Performance of High Temperature PEM Fuel Cell Materials.
Part 1: Effects of Temperature, Pressure and Anode Dilution

Michael G. Waller, Mark R. Walluk, Thomas A. Trabold*

Golisano Institute for Sustainability and Center for Sustainable Mobility
Rochester Institute of Technology
Rochester, New York 14623

***Corresponding Author**

tatasp@rit.edu, Tel: 001-585-475-4696
111 Lomb Memorial Drive, Rochester, NY 14623

Abstract

High temperature proton exchange membrane (HT-PEM) fuel cells operate most effectively at temperatures 160°C or greater and can tolerate high carbon monoxide concentrations in fuel feeds. For practical mobile fuel cell systems, the ability to tolerate high levels of carbon monoxide enables a simplified integrated reformer fuel cell design, where a one-step reforming process can directly feed the fuel cell. This creates the potential for practical fuel cell systems to be designed that are capable of operating using an on-board hydrocarbon fuel. Hydrocarbon reforming processes (i.e., partial oxidation, steam reforming, or autothermal reforming) generate effluent gas compositions that typically contain various amounts of hydrogen, carbon monoxide, carbon dioxide, nitrogen, and water. While there are several studies that have examined the effects of CO dilution on HT-PEM fuel cell performance, there are very few that have examined the effects of other common reformat species, particularly while operating at varying temperatures and pressures. This work aims to fill the research gap in published data through evaluation of the performance exhibited by two HT-PEM membrane-electrode assembly (MEA) types, Advent's TPS[®]-based MEA and the BASF Celtec series MEA, based on acid-doped polybenzimidazole (PBI). In Part I of this series, the effects of temperature and pressure for various percentages of anode dilution were investigated. Temperatures and pressures were varied from 160 to 200°C and 101.3 to 200 kPa, respectively. The effect of hydrogen diluted with nitrogen in the anode feed was examined with nitrogen concentrations up to 70%. Overall, the PBI MEA provided greater performance than the TPS for all tested conditions. Our results show that the performance loss due to high dilution levels can be wholly mitigated by an increase in operating temperature, pressure, or a combination thereof. For example, even at a dilution level containing 70% nitrogen, operating the cell at 200°C and at 200 kPa provides the same power output as running the cell on pure hydrogen at 160°C and at atmospheric pressure. This data can be used to model the performance effect of high diluent concentrations in the anode gas feed when developing an integrated reformer/fuel cell system.

Keywords

High temperature PEM fuel cell, PBI, TPS, nitrogen dilution

Introduction

System designs integrating an on-board fuel reformer with a conventional PEM fuel cell using Nafion[®]-based MEAs are very complex, involving multiple fuel reforming and shift reactors to purify the hydrogen stream entering the fuel cell. Most single-step reforming processes tend to generate large amounts of carbon monoxide (CO), which adsorbs strongly onto platinum (Pt) at low temperatures, poisoning the electrode catalyst. For conventional polymer electrolyte membrane (PEM) fuel cells (PEMFCs) that operate around 80°C, significant performance loss is observed at CO concentrations in the anode feed of 10 ppm [1], [2]. To reduce CO concentrations below 10 ppm, multiple reactors such as water gas shift (WGS) [3], preferential oxidation (PROx) [4], and pressure swing adsorption (PSA) [5] are required to clean up the reformat after the initial reforming reaction. Operating several reactors to produce dynamic power for mobile applications is impractically complex, and a CO-tolerant PEMFC technology would greatly simplify the overall system design.

High temperature PEM fuel cells (HT-PEMFC) offer numerous advantages over conventional PEM fuel cells including fuel flexibility and reduction in balance of plant (BoP) equipment required at the system level. Operating at temperatures typically between 160 and 200°C allows the fuel cell to generate electricity using hydrogen feeds that contain much higher concentrations of contaminants than can be tolerated with conventional Nafion-based PEM fuel cells [6], [2], [7]. For example, Li et al. [2] considered the effect of CO concentrations up to 16% in a HT-PEM fuel cell. Although the performance of the fuel cell with CO concentrations of 16% was the lowest of all the tested operating conditions, useful amounts of power were generated nonetheless. This demonstrates that high power outputs are achievable with HT-PEM fuel cells, even when operating on very high concentrations of diluents. Additionally, operating at temperatures above the boiling point of water reduces complex water management BoP equipment because water can easily be removed from the cell as a vapor rather than as a liquid. These benefits allow for a much simpler integrated fuel reformer and fuel cell stack design.

Novel types of membranes used for HT-PEMFCs such as those described in [8], [9], [10], and [11]; however, only a few have seen some commercial success. One of the commercially available membranes is based on a pyridine containing poly(ether sulfone) [12], [13], [14], also known as TPS[®], and is currently produced by Advent Technologies Inc. [15]. A large focus of researchers using TPS-based membrane electrode assembly (MEAs) has been on developing direct methanol fuel cells (DMFC) such as in [14] and [16]. While commercially available, there is, however, limited MEA performance data based on Advent's TPS technology in published literature.

The most widely studied HT-PEMFC membrane is the Celtec-P series developed by BASF based on acid-doped polybenzimidazole (PBI) [17], and it has seen some commercial success [18]. Other commercially available PBI based MEAs are offered by Danish Power System [19], and was investigated in [20]. The Celtec MEAs were chosen for use in our research as they appear to be more widely used in prior published research and they represent the state-of-the-art in commercially available HT-PEM MEAs.

Numerous performance studies have been conducted using the Celtec series MEAs investigating parameters such as temperature [21], [22] CO concentration [17], [23], [24], relative humidity [25], [26], and durability [27], [28], [29]. Most performance studies for PBI-

based HT-PEMFCs have focused largely on cell performance when operating on pure H₂, or H₂ mixed with various amounts of CO, and at atmospheric pressure. However, if hydrogen is generated from an on-board fuel processor using a catalytic partial oxidation (cPOx), steam reforming (SR), or autothermal reforming (ATR) process, other gases may be produced that will enter into the anode of the fuel cell stack such as N₂, CO₂, H₂O, CH₄, C₂H₄, and C₂H₆. For example, under optimal reforming operating conditions, propane cPOx will produce effluent gas composed of 28% H₂, 23% CO, and 49% N₂ [30].

Presently, very little data for HT-PEM fuel cells can be found while operating on high concentrations of N₂ in the anode, as well as under high pressures up to 200 kPa. If future integrated reformer HT-PEMFC systems are to be developed, the impact of N₂ dilution on a HT-PEMFCs performance should be investigated, as well as the effect of operating pressure. This article is the first in a series that attempts to fill this gap by investigating the performance of commercial TPS and PBI-based MEAs while varying the temperature, pressure, and different anode dilution concentrations with nitrogen (N₂). It is important to note that the effect of anode dilution is the focus of this study rather than CO₂, another common fuel reforming effluent gas; this is for two reasons. The first is because some fuel reforming processes generate significant amounts of N₂ in the effluent, and very little if any CO₂ as described in the previous paragraph. The second is that several other works that investigate the effect of CO₂ concentrations in the anode up to 25% versus N₂ concentrations at the same level, show that N₂ and CO₂ result in the same performance loss when operating at the temperatures investigated in this study [2]. Although, the performance loss from CO₂ versus N₂ when operating at lower cell temperatures, such as 60°C, do show that CO₂ greater negative impact than N₂ [31]. In this work, the H₂ concentration was varied from 30-100%, the temperature was varied from 160-200°C, and the operating pressure was changed from atmospheric to 200 kPa.

1.0 Experimental

All experiments were performed using a modified Hydrogenics fuel cell test stand. Several TPS and PBI-based MEAs were purchased from Advent Technologies with active cell areas of 45.2 cm² [15]. BASF has stopped manufacturing the Celtec series MEAs, but has licensed their technology to Advent Technologies who manufactured the MEAs used in our experiments. The MEAs purchased were the Celtec P1100W and Advent's TPS series MEA, with total precious metal loadings of 1.7 and 3.0 mg/cm², respectively. The manufacturer did not provide the specific amount of precious metal loading on the anode/cathode, nor the catalyst composition. The MEAs were placed in a test cell, shown in Figure 1, comprised of two graphite plates with flow channels cut in a quad serpentine pattern, supplied by Fuel Cell Technologies. The end plates contain heating rods in order to control the cell temperature through a computer controlled relay.

Figure 1: Picture of the actual test cell supplied by Fuel Cell Technologies

According to the manufacturer's specifications, a break-in period of 24 hours operating on pure hydrogen was completed for each cell where power was drawn at a current density of 0.2 A/cm^2 at a temperature of 160°C for the PBI, and 180°C for the TPS. Figure 2 displays a schematic representation of the test cell system. Gases N_2 , H_2 , and Air were metered using Brooks mass flow controllers calibrated to control the desired gases. Cell back pressure was controlled using diaphragm regulators. The temperatures at the inlet and exit ports of the cell were maintained above 120°C so water would not condense within the test cell, as liquid water formation is a well-known degradation phenomena [32]. Water generated in the cell was condensed and removed downstream of the exhaust, as shown in Figure 2.

A Labview[®] control and data acquisition system was developed to automatically measure polarization curves and control gas flows. After the break-in, polarization curves were run from $0 - 1.5 \text{ A/cm}^2$ for the PBI MEAs, and $0 - 0.9 \text{ A/cm}^2$ for the TPS. All tests were run with a stoichiometric ratio of 1.5 at the anode using either pure hydrogen or a specified mixture of H_2 and N_2 , and a stoichiometric ratio of 2.0 at the cathode using air. Polarization curves were obtained by current step potentiometry, and were measured beginning with the open circuit voltage. Because of the maximum flow rate capabilities of the hydrogen flow controller used, polarization curves with anode feeds containing 30% H_2 and 70% N_2 could only be measured up to 0.9 A/cm^2 while still maintaining a stoichiometry of 1.5 at the anode.

Figure 2: Schematic of the HT-PEMFC single cell test setup

All tests were performed on two MEAs for each cell type. For each different anode concentration, polarization curves were taken at three different temperatures, and three different pressures. The sequence for setting the test parameters was to first select the anode feed concentration, then the cell temperature, and finally cycle through the experimental pressures. The first polarization curve taken was run at an H_2/N_2 concentration of 100/0, a temperature of 160°C , and at atmospheric pressure of 101.3 kPa. The last polarization curve was taken at an H_2/N_2 concentration of 30/70, a temperature of 200°C , and at a pressure of 200 kPa. Including the 24 hour break-in procedure, the test protocol run on each cell required approximately 65 hours to complete.

2.0 Results and Discussion

Figure 3 compares several baseline polarization curves from our experiments with data generated by the manufacturers of the MEAs tested under similar operating conditions. The data obtained from our tests compares well with data from the manufacturers, indicating our experimental setup functions properly.

Figure 3: Performance of baseline RIT polarization curves of the tested MEAs as compared to data provided by the manufacturer. Each curve is labeled with the research organization and MEA type, the anode and cathode stoichiometric ratios, the operating temperature, and the publication year for the data source. The sources for each curve are as follows: this work, [33], [18], this work, [34].

Figure 4 displays the effects of temperature, pressure, and anode dilution for all tests run on the PBI type membrane. Increasing the temperature of the cell as well as operating pressure results in greater performance. The maximum power density of the lowest performing curve is 252 mW/cm^2 , and occurs at a 30/70 H_2/N_2 anode concentration mix, 160°C , and 101.3 kPa. Conversely, the maximum power density of the highest performing curve of 754 mW/cm^2 was achieved at a 100/0 H_2/N_2 anode concentration mix, 200°C , and 200 kPa. The maximum power densities of the lowest and highest performance curves are simultaneously the high and low boundary conditions for all experimental variables.

Figure 4: PBI MEA performance curves as a function of anode dilution, temperature, and pressure

As can be seen in each sub figure of Figure 4, anode dilution has a significant impact on performance for the given test conditions, particularly at lower temperatures and pressures. This can be interpreted when looking at the typical relationships used to model fuel cell polarization curves which can be written as:

$$V_{cell} = E^0 + \frac{RT}{2F} \ln \left(\frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} \right) - \frac{RT}{2\alpha F} \ln \left(\frac{i}{i_o} \right) - ir - m \exp(ni) \quad (1)$$

The first two terms represents the Nernst voltage, where E^0 is the cell voltage at standard operating temperature and pressure, R is the universal gas constant, and F is Faraday's number, and P is the partial pressure of the different gas species. The third term is the Tafel equation used to determine the activation overpotential where α is the charge transfer coefficient, i is the current density, and i_o is the exchange current density. The fourth term defines the ohmic losses that are linearly related to the current density where r is the ohmic resistance. The final term is an empirical relationship used to represent the mass transport losses, and is one of the more common models, because it provides an excellent fit [35]. While the mass transport term is useful for modeling polarization data, it is not very helpful in determining how increases in operational parameters such as cell temperature, will effect these losses.

From a thermodynamic perspective, high dilution levels or low overall system pressures result in a decrease of the reactants partial pressures. This reduction in pressure effects multiple

terms in the equation used to model the fuel cell voltage. This impacts the Nernst voltage term resulting in a reduced open circuit voltage. Additionally, it is presumed operating at lower reactant pressures results in lower catalyst site occupancy, thereby reducing the value of the exchange current density, i_o , and increasing the activation polarization losses [36]. The mass transport losses are also affected by pressure changes, and increase from reduced partial pressures of the reactants as they are consumed. The mass transport effect is typically seen on the polarization curve at high current densities, but with a reduction in overall system pressure, the mass transport loss will be observed earlier on the polarization curve. Conversely, an increase in the overall system pressure, which in turn increases the partial pressure of the reactants, pushes the mass transport effect further out on the polarization curve. This is evident in Figure 4 as the pressure increases from left to right.

Figure 5: Differential voltage data and fitted models for the PBI MEA due to higher pressures relative to operation at atmospheric pressure for dilution levels of 0% and 20% at cell temperatures of 160°C

Figure 5 shows the differential voltage for the PBI MEA due to higher pressures relative to operation at atmospheric pressure for dilution levels of 0% and 20%, and at cell temperatures of 160°C. Modeling the increase in voltage due to an increase in pressure for the open circuit voltage is relatively straightforward using the Nernst term in Eq.1. If the system pressure changes from P_1 to P_2 , the resulting change in OCV will be equal to:

$$\Delta V = \frac{RT}{4F} \ln \left(\frac{P_2}{P_1} \right) \quad (2)$$

When increasing the pressure from 101.3 to 150 and 200 kPa respectively, at 160°C the resulting increase in voltage due to the Nernst potential is 3.7 and 6.3 mV respectively. The rest of the voltage increase due to pressure can be attributed to a reduction in the activation overpotential and the mass transport losses. However, there is no explicit relationship defining the effect pressure has on the exchange current density or the mass transport loss coefficients. Nevertheless, an empirical model can be developed that fits the data well by combining Eq. 2

with the activation and mass transport overpotential terms found in Eq. 1. The effect pressure has on the voltage of the cell can be modeled as:

$$\Delta V = V_2 - V_1 = \frac{RT}{4F} \ln \left(\frac{P_2}{P_1} \right) + A \ln(B) + C \exp(Di) \quad (3)$$

where A , B , C , and D are empirically determined coefficients. The coefficient A represents the effect pressure has on the charge transfer coefficient α where α must be between 0 and 1 and is typically between 0.1 and 0.5. From the Tafel equation, $A = \frac{RT}{2\alpha F}$, and since α is between 0.1 and 1, then A must be between 0.0187 and 0.187. The coefficient B incorporates the effect the change in pressure has on the exchange current density and is equal to the ratio of exchange current densities at different pressures, ($B = \frac{i_{o,2}}{i_{o,1}}$). As it is not expected that pressure will have a positive impact on the exchange current density, $B > 1$. C and D describe the impact the change in pressure has on the coefficients m and n used in Eq. 1. This model provides an excellent fit to the data (within +/- 5 mV) and is plotted in Fig. 4. Table 1 shows the parametric coefficients used for the empirical models shown in Fig. 5. Note that in the model, i is in units of mA/cm².

Table 1: Parametric coefficients used for models in Figure 4.

Model (H ₂ /N ₂ %, kPa)	A	B	C	D
80/20, 150	0.0771	1.24	5.15E-3	1.80E-3
80/20, 200	0.0801	1.29	1.56E-2	1.39E-3
100/0, 150	0.0622	1.12	1.39E-2	5.41E-4
100/0, 200	0.0814	1.14	2.74E-2	5.08E-4

Increasing the operating temperature of the cell also increases the performance of the cell. Particularly noticeable in Fig. 3 is the effect temperature has on performance at anode dilution levels of 70% N₂. Increasing the cell operating temperature from 160 to 200°C, while keeping the system pressure at 101.3 kPa, results in an increased voltage level of 342 mV at a current density of 0.9 A/cm². This equates to a power density increase of 308 mW/cm². At higher operating pressures though, this effect is not as pronounced. When operating under 70% anode dilution at 200 kPa, increasing the cell temperature from 160 to 200°C provides a voltage increase of 74 mV at 0.9 A/cm², a power density increase of 67 mW/cm².

Although not apparent from Eq. 1, the increase in temperature effects each term, including the ohmic resistance and mass transport overpotentials. As seen in Eq. 1, the temperature of the cell is directly proportional to the Nernst voltage and activation polarization; however, its relationships with the exchange current density, ohmic resistance, and mass transport losses are not as well understood.

Several authors have investigated the effect of temperature on the exchange current density, developing complex models to account for many different parameters including temperature, pressure, electrochemical rate reactions, etc. [37]. Others, such as Korsgard et al. [22], have developed simple models that are a function of temperature only where the authors suggest the exchange current density has an exponential relationship with temperature. Whatever the relationship is, it is clear that a higher operating temperature of the fuel cell leads to a larger exchange current density, which in turn reduces the activation losses.

It has also been suggested that an increase in temperature has a positive correlation with the ohmic losses. In [25] and [38], the authors suggest that the membrane temperature dependency of conductivity obeys an Arrhenius relation. In [22], the authors empirically determined a linear relationship between temperature and the ohmic loss parameter for a PBI MEA. The positive effect of temperature on the ohmic loss is also evidenced in this work.

The mass transport losses are also reduced by increasing the cell operating temperature, particularly at high dilution levels as is evidenced when comparing the 30/70 H₂/N₂ polarization curve at 160°C, 101.3 kPa to the 30/70 H₂/N₂ curve at 200°C, 101.3 kPa. Mass transport losses are a result of reactant depletion at catalyst sites, and begin to appear when the reactant concentration at the surface of the catalyst approaches 0, or when the catalyst reaction cannot occur quickly enough for the desired current draw. Since increases in operating temperatures do not affect the reactant surface concentration, the positive effect an increase in fuel cell temperature has on the mass transport losses is likely a result from an increase in the reaction rate of the electrode catalysts.

While the negative performance effects of anode dilution are most strongly seen at low temperatures and pressures, even at anode concentrations of 30/70 H₂/N₂, increasing the temperature and/or pressure can drastically improve the performance of the MEA. For example, Figure 6 shows performance curves of diluted anode feeds that produce similar power levels (within a voltage range of +/- 20 mV at 0.9 A/cm²) for a PBI MEA operated on pure H₂ at 160°C. Figure 10 shows similar results but for the TPS MEA.

Figure 6: Performance curves of a PBI MEA under various operating conditions of anode dilution, temperature, and pressure, but with similar power outputs.

Even at high dilution levels of 70% N₂, similar performance can be obtained as operating on pure H₂ at 101.3 kPa through varying the cell temperature and pressure. This is a very interesting finding, particularly when designing a system capable of running on a reformed fuel feed. For some reforming processes, hydrogen concentrations in the effluent stream can be as low as 30%. To increase the hydrogen content to higher levels and boost performance, additional reactors are needed, further complicating a system. A relatively simpler approach might be to either increase

the temperature, operating pressure, or some combination of the two, to realize greater performance. Ultimately, an energy, durability, and economic tradeoff analysis would be needed to determine the optimal design strategy, including the durability implications of operation at higher temperatures and pressure.

Figure 7: TPS MEA Performance curves as a function of anode dilution, temperature, and pressure

Figure 7 presents the performance curves measured for the TPS MEA under the same conditions used for the PBI MEA. Many of the general trends of the TPS MEA were similar to the PBI, but with some notable differences. Overall, the TPS did not perform as well as the PBI-based MEA. Additionally, the TPS MEA would not generate stable voltages beyond 0.9 A/cm² for most polarization curves, due to significant mass transport losses. As a result, the maximum power point for most curves occurred between 0.6 and 0.8 A/cm². The reasons for this are unclear and outside the scope of this work. Further investigation is necessary. The maximum TPS power point of the lowest performing curve of 157 mW/cm² was measured at the same conditions as the PBI MEA at a 30/70 H₂/N₂ anode concentration mix, 160°C, and 101.3 kPa. The maximum power density for the highest performing TPS curve was 418 mW/cm² and occurred at 100/0 H₂/N₂ anode concentration mix, 180°C, and 200 kPa. This maximum power density was 336 mW/cm² lower than the maximum power density achieved by the PBI, almost 45% lower performance.

Figure 8: Performance of TPS MEA for various pressures at 180°C and a 30/70 H₂/N₂ dilution level.

Increasing the operating pressure of the TPS cell has a similar effect as for the PBI, and is most notable at high dilution levels, particularly at 180°C, as shown in Figure 8. At a current density of 0.7 A/cm², increasing the system pressure from 101.3 to 200 kPa results in a voltage increase of 242 mV, or a power density increase of 170 mW/cm² for the TPS MEA. The change in voltage due to pressure can similarly be modeled using Eq. 3.

The effect temperature has on the cell performance for the TPS was not as pronounced as for the PBI. In some cases, performance of the TPS MEA at 200°C was almost the same if not slightly lower than the performance at a temperature of 180°C. As an example, Figure 9 displays the performance curves for the TPS MEA operating on pure H₂ at 150 kPa for various temperatures. For many of the tests conducted, increasing the operating temperature appeared to increase the performance of the cell at lower current densities, but decrease performance at high current densities.

Figure 9: Performance of TPS MEA for various temperatures at 101.3 kPa operating on pure H₂ at the anode

This trend is seen at various dilution levels and pressures and appears to result from a reduction in the activation losses coupled with an increase in the mass transport losses. The underlying reason for this trend is unclear as an increase in temperature is expected to reduce both the activation and mass transport losses through an increase in catalytic activity as a result of higher temperatures. Further investigation is necessary to better comprehend the effects of operating conditions on performance of TPS-based MEAs.

Figure 10: Performance curves of a TPS MEA under various operating conditions of anode dilution, temperature, and pressure, but with similar power outputs

Figure 10 displays several polarization curves that produced similar performance results (within a voltage range of +/- 20 mV at 0.6 A/cm²) for the TPS MEA, but under different anode

dilution levels, temperatures, and pressures. Similar to the performance curves presented in Figure 6 for the PBI MEA, varying the operating temperature and/or pressure within reasonable limits is an effective way to increase the performance even when operating on highly diluted anode gas concentrations.

Figure 11: Comparison of the lowest and highest performing polarization curves for the PBI and TPS MEAs

Figure 12: Power density curves of the lowest and highest performing polarization curves for the PBI and TPS MEAs

Figure 11 and Figure 12 compare the highest and lowest performance polarization and power density curves respectively of the tested conditions for both the PBI and TPS MEAs. The PBI

MEA outperforms the TPS MEA at both the “best” and “worst” test conditions. Additionally, higher operational current densities are achievable when using the PBI material, as the mass transport losses become too large for stable voltage performance of the TPS MEA. The data presented in this paper do not address the MEA tolerance of other contaminants, or durability under long-term operation. Durability issues, such as CO tolerance and long term performance, are important considerations when designing an overall system, and will be considered in future studies of integrated reformer/HT-PEM fuel cell systems.

Several authors have investigated the long-term durability of PBI MEAs, such as [11], [27], [29], and [32], but have only investigated the impact of a few variables. In [11], the authors investigate a novel TiO₂ composite PBI membrane for over 1100 hours. While operating at 150°C, Their results revealed that acid loss was reduced by 2% when 2 wt.% of TiO₂ was added to the membrane. In [27], it is shown that the phosphoric acid evaporation rate of PBI MEAs increases exponentially as the temperature increases. At 200°C, the phosphoric acid evaporation rate was found to be roughly six times the evaporation rate of operation at 160°C. The same study reports a voltage loss of 40 mV after more than 6000 continuous hours (a loss of 6.67 μ V/hr) while operating at 160°C and a current density of 0.2 A/cm². Assuming the voltage loss over time was largely due to phosphoric acid evaporation, operation at 200°C might still allow for over 1000 hours of continuous operation with a voltage drop of 40 mV. However, further investigation of this theory is necessary. To the authors’ best knowledge, there are no long-term studies in the public literature on TPS performance. The cells tested in this work were only operated for 65 hours, exhibiting essentially no performance loss over the tested lifetime. This was surprising given the high temperature operation however, the evaporation rate of phosphoric acid was likely reduced due to the high pressure operations at 200°C. Further investigation into longer lifetimes, and the effects of operating pressure on evaporation rate, is a topic of future research, and may have substantial system level design implications.

Perhaps the most important result from the current study is that even while operating on highly diluted anode feed concentrations, modifications to the operating parameters, such as temperature and system pressure, can improve performance to the levels achieved under typical operating conditions (i.e. 160°C, 101.3 kPa for the PBI). When designing a functional system using a HT-PEMFC to run on a hydrocarbon fuel, it may be less costly, both energetically and economically, to increase either the operating temperature or pressure of the fuel cell rather than incorporating a complex fuel reforming system to improve the quality of the anode feed gas stream. These trade-offs for practical HT-PEM systems will be explored in future papers.

3.0 Conclusions

This paper presents performance data for two commercial HT-PEM MEA materials, BASF’s Celtec P1100W and Advent’s TPS[®] based MEA, under a wide array of testing conditions. The effects of temperature and pressure for various levels of anode dilution were investigated. Temperatures and pressures were varied from 160 to 200°C, and 101.3 to 200 kPa, respectively. The hydrogen concentration examined was varied from 30-100%. Increases in pressure and temperature greatly enhance fuel cell performance for both the PBI and TPS MEAs, with the PBI outperforming the TPS under all tested conditions. While there may be a significant performance impact resulting from anode feed dilution, voltage losses can be overcome through increasing the operating temperature and/or pressure of the fuel cell within reasonable limits, even at high anode dilution levels of 70%. However, the energy cost, economic cost, durability, and system

level complexity must all be considered when making a final design decision. The data generated from this work will be useful in predicting the values of these tradeoffs for full system designs.

4.0 Acknowledgement

This work was performed under the financial assistance of award #60NANB13D71 from U.S. Department of Commerce, National Institute of Standards and Technology, which provided a Graduate Research Assistantship for Michael G. Waller. Dr. Muhammad Arif of the NIST Center for Neutron Research (NCNR) is acknowledged for supporting this effort, and for his group's ongoing support of research and development advancing fuel cell technology in the U.S.

References

- [1] Chandan A, Hattenberger M, El-Kharouf A, Du D, Dhir A, Self V, Pollet BG, Ingram A, Bujalski W. High temperature (HT) polymer electrolyte membrane fuel cells (PEMFC) – A review. *J. Power Sources* 2013; 231:264–278.
- [2] Li Q, He R, Gao J-A, Jensen JO, Bjerrum NJ. The CO poisoning effect in PEMFCs operational at temperatures up to 200°C. *J. Electrochem. Soc.* 2003; 150:A1599–A1605.
- [3] Luengnaruemitchai A, Osuwan S, Gulari E. Comparative studies of low-temperature water–gas shift reaction over Pt/CeO₂, Au/CeO₂, and Au/Fe₂O₃ catalysts. *Catal. Commun.* 2003; 4:215–221.
- [4] Recupero V, Pino L, Vita A, Cipiti F, Cordaro M, Laganà M. Development of a LPG fuel processor for PEFC systems: Laboratory scale evaluation of autothermal reforming and preferential oxidation subunits. *Int. J. Hydrog. Energy* 2005; 30:963–971.
- [5] Grande CA. Advances in pressure swing adsorption for gas separation. *Int. Sch. Res. Not.* 2012; 2012: e982934.
- [6] Qi Z, He C, Kaufman A. Effect of CO in the anode fuel on the performance of PEM fuel cell cathode. *J. Power Sources* 2002; 111:239–247.
- [7] Li Q, Jensen JO, Savinell RF, Bjerrum NJ. High temperature proton exchange membranes based on polybenzimidazoles for fuel cells. *Prog. Polym. Sci.* 2009; 34:449–477.
- [8] Park SJ, Lee DH, Kang YS. High temperature proton exchange membranes based on triazoles attached onto SBA-15 type mesoporous silica. *J. Membr. Sci.* 2010; 357:1–5.
- [9] Li M, Scott K. A polymer electrolyte membrane for high temperature fuel cells to fit vehicle applications. *Electrochimica Acta* 2010; 55:2123–2128.
- [10] Lobato J, Cañizares P, Rodrigo MA, Úbeda D, Pinar FJ. Enhancement of the fuel cell performance of a high temperature proton exchange membrane fuel cell running with titanium composite polybenzimidazole-based membranes. *J. Power Sources* 2011; 196:8265–8271.
- [11] Pinar FJ, Cañizares P, Rodrigo MA, Úbeda D, Lobato J. Long-term testing of a high-temperature proton exchange membrane fuel cell short stack operated with improved polybenzimidazole-based composite membranes. *J. Power Sources* 2015; 274:177–185.
- [12] Pefkianakis EK, Deimede V, Daletou MK, Gourdoupi N, Kallitsis JK. Novel polymer electrolyte membrane, based on pyridine containing poly(ether sulfone), for application in high-temperature fuel cells. *Macromol. Rapid Commun.* 2005; 26:1724–1728.
- [13] Gourdoupi N, Triantafyllopoulos N, Deimede V, Pefkianakis L, Daletou M, Neophytides S, Kallitsis J, Aromatic polyether copolymers and polymer blends and fuel cells comprising same. United States Patent Application US20080063923 A1, March 13, 2008.
- [14] Avgouropoulos G, Papavasiliou J, Daletou MK, Kallitsis JK, Ioannides T, Neophytides S. Reforming methanol to electricity in a high temperature PEM fuel cell. *Appl. Catal. B Environ* 2009; 90:628–632.
- [15] “Advent Technologies Inc.,” 2014. [Online]. Available: <http://www.advent-energy.com/>. [Accessed: 22-Apr-2014].
- [16] Avgouropoulos G, Ioannides T, Kallitsis JK, Neophytides S. Development of an internal reforming alcohol fuel cell: Concept, challenges and opportunities. *Chem. Eng. J.* 2011; 176–177:95–101.

- [17] Korsgaard AR, Nielsen MP, Bang M, Kær SK. Modeling of CO Influence in PBI electrolyte PEM fuel cells. Proc. 4th Int. Conf. on Fuel Cell Science, Engineering and Technology. ASME 2006: 911–915.
- [18] De Castro E. PBI-phosphoric acid based membrane electrode assemblies: Status update. PAFC Workshop, 16-Nov-2009.
- [19] “Danish Power Systems | Danish Power Systems.” [Online]. Available: <http://daposy.com/>. [Accessed: 10-Nov-2015].
- [20] Lobato J, Zamora H, Cañizares P, Plaza J, Rodrigo MA. Microporous layer based on SiC for high temperature proton exchange membrane fuel cells. J. Power Sources 2015; 288:288–295.
- [21] Chen C-Y, Lai W-H. Effects of temperature and humidity on the cell performance and resistance of a phosphoric acid doped polybenzimidazole fuel cell. J. Power Sources 2010; 195:7152–7159.
- [22] Korsgaard AR, Refshauge R, Nielsen MP, Bang M, Kær SK. Experimental characterization and modeling of commercial polybenzimidazole-based MEA performance. J. Power Sources 2006; 162:239–245.
- [23] Das SK, Reis A, Berry KJ. Experimental evaluation of CO poisoning on the performance of a high temperature proton exchange membrane fuel cell. J. Power Sources 2009; 193:691–698.
- [24] Andreasen SJ, Vang JR, Kær SK. High temperature PEM fuel cell performance characterisation with CO and CO₂ using electrochemical impedance spectroscopy. Int. J. Hydrog. Energy 2011; 36:9815–9830.
- [25] Ma Y-L, Wainright JS, Litt MH, Savinell RF. Conductivity of PBI membranes for high-temperature polymer electrolyte fuel cells. J. Electrochem. Soc. 2004; 151:A8–A16.
- [26] Daletou MK, Kallitsis JK, Voyiatzis G, Neophytides SG. The interaction of water vapors with H₃PO₄ imbibed electrolyte based on PBI/polysulfone copolymer blends. J. Membr. Sci. 2009; 326:76–83.
- [27] Schmidt TJ, Baurmeister J. Properties of high-temperature PEFC Celtec®-P 1000 MEAs in start/stop operation model. J. Power Sources 2008; 176:428–434.
- [28] Moçotéguy P, Ludwig B, Scholta J, Barrera R, Ginocchio S. Long term testing in continuous mode of HT-PEMFC based H₃PO₄/PBI Celtec-P MEAs for μ -CHP applications. Fuel Cells 2009; 9:325–348.
- [29] Moçotéguy P, Ludwig B, Scholta J, Nedellec Y, Jones DJ, Rozière J. Long-term testing in dynamic mode of HT-PEMFC H₃PO₄/PBI Celtec-P based membrane electrode assemblies for micro-CHP applications. Fuel Cells 2010; 10:299–311.
- [30] Waller MG, Walluk MR, Trabold TA. Operating envelope of a short contact time fuel reformer for propane catalytic partial oxidation. J. Power Sources 2015; 274:149–155.
- [31] Hedström L, Tingelöf T, Alvfors P, Lindbergh G. Experimental results from a 5 kW PEM fuel cell stack operated on simulated reformat from highly diluted hydrocarbon fuels: Efficiency, dilution, fuel utilisation, CO poisoning and design criteria. Int. J. Hydrog. Energy 2009; 34:1508–1514.
- [32] Galbiati S, Baricci A, Casalegno A, Marchesi R. Degradation in phosphoric acid doped polymer fuel cells: A 6000 h parametric investigation. Int. J. Hydrog. Energy 2013; 38: 6469–6480.

- [33] BASF. Celtec MEAs. Membrane Electrode Assemblies for High Temperature PEM Fuel Cells. 2012.
- [34] Advent Technologies. Advent TPS HT MEAs Product Sheet. 2013.
- [35] Kim J, Lee S-M, Srinivasan S, Chamberlin CE. Modeling of proton exchange membrane fuel cell performance with an empirical equation. J. Electrochem. Soc. 1995; 142:2670–2674.
- [36] Larminie J, Dicks A, McDonald MS. *Fuel cell systems explained*, vol. 2. Wiley New York, 2003.
- [37] Hosoi T, Yonekura T, Sunada K, Sasaki K. Exchange current density of SOFC electrodes: Theoretical relations and partial pressure dependencies rate-determined by electrochemical reactions. J. Electrochem. Soc. 2015; 162:F136–F152.
- [38] Bouchet R, Siebert E. Proton conduction in acid doped polybenzimidazole. Solid State Ion. 1999; 118:287–299.