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Parametric Analysis of the Optimal CO content in A High Temperature PBI membrane

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Abstract
An experimental investigation is conducted on a high temperature, single cell PEM with three different concentrations of CO with the intent of establishing acceptable carbon monoxide content from reformates. Hydrogen of 99.997% purity is used as a baseline fuel while 2 and 5 % CO contents are tested at 150 ^{o}C to 190 ^{o}C. Results from these tests reveal significant and unacceptable reduction of cell performance with temperature below 150 ^{o}C while the performance characteristic of the tested blends tends to converge at higher temperatures around 190 ^{o}C and above. Prior work characterized the operation of the system over a sparse range of CO operational envelope. The current work will fill the gap to generate an operational envelope of CO percentage good for high temperature PEM fuel cell operation.

Key words: CO poisoning, PBI membrane, PEM fuel cell

1. Introduction

The aim of this paper is to experimentally demonstrate on the CO concentration in hydrogen fuel that is considered unacceptable in high temperature polybenzimidazole proton exchange membrane HT-PBI-PEM. That value is set at 5% below the baseline fuel (hydrogen of 99.997% purity) threshold. Most reports in the literature on high temperature membrane performances are based on simulated model outcomes and model results are as good as their assumptions. The nature of the high temperature membranes is complex and the physio-chemical properties and reactions are complex. An experimental approach is adopted here with a single cell with convectional air cooling. A departure from the baseline fuel performance of more than 5mV at every current density tested is considered unacceptable.

Much attention has been given to the fuel cells as the alternate power system for various reasons: environmental, renewability, freedom from foreign oil, national security, etc. Some countries have even taken further steps to ditch internal combustion engine ICE) within the next 20 years. Electrochemical method of power generation is preferred to combustion that generates pollutants. However, the road map to hydrogen economy is not without hurdles. Absence of hydrogen dispensing

infrastructure, sustainable source of hydrogen without using petro-products, reliable membranes that can last up to 40,000 hours without developing pinholes, ability to withstand sub-zero temperatures or desert conditions, tolerance of impurities and using of flex-fuel to say the least are some of the concerns.

The improvement of the sulfonated membranes has been enormous since the early 90s. In the past decade, significant advancement towards integration of fuel cells into automobiles (passenger vehicles and buses), golf carts, forklifts, trains, portable devices, soldier power has been reported. The deficiencies of the low temperature LT-PEM membranes led to the improvement of the high temperature membranes which are widely reported in literature. This report will highlight the advantages of both membranes and then set an operational range around the HT-PEM that will serve a template for further research efforts with the membrane.

2. Literature review

Wang et-al /1/ developed a–one-dimensional transient model and used it to predict the impact of carbon monoxide tolerance of a PBI membrane and validated it with experiment. He found higher CO content in hydrogen influencing CO coverage with subsequent potential loss with time under various hydrogen and CO mixtures. The temperature range tested was 150-190 ^{o}C. Wainright et-al. /2/ found PBI membranes doped in sulfuric and phosphoric acids to exhibit high conductivity. Ubong et-al. /3,4/ experimented on three different hydrogen and CO mixtures to determine the impact of variables, such as temperature, pressure, stoichiometry on the performance of PBI membrane.

At lower temperatures, the cell performance deteriorated with increase of CO in the mixture. While increase in pressure generally improved the cell performance. Dhar et-al. /5, 6,/ found adsorption of CO on platinum catalyst to occur at low temperature. These research activities have one theme in common that the presence of CO in fuel degrades the cell performance. However, the premise of this study lays the ground work that future fuels will be degraded as such, membranes should be developed to withstand varying quality of fuels from different sources, such as manufacture's inability to maintain a standardized product quality, storage, transportation platforms and dispensing equipment of the fuel.

2.1 Characteristics of the low temperature PEM

The low temperature LT-PEM fuel cells with sulphonated membranes exhibit very vast response, as such, is suitable for automotive applications, modular power unit, auxiliary power unit (APU) and generally for the distributive power generation. They are environmentally very friendly. If hydrogen is used as fuel for hydrogen/air fuel cell, the end product is water. They do not have movable parts, as such exhibit low noise levels from the balance of plant. However, on the contrary, the exit product from the anode and cathode terminals is warm water of low heat value. The membrane requires humidification, thereby increasing the complexity of the balance of plant (BOP).

The electro-chemical reactions are slow due to its low temperature operation. The membrane is expensive and develops pinholes after hundreds of hours of its operation. LT-PEM is susceptible to CO poisoning, if its concentration is above 10

ppm in the fuel. Carbon dioxide deactivates the Pt catalyst used in the proton exchange membranes. This results in low cell performance and finally breakdown of the membrane. Also, LT-PEM is susceptible to flooding at high current densities leading to incipient mass transport concentration. This is absent in HT-PEM, Ubong, et-al./3,4/.

Despite all these shortcomings, it is a clean and reliable energy source that requires years of further development and perfection. It's the limitation of LT-PEM that mitigated the development of the HT-PEM. The advantages of the high temperature PEM are: (i) increase electro-chemical kinetics (ii) water and cooling systems management are simplified (iii) absence of humidifier and the cost associated with the hardware (iv) waste heat has sensible energy that can be harnessed for process analysis (v) flexibility to use fuels with higher CO content (vi) simplicity in coupling reformates to the HT-PEM without PROX preprocessing (vii) two phase flow of the reactants are eliminated and simplified (viii) The cell exhibits steady and repeatable voltage output at steady state conditions (ix) vapor is the exit product (x) tolerance of up to 5% CO in the fuel at an elevated temperature of 190 ^{o}C and above.

The high temperature membrane also exhibits the following shortcomings: (i) on accidental shutdown of the fuel cell without properly purging the system with inert gas, the acid leaches and degrades the cell performance (ii) the cost of the membrane is prohibitive (iii) the vapor from the cell is not pure water when condensed as the cell is chemically doped in either suphuric or phosphoric acid (iv) water cannot be used as the coolant as the operational temperature of the cell is above the saturation temperature of water thereby adding cost to the BOP.

Figure 1. Experimental set up

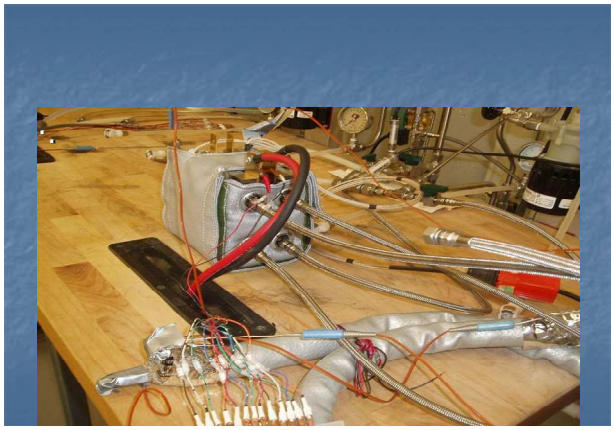

Figure 2. High temperature proton exchange PBI membrane

3. Experimental setup and procedure

The experimental hardware consists of the Schatz Energy Research Center (SERC) multi-stand test bench. The bench comprises four test station (TS) with the first two stations (TS 1-2) designed to test low end stacks up to 200W and single cells. They are dead–ended in design. Test stations TS 3 - 4 are open-ended and can test up to 1kW stack at pressures up to 2barg. The fourth test station (TS4) was reconfigured to test single cells and to comply with the US Fuel Cell Council's Test Protocol for Testing single cells. The test equipment is shown in Figure

1, while Figure 2 presents the HT- PEMFC on TS 4.

The test bench integrates seven support systems. The air and hydrogen systems are supplied through MKS mass flow controllers (MFC) rated at 0-2 SLPM (standard liter per minute) and 0-10 SLPM respectively at appropriate pressure levels required by the cell. The cell is equipped with a heating pad and the OMEGA CSi8D bench-top heater temperature controller is used for regulating the cell temperature, while the computer monitors the cell temperature at the same time. The electrical system controls the fuel cell load by dissipating the output energy through an electronic load. The coolant system was disabled. A single computer with an analog and digital interface controls and monitors

Table 1. Test matrix

	Flow rate	Stoichiometry	Pressure
Air	Varies with load	200%	atmospheric
Hydrogen	Varies with load	120%	atmospheric
Temp	150-190 ^{o}C		

parameters (current and individual cell voltages, hydrogen/air inlet flows and pressures and cell/stack temperatures) of the four TS on the bench simultaneously.

The safety system is monitored by the computer watchdog timer which flags any parameter that operates outside the stated limits and signals an alarm such as low voltage, high temperature, etc. The entire hardware safety system triggers an alarm signaling hydrogen sensor, smoke detector or low backup power in the uninterruptible power supply. The safety system also signals alarms with (i) auto-emergency shutdown and hydrogen leak.

The computer enables automatic long term data logging. The test was conducted at constant current mode from OCV (open circuit voltage) to 45Amps. A 120% stoichiometry at the anode and 200% at the cathode with atmospheric pressure set at the exits. The HT-PEM poco-graphite hardware has a triple serpentine flow channel with a 45 cm^2 active area and width/depth channel sizes of 1 mm x 1 mm. The end plates are of aluminum alloy.

4. EXPERIMENTAL MATRIX AND TEST PROCEDURES

The test was conducted using three sets of gas mixtures. The baseline test consisted of hydrogen with 99.997% purity. This was followed by 2 and 5% concentration of CO respectively in hydrogen. A five layered MEA PBI from BASF (USA) assembly with PBI membrane was used. Fuel cell temperatures were maintained between 150-190 ◦C. Prior to data logging, the cell was equilibrated at 130 ◦C at 9 amps for 100 hours. Table 1 below presents
the test parameters for this work.

5. Analysis of the report

A voltage–temperature evaluation conducted at 500 mA/cm^2 with three samples of pure hydrogen (0%), 2% and

5% concentrations of CO (in the fuel) respectively, reveals that as the temperature approaches 200 ^{o}C, all the tested samples approach a convergent curve/line. The implication is that at higher temperatures above 190 ^{o}C, the effect of CO covering the surface of the catalyst gradually diminishes. That is shown in Figure 3. Conversely, at a lower temperature below 180 ^{o}C, the 5% concentration drops off rapidly, followed by that of the 2% concentration at 160 ^{o}C That observation is consistent with the research results of Das-et-al /8/.

The above suggests raising the temperature of operation of HT-PEM above 200 ^{o}C. The advantage is that reformates can be coupled directly into the cell without PROXing, i.e. without going through additional preprocessing (PROX) of the reformate to reduce the CO content to approximately 10 ppm. This minimizes the complexity of the balance of plant.

Figure 4 presents a plot of voltage versus temperature of two samples of 2 and 5% CO in the fuel at 200 mA/cm^2. At low current density of 200 mA/cm^2, both samples generated voltages above 0.6V at 140 ◦C. The two samples performance is identical at 180 ◦C and above, which strongly suggests that temperature has a strong effect on the CO composition and optimal operation of the HT-PEM. However, most fuel cells operate at higher current densities than 200 mA/cm^2, as such low current density regions are of less value to an operational cell unless, and it is a special purpose power source.

For brevity reasons, the following were additional findings on power density versus temperature curves for two concentrations of 2 and 5% CO in the fuel. At 200 mA/cm^2, 175 ◦C, both power density curves converge. This shows that further temperature increase at that load does not give any advantage or preference of one fuel composition over the other. At higher loading level of 500 mA/c m^2, all the three samples tested tend to converge at a temperature above 180 ◦C. A pointer that at approximately 200 ◦C and above, higher CO concentration of 5% in the fuel does not degrade the performance of the fuel cell. This stretches the limits of the current PBI membranes which are limited by maker's instructions to operate below 200 ◦C.

5. Conclusions

The following conclusions can be made about the allowable concentrations of carbon monoxide in high temperature fuel cells. Within the test matrix performed in this experiment, carbon monoxide concentration from 1-5% can be run in a PBI membrane as long as the temperature is above 180 ◦C. Lower than the stated temperature, a concentration of 2% or lower is preferred as long as the temperature is above 170 ◦C. Finally, the operation of PBI membranes favors high temperature environment over low temperatures.

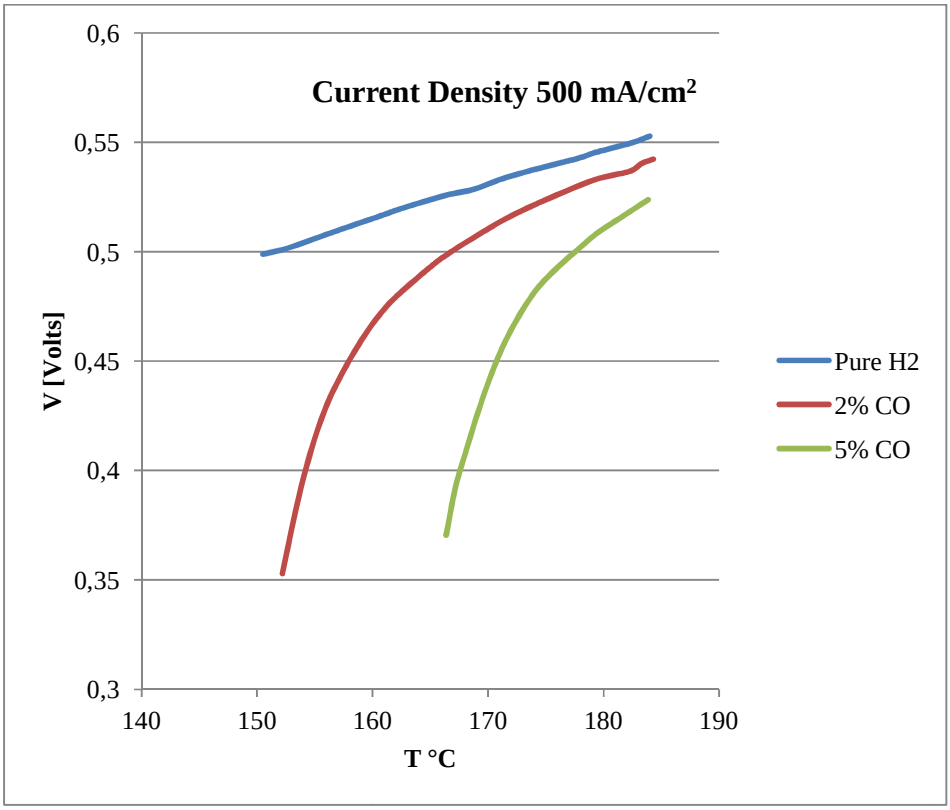

Figure 3. Voltage versus cell temperature at 500mA/cm^2.

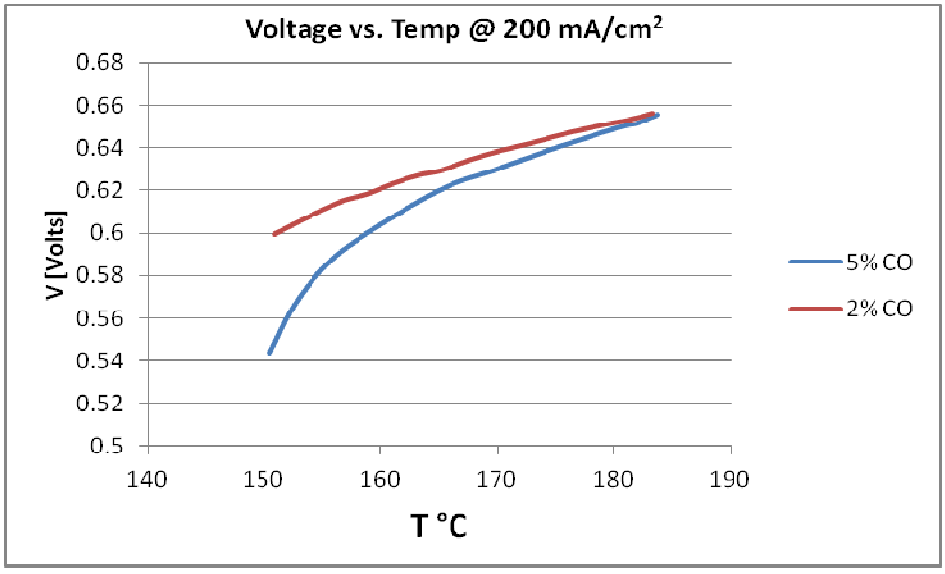

Figure 4. Voltage versus temperature at 200 mA/cm^2 at 2 and 5% CO concentration in the fuel

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