replaced by a CPE [33,47]. It has been validated in [45] that increasing the value of \(q\) decreases the value of real part of impedance at any frequency and decreasing the value of \(\hat{n}\) flattens the arc of the semi-circle and displaces it to higher \(Z'\) values at the same frequencies. [45]

4.3.2 Experimental set-up

In this study, impedance data was collected at atmospheric pressure, with flow rates of \(H_2\) and \(O_2\) at 0.2 l/min. The temperature of the cell was varied from 80°C to 100°C and from 68°C to 100°C for the humidifiers, depending on the required relative humidity at each cell temperature. The instruments used for this experiment were the
Solartron 1260 Frequency Response analyzer (Solartron Analytical) coupled with the Solartron Electrochemical interface, both of which were interfaced with the computer through the GPIB port [31]. The fuel cell was operated in a potentiostatic mode, at a bias potential of 0.8 V superimposed with AC signal amplitude of 15 mV and the frequency was varied from 4000 to 0.1 Hz.

4.3.3 EIS analysis

The equivalent circuit used to evaluate the impedance characteristics of the fuel cell at different temperatures is given above in Figure 5. $R_{hf}$ represents the ohmic resistance, the dominant factor being the resistance of the membrane to proton conduction and is the value of the high frequency intercept on the real axis. CPE replicates the non-ideal double layer behavior at the electrode-electrolyte interface; the charge transfer resistance at the electrode is depicted by $R_{ct}$. These characteristic variables quantify the responses to grasp the nature of inner workings of the cell. Series arrangement is for processes occurring sequentially while simultaneous processes are represented in parallel arrangement of elements [48].

The result of the impedance measurements is depicted as a Nyquist plot, which is a plot of the real ($Z'$) and imaginary ($Z''$) part of the total impedance in the range of frequencies tested. A typical plot is displayed in Figure 6.
Figure 6. Typical impedance spectra obtained at 80°C and 100% RH for MEA-1 at 0.8 V (adapted from [38]).

The intercept of the arc at high frequency is a measure the ohmic resistance of the cell, $R_{hf}$, and width of the arc is the charge transfer resistance, $R_{ct}$. Deviation from ideal capacitive behavior generates a “suppressed semicircle”, which is expressed in the deviation of $\hat{n}$ from 1. The values of the parameters were obtained by fitting using the Zview software. $R_{hf}$ generated from the fit was used to estimate the total ohmic resistance. From the values of $q$ and $\hat{n}$, the capacitance was calculated from the equation (5) [49,50].

$$C^{\hat{n}} = \frac{q}{\left[ \frac{1}{R_{hf}} + \frac{1}{R_{ct}} \right]^{1-\hat{n}}} \tag{5}$$

Subsequently, the charge transfer time constant ($\tau$) can be evaluated as the product of $R_{ct}$ and $C$ [44]. The impedance spectra obtained for this experiment are
presented in Appendix B. The ohmic losses as indicated by $R_{hf}$ and activation time constant ($\tau$) are presented in Chapter 6 (Results and Discussions) in Figure 17 and Figure 23 respectively.
CHAPTER 5: ASSESSMENT OF PERFORMANCE LOSSES IN PEMFCs BY POLARIZATION MODELS

Susmitha Gopu and Anima Bose

(To be submitted to J. Power Sources)

5.1 Abstract

Single cell performances of PEMFC were measured and their performance losses were analyzed based on several established analytical models. As commonly observed, these losses are due to activation, ohmic, and mass transport overpotentials. Four models were used in fitting the performance curves. Three of the models used the same parameters to fit the observed activation and ohmic losses. Among these models, Model-1 exhibited better fit of the three components of performance losses, while Model-2 and Model-3 failed to adequately account for mass transport losses. The flexible nature of two parameters, ‘m’ and ‘N’, in Model-1 makes adjustments for the variable permeability and ionomer conductivity in the electrode layers. Model-4 separates the contribution of electrode and non-electrode components to estimate the losses. Detailed comparative analysis of performance data based on these four models is discussed in the context of nature of the cells, operating conditions, and relative contributions of the individual components of overpotential.

Keywords: PEMFC, data analysis, analytical model, Polarization losses

5.2 Introduction

Proton Exchange Membrane Fuel Cells (PEMFCs) have been considered as promising non-polluting energy devices for transportation [12,51] as well as some
stationary applications [12]. To improve the system efficiency, attempts are being made to understand the processes occurring in PEMFCs. One of the basic measures of cell performance is the polarization curve, a plot of voltage versus current density from which preliminary information on the various losses associated with the cell components can be obtained. However, collecting polarization data is a time consuming process and the contribution of different components to the overall loss in power is not directly discernible, and therefore, mathematical models are employed to identify the sources of polarization losses [52]. Numerous efforts have been made to develop an accurate model to represent the effect of the different factors involved in polarization losses. All the models are based on assumptions made to reduce complexity, sometimes by considering ideal behavior in certain respects. The validity of these assumptions is not justified for all experimental conditions and a calculated choice has to be made to select the appropriate model. In this article, some commonly used models have been compared to fit two sets of experimental data to determine the best choice for representation and to evaluate key parameters such as the Tafel slope, exchange current density, ohmic resistance and mass transfer resistance. A brief explanation of polarization and its causes is followed by a section explaining the use of model for extracting the parameters that are not directly obtained from data.

5.3 Polarization

Polarization [12] is the deviation of voltage over a range of current densities from the theoretical value. The operating conditions such as temperature, pressure and concentration of the reactants control the theoretical value, which is calculated from the
Nernst equation (17). For example, at 80°C and 100% Relative Humidity (RH) of the supplied gases, the ideal voltage is 1.16 V. This value is never achieved due to losses occurring in the fuel cell, some of which are irreversible. The highest voltage is obtained when no current is drawn from the system and is termed the Open Circuit Potential (OCP). The difference between the output voltage and the OCP is labeled ‘polarization’. The difference is called ‘overpotential’ when OCP is compared with the Nernst Potential of the cell [53], although both terms, polarization and overpotential, are usually considered equivalent. Several factors are responsible for these losses and are summarized below.

5.3.1 Types of voltage losses

Overpotentials or polarization losses are divided in three broad categories namely, activation losses, ohmic losses, and mass transfer losses, based on the processes dominating within a certain current density range. They are influenced by several factors including catalyst and membrane properties, their morphology, conductivity of the hardware components and flow rates of the reactants [52]. A typical polarization curve depicting the segregation of current densities annotated with the dominant losses is shown in Figure 7.

5.3.2 Activation losses

The departure of OCP from Nernst potential [52] in conjunction with the additional voltage drop at low current densities is collectively referred to as activation polarization. This occurs due to slow reaction kinetics. The anodic effects are usually neglected, as they are insignificant compared to the losses at the cathode. The losses are
attributed to reduced catalytic activity [53] and kinetic losses. Some of the kinetic energy of the supplied reactants is utilized by the molecules to overcome the activation barrier to form new bonds in the products. This part of the fuel’s energy becomes unavailable and results in decreased power [52,54]. Activation losses can be minimized by increasing the catalytic activity or the kinetic energy of the fuel, which can be achieved by increasing the operating temperature [52].

5.3.3 **Ohmic losses**

As the current drawn from the cell is increased, the activation polarization becomes steady [35]; the number of electrons and protons generated increases. The resistance to the flow of these charged species in the system causes reduction in current and these losses are categorized as ohmic losses. In this region, the relationship between current and voltage follows Ohm’s law [52,54]. The magnitude of the ohmic resistance includes resistance to the flow of protons and electrons by the fuel cell components such as end plates, flow fields, gas diffusion layer and electrode and membrane layers [52].

5.3.4 **Mass transport losses**

When higher currents are drawn from the cell, the ohmic losses stabilize; the rate of reactant consumption and product generation at the electrode surface increases. If the diffusion of the reactants to the catalyst surface and removal of products from the electrode do not match the rates of the reaction, a concentration gradient develops between the bulk region and electrode surface. It leads to a rapid fall in the output voltage at high current densities due to inefficient supply of reactants to the electrode surface. This diversion from OCP is termed as mass transfer overpotential [52,54]. It is reduced
by increasing operating pressure, increasing electrode surface area, and using thinner electrodes [52].

![Typical polarization curve showing the occurrence of the typical losses at different ranges of current densities; data obtained at 80°C and 100% RH of the H₂ and O₂, at flow rates of 0.2 l/min and 1 atm pressure. (redrawn from [52]).](image)

**Figure 7.** Typical polarization curve showing the occurrence of the typical losses at different ranges of current densities; data obtained at 80°C and 100% RH of the H₂ and O₂, at flow rates of 0.2 l/min and 1 atm pressure. (redrawn from [52]).

### 5.4 Use of polarization model in system analysis

As explained in Section 5.3, the output voltage and hence, the power of a fuel cell is dependent on multiple factors. It is not feasible to test the separate or compound effects of all of these factors. A more practical solution would be to develop mathematical expression that can explain the influence of these parameters on the total polarization. In this context, the purpose of employing a mathematical model is to quantify the performance in terms of variables that represent the physical processes occurring in the system [55]. The drawback is that it is difficult to find the exact equation that will
duplicate the real system as all the experimental errors and non-idealities have to be taken into consideration. However, a very good approximation of the existing system can be achieved through a reasonable set of assumptions based on the understanding of the processes occurring in the fuel cell. The relevance of a model can be verified by comparison with experimental data. The verified model can be used to calculate parameters that cannot be explicitly derived through experiments [52]. The various categories of the developed models and the benefits and limitations of the fuel cell models are more comprehensively explained in [55].

5.4.1 Models for polarization curve

Among the several analytical expressions that have been developed to describe the polarization curve, four commonly adopted models were examined and are briefly described. The semi-empirical model or Model-1 was one of the first attempts to represent the polarization model for the entire current density range [56]. Model-2 [57] and Model-3 [58] are extensions of Model-1 but replace the empirical terms that describe mass transport losses with more meaningful parameters. The difference between experimental data (obtained in this study) and fitted data from each of these models is shown in Figure 8. Model-4 [53] is outlined and compared with the experimental data individually as the model formulation and analysis is more detailed although the basic concept is the same. It delineates each of the three broadly classified losses into electrode contributions and non-electrode contributions.
5.4.2 Semi-empirical model (Model-1)

The semi-empirical model (designated as Model-1 in this study) describes the polarization curve by a semi-empirical equation (6) [56]

$$E = E_r - b \log \left( \frac{i}{i_0} \right) - R_\Omega i - m \exp(Ni)$$

(6)

$E$ (V) is the experimental voltage, $E_r$ (V) is the reversible potential of the cell calculated from Nernst equation (17), $i$ (mA/cm$^2$) is the experimental current density, $i_o$ (mA/cm$^2$) is the exchange current density, $b$ (V/decade) is the Tafel slope calculated for $i \leq 100$ mA/cm$^2$, $R_\Omega$ (ohms-cm$^2$) is the ohmic resistance of the cell, $m$ (V) and $N$ (cm$^2$/mA) are empirical terms representing mass transfer losses. This model has been used as a preliminary evaluation tool for quantifying the losses in numerous studies. (see [11,25,44,59-61]). Equation (6) is the theoretical potential minus the activation, ohmic and mass transfer losses. The relationship between the overpotential and current density in the activation controlled region is described by the Tafel equation (equation (7)) assuming concentration polarization effects are negligible and it is given by

$$\Delta E = b \log \left( \frac{i}{i_0} \right)$$

(7)

$\Delta E$ (V) is the overpotential due to activation losses only, $i$ (mA/cm$^2$), is the experimental current density, $i_0$ (mA/cm$^2$) is the exchange current density. The exchange current density is the current ‘shuttled’ between the two electrodes when the cell is operating reversibly [62] and is influenced by electrode and catalyst properties [63]. Higher exchange current densities are due to a higher rate of the reaction and better catalytic activity [63]. The Tafel slope signifies the initial steep decrease in potential and high
values imply reduced kinetics, high resistance to oxygen transport at the cathode, changes in the rate-controlling step of the electrochemical reaction, among other factors. [64].

The ohmic loss in the fuel cell is represented by the term ‘$R_{\Omega} \ i$’ in equation (6). $R_{\Omega} \ (\text{ohm-cm}^2)$ includes the resistance of the membrane, which is greatly dependent on the extent of humidification [2] and hence changes with current density [63]. Sena et al [65] developed an expression for the variation of electrolyte resistance with current density, which controls the water balance in the membrane. During the operation of a fuel cell, the ohmic loss is monitored by the current interrupt technique [35]. In this method the current is interrupted for a less than 10 nano-seconds and the increased value of the voltage is recorded. It is believed that ohmic losses instantly disappear on interruption while the activation losses reduce eventually with the discharging of double layer acting as a capacitor, which occurs over a relatively longer time period. Hence the voltage recorded by the current interruption is devoid of the ohmic losses and the voltage change is considered as the ‘$R_{\Omega} \ i$’ loss. In many cases, the resistance is taken as a constant value to simplify the equation.

Having accounted for activation and ohmic losses, the remaining mass transport losses are given by the constants ‘$m$’ and ‘$N$’. They are estimated to fit the experimental values to equation (6) in the high current density region. The difference between the experimental voltage and the voltage corrected for only activation and ohmic losses is fitted to an exponential curve and the values of ‘$m$’ and ‘$N$’ are determined. The physical meanings of the parameters, ‘$m$’ and ‘$N$’, are given by Bevers et al [66]. The value of ‘$m$’ dictates the point of occurrence of mass transport losses which changes the slope of the
curve. It is understood to be a manifestation of the porosity and tortuosity of the Gas Diffusion Layer (GDL). For low permeability of the GDL, mass transport losses occur at much lower current densities. The GDL permeability changes with the water accumulation and hence ‘m’ varies for different operating conditions even while employing the same GDL.

‘N’ affects the slope of the high current density region only, where concentration polarization losses become dominant as shown in Figure 7. Higher values correspond to steeper curves in this region, resulting in much lower limiting current densities. It was reasoned through simulations that it is indicative of the electrolyte conductivity present in the electrode layer [66]. For poor ionomer conductivity, the effective surface conductivity is compromised and species are not transferred efficiently, leading to reduced current densities. Some numerical results reported in [56] are presented in Table 3 for comparison with experimentally obtained data.

Table 3. Comparison of parameter values from [56] with experimentally obtained data.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>As reported in [56] in Table II at 70°C and 1atm</th>
<th>As reported in [56] in Table III at 60°C and 1atm for O₂/N₂ (90% O₂)</th>
<th>Experimental data at 80°C and 1atm for MEA-1</th>
<th>Experimental data at 80°C and 1atm for MEA-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b$ (mV/dec)</td>
<td>60</td>
<td>54</td>
<td>92</td>
<td>82</td>
</tr>
<tr>
<td>$R_Ω$ (ohm-cm²)</td>
<td>0.259</td>
<td>0.232</td>
<td>0.047 ± 0.005</td>
<td>0.053 ± 0.009</td>
</tr>
<tr>
<td>$m$ (V)</td>
<td>$1.25 \times 10^1$</td>
<td>$1.59 \times 10^{-9}$</td>
<td>$9.40 \times 10^{-3}$</td>
<td>$2.90 \times 10^{-3}$</td>
</tr>
<tr>
<td>$N$ (cm²/mA)</td>
<td>$2.10 \times 10^{-3}$</td>
<td>$2.16 \times 10^{-3}$</td>
<td>$3.60 \times 10^{-3}$</td>
<td>$5.00 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
The value of Tafel slopes in this experiment are about 40-70% higher compared to values calculated for the data obtained in reference [56] while the resistance is reported to be 10 times smaller. It can be deduced that the dominating source of losses in the tested MEAs is from activation polarization. ‘m’ appears to be varying over several orders of magnitude from the order of $10^{-9}$ (V) to $10^{1}$ (V) as presented in [56]. ‘N’ is found to be in the same order of $10^{-3}$ (cm$^2$/mA) as compared to the values reported in [56], but slightly higher.

In conclusion, this model is intuitive, easy to adopt and is useful as an evaluation tool to determine the contribution of different losses. However, the terms ‘m’ and ‘N’ do not signify any particular phenomena and are essentially numerically fitted factors, and for this reason the accuracy of the values cannot be ascertained. They also account for random variation and the losses that have not been taken into consideration, which could explain the wide range of reported ‘m’ values. To sum up, this equation serves best as a fitting equation for obtained data at steady state but is not useful for optimization or for representing non-steady state operation [67]

5.4.3 Thin film model (Model-2)

The second polarization model examined in this study is taken from reference [57] and referred to as Model-2 henceforth.

$$E = E_r - b \log\left(\frac{i}{i_0}\right) - R_\Omega i + b \log\left(1 - \frac{i}{i_{lim}}\right)$$

(8)

$i_{lim}$ is the limiting current density (mA/cm$^2$). The activation and ohmic losses are represented exactly as in Model-1. Although the ohmic resistance changes with the
current density [65], it was considered to be constant as a simplification. The limiting current density introduced here is the maximum value of current that is achieved when the gases at the reacting sites are completely consumed. The mass transport effects are represented by the third term, which was developed based on a set of assumptions stated below. The electrode layer was modeled as a hydrophobic region and an agglomerate region, with the agglomerate consisting of the three phases: carbon, catalyst and electrolyte. The two regions were assumed to be segregated by a thin film of electrolyte [57]. The directions of gas transport in this layer and the current flow were regarded to be perpendicular to each other. The ohmic resistance of the agglomerate layer was presumed to be minimal because the local current generated was found to be a function of concentration of the reactants only. The absence of reverse current was confirmed from the deviation of OCP from equilibrium potential along with very low current in the activation controlled region. The current generated was calculated from the Tafel relation and considered to be a function of the concentration of the reactant. The reactant concentration was taken as the steady state value and a function of agglomerate and electrolyte thickness, diffusion coefficient in the two layers and rate of the reaction. The obtained expression was then simplified for the agglomerate diffusion parameter (defined in Springer and Raistrick [57]) approaching a value near zero. The film diffusion parameter [57] was found to be a ratio of \( i_0 \) (defined in [57]) to \( i_{lim} \) (defined in [68]) when substituted as per the defining variables. Taking all the above into account, the current density as a function of overpotential, \( \eta \), assuming no ohmic losses was given by
Expressing equation (10) explicitly for $\eta$ gives

$$\eta = b \log\left(1 - \frac{i}{i_{lim}}\right)$$

(10)

The mass transport losses represented by equation (10) were combined with ohmic losses and activation losses and the resulting expression for voltage is shown in equation (8). Polarization data as obtained for two MEAs in the present work was analyzed using Model-2; the results are highlighted in Table 4 and for comparison, the results as evaluated in [65] are presented.

### Table 4. Comparison of polarization parameters obtained using Model-2 with experimental data

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Polarization fitting parameters reported in [65] for Nafion® 112 membrane with 100% oxidant at 80°C in air (Table 4)</th>
<th>From experimental data obtained in this study at 80°C and 1 atm for MEA-1</th>
<th>From experimental data obtained in this study at 80°C and 1 atm for MEA-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b$ (mV/dec)</td>
<td>70 - 240$^a$</td>
<td>92</td>
<td>82</td>
</tr>
<tr>
<td>$i_0$ (mA/cm$^2$)</td>
<td>$0.010 \times 10^{-3}$</td>
<td>$0.008 \times 10^{-3}$</td>
<td>$0.005 \times 10^{-3}$</td>
</tr>
<tr>
<td>$R_\Omega$ (ohm-cm$^2$)</td>
<td>0.08$^b$</td>
<td>$0.047 \pm 0.005$</td>
<td>$0.053 \pm 0.009$</td>
</tr>
<tr>
<td>$i_{lim}$ (mA/cm$^2$)</td>
<td>$2.3 \times 10^3$</td>
<td>$1.0 \times 10^3$</td>
<td>$1.0 \times 10^3$</td>
</tr>
</tbody>
</table>

$^a$ Tafel slopes were calculated at different ranges of current density  

$^b$ $R_\Omega$ at $1.2 \times 10^3$ A/cm$^2$ was taken as the constant value
As reported by Sena et al. [65], the three values of Tafel slope calculated for corresponding ranges of current density were used in a different equation, which did not include oxygen diffusion effects. The purpose of listing these results from [65] is to gain insight into the order of magnitude of the estimated parameters. The more appropriate equation (8) employs a specific value of the slope; therefore, a single value was computed for the observed data, for current densities up to 100 mA/cm$^2$ particular to this case. The resistance at 1200mA/cm$^2$ was taken as the constant value in Sena et al. [65], while for MEA-1 and 2; average values are noted for better fitting with the data.

On comparing the fit obtained using equation (8) and the actual polarization data (‘V model-2’ with ‘V exp’ in Figure 8), it was observed that the departure of the model from the data at higher current densities was large and the model equation differed by a factor of 2.5 from the data at high current densities (for both MEAs). This demonstrates that the mass transport losses determined by the model were severely underestimated compared to the actual losses occurring in the electrode indicating major flaw in the assumptions. For the real system, the path of diffusion could be greater than estimated by the model, causing higher concentration gradient across the layer with the result that fewer reactants reach the triple phase boundaries. As a consequence, the current generated is much lesser and the potential drop is greater. The limiting current densities in Table 4 are low reiterating the additional mass transfer losses. Also, there might be residual effect of the ohmic and activation losses in the mass transport limited region.

Recapitulating the above findings, the mass transfer loss terms in this model have a better physical interpretation compared to Model-1. The limiting current density is a
direct representation of the oxygen diffusion effects, in that the maximum value is limited by the inadequate reactant supply. However, based on the fitting results and the above explanation, it can be deduced that before adopting this model, the validity of the assumptions needs to be verified, as it is not applicable for all polarization data. This model has been applied in some studies [4,65,69] and was reasoned to be a logical approach when the mass transfer loss is controlled by the thin film of ionomer bridging the agglomerate region with the hydrophobic domain [4].

5.4.4 Canaday et al model (Model-3)

The third model (Model-3) that was inspected [58], similar to Model-2, replaces the mass transport voltage loss with modified terms. These terms are arrived at by a combination of Fick’s first law of diffusion, limiting current density and Nernst equation (17). However, the implementation of Nernst equation in this context is pertinent only when the concentration polarization is the only type of polarization [62]. In this model, the gases are assumed to behave ideally and the partial pressure of the reacting species at the electrode surface is estimated from Fick’s first law of diffusion. The distance through which they diffuse to the reacting site is taken to be equal to the thickness of the electrode. The rate of diffusion is taken to be a function of porosity, tortuosity and thickness of the electrode. The current obtained is calculated from the concentration of the species that have penetrated to the electrode surface, employing Faraday’s law of electrolysis, which correlates the charge produced with the amount of gases reacting. The current can then be expressed in terms of the limiting current density and partial pressure at the bulk and surface. Finally, the Nernst equation is used to calculate the voltage drop
across pressure gradient of the reactant, and substituting for the pressure gradient in terms of $i_{lim}$, we have

$$V_{conc} = \frac{RT}{nF} \ln \left( 1 - \frac{i}{i_{lim}} \right)$$

(11)

The resulting equation for voltage is

$$E = E_r - b \log \left( \frac{i}{i_0} \right) - R_\Omega i + \frac{RT}{nF} \log \left( 1 - \frac{i}{i_{lim}} \right)$$

(12)

This is another widely accepted model [58,70-72] and in contrast to Model-1, it follows a cognitive approach as supported by the use of physical parameters for mass transport losses. It postulates that at the same operating temperature and pressure, the morphological characteristics, such as porosity and tortuosity of the GDL and electrodes are the controlling factors for mass transport losses. However, as seen in Figure 8, this model shows the highest deviation from the data, and could be corrected by multiplying the last term by a factor of 12.5. The plausible explanations could be that the actual concentration profiles might be more complex than described by Fick’s law or it might be misleading to assume that only concentration polarization effects exist at high current densities. Basically, the moles of gases reaching the reactant surface are much less than predicted by this equation, entailing a steeper drop in the mass transport loss region and the limiting current densities achieved are also less in magnitude than expected. In short, Model-3 is more reflective of the mechanisms at the electrode but the authors suggest that it has to be selectively applied only when other losses are practically inappreciable and when this partial voltage loss concurs with the Nernst equation.
5.4.5 Williams et al model (Model-4)

A separate section has been devoted for the description of this model, designated as Model-4 henceforth, because although the underlying concept applied is similar, the estimation of losses is tackled in a reverse manner. In the previous sections, the key parameters are first calculated by data fitting to assess the losses and subsequently subtracted from the theoretical value to predict the experimental voltage. The predicted experimental voltage is then compared with actual data to gauge the dissimilarity. In this case, the experimentally obtained voltage is corrected in a step wise manner to match the theoretical value. Also, Model-4 gives an extensive dissection of the polarization losses and is adopted in other studies as well [73-76]. The three types of losses are further divided as the contributions of the electrode and non-electrode components to gain a better understanding of the dominant causes [53]. The six losses computed were (i) ohmic overpotential due to the non-electrode components; (ii) ohmic overpotential due to
cathodic resistance; (iii) concentration overpotential due to non-electrode layers such as the flow fields, gas diffusion layers etc; (iv) concentration overpotential in the cathode layer; (v) activation overpotential at the cathode due to sluggish kinetics, and (vi) cathodic activation overpotential due to inefficient activity of the catalyst.

Cell voltage was represented as
\[ V_{\text{cell}} = V_{\text{eq}} - \eta \]  \hspace{1cm} (13)

where \( V_{\text{cell}} \) is the cell voltage obtained experimentally and \( V_{\text{eq}} \) is the theoretical cell voltage calculated by the Nernst equation at the operating temperature and concentration of the reactants and products. \( \eta \) is the total polarization, which is given as
\[ \eta = \eta_{\text{ohm,nonelectrode}} + \eta_{\text{ohm,electrode}} + \eta_{\text{conc,nonelectrode}} + \eta_{\text{conc,electrode}} + \eta_{\text{act,tafel}} + \eta_{\text{activity}} \]  \hspace{1cm} (14)

The assumptions and the series of steps to calculate the losses are briefly given below.

i) \( \eta_{\text{ohm,nonelectrode}} \) is contributed by the resistance of the non-electrode components of the cell and is automatically calculated by the current-interrupt technique [35] by the fuel cell software.
\[ \eta_{\text{ohm,nonelectrode}} = iR_{\text{nonelectrode}} \]  \hspace{1cm} (15)

ii) The \( iR \) compensated voltage is the voltage obtained after correcting for \( \eta_{\text{ohm,nonelectrode}} \) and is plotted as \( V_{\text{corr1}} \) in Figure 10 and Figure 10.
\[ \eta_{\text{ohm,electrode}} = iR_{\text{electrode}} \]  \hspace{1cm} (16)

\( R_{\text{electrode}} \) is calculated assuming constant utilization [54] of \( \text{O}_2 \) at the cathode and first order reduction with respect to oxygen concentration, which is valid at high
current densities. The value of $R_{\text{electrode}}$ is determined by a trial and error procedure such that at a particular value of $V_{\text{corr1}}$, the ratio of current densities obtained using $O_2$ and using air is 4.8 (which is the ratio of mole percent of $O_2$ in pure oxygen and air).

iii) To compute the mass transfer losses caused by the non-electrode components, the current term in the Butler Volmer equation [62] was corrected by introducing limiting current density. This modified Butler Volmer equation is valid when the following assumptions are true. (a) Oxygen diffusing to the cathode obeys Fick’s Law of diffusion, (b) The reduction reaction is first order and follows the Butler Volmer equation.

iv) Tafel slope is used to represent activation losses occurring at the cathode, and the exchange current density in the Tafel equation (7) is replaced by 10mA/cm$^2$, taken as the reference value at which activation losses become prominent.

v) The difference between the Tafel slope and the modified Tafel slope (from the modified Butler Volmer equation) is used to estimate concentration polarization losses occurring in the electrode layer.

vi) The difference between the theoretically calculated value from Nernst Equation and the voltage attained at 10mA/cm$^2$ is assumed to be the loss due to catalyst activity. This was not justified mathematically and hence the reasoning is not completely established.

The implementation of this step-wise procedure for the two MEAs is graphically shown in Figure 10 and Figure 10. The reference value that the data is corrected for is the
Figure 9. Using Model-4 to de-compound polarization data obtained at 80°C and 100% RH with H₂/air at flow rates of 0.2 l/min and atm pressure for MEA-1 containing Nafion® and composite in the membrane and electrodes.
The causes of losses and the percentage for which they are accountable can be easily inferred from the figure above, nevertheless, the inadequacy of this method is explained in the subsequent paragraph.

This analysis can be applied if the current ratio is less than or equal to 4.8 as explained above. A more accurate current ratio can be determined from the log mean average values of the inlet and outlet concentrations of oxygen and air. However, flow-rates of the gases at the outlet could not be monitored due to limitations of data collection. Since the calculated current ratio was found to be greater than 4.8, the trial and error routine to iterate the electrode ohmic resistance could not be completed. The causes
for this nonconformity could likely be that the mass transport effects are significant at lower current densities than expected. Hence, the current obtained with air was less than predicted by the first order oxygen reduction reaction, resulting in a current ratio greater than 4.8. Such situations make this analysis inapplicable. Another circumstance of ambiguity is determination of breaking current density or the current density at which the mass transport losses become significant. There is no fixed criterion to mark this value precisely as it is approximated only by judging from the polarization plot. Based on these accounts this approach cannot be implemented for every set of experimental data.

5.4.6 Conclusion

Some popular model equations for quantifying the losses were applied to find the best fit for obtained polarization data. These models do not strictly duplicate the occurrence of electrochemical processes but are adequate when the sole purpose of the model is to extract the losses in numeric figures for comparative purposes. Among these, Model-1 represented the mass transfer losses with empirical terms, while the other models had variables representative of the experimental data. Since numerous assumptions are made to develop a model, they could not be validated and Models 2, 3 and 4; although more intuitive and provided more useful information, failed to represent the real data. Hence, Model-1 proved to be suitable as it accounted for any unknown sources of losses, experimental errors and uncertainties involved. Models with more rigorous calculations, expressing intricate processes have been developed, some of which are discussed in references [35,57,63,68,77,78]. However, such models have not yet been explored in this study.
CHAPTER 6: RESULTS AND DISCUSSIONS

6.1 Nernst potential

The theoretical potential \( E_r \) that should be obtained at any operating condition is calculated from the Nernst Equation given by

\[
E_r = E^0 - \frac{RT}{4F} \ln \left( \frac{[H_2O]}{[H_2]^2[O_2]} \right)
\]

where \( E^0 \) is the theoretical potential at temperature \( T \) and is calculated from Gibbs free energy change at \( T \), for this electrochemical reaction, considering that water vapor is generated as the product [79]. Equation (17) asserts that \( E_r \) changes with the temperature and concentration of the reactants. The variation in partial pressure of the feed gases at each tested temperature and the calculated Nernst potential is given in Table 5 and Figure 11.
Figure 11. Theoretical values of Nernst potential at the required temperatures and RH calculated for 1 atm. Solid lines depict constant cell temperature and dotted lines connect values at same relative humidity. $T_{FC}$ denotes the temperature of the cell and $T_{RH}$ denotes the temperature set for both the anode and cathode humidifiers to attain the required RH indicated below each condition.

Obviously, on increasing cell temperature the Nernst potential falls, indicated by the dotted line in Figure 11. On the other hand, at a constant cell temperature (e.g. 90°C), $E_r$ decreases with higher RH because the partial pressure of the humidifying water is greater, and the partial pressure of the $H_2$ and $O_2$ reduces [27] as shown in Table 5. For e.g. at 90°C, as RH is changed from 40% to 100%, $pH_2O$ increases from 0.29 atm to 0.69 atm and $pH_2$ and $pO_2$ correspondingly decreases from 0.71 to 0.31 atm.
Table 5. Calculated values of Nernst Potential from equation (17) at each operating condition and corresponding feed gas partial pressures. $T_{\text{FC}}$ denotes the temperature of the cell and $T_{\text{RH}}$ denotes the temperature set for both the anode and cathode humidifier to attain a required RH (row 2).

<table>
<thead>
<tr>
<th>$T_{\text{FC}}/T_{\text{RH}}$ (°C/°C)</th>
<th>80/62</th>
<th>80/72</th>
<th>80/80</th>
<th>90/68</th>
<th>90/72</th>
<th>90/82</th>
<th>90/90</th>
<th>100/82</th>
<th>100/92</th>
<th>99/99</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH (%)</td>
<td>50</td>
<td>75</td>
<td>100</td>
<td>50</td>
<td>75</td>
<td>100</td>
<td>50</td>
<td>75</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>$p_{\text{H}<em>2}$ or $p</em>{\text{O}_2}$ (atm)</td>
<td>0.77</td>
<td>0.64</td>
<td>0.53</td>
<td>0.71</td>
<td>0.64</td>
<td>0.46</td>
<td>0.31</td>
<td>0.49</td>
<td>0.25</td>
<td>0.03</td>
</tr>
<tr>
<td>$p_{\text{H}_2\text{O}}$ (atm)</td>
<td>0.23</td>
<td>0.36</td>
<td>0.47</td>
<td>0.29</td>
<td>0.36</td>
<td>0.54</td>
<td>0.69</td>
<td>0.51</td>
<td>0.75</td>
<td>0.97</td>
</tr>
</tbody>
</table>

The voltage obtained when current is drawn from the fuel cell is always less than the theoretically computed value and the causes for this deviation are due to polarization losses which are briefly explained in Section 5.3. These losses are categorized based on the dominating process at a particular current density and can be quantified by fitting the experimental data to an empirical model equation (6) (Chapter 5) [56]. The actual voltage versus current density (V-i) data obtained for the three MEAs in this experiment is presented below in Section 6.2. The performance of the MEAs is compared by analyzing the different sources of losses evaluated using polarization, CV and EIS techniques.

### 6.2 Polarization curves

Polarization data was collected for the 3 sample MEAs at temperatures of 80°C, 90°C and ~100°C and varying the relative humidity (RH) of the fuel and oxidant gases as 50%, 75% and 100%. The required RH was set by changing the temperature of the humidifiers. The data was recorded after steady state was achieved as confirmed by unchanging values of current and resistance at a fixed applied potential [28] for each start-up. The variability in performance for each individual start-up of the fuel cell were averaged and the standard deviation has been indicated for each value in the results and
discussions. The effect of altering 3 factors; RH, composition and temperature on polarization are presented in Figure 12, Figure 13 and Figure 14.

Figure 12. Polarization curves recorded for MEA-1, MEA-2 and MEA-3 at different temperatures and RH with H2/O2 and H2/air at 0.2 l/min and at atmospheric pressure. (a) 80°C and 100% RH; (b) 80°C and 75% RH; (c) 80°C and 50% RH. Line color represents MEA composition (Blue-MEA-1; Red-MEA-2; Purple-MEA-3). Line pattern indicates data at a particular temperature (Solid lines-80°C, dashed lines - 90°C and dotted lines-~100°C). Symbol (X) represents data taken with H2/air at the indicated operating condition.
Figure 13. Polarization curves recorded for MEA-1, MEA-2 and MEA-3 at different temperatures and RH with H$_2$ / O$_2$ and H$_2$ / air at 0.2 l/min and at atmospheric pressure. (a) 90°C and 100% RH; (b) 90°C and 75% RH; (c) 90°C and 50% RH; (d) 90°C and 40% RH. Line color represents MEA composition (Blue-MEA-1; Red-MEA-2; Purple-MEA-3). Line pattern indicates data at a particular temperature (Solid lines - 80°C, dashed lines - 90°C and dotted lines - ~100°C). Symbol (X) represents data taken with H$_2$ / air at the indicated operating condition.
Polarization curves or V-\(i\) curves represented by symbol (X) in Figure 12-Figure 14; depict data obtained with air at the cathode while the other curves were obtained with \(O_2\) at the cathode. When air is used as the oxidant, the degree of losses is greater because the process is limited by the decreased availability of oxygen, causing mass transport deficient behavior [3], and is indicated by the low limiting current densities. Limiting current density is taken as the current drawn from the cell at voltages below 0.3 V; for
MEA-1 at 90°C and 50% RH, the current density at ~0.2 V was 2760 mA/cm² with H₂/O₂ and 940 mA/cm² with H₂/air. The relatively low value for air data is due to reduced partial pressure of O₂ supplied from air. H₂/air polarization data is shown primarily for comparison and was observed to follow the same trend when plotted at a reduced scale of current density. The polarization losses were evaluated from data collected with oxygen in order to eliminate the additional mass transport losses caused by utilizing air. Thus, the effect of the additive on activation and ohmic losses can be comprehended more accurately.

For each MEA, as the temperature is increased at the same RH, there is a drop in performance and in the limiting current densities. The lines of the same color between graphs Figure 12 (a) Figure 13 (a) and Figure 14 (a) depict the change in polarization curves at 100% RH with increase in temperature from 80°C to 100°C. On observing plots labeled as (b) in Figure 12-Figure 14, the effect with increase in temperature at 75% RH can be observed and similarly variation at 50% RH can be observed between plots labeled as (c) in Figure 12-Figure 14. The temperature controls the percentage of water in the ionomer, which in turn affects proton conductivity, and to that end the V-i characteristics are affected. Thus, operating the cell at lower temperature results in better performance.

RH effect at a fixed cell temperature can be perceived by comparing the plots (a), (b) and (c) in Figure 12 or in Figure 13 or Figure 14. The effect can be clearly interpreted from the current densities at 0.7 V given in Table 6. With the decrease in RH there is a drop in the current density and hence the output power at the fixed voltage of 0.7 V. RH
being directly related to the water content in the membrane regulates its proton conductivity [2] and consequently, the output from the cell.

The influence of MEA composition on performance can be understood by observing the curves within each graph or by observing the current density values in Table 6. For a majority of the operating conditions, MEA-1 (blue: having proposed additive in the membrane and electrodes) demonstrates better output over the entire current density range; in comparison MEA-2 has the lowest performance. Such response could be a result of MEA morphology, homogeneity of the adjoining components and the presence of the PWA additive in MEA components. Identical composition in the two adjacent layers enables better contact and is conducive for proton (H⁺) shuttling from electrode layer to bulk electrolyte. MEA-1 (heteropolyacid/Nafion® in membrane and electrodes) and MEA-3 (only Nafion® in membrane and electrodes) both contain identical ionomer composition in their respective adjacent layers and offer better performance than MEA-2. Furthermore, heteropolyacid additive in all components in MEA-1 offers better V-i characteristics than MEA-2 particularly at higher temperatures and lower humidities. Comparing the values at the optimum condition (80°C and 100% RH) from Table 6, MEA-1 and MEA-3 have nearly the same values; while at a highest temperature and lowest RH (100°C and 50% RH), the current density for MEA-1 is at least 35% higher. Table 6 also presents the maximum power density that was drawn from the cell with the corresponding MEA. The highest power was obtained predictably from MEA-1 at 80°C and 100% RH, confirming the performance from V-i data. At 100°C and
50% RH, MEA-1 generates at least 63 mW/cm$^2$ higher power density than MEA-2 or MEA-3.

Table 6. Current density at 0.7 V and peak power density obtained for MEA-1, MEA-2 and MEA-3; with $\text{H}_2/\text{O}_2$ at 0.2 l/min for the operating conditions given in columns 1 and 2. $T_{\text{FC}}$ denotes the temperature of the cell and $T_{\text{RH}}$ denotes the temperature set for both the anode and cathode humidifier to attain the required RH (column 2).

<table>
<thead>
<tr>
<th>$T_{\text{FC}}/T_{\text{RH}}$ ($^\circ$C/$^\circ$C)</th>
<th>RH (%)</th>
<th>$i@0.7$ V (mA/cm$^2$)</th>
<th>Peak power density (mW/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MEA-1</td>
<td>MEA-2</td>
</tr>
<tr>
<td>80/62</td>
<td>50</td>
<td>390 ± 34</td>
<td>180 ± 12</td>
</tr>
<tr>
<td>80/72</td>
<td>75</td>
<td>560 ± 37</td>
<td>320 ± 24</td>
</tr>
<tr>
<td>80/80</td>
<td>100</td>
<td>710 ± 53</td>
<td>520 ± 46</td>
</tr>
<tr>
<td>90/68</td>
<td>40</td>
<td>260 ± 22</td>
<td>100 ± 6</td>
</tr>
<tr>
<td>90/72</td>
<td>50</td>
<td>340 ± 23</td>
<td>210 ± 21</td>
</tr>
<tr>
<td>90/82</td>
<td>75</td>
<td>410 ± 26</td>
<td>280 ± 24</td>
</tr>
<tr>
<td>90/90</td>
<td>100</td>
<td>520 ± 47</td>
<td>400 ± 29</td>
</tr>
<tr>
<td>100/82</td>
<td>50</td>
<td>290 ± 18</td>
<td>150 ± 15</td>
</tr>
<tr>
<td>100/92</td>
<td>75</td>
<td>260 ± 21</td>
<td>240 ± 17</td>
</tr>
<tr>
<td>99/99</td>
<td>100</td>
<td>305 ± 29</td>
<td>300 ± 30</td>
</tr>
</tbody>
</table>

These V-$i$ curves are used to calculate activation, ohmic and mass transfer losses occurring in the 3 MEAs by fitting the experimental data to an empirical model equation (6) (Chapter 5) [56]. Parameters evaluated from the experimental fit aid in verifying the effectiveness of the added composite at different temperatures and RH. Section 6.3 emphasizes the improvement in the ohmic resistance due to the presence of the composite in the electrodes. The influence on activation losses due to the added composite (Section 5.3.2) can be comprehended from Open Circuit Potential (OCP), Effective Catalytic
Surface Area (ECSA), Tafel slope, charge transfer resistance. The other parameters apart from those already mentioned, which are also calculated by applying the model equation (6) to polarization data are examined in Section 6.5.

6.3 Effect of the composite electrodes on ohmic resistance

The purpose of adding composite to the electrode layer was to enhance proton conductivity and consequently a reduction in ohmic resistance, particularly at elevated temperature and low humidity conditions. The total ohmic resistance for the three MEAs was computed by two techniques: current interrupt technique applied while recording polarization curves and EIS technique. The results from these techniques are presented in Sections 6.3.2 and 6.3.3. Section 6.3.4 sheds light on the ohmic resistance of the electrode layer which is believed to be represented by ‘N’, the empirical term related to mass transfer losses in equation (6).

6.3.1 Total ohmic resistance

At the intermediate current density region; the electrons and protons generated at the anode create a gradient for transport to the cathode through their respective paths as shown in Figure 2 of Chapter 3 (Experimental Section). The electron flow is hindered by the resistance of electronic conductors such as bipolar plates, current collectors, gas diffusion layers and electrodes. The resistance to proton flow occurs in the membrane and in the ionomer network in the electrode layers. The sum of the electronic and protonic resistance in this fuel cell system is the total ohmic resistance. This resistance value changes with: the extent of membrane/ionomer hydration, the materials of the electronic conductors and the thickness of the membrane and electrodes [63,80]. The major
contribution of ohmic resistance is provided by the ionomer in the membrane and electrodes. Mathematical expressions for variation of membrane/ionomer ohmic resistance with temperature, with current density and with degree of humidification have been reported [63,65]. The membrane/ionomer water content and proton transfer through the membrane/ionomer are strongly correlated because protons are transferred as solvated ions in this component [81]. Thus, the hydration level has a significant effect on ohmic resistance. Estimation of this resistance by current interrupt technique and by EIS technique is described below.

6.3.2 Ohmic resistance from current interrupt

The dynamic ohmic resistance of the cell changes with the increase in the current drawn from the cell and is calculated by the current interrupt technique [38]. In this method, current is interrupted for a few nano-seconds and the instantaneous increase in voltage that occurs is recorded. The rationale behind this approach is as follows. On obstructing the current, ohmic resistance immediately disappears. If the duration of this obstruction is increased, the other losses also eventually vanish and for this reason the time of current interrupt is maintained in the range of $10^{-9}$ seconds. The difference between the actual voltage and instantaneous increase is used to estimate the ohmic resistance at each current density [38].

The increase in the ohmic resistance causes a decrease in voltage at intermediate current densities and the relationship between the voltage and current is given by Ohm’s law, equation (18)

$$E = R_{\alpha}I$$

(18)
where $E$ (V) is the voltage, $R_Ω$ (ohm-cm$^2$) is the ohmic resistance and $i$ (mA/cm$^2$) is the current density. $R_Ω$ is not constant over the entire range of current density due changes in the level of hydration. The extent of the variation in $R_Ω$ for each operating condition and for each MEA is plotted in Figure 15, and is displayed by the error bars. Evidently, at lower RH the resistance variation is wider. At 90°C and 40% RH, the deviation from average is highest; the deviation is minimum at 80°C and 100% RH, reiterating that RH has a more pronounced effect on performance [28].

![Figure 15. Average values of the resistance recorded using current interrupt technique applied while collecting polarization data with H$_2$/O$_2$ at 0.2 l/min. Error bars indicate highest and lowest values at each operating temperature for the particular MEA. T$_{FC}$ denotes the temperature of the cell and T$_{RH}$ denotes the temperature set for both the anode and cathode humidifiers to attain the required RH indicated below each condition.](image)
The degree of fluctuation being unequal for different conditions, the $R_Ω$ at one selected voltage of 0.8 V (designated as $R_Ω, 0.8V$ for clarity) is compared in Figure 16 to get better information on the ohmic resistance variation for each of 3 factors monitored in this experiment: temperature, RH and MEA composition.

![Figure 16. Resistance values at 0.8 V recorded using current interrupt technique applied while collecting polarization data with $H_2/O_2$ at 0.2 l/min for the 3 MEAs at depicted operating conditions. $T_{FC}$ denotes the temperature of the cell and $T_{RH}$ denotes the temperature set for both the anode and cathode humidifiers to attain the required RH indicated below each condition.]

At 100% RH, the value of $R_Ω, 0.8V$ does not change significantly with increase in temperature; as seen from Table 7, for MEA-1 this resistance is $0.053 \pm 0.004$ ohm-cm$^2$. 
at 80°C and 0.052 ± 0.002 ohm-cm² at 100°C which are considered as similar within the experimental error. At 50% RH, for an increase in temperature from 80°C to 100°C the increase in the average $R_{Ω, 0.8V}$ is in the range of 5-15%, where 5% change is for MEA-1. On the other hand, at any particular temperature with increasing level of humidification, there is a much greater drop in the ohmic resistance value indicating the stronger influence of level of hydration on ohmic resistance. At 100°C, a decrease from 100% RH to 50% RH, the $R_{Ω, 0.8V}$ value decreases by 128% for MEA-1 to 180% for MEA-2. The effectiveness of the composite added to the electrode layer can be directly understood by comparing the ohmic resistance of the MEAs in the Figure 16 and Table 7. MEA-1 has the least resistance at all conditions and the separation is greater at lower RH values (Figure 16). At the highest temperature of 100°C and lowest humidity of 50% RH, the average $R_{Ω, 0.8V}$ of MEA-1 is 27% lower than MEA-3 and 58% lower than MEA-2. These results validate better water retention for the components of MEA-1 containing the PWA-nano-composite.
Table 7. Resistance values (current interrupt) at 0.8 V for the 3 MEAs at indicated operating conditions as given in columns 1 and 2. $T_{FC}$ denotes the temperature of the cell and $T_{RH}$ denotes the temperature set for both the anode and cathode humidifier to attain the required RH (column 2).

<table>
<thead>
<tr>
<th>$T_{FC}/T_{RH}$ (°C/°C)</th>
<th>RH(%)</th>
<th>$R_{Ω,0.8V}$ from Current Interrupt (ohms-cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MEA-1</td>
</tr>
<tr>
<td>80/62</td>
<td>50</td>
<td>0.112 ± 0.006</td>
</tr>
<tr>
<td>80/72</td>
<td>75</td>
<td>0.062 ± 0.003</td>
</tr>
<tr>
<td>80/80</td>
<td>100</td>
<td>0.053 ± 0.004</td>
</tr>
<tr>
<td>90/68</td>
<td>40</td>
<td>0.141 ± 0.011</td>
</tr>
<tr>
<td>90/72</td>
<td>50</td>
<td>0.120 ± 0.005</td>
</tr>
<tr>
<td>90/82</td>
<td>75</td>
<td>0.073 ± 0.005</td>
</tr>
<tr>
<td>90/90</td>
<td>100</td>
<td>0.050 ± 0.002</td>
</tr>
<tr>
<td>100/82</td>
<td>50</td>
<td>0.118 ± 0.006</td>
</tr>
<tr>
<td>100/92</td>
<td>75</td>
<td>0.079 ± 0.005</td>
</tr>
<tr>
<td>99/99</td>
<td>100</td>
<td>0.052 ± 0.002</td>
</tr>
</tbody>
</table>

The current interrupt method is advantageous over EIS technique because it is relatively faster and can be implemented by simply incorporating a switch in the circuit. However, it disturbs the operation of the cell and is not reliable for extensive analysis [82]. The actual resistance of the ionomer cannot be isolated from either of the techniques (current interrupt technique and EIS technique); the value of the resistance evaluated in both cases is the sum of the ohmic resistance of the components in the cell.

6.3.3 Ohmic resistance from EIS

The ohmic resistance offered by the fuel cell is estimated from EIS measurements by noting the high frequency intercept of the impedance spectrum. To enable comparison of the values from both techniques, the resistance at 0.8 V was selected in both cases. The
impedance spectra from which $R_{hf}$ was estimated are given in Appendix B (Figure 31-Figure 33). The same trend was also observed from EIS data as shown in Figure 17. The magnitude for EIS derived values is generally higher because it might include some resistance that is not entirely ohmic. The mathematical relation between the numerical values from the two methods was given in detail in [38]. Figure 17 demonstrates the effect of operating conditions on ohmic resistance for the MEAs through the EIS technique.

![Figure 17](image)

**Figure 17.** Ohmic resistance variation as obtained from the high frequency intercept of the EIS spectrum recorded for the 3 MEAs at the depicted operating conditions. $T_{FC}$ denotes the temperature of the cell and $T_{RH}$ denotes the temperature set for both the anode and cathode humidifiers to attain the required RH indicated below each condition.
Figure 17 indicates that at a fixed temperature, increasing the RH brings about a much sharper decrease in the ohmic resistance value $R_{hf}$, derived from the EIS technique. However, at fixed RH of the cell, an increase in temperature from 80°C to 100°C causes a much lesser change in the value of $R_{hf}$. Using the values from Table 8 for quantitative comparison, $R_{hf}$ at a constant temperature of 100°C falls by about 59-150% when RH is increased from 50% to 100%. In contrast, at a fixed RH of 50%, $R_{hf}$ increases by only 6-33% for a temperature increase of 80°C to 100°C. Focusing on the MEA composition effect, the ohmic resistance of MEA-1 is clearly lesser than MEA-2 and MEA-3, particularly at lower RH. At 100°C and 50% RH, MEA-1 has 73% lower $R_{hf}$ value than MEA-2 and 50% lower than MEA-3. Again, such a result establishes that the presence of the additive in the electrode of MEA-1 improves its proton conductivity and causes reduction in the overall ohmic resistance. Also, with reduction in RH or increase in temperature, the increase in $R_{hf}$ value for MEA-1 is at the lower value of the reported range than for MEA-2 or MEA-3.
Table 8. High frequency intercept of the impedance spectrum recorded at 0.8 V for the 3 MEAs at indicated operating conditions columns 1 and 2. $T_{FC}$ denotes the temperature of the cell and $T_{RH}$ denotes the temperature set for both the anode and cathode humidifier to attain the required RH (column 2).

<table>
<thead>
<tr>
<th>$T_{FC}/T_{RH}$ ($°C/°C$)</th>
<th>RH (%)</th>
<th>$R_{hf}$ (ohm-cm$^2$)</th>
<th>MEA-1</th>
<th>MEA-2</th>
<th>MEA-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>80/62</td>
<td>50</td>
<td>0.176 ± 0.002</td>
<td>0.242 ± 0.003</td>
<td>0.256 ± 0.005</td>
<td></td>
</tr>
<tr>
<td>80/72</td>
<td>75</td>
<td>0.112 ± 0.001</td>
<td>0.140 ± 0.003</td>
<td>0.151 ± 0.003</td>
<td></td>
</tr>
<tr>
<td>80/80</td>
<td>100</td>
<td>0.098 ± 0.002</td>
<td>0.111 ± 0.002</td>
<td>0.117 ± 0.002</td>
<td></td>
</tr>
<tr>
<td>90/68</td>
<td>40</td>
<td>0.233 ± 0.003</td>
<td>0.327 ± 0.003</td>
<td>0.332 ± 0.006</td>
<td></td>
</tr>
<tr>
<td>90/72</td>
<td>50</td>
<td>0.194 ± 0.002</td>
<td>0.338 ± 0.004</td>
<td>0.233 ± 0.003</td>
<td></td>
</tr>
<tr>
<td>90/82</td>
<td>75</td>
<td>0.128 ± 0.003</td>
<td>0.206 ± 0.004</td>
<td>0.177 ± 0.003</td>
<td></td>
</tr>
<tr>
<td>90/90</td>
<td>100</td>
<td>0.096 ± 0.002</td>
<td>0.171 ± 0.002</td>
<td>0.110 ± 0.001</td>
<td></td>
</tr>
<tr>
<td>100/82</td>
<td>50</td>
<td>0.188 ± 0.002</td>
<td>0.324 ± 0.006</td>
<td>0.280 ± 0.005</td>
<td></td>
</tr>
<tr>
<td>100/92</td>
<td>75</td>
<td>0.118 ± 0.002</td>
<td>0.157 ± 0.003</td>
<td>0.186 ± 0.004</td>
<td></td>
</tr>
<tr>
<td>99/99</td>
<td>100</td>
<td>0.118 ± 0.002</td>
<td>0.130 ± 0.002</td>
<td>0.117 ± 0.002</td>
<td></td>
</tr>
</tbody>
</table>

The two techniques that have been described in this section allow for the assessment of total ohmic resistance. The exact results of this experiment can be comprehended if the ohmic resistances of the electrodes can be estimated and compared for the 3 sample MEAs. This can be realized by examining the ‘$N$’ value obtained for the 3 MEAs by fitting their corresponding polarization curves to the chosen mathematical model.

### 6.3.4 ‘$N$’ variation

Although ‘$N$’ is an empirical tem computed primarily to account for the mass transport losses, its physical meaning of was described by the authors, Bevers et al. [66]. In their analysis, the decrease in the ionomer conductivity of the electrode layer made the V-i curve fall more rapidly in the mass transfer limited region. The same behavior was observed by increasing the magnitude of ‘$N$’ in the simulation of equation
(6) (Chapter 5). Correlating the two observations, ‘\(N\)’ was proposed to be a function of the electrolyte resistance in the electrode layer. At fixed flow rates of the gases ‘\(N\)’ fluctuates with the operating conditions and ionomer quantity in the electrode layer as seen in Figure 18.

The effect of the electrode composition, which is the main objective of this study, is recognizable from the colored lines in Figure 18. MEA-1 (blue lines) shows favorable
outcome as seen from the minimum values of this variable ‘$N$’. The other two MEAs have equivalent at some conditions due to identical electrode compositions. It can be concluded that the addition of the PWA nano-composite enhances electrode proton conductivity and thereby the area of current generation in the electrode, thus shifting the polarization curve to higher limiting current densities. The numerical values of all the measured variables from this analysis are presented in Table 9. ‘$N$’ is at a minimum of $(60 \pm 3) \times 10^{-5}$ (cm$^2$/mA) for MEA-1 at 80°C and 100% RH and is at a maximum for MEA-3 at low humidity conditions i.e. 90°C and 40% RH and 80°C and 50% RH. At 100°C and 50% RH, the value of ‘$N$’ for MEA-1 is 50% lower than MEA-2 and 70% lower than MEA-3. It is an implication of the increase in the proton resistance of electrodes of MEA-2 and MEA-3 in the absence of the composite at low hydration levels. The temperature and RH effect cannot be precisely established from the above figure. It has to be remembered that the method in which ‘$N$’ is computed allows for considerable uncertainty in its numerical value which cannot be eliminated. This could account for the lack of clarity on the effect of temperature and RH on ‘$N$’. 
Table 9. Numerical values of the mass transfer loss term ‘N’ for 3 MEAs at the temperatures indicated in columns 1 and 2. $T_{FC}$ denotes the temperature of the cell and $T_{RH}$ denotes the temperature set for both the anode and cathode humidifier to attain the required RH (column 2).

<table>
<thead>
<tr>
<th>$T_{FC}/T_{RH}$ ($^\circ$C/$^\circ$C)</th>
<th>RH (%)</th>
<th>MEA-1 $x10^5$ (cm$^2$/mA)</th>
<th>MEA-2 $x10^5$ (cm$^2$/mA)</th>
<th>MEA-3 $x10^5$ (cm$^2$/mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80/62</td>
<td>50</td>
<td>70 ± 2</td>
<td>91 ± 4</td>
<td>270 ± 11</td>
</tr>
<tr>
<td>80/72</td>
<td>75</td>
<td>80 ± 4</td>
<td>130 ± 6</td>
<td>150 ± 3</td>
</tr>
<tr>
<td>80/80</td>
<td>100</td>
<td>60 ± 3</td>
<td>100 ± 6</td>
<td>200 ± 7</td>
</tr>
<tr>
<td>90/68</td>
<td>40</td>
<td>110 ± 5</td>
<td>180 ± 6</td>
<td>260 ± 9</td>
</tr>
<tr>
<td>90/72</td>
<td>50</td>
<td>120 ± 4</td>
<td>160 ± 8</td>
<td>200 ± 8</td>
</tr>
<tr>
<td>90/82</td>
<td>75</td>
<td>110 ± 3</td>
<td>160 ± 6</td>
<td>150 ± 5</td>
</tr>
<tr>
<td>90/90</td>
<td>100</td>
<td>110 ± 5</td>
<td>160 ± 8</td>
<td>150 ± 3</td>
</tr>
<tr>
<td>100/82</td>
<td>50</td>
<td>100 ± 3</td>
<td>150 ± 7</td>
<td>170 ± 10</td>
</tr>
<tr>
<td>100/92</td>
<td>75</td>
<td>120 ± 6</td>
<td>190 ± 11</td>
<td>160 ± 4</td>
</tr>
<tr>
<td>99/99</td>
<td>100</td>
<td>150 ± 8</td>
<td>220 ± 13</td>
<td>200 ± 6</td>
</tr>
</tbody>
</table>

The usefulness of the composite can be easily established by examining the effect on the ohmic resistance, but the way in which it modifies the remaining parameters related to activation and mass transport losses has to be taken into consideration. Such a study will determine the impact on the performance in general. The change in the parameters related to activation losses are discussed in Section 6.4, and the other parameters are discussed in Section 6.5.

### 6.4 Effect of the composite on activation losses

The activation losses (Section 5.3.2, Chapter 5) can be comprehended from Open Circuit Potential (OCP), Effective Catalytic Surface Area (ECSA), Tafel slope, charge transfer...
resistance; all of which are defined and explained in the subsequent paragraphs in this chapter.

6.4.1 **Open Circuit Potential (OCP) variation**

Open Circuit Potential (OCP) is the voltage obtained when no power is drawn from the cell. In theory, it is difference between the two electrode potentials, and should ideally equal the Nernst potential [38]. Operating conditions (temperature and RH) and composition of the MEAs induce deviation in this value. The OCP of MEAs in discussion, are displayed in Figure 19 and Table 10 for the present set of conditions.

![Figure 19. OCP obtained with H2/O2 at 0.2 l/min, 1 atm at given conditions for MEA-1, MEA-2 and MEA-3. TFC denotes the temperature of the cell and TRH denotes the temperature set for both the anode and cathode humidifiers to attain the required RH indicated below each condition.](image-url)
The change in OCP with temperature or with RH or between MEAs is less than 7%. However, within this small change, there is an observable trend in the variation with increase in RH and between different MEAs. RH affects the hydration state of the ionomer, which can control the maximum attainable potential [83]. The positive influence of hydration is observed from the increase of OCP with RH (Figure 19). In Table 10, at 90°C, OCP is ~0.916 V at 40% RH and increases to ~0.946 V at 100% RH for the reference MEA (MEA-3). OCP is also subject to the extent of hydrogen crossover [66], in that an increase in crossover will result in lower OCP. This correlation is consistent with observed RH variations of OCP and H₂ crossover for MEA-3 at 90°C given in Table 10 and Table 11. Hydrogen crossover increases from ~1.9×10⁻⁸ moles H₂/cm².s at 100% RH to ~4.6×10⁻⁸ moles H₂/cm².s at 40% RH while OCP decreases for the same decrease in RH. For each MEA, dissimilarities due to the extent of contamination (due to organic or metallic impurities present in the MEA [84,85] that have not be removed during pre-treatment) effective catalytic surface area (ECSA), crossover of the fuel and oxidant, and occurring parasitic reactions [86], manifest as a change in OCP [38,66]. At 50% RH for all the temperatures, MEA-1 generates the higher OCP compared to the other two MEAs. For 100°C and 50% RH, the OCP attained for MEA-1 is about 6% greater compared to MEA-2 and about 5% greater with respect to MEA-3. Since Nafion® works effectively at 100% RH and tends to get dehydrated as the humidity levels are reduced, the positive effect of the composite will be pronounced at lower RH.
Table 10. Open Circuit Potential achieved with $\text{H}_2/\text{O}_2$ at flow rates of 0.2 l/min, obtained for MEA-1, MEA-2 and MEA-3 at the operating conditions given in columns 1 and 2. $T_{\text{FC}}$ denotes the temperature of the cell and $T_{\text{RH}}$ denotes the temperature set for both the anode and cathode humidifier to attain the required RH (column 2).

<table>
<thead>
<tr>
<th>$T_{\text{FC}}/T_{\text{RH}}$ (°C/°C)</th>
<th>RH (%)</th>
<th>Open Circuit Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MEA-1</td>
</tr>
<tr>
<td>80/62</td>
<td>50</td>
<td>0.938 ± 0.007</td>
</tr>
<tr>
<td>80/72</td>
<td>75</td>
<td>0.956 ± 0.004</td>
</tr>
<tr>
<td>80/80</td>
<td>100</td>
<td>0.966 ± 0.002</td>
</tr>
<tr>
<td>90/68</td>
<td>40</td>
<td>0.941 ± 0.006</td>
</tr>
<tr>
<td>90/72</td>
<td>50</td>
<td>0.955 ± 0.006</td>
</tr>
<tr>
<td>90/82</td>
<td>75</td>
<td>0.956 ± 0.006</td>
</tr>
<tr>
<td>90/90</td>
<td>100</td>
<td>0.962 ± 0.005</td>
</tr>
<tr>
<td>100/82</td>
<td>50</td>
<td>0.947 ± 0.005</td>
</tr>
<tr>
<td>100/92</td>
<td>75</td>
<td>0.945 ± 0.004</td>
</tr>
<tr>
<td>99/99</td>
<td>100</td>
<td>0.946 ± 0.004</td>
</tr>
</tbody>
</table>

6.4.2 Hydrogen crossover from LSV

The Nafion® membrane is known to have a limited permeability to $\text{H}_2$ and $\text{O}_2$ enabling crossover of gases from one electrode to the other which will lead additional losses including OCP decline [86]. In some cases, the formation of radicals due to crossed over reactants [87] create pinholes [88] in the membrane and might also lead to short circuit of the cell [86]. The degree of crossover is useful in detecting the micro-structural integrity of the membrane. The losses caused by oxygen crossover considered to be rather minute compared to that of $\text{H}_2$ crossover [86]. From the LSV data crossover of hydrogen from anode to cathode was calculated from equation (2) of Chapter 4 (Analysis Techniques) and the results are presented in Figure 20.
It is seen from Figure 20 and Table 11 that crossover decreases with rising cell temperature and increasing RH. At the same RH of 50%, as temperature is increased from 80°C to 100°C, the flux of H₂ crossover decreases 20-73% for the 3 MEAs. At the temperature of ~100°C, from 50% RH to 100% RH, the percentage decrease in crossover is 155% to 338%. The effect of RH is much higher. This behavior with temperature and RH can be rationalized by the partial pressure of hydrogen in the feed. At higher temperatures and higher RH, the partial pressure of water in the feed mixture increases, and that of hydrogen decreases (Table 5), hence the negative slope of the curves. MEA-1
and MEA-2 appear to have the same extent of crossover for most of the conditions. MEA-3 has marginally lower values. At 100°C and 50% RH, the change in crossover values is about 7% between MEA-1 and MEA-2 and is about 60% between MEA-1 and MEA-3. Since the membrane composition is identical for MEA-1 and MEA-2, this factor can be suspected to cause a slightly higher H₂ crossover. Verma and Scott [17] have reported increased crossover for the phosphoric acid doped membranes containing HPAs and accounted that as higher permeability of H₂ in the presence of excess acid molecules that attach to HPA molecules. By drawing analogy between the two cases, the hybrid PWA membranes in this study could also enhance crossover due to higher number of sulphuric acid molecules adhering to PWA particles in the membrane during pretreatment. The influence of crossover on OCP has been related in Section 6.4.1. Despite the minor loss of crossover in MEA-1, it has higher OCP. MEA-2 has equivalent values with MEA-3. Hence the observed crossover reduction for MEA-2 can be considered inconsequential.
Table 11. H₂ crossover calculated from LSV data with H₂ / N₂, at flow rates 0.2 l/min, obtained for MEA-1, MEA-2 and MEA-3 at the list of conditions given in columns 1 and 2. T_{FC} denotes the temperature of the cell and T_{RH} denotes the temperature set for both the anode and cathode humidifier to attain the required RH (column 2).

<table>
<thead>
<tr>
<th>T_{FC}/T_{RH} (°C/°C)</th>
<th>RH(%)</th>
<th>Moles of H₂ crossover \times 10^8 (moles/cm² . s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MEA-1</td>
</tr>
<tr>
<td>80/62</td>
<td>50</td>
<td>3.8 ± 0.1</td>
</tr>
<tr>
<td>80/72</td>
<td>75</td>
<td>4.1 ± 0.2</td>
</tr>
<tr>
<td>80/80</td>
<td>100</td>
<td>2.3 ± 0.1</td>
</tr>
<tr>
<td>90/68</td>
<td>40</td>
<td>3.4 ± 0.1</td>
</tr>
<tr>
<td>90/72</td>
<td>50</td>
<td>3.6 ± 0.1</td>
</tr>
<tr>
<td>90/82</td>
<td>75</td>
<td>3.0 ± 0.1</td>
</tr>
<tr>
<td>90/90</td>
<td>100</td>
<td>2.0 ± 0.0</td>
</tr>
<tr>
<td>100/82</td>
<td>50</td>
<td>3.0 ± 0.1</td>
</tr>
<tr>
<td>100/92</td>
<td>75</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>99/99</td>
<td>100</td>
<td>0.7 ± 0.0</td>
</tr>
</tbody>
</table>

6.4.3 **ECSA measurement**

The activity of the catalyst is determined by ECSA calculated from CV data as described in Section 4.2.4. The CVs recorded at operating conditions of interest for the tested MEAs are presented in the Appendix A (Figure 28-Figure 30). The charge for H₂ desorption was estimated from the CV data according to the method in Section 4.2.4. Consequently ECSA was calculated from equation (3) of Chapter 4 (Analysis Techniques) and the results are shown in Figure 21. There is a 25% uncertainty in the platinum loading of the cathode due to the difficulty in determining the exact weight of the membrane and electrodes. The Pt weight in the cathodes of the MEAs is taken as 0.4±0.1 mgPt/cm². The fluctuation in the weights of the membrane and electrodes arises
from absorption of water by Nafion® from the ambient air. The uncertainty in calculated ECSA is computed by error propagation and is displayed by the error bars in Figure 21. The numerical values of calculated ECSA are given in Table 12.

![Figure 21. ECSA variation with temperature for MEA-1, MEA-2 and MEA-3; calculated from CV with H₂ at the anode and N₂ at the cathode, fed at flowrates of 0.2 l/min. T_FC denotes the temperature of the cell and T_RH denotes the temperature set for both the anode and cathode humidifiers to attain the required RH indicated below each condition.](image)

The ECSAs of MEA-1 and MEA-2 cannot be distinguished due to huge uncertainties in measurement and fabrication. But MEA-3 has lower values even considering the experimental error. Excluding the ECSA calculated at 80°C and 50% RH, the active surface area is at least 20% lower for MEA-3 compared to both MEA-1 and
MEA-2. An important inference from ECSA measurement is that PWA additive does not poison the catalyst [24] when added to the components of an MEA, as clarified by the higher ECSAs obtained for MEA-1 and MEA-2. This ensures that the composite added is adequately embedded within the membrane by employing the sol-gel method (Chapter 2: Literature Review) and does not leach out causing electrode contamination as reported in Ramani et al. [10].

Table 12. Cathode active surface areas determined by CV for MEA-1, MEA-2 and MEA-3 at the operating conditions given in columns 1 and 2. \( T_{\text{FC}} \) denotes the temperature of the cell and \( T_{\text{RH}} \) denotes the temperature set for both the anode and cathode humidifier to attain the required RH (column 2).

<table>
<thead>
<tr>
<th>( T_{\text{FC}}/T_{\text{RH}} ) ( (^{\circ}\text{C}/^{\circ}\text{C}) )</th>
<th>RH(%)</th>
<th>ECSA ( \times 10^{-5}(\text{cm}^2\text{Pt/gPt}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>80/62</td>
<td>50</td>
<td>2.5 ± 1.2</td>
</tr>
<tr>
<td>80/72</td>
<td>75</td>
<td>2.5 ± 1.2</td>
</tr>
<tr>
<td>80/80</td>
<td>100</td>
<td>2.8 ± 1.4</td>
</tr>
<tr>
<td>90/68</td>
<td>40</td>
<td>2.1 ± 0.8</td>
</tr>
<tr>
<td>90/72</td>
<td>50</td>
<td>2.2 ± 0.7</td>
</tr>
<tr>
<td>90/82</td>
<td>75</td>
<td>2.2 ± 0.7</td>
</tr>
<tr>
<td>90/90</td>
<td>100</td>
<td>2.4 ± 0.8</td>
</tr>
<tr>
<td>100/82</td>
<td>50</td>
<td>1.9 ± 0.8</td>
</tr>
<tr>
<td>100/92</td>
<td>75</td>
<td>2.0 ± 0.8</td>
</tr>
<tr>
<td>99/99</td>
<td>100</td>
<td>2.1 ± 0.8</td>
</tr>
</tbody>
</table>
6.4.4 Tafel slope

Tafel slope, ‘b’ from equation (7) (Chapter 5) is a straight-forward depiction of the drastic decrease in potential due to activation losses. Theoretically the slope value can be calculated from equation (19) [80,89].

\[ b = \frac{RT}{2\alpha F} \]  

(19)

where \( \alpha \) is the transfer coefficient, the fraction of the electrical energy that is consumed to actuate the reaction [80,89]. The other terms have their usual meaning. \( \alpha \) is assumed to be 0.5 for simplicity but in reality it varies with different materials [80], with the rate determining step and with the formation of oxide films [89]. The numerical values of Tafel slopes from equation (19) at the required cell temperatures are shown in Table 13.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical ( b ) (mV/dec)</td>
<td>70</td>
<td>72</td>
<td>74</td>
</tr>
</tbody>
</table>

Experimentally obtained slopes are not always in agreement with the values in Table 13 estimated from equation (19) [89]. The range of current density for which they are calculated has to be taken into account [90,91]. In this analysis, the Tafel slope was calculated for \( i <100\text{mA/cm}^2 \). The variation of ‘b’ with different temperatures, RH and MEA composition is shown in Figure 22.
Higher values of the slope can be attributed to several reasons namely; greater sum of activation and ohmic resistances [3], low activity of protons, insufficient oxygen transport through the electrodes or a change of the step in the reaction sequence that determines the reaction rate [64]. In other words, the loss in voltage at low current densities indicated by ‘b’ is not purely due to activation related losses. The possible contribution of ohmic and mass transport losses to the Tafel slope has to be considered. For better performing electrodes, ‘b’ decreases and causes the polarization curve to shift to higher voltages [80]. The numerical values of the slopes are presented in Table 14 and
are in the range of 70 mV/dec to 180 mV/dec. Tafel slopes approach double the theoretical values when the cathode is affected by mass transfer limitations along with activation losses [38].

From Figure 22, at 50% RH, with increase in temperature from 80°C to 100°C, the variation of Tafel slope was between 5% and 14%. As the relative humidity is varied, the change is more perceptible. For an increase from 50% RH to 100% RH at 100°C, the Tafel slope reduced by about 16-52% for the 3 MEAs. Better hydration improves the activity of the protons as mentioned earlier and reduces activation overpotential. The effect of the composition is established by comparing all MEAs, MEA-1, MEA-2 and MEA-3. The purpose of the composite is to improve performance at lower RH and higher temperatures which can be understood by observing the significant reduction in these losses at 50% RH for MEA-1. At 100°C and 50% RH, the Tafel slope of MEA-1 is lower by 40% compared to MEA-2 and 20% compared to MEA-3. As observed for OCP values, the Tafel slopes are not distinctly different at 100% because the role of the additive in the electrode is anticipated to be beneficial at lower humidity conditions.
Table 14. Numerical values of Tafel slopes calculated from experimental data for MEA-1, MEA-2 and MEA-3 at the operating conditions given in columns 1 and 2. $T_{FC}$ denotes the temperature of the cell and $T_{RH}$ denotes the temperature set for both the anode and cathode humidifier to attain the required RH (column 2).

<table>
<thead>
<tr>
<th>$T_{FC}/T_{RH}$ ($^\circ$C/$^\circ$C)</th>
<th>RH (%)</th>
<th>Tafel Slope (mV/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MEA-1</td>
</tr>
<tr>
<td>80/62 50</td>
<td></td>
<td>94 ± 2</td>
</tr>
<tr>
<td>80/72 75</td>
<td></td>
<td>86 ± 1</td>
</tr>
<tr>
<td>80/80 100</td>
<td></td>
<td>78 ± 2</td>
</tr>
<tr>
<td>90/68 40</td>
<td></td>
<td>118 ± 6</td>
</tr>
<tr>
<td>90/72 50</td>
<td></td>
<td>102 ± 1</td>
</tr>
<tr>
<td>90/82 75</td>
<td></td>
<td>90 ± 2</td>
</tr>
<tr>
<td>90/90 100</td>
<td></td>
<td>81 ± 3</td>
</tr>
<tr>
<td>100/82 50</td>
<td></td>
<td>102 ± 4</td>
</tr>
<tr>
<td>100/92 75</td>
<td></td>
<td>98 ± 3</td>
</tr>
<tr>
<td>99/99 100</td>
<td></td>
<td>88 ± 2</td>
</tr>
</tbody>
</table>

The higher activation losses of MEA-2 are attributed to higher charge transfer resistance as compared to the other MEA-1 and MEA-3 and this is verified from the time constant for charge transfer evaluated from EIS data, Figure 23 and Table 15.

6.4.5 **Time constant for charge transfer from EIS**

The time taken for the transfer of charge between the electrode and the reacting species is given by this variable ‘$\tau$’ [44] and should be low to minimize activation losses. It is the product of charge transfer resistance and double layer capacitance from EIS measurements (Chapter 4: Analysis Techniques). The EIS spectra obtained for the MEA-1, MEA-2 and MEA-3 are presented in Figure 31 in the Appendix B.
Figure 23 and Table 15 depict the variation of time constant for charge transfer with temperature, RH and MEA composition. Raising the temperature causes higher ‘$\tau$’ as a result of increased charge transfer resistance. At 50% RH, as the temperature is raised from 80°C to 100°C, the increase in average time taken for charge transfer for the 3 MEAs is between 45% and 141%. The increase in charge transfer time constant with higher temperature can be explained from the decrease in the extent of “wettability” in the electrodes [27]. On increasing RH, MEA-1 shows lowering of the time constant at 80°C and 90°C which can be again related to higher wettability of the TPBs in the
electrode layer of this MEA. It is a consequence of improved water retention of the
ionomer in the electrode due to addition of the composite in this layer. At 100°C on
decreasing the hydration level from 100% RH to 50% RH, the time constant increases by
12% for MEA-1 as compared to 51% for MEA-2 and 24% for MEA-3. The increase in
‘\(\tau\)’ is much less for MEA-1; also at 100°C and 50% RH, the charge transfer time constant
for this MEA is lower by 4% in comparison to MEA-2 and 66% lower compared to
MEA-3 at 100°C and 50% RH. MEA-1 indicates the fastest charge transfer due to
increased number of wetted TPBs. MEA-2 and MEA-3 show higher charge transfer
resistances which demonstrate the reduced hydration levels in the absence of the PWA
composite. Thus, the added composite reduces the time constant for charge transfer.

Table 15. Time constant for charge transfer determined from EIS analysis for MEA-1,
MEA-2 and MEA-3 at indicated operating conditions in columns 1 and 2. \(T_{\text{FC}}\) denotes the
temperature of the cell and \(T_{\text{RH}}\) denotes the temperature set for both the anode and
cathode humidifier to attain the required RH (column 2).

<table>
<thead>
<tr>
<th>(T_{\text{FC}}/T_{\text{RH}}) (^{\circ}\text{C}/^{\circ}\text{C})</th>
<th>RH(%)</th>
<th>Time constant for Charge Transfer (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MEA-1</td>
</tr>
<tr>
<td>80/62</td>
<td>50</td>
<td>0.006 ± 0.0001</td>
</tr>
<tr>
<td>80/72</td>
<td>75</td>
<td>0.004 ± 0.0001</td>
</tr>
<tr>
<td>80/80</td>
<td>100</td>
<td>0.004 ± 0.0002</td>
</tr>
<tr>
<td>90/68</td>
<td>40</td>
<td>0.008 ± 0.0002</td>
</tr>
<tr>
<td>90/72</td>
<td>50</td>
<td>0.009 ± 0.0002</td>
</tr>
<tr>
<td>90/82</td>
<td>75</td>
<td>0.009 ± 0.0004</td>
</tr>
<tr>
<td>90/90</td>
<td>100</td>
<td>0.007 ± 0.0002</td>
</tr>
<tr>
<td>100/82</td>
<td>50</td>
<td>0.011 ± 0.0004</td>
</tr>
<tr>
<td>100/92</td>
<td>75</td>
<td>0.011 ± 0.0002</td>
</tr>
<tr>
<td>99/99</td>
<td>100</td>
<td>0.012 ± 0.0003</td>
</tr>
</tbody>
</table>
From the study of the activation losses occurring in the 3 MEAs; OCP, H\textsubscript{2} crossover, and ECSA validate that addition of the composite in the electrodes of the MEA does not affect material compatibility of the electrode layer. Tafel slope and charge transfer time constant demonstrate the advantage of the composite MEA at lower humidity conditions, which was also confirmed from the ohmic resistances of the MEAs. The other parameters computed from the polarization data, which have not been included in the previous paragraphs are addressed in Section 6.5.

**6.5 Effect of the composite on other parameters**

**6.5.1 Exchange current density and parasitic currents**

The effectiveness of an electrode is a function of its morphology and the properties of the catalyst used. It manifests as an apparent variation in the exchange current density [63] given by \(i_0\) in equation (7). In principle, it is the current transferring back and forth between the two electrodes at equilibrium [62]. \(i_0\) is determined by the concentrations of the reactants at the reaction site and the electrochemical rate constant. When simplified assuming bulk concentrations of the reacting species at the interface, the value can be determined by [57]

\[
i_0 = nFk^0C^* \tag{20}
\]

where \(k^0\) is the specific rate constant and \(C^*\) is the bulk concentration. From the above equation (20), \(i_0\) is proportional to reaction rate constant and the concentration of the reactants. The rate constant being an exponential function of temperature, a higher value of exchange current density must result with rise in temperature [63,90].
The common opinion is that higher exchange current density is a feature of better electrode characteristics as stated above in this section. Based on this opinion, when the Tafel slope is high, the exchange current density should be low. Interestingly, in this study, there is parallel decrease between Tafel slopes and exchange current density which is contrary to the generally expected trends between the two parameters. An explanation for such an incongruity is attempted from understanding the report by Arato and Costa [81]. In their analysis of the losses causing a drop in open circuit potential, they proposed that parasitic currents arising from crossover of hydrogen to the cathode could contribute to the exchange current density at the cathode. Typically the exchange current density for Oxygen Reduction Reaction (ORR) is in the range of $10^{-6}$ mA/cm$^2$, while that of hydrogen is about $10^{-3}$mA/cm$^2$ [81,92]. On the basis of their proposed theory, the oxidation of crossed over hydrogen at the cathode can appear as exchange current density at open circuit conditions. Since the exchange current density in this experiment is much higher than that of the ORR, and the trend of $i_0$ partially resembles H$_2$ crossover, it is deduced that the apparent values of exchange current density can be due to parasitic reactions rather than the pure exchange current originating from equilibrium current at zero overpotential. Considering that the calculated $i_0$ could be parasitic currents, its variation with the effect of temperature, RH and MEA composition are shown in Figure 24.
As the cell temperature is changed from 80°C to 100°C, the magnitude of $i_0$ increases by 93-167% for all tested MEAs at 50% RH (Figure 24 and Table 16). At the same cell temperature, the curve usually has a negative slope with increasing RH. However, at 100°C, the $i_0$ value increases with increase in RH only for MEA-1. By comparing columns 3, 4 and 5 in Table 16, and lines of different colors in Figure 24 for 50% RH, it can be observed that MEA-1 has the least value of $i_0$ and MEA-3 has the highest. At 100°C and 50% RH, the calculated $i_0$ value for MEA-1 is 518% less than MEA-2 and 70% lesser than MEA-3. The high values of exchange current for MEA-3 ...
could reflect higher parasitic currents as opposed to better catalyst activity. From this point of view, even though MEA-1 has the similar H₂ crossover characteristics as MEA-2, and higher than MEA-3, it still has lower i₀ values, suggestive of lower parasitic currents. However, this discussion needs to be corroborated with definitive experiments, as stated in reference [81].

Table 16. Numerical values of calculated exchange current density for MEA-1, MEA-2 and MEA-3 at the indicated operating conditions in columns 1 and 2. T_{FC} denotes the temperature of the cell and T_{RH} denotes the temperature set for both the anode and cathode humidifier to attain the required RH (column 2).

<table>
<thead>
<tr>
<th>T_{FC}/T_{RH} (°C/°C)</th>
<th>RH(%)</th>
<th>Exchange Current Density (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MEA-1</td>
</tr>
<tr>
<td>80/62</td>
<td>50</td>
<td>0.009 ± 0.002</td>
</tr>
<tr>
<td>80/72</td>
<td>75</td>
<td>0.007 ± 0.001</td>
</tr>
<tr>
<td>80/80</td>
<td>100</td>
<td>0.004 ± 0.001</td>
</tr>
<tr>
<td>90/68</td>
<td>40</td>
<td>0.042 ± 0.006</td>
</tr>
<tr>
<td>90/72</td>
<td>50</td>
<td>0.021 ± 0.002</td>
</tr>
<tr>
<td>90/82</td>
<td>75</td>
<td>0.009 ± 0.001</td>
</tr>
<tr>
<td>90/90</td>
<td>100</td>
<td>0.006 ± 0.001</td>
</tr>
<tr>
<td>100/82</td>
<td>50</td>
<td>0.023 ± 0.004</td>
</tr>
<tr>
<td>100/92</td>
<td>75</td>
<td>0.019 ± 0.004</td>
</tr>
<tr>
<td>99/99</td>
<td>100</td>
<td>0.030 ± 0.006</td>
</tr>
</tbody>
</table>

Under the assumption that the calculated i₀ represents parasitic currents, MEA-1 exhibits better MEA characteristics.
6.5.2 ‘m’ Variation

The last term in the equation (6) of Chapter 5, containing ‘m’ and ‘N’ represents the mass transfer losses occurring in the cell. ‘N’ has been addressed in Section 6.3.4. ‘m’ (as with ‘N’) is also determined by fitting an exponential curve to the difference between experimentally obtained data and voltage corrected for only activation and ohmic losses from equation (6) (Chapter 5) [56]. ‘m’ is empirically calculated to fit the experimental data and captures the variability arising from experimental uncertainties. Thus, variation of ‘m’ with the testing factors of the experiment, namely, temperature, RH and MEA composition; might not be definite. The physical significance of the empirical terms was suggested by Bevers et al. [66]. As seen from equation (6) (Chapter 5) changing the value of ‘m’ changes the slope of the curve in the mass transport controlled region and also the value of current density at which the output becomes mass transport controlled. Bevers and coworkers [66] have validated through simulations that the point of diffusion control and the slope of the curve in the current density region are greatly affected by the porosity and pore size of the gas diffusion layer. Reduced porosity and pore size can limit the partial pressure of the gases at the electrode interface thus modifying the slope of the high current density region. Thus, ‘m’ is associated with the pore characteristics of the GDL. These characteristics become more dominant in determining the point of diffusion control only when the electrolyte conductivity is very low. Even when the same GDL is employed, due to changes in water accumulation in the electrodes with different electrode compositions and operating conditions, ‘m’ value can change and the variation can be seen in Figure 25.
Figure 25. Empirical mass transport parameter ‘m’ in equation (6) of Chapter 5, calculated from experimental V-i curve recorded at the specified operating conditions. T_{FC} denotes the temperature of the cell and T_{RH} denotes the temperature set for both the anode and cathode humidifiers to attain the required RH indicated below each condition.

Although the effects of temperature and RH are not discernible for ‘m’, MEA composition produces a noticeable trend. The MEAs containing the composite (MEA-1 and MEA-2) appear to have similar degree of mass transport related losses given by ‘m’ at most of the temperatures and the reference MEA (MEA-3) appears to have minimum losses irrespective of the operating condition. In the case that the additive enhances greater water retention for MEA-1 and reduces the porosity of the GDL, it accounts for the diffusion related losses at lower current densities. Extending the same explanation for MEA-3, the absence of the composite in its elements should give the least values of ‘m’,
which is verified in Figure 25. The magnitude of potential loss attributed to mass transport limitations is in the range of $10^{-3}$ V to $10^{-2}$ V for the tested samples as given in Table 17 below. At 100°C and 50% RH, the value of ‘$m$’ is 55% greater for MEA-1 compared to MEA-3 and 7% greater than MEA-2.

Table 17. Numerical values of ‘$m$’, the mass transport related losses obtained for the three MEAs at indicated operating conditions in columns 1 and 2. $T_{\text{FC}}$ denotes the temperature of the cell and $T_{\text{RH}}$ denotes the temperature set for both the anode and cathode humidifier to attain the required RH (column 2).

<table>
<thead>
<tr>
<th>$T_{\text{FC}}/T_{\text{RH}}$ ($^\circ\text{C}/^\circ\text{C}$)</th>
<th>RH(%)</th>
<th>Mass transfer loss ‘$m$’ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MEA-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MEA-2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MEA-3</td>
</tr>
<tr>
<td>80/62</td>
<td>50</td>
<td>0.0122 ± 0.0010</td>
</tr>
<tr>
<td></td>
<td>0.0040 ± 0.0003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0000 ± 0.0000</td>
<td></td>
</tr>
<tr>
<td>80/72</td>
<td>75</td>
<td>0.0110 ± 0.0012</td>
</tr>
<tr>
<td></td>
<td>0.0090 ± 0.0009</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0013 ± 0.0001</td>
<td></td>
</tr>
<tr>
<td>2580/80</td>
<td>100</td>
<td>0.0169 ± 0.0018</td>
</tr>
<tr>
<td></td>
<td>0.0100 ± 0.0009</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0032 ± 0.0003</td>
<td></td>
</tr>
<tr>
<td>90/68</td>
<td>40</td>
<td>0.0059 ± 0.0006</td>
</tr>
<tr>
<td></td>
<td>0.0060 ± 0.0006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0003 ± 0.0000</td>
<td></td>
</tr>
<tr>
<td>90/72</td>
<td>50</td>
<td>0.0084 ± 0.0007</td>
</tr>
<tr>
<td></td>
<td>0.0070 ± 0.0005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0004 ± 0.0000</td>
<td></td>
</tr>
<tr>
<td>90/82</td>
<td>75</td>
<td>0.0083 ± 0.0007</td>
</tr>
<tr>
<td></td>
<td>0.0070 ± 0.0006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0030 ± 0.0003</td>
<td></td>
</tr>
<tr>
<td>90/90</td>
<td>100</td>
<td>0.0090 ± 0.0009</td>
</tr>
<tr>
<td></td>
<td>0.0075 ± 0.0005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0040 ± 0.0003</td>
<td></td>
</tr>
<tr>
<td>100/82</td>
<td>50</td>
<td>0.0150 ± 0.0013</td>
</tr>
<tr>
<td></td>
<td>0.0140 ± 0.0013</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0068 ± 0.0006</td>
<td></td>
</tr>
<tr>
<td>100/92</td>
<td>75</td>
<td>0.0155 ± 0.0013</td>
</tr>
<tr>
<td></td>
<td>0.0130 ± 0.0013</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0084 ± 0.0009</td>
<td></td>
</tr>
<tr>
<td>99/99</td>
<td>100</td>
<td>0.0129 ± 0.0012</td>
</tr>
<tr>
<td></td>
<td>0.0120 ± 0.0009</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0094 ± 0.0009</td>
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</tbody>
</table>

From the analysis of the results obtained from different techniques to ascertain the performance of the 3 sample MEAs, it has been inferred that incorporating the PWA nano-composite in the membrane and electrodes reveals better performance than the MEAs with the composite only in the membrane or no composite in membrane or electrodes. This effect is more evident at low humidity conditions. The validity of this
inference can be confirmed if the same conclusion can be drawn from repetition of this experiment.

To verify the reproducibility of the results, a second set of the 3 MEAs were fabricated following the same procedure described in Chapter 3 (Experimental Section). Since repetition of the entire experiment is very time consuming, the MEAs were tested at one selected operating condition of 90°C and 50% RH, satisfying both factors of elevated temperature and low RH condition.

### 6.6 Sources of variability

One of the main causes of variability is the difference in the morphology of the membranes and electrodes arising from fabrication uncertainties, which could likely be reduced if the process were automated. Since the membrane and electrodes for every tested MEA were prepared in the lab, duplicating the microstructure of the components between two MEAs is not feasible. In addition for a particular MEA, each “start-up” of the cell leads to distinctive formation of transport pathways for species within the components and at the interfaces [93]. Dissimilarities at this minute level have been reported as the cause of 8% variation in charge transfer resistances of the same MEA [93]. Consequently, a different approach was taken to examine the reproducibility of the results. The performance of the different MEAs with the same composition improved with practice, to that end the effect of the composite was tested between the three samples prepared for one complete experiment. The best performing MEAs of each composition were evaluated and the variation in performance is considered to be primarily due to the effect of the composition, assuming that the level of skill in fabrication is consistent.
among samples of a particular set. The extent of improvement observed from a different set of the three MEAs was found to be similar to the final results reported in this chapter. Figure 26 demonstrates the similarities in the improvement of polarization data for 2 sets of MEAs compared at the reference operating temperature of 80°C and 100% RH, and two other operating conditions of interest; 90°C-50% RH and 100°C-50% RH. From these results, addition of the PWA-composite to the ionomer of the electrode shows promise of improving performance at low humidity conditions.
To examine the prospect of achieving higher proton conductivity by increasing the additive concentration in the electrode, another experiment was conducted as summarized in the following section.
6.7  Optimization of PWA/TEOS composite in the electrode

The objective was to explore the optimum composition of the additive in the electrodes. Two other MEAs with the same membrane composition as the MEA-1, but with a higher percentage of the PWA nano-composite in the electrode layer were fabricated. MEA-4 and MEA-5 were prepared in the same procedure as MEA-1 but with higher amount of TEOS and PWA in the electrode ink. The electrode component of MEA-4 had twice the PWA/TEOS weight and MEA-5 had 4 times the amount of the nano-composite with respect to MEA-1. The V-i curves collected for the new MEAs were recorded and compared with the data of the 3 sample MEAs and are displayed in the Figure 27 (a), (b), and (c) below. Data was recorded at selected operating conditions of 80°C and 100% RH, 90°C and 50% RH and 100°C and 50% RH.
Figure 27. Polarization data with H₂/O₂ at 0.2 l/min and 1 atm, comparing MEAs with variation in the amount PWA composite in the electrode layer at 5 levels. MEA-1 (blue), MEA-2 (red) and MEA-3 (purple) have the PWA content indicated in Chapter 4 (Experimental Section). MEA-4 (orange) has the twice the PWA content as MEA-1 and MEA-5 (green) has 4 times the PWA content as MEA-1. (a) V-i data recorded at 80°C and 100% RH (solid lines), (b) V-i data recorded at 90°C-50% RH (dashed lines) and (c) V-i data recorded at 100°C-50% RH (dotted lines).

MEA-5 (orange line) shows contrastingly low performance at all the examined conditions. MEA-4 (green line) is relatively better than MEA-5 but is inconsequential in terms of output. It is speculated that higher quantity of the composite could form a separate network of SiO₂ instead of being dispersed as individual particles attached to the ionomer [21]. This can disrupt the formation of TPBs making the MEA unproductive. The other plausible explanation is that the excess amount of PWA could get adsorbed on
the carbon substrate, leading to deactivation of the catalyst [24] and subsequently large activation losses. Therefore, the quantity of PWA-SiO$_2$ in the ionomer of the electrode is in the same ratio as suggested by Mahreni et al. [11] because the addition of higher amounts was detrimental to MEA performance. An interesting observation from Figure 27 (c) is that, MEA-5 demonstrates an improvement in performance at the corresponding operating condition of 100°C and 50% RH as compared to 80°C and 100% RH in Figure 27 (a) and 90°C and 50% RH in Figure 27 (b). It is likely that the function of PWA composite to enhance the proton conductivity becomes significant on increasing temperature and reducing the RH. Such a hypothesis can be confirmed by testing a wider range of operating conditions.
CHAPTER 7: CONCLUSION AND FUTURE WORK

Nafion® is the common polymer electrolyte membrane used in PEMFCs and is also added in the electrode layer to enhance catalyst utilization. Proton conductivity of the membrane at higher temperature and lower humidity was found to improve on incorporation of a PWA/TEOS nanocomposite. As an extension of this study, the effect of PWA/TEOS in the electrode layer was explored. Three MEAs, one with the composite in the electrode and membrane, a second one with composite only in the membrane and the third (reference MEA) with no composite in either of its components were prepared and tested. Considering the huge uncertainties arising from fabrication of each individual component, reproducibility of the results was established by comparing the performances of between 3 MEAs of a single set. The variation in performances between 3 MEAs was found to be in agreement with other sets. Polarization, CV and EIS measurements were conducted and compared for the 3 MEAs at different operating conditions ranging for 80°C to 100°C, each at relative humidities of 50% RH, 75% RH and 100% RH.

The realization of the objective of this experiment was verified instinctively by comparing the overall ohmic resistance and the ohmic resistance of the electrodes between MEAs. Overall ohmic losses was determined by comparing these resistances at 0.8 V measured from current interrupt technique ($R_\Omega$) and the high frequency intercept ($R_{hf}$) of EIS spectrum. The extent of ohmic losses ascribable only to the electrodes could not be measured directly and was assessed by observing the values of ‘$N’$. For the overall ohmic resistances, $R_\Omega$ and $R_{hf}$, the temperature effect is not very distinguishable within the range tested. The effect of changing the RH was more distinct. At 50% RH, the
improvement in these values for MEA-1 is evident. The result observed from ‘N’ values of MEA-1 in comparison to MEA-2 and MEA-3 is also optimistic. MEA-1 generates least electrode ohmic resistance relative to MEA-2 and MEA-3 at all operating conditions.

The effect on activation losses were estimated from OCP, H₂ crossover, ECSA values, Tafel slopes and charge transfer resistances. With the change in cell temperature or RH, the percentage of variation in OCP was below 7%. However, even within this small range, MEA-1 had higher OCP values at 50% RH. The moles of H₂ crossover for MEA-1 and MEA-2 were marginally higher compared to MEA-3. In spite of such a result from hydrogen crossover, the Tafel slopes and charge transfer time constant verify that among the three MEAs, MEA-1 has the lowest activation losses, particularly prominent at 50%RH. The ECSA values which can be used to understand activation losses substantiates that the catalyst active surface area of MEA-1 is not compromised due to the addition of the PWA composite in the electrodes.

The computed values of exchange current density were argued to be a possible reflection of parasitic currents. Based on this assumption, MEA-1 demonstrated lower currents generated by undesirable reactions as compared to the other samples at 50% RH conditions.

The value of ‘m’ which is a representation of mass transfer losses was calculated from the mass transport limited region in the polarization curve. MEA-1 and MEA-2 displayed higher values of this parameter compared to MEA-3. The presence of the
composite probably caused greater water retention in the gas diffusion layers or interfaces leading to higher mass transport losses.

Despite minor losses due to H₂ crossover and mass transport limitations, in effect MEA-1 demonstrated best results, particularly at low relative humidity promoting the benefits of adding PWA nanocomposite to the electrode and membrane. The highest performance was still obtained at 80°C and 100% RH even for the best performing MEA. Although, the optimum operating temperatures did not change upon PWA addition, comparison of the three MEAs at 50% RH showed promise of the PWA as an additive in the ionomer to improve output.

As a continuation of this study, higher temperatures i.e. upto 120°C or 140°C, can be tested to observe the performance of the MEA containing the PWA composite in its constituents. The results at these conditions will be more useful in evaluating the application of this composite MEA (MEA-1 in this study) for high temperature operation. If the results from such an experiment demonstrate the expected results of improved output, durability studies have to be conducted to verify its use for real-world applications. In addition to testing the durability, the effect of CO poisoning on MEA performance at high temperature, can also be observed by using industrial H₂ as a fuel instead of high purity H₂.

Physical characterizations such as Thermogravimetric analysis (TGA) to examine the thermal stability of the MEA and Scanning Electron Microscopy (SEM) to examine the micro-structure of the membrane and electrodes can also be conducted.
REFERENCES


APPENDIX A: CYCLIC VOLTAMMOGRAMS

The cyclic voltammograms obtained for MEA-1, MEA-2 and MEA-3 at the same operating conditions as the polarization curves are presented in Figure 28, Figure 29 and Figure 30. The experimental set up is given in detail in Section 4.2.2. The ECSA values for each tested MEA at the indicated operating conditions were calculated from this data as per the method described in Section 4.2.4.

Figure 28. CV data recorded for MEA-1, MEA-2 and MEA-3 at 80°C and different RH with H₂/N₂ at 0.2 l/min and at atmospheric pressure at a scan rate of 50 mV/s. a) 80°C and 100% RH; (b) 80°C and 50% RH; Line color represents MEA composition (Blue-MEA-1; Red-MEA-2; Purple-MEA-3). Line pattern indicates data at a particular temperature (Solid lines-80°C, dashed lines - 90°C and dotted lines- ~100°C).
Figure 29. CV data recorded for MEA-1, MEA-2 and MEA-3 at 90°C and different RH with H\textsubscript{2} / N\textsubscript{2} at 0.2 l/min and at atmospheric pressure at a scan rate of 50 mV/s. a) 90°C and 100% RH; (b) 90°C and 40% RH. Line color represents MEA composition (Blue-MEA-1; Red-MEA-2; Purple-MEA-3). Line pattern indicates data at a particular temperature (Solid lines-80°C, dashed lines - 90°C and dotted lines- ~100°C).

Figure 30. CV data recorded for MEA-1, MEA-2 and MEA-3 at 100°C and different RH with H\textsubscript{2} / N\textsubscript{2} at 0.2 l/min and at atmospheric pressure at a scan rate of 50 mV/s. a) 100°C and 100% RH; (b) 100°C and 50% RH. Line color represents MEA composition (Blue-MEA-1; Red-MEA-2; Purple-MEA-3). Line pattern indicates data at a particular temperature (Solid lines-80°C, dashed lines - 90°C and dotted lines- ~100°C).
APPENDIX B: IMPEDANCE SPECTRA

The impedance spectra obtained for MEA-1, MEA-2 and MEA-3 at the operating conditions used for the polarization curves and CV are displayed in Figure 31-Figure 33. The experimental set up is given in Section 4.3.2. The ohmic resistance and charge transfer time constant were calculated from this data as described in Section 4.3.3.

Figure 31. Impedance spectra recorded for MEA-1, MEA-2 and MEA-3 at 80°C and different RH with the following conditions: H\textsubscript{2} / O\textsubscript{2} at 0.2 l/min, atmospheric pressure, biased potential of 0.8 V, AC signal amplitude of 15 mV, frequency range from 4000 Hz to 0.1 Hz. (a) 80°C and 100% RH; (b) 80°C and 75% RH; (c) 80°C and 50% RH. Line color represents MEA composition (Blue-MEA-1; Red-MEA-2; Purple-MEA-3). Line pattern indicates data at a particular temperature (Solid lines-80°C, dashed lines-90°C and dotted lines- ~100°C).
Figure 32. Impedance spectra recorded for MEA-1, MEA-2 and MEA-3 at 90°C and different RH with the following conditions: H$_2$ /O$_2$ at 0.2 l/min, atmospheric pressure, biased potential of 0.8 V, AC signal amplitude of 15 mV, frequency range from 4000 Hz to 0.1 Hz. (a) 90°C and 100% RH; (b) 90°C and 75% RH; (c) 90°C and 50% RH; (d) 90°C and 40% RH. Line color represents MEA composition (Blue-MEA-1; Red-MEA-2; Purple-MEA-3). Line pattern indicates data at a particular temperature (Solid lines-80°C, dashed lines-90°C and dotted lines- ~100°C).
Figure 33. Impedance spectra recorded for MEA-1, MEA-2 and MEA-3 at 100°C and different RH with the following conditions: H₂/O₂ at 0.2 l/min, atmospheric pressure, biased potential of 0.8 V, AC signal amplitude of 15 mV, frequency range from 4000 Hz to 0.1 Hz. (a) 100°C and 100% RH; (b) 100°C and 75% RH; (c) 100°C and 50% RH. Line color represents MEA composition (Blue-MEA-1; Red-MEA-2; Purple-MEA-3). Line pattern indicates data at a particular temperature (Solid lines-80°C, dashed lines-90°C and dotted lines-~100°C).