Anode Pressurization of PEM Fuel Cells at Elevated Temperatures

Hui Xu, H. Russell Kunz, and James. M. Fenton
Department of Chemical Engineering
University of Connecticut
Storrs, CT 06269

ABSTRACT

PEM fuel cells operated at elevated temperatures (120-150 °C) can greatly alleviate CO poisoning on anode catalysts. However, at elevated temperature and ambient pressure, the cells must be operated at low relative humidity (RH), which significantly increases membrane and electrode resistance. To operate PEM fuel cells at elevated temperature and high RH, extra work is needed to pressurize the anode and cathode reactant gases. This will decrease the efficiency of the PEM fuel cell system. A hydrocarbon-fuel processor in series with a PEM fuel cell can produce reformed gases at high pressure with a high relative humidity without compression of gasses. The water in the anode compartment will transport through the membrane and into the cathode structure decreasing the cell resistance. This work studied the effect of anode pressurization on the cell resistance and performance. The results show that high RH from anode pressurization at both 120°C and 150°C can decrease the membrane resistance and therefore increase the cell voltage. The cell running at 150°C obtains a cell voltage of 0.43V at 400mA/cm² even with 1% CO in H₂. These results provide instructions for the application of a coupled fuel processor-fuel cell system.

INTRODUCTION

A Proton Exchange Membrane (PEM) fuel cell converts chemical energy to electrical energy using a solid ionomer (such as Nafion®) as the electrolyte. Usually, PEM fuel cells are operated at low temperatures (<80°C) and 100% RH. However, PEM fuel cells operated at elevated temperatures (>100 °C, atmospheric pressure and therefore dry conditions) have significant advantages over low temperature PEM fuel cells as CO poisoning at the anode is effectively alleviated. A quantitative analysis of the free energy for H₂ and CO adsorption suggests that CO tolerance at the anode should possibly increase by a factor of 20, by elevating the operating temperature to higher than 100°C. CO tolerance is affected not only by the cell temperature, but by the relative humidity (RH) of reactant gases. Higher temperature operation also increases the energy efficiency, improves heat rejection, provides higher quality waste heat, and permits easier water management. However, at elevated temperatures and ambient pressure, the PEM fuel cell must be operated at low RH, which dries out the membrane and electrodes, thus results in significant membrane and electrode resistance. At elevated temperature, PEM fuel cells can also be operated at high RH as long as the fuel cell system can be pressurized. However, pressurization of the fuel cell system requires extra pump work, which reduces the total efficiency of the fuel cell system.
In practice, the hydrogen for a fuel cell is frequently obtained from the processing of hydrocarbon fuels by way of steam reforming. Considerable efforts have been made to integrate a fuel processor with the fuel cell in residential and automobile applications. The fuel processor is usually operated at a very high temperature and pressure (up to 1000°C and 30atm). The reformed gases, including hydrogen, carbon dioxide, carbon monoxide, water, etc., are at this high pressure before they enter the anode of the fuel cell system. Therefore, it is possible to run a fuel cell with the anode pressurized and the cathode at ambient pressure without lowering the system efficiency. Pressurization of the anode makes it possible to increase the anode RH while running a fuel cell at elevated temperature. The increased RH at the anode results in more water at the anode side. Due to the gradient of the water concentration between the anode and the cathode, the water in the anode side may go through the membrane and reach the cathode, wetting the whole membrane and the cathode.

This study investigated anode pressurization for hydrogen-air and hydrogen-carbon monoxide-air systems. The effects of anode pressurization on membrane resistance, cell voltages, hydrogen crossover and electrochemical area (ECA) were evaluated. These results provide a reference for operation of a coupled fuel processor – fuel cell system.

**EXPERIMENTAL**

**Membrane and Electrode Assembly (MEA)**

The membrane electrode assemblies were prepared by applying both the anode and the cathode catalyst layers directly onto a composite membrane: Nafion® and phosphotungstic acid impregnated into porous Teflon® (NTPA), with a thickness of 25–50μm. The cathode catalyst, 46.6 wt% Pt/C (Tanaka Kikinzoku Kogyo, Tokyo, Japan), was mixed with 5% Nafion® solution (Solution Technologies, Mendenhall, PA) by stirring and ultrasonic dispersion before it was applied onto the membrane. The cathode loading of precious metal was 0.25 mg/cm² and the Nafion® content was 35wt %. On the anode, Pt-Ru black (Alfa Aesar, Ward Hill, MA) was applied onto the membrane with 1.0 mg/cm² catalyst loading and 10wt% Nafion® content. The catalyst-coated membrane was sandwiched between two SGL gas diffusion layers (SGL Carbon Group, Wiesbaden, Germany) to obtain a 5cm² MEA for the single cell polarization measurement. The gasket pinch was 300 μm each on both sides of the MEA for a total pinch of 600 μm. A single serpentine 5 cm² active area graphite flow field was used (ElectroChem., Inc, Woburn, MA).

**Linear Sweep Voltammetry and Cyclic Voltammetry**

Linear sweep voltammetry and cyclic voltammetry (CV) were performed using a PAR 273A potentiostat (Princeton Applied Research, Oak Ridge, TN) with hydrogen at the anode and nitrogen at the cathode first at 80/80/80 °C (100% RH, cell temperature/anode saturator temperature/cathode saturator temperature) and then 120 °C and 150°C with different RHs. The RHs of anode and cathode gases were controlled by saturators in a MEDUSA ™ test station (Teledyne Energy Systems, Inc, Los Angeles, CA). Before the
measurement, the MEA was equilibrated at the experimental condition for 1 hour. Electrochemical area was calculated based on the following equation.

\[
ECA = \frac{Q_n}{[Pt] \times 0.21}
\]

Here \([Pt]\) represents the platinum loadings (mg/cm²) in the cathode, \(Q_n\) the charge for hydrogen desorption (mC/cm²), which can be calculated from the CVs, and 0.21 in mC/cm² platinum represents the charge required to oxidize a monolayer of hydrogen on bright Pt¹.

**Cell Voltages and Resistances**

A 890C load box (Scribner Associates, Inc., Southern Pines, North Carolina) was used to measure cell voltage and resistance. Five minutes were spent at each current density with the cell voltage collected every 20s. Cell internal resistance, \(R\), was measured and recorded at current densities higher than 100mA/cm² using the current interrupt technique with the load box and the Fuel Cell V3.2 software (Scribner Associates, Inc., Southern Pines, North Carolina). IR-corrected cell voltages are equal to the cell voltages plus \(iR\). The utilization of hydrogen was 33%; for current densities below 1000mA/cm², a minimum flow rate of 0.1 cm³/min was used. The utilization of oxygen was 25%; for current densities below 300mA/cm², a minimum flow rate of 0.1 cm³/min was used.

**RESULTS AND DISCUSSIONS**

**Cell Resistance and Voltages at Ambient Pressure**

Figure 1 shows the cell voltages and resistances at two temperatures, 80°C and 120°C, and ambient pressure. The thickness of the NTPA membrane was 24μm. The first condition, 80/80/80°C (cell/anode saturator/cathode saturator temperature), is frequently used for low temperature PEM fuel cells. It corresponds to 100% RH, with a 0.53 atm air partial pressure, 0.53 atm hydrogen partial pressure and 0.47 atm water partial pressure. The second condition, 120/90/90°C, has a relative humidity of 35% at the inlet with a 0.3 atm oxygen partial pressure, 0.3 atm hydrogen partial pressure and 0.7 atm water partial pressure. At ambient pressure, this is close to the highest RH that can be obtained for a cell operated at 120°C without severe performance loss due to low reactant partial pressures. The cell voltage and resistance at a current density of 400mA/cm² will be selected to make comparisons. At 80/80/80°C, the membrane resistance is 0.07 Ohm-cm², and the cell voltage is 0.7V at 400mA/cm². At 120/90/90°C, the membrane resistance is 0.21 Ohm-cm² and the cell voltage is 0.56V. The low cell voltage at 120/90/90°C is due in large part to the high membrane resistance at low RH. The higher cell voltage could be partially due to higher hydrogen and air partial pressure (0.53 atm) at 80°C than that (0.3 atm) at 120°C. The condition 120/90/90°C will be used as a base-line condition in the following study. The cell voltage and resistance at the anode pressurization in both 120°C and 150°C were compared to those at this base line condition.
To increase the RH of the MEA, the total pressure of the anode was increased to 1.7 atm and the anode saturator temperature was elevated to 110°C, but the cathode saturator was still kept at 90°C and the cathode pressure was kept at 1 atm. The thickness of the NTPA membrane used here was 36 μm. The condition, as represented by 120/110/90°C, has 72% RH at the anode and 35% RH at the cathode. The water partial pressure at the anode is 1.4 atm and the hydrogen partial pressure is 0.3 atm. At the cathode, the water partial pressure is still 0.7 atm and the air pressure is 0.3 atm. Figure 2 shows the cell voltages and resistances at 120/110/90°C, as compared to the base line 120/90/90°C. At 120/110/90°C, the membrane resistance is 0.16 Ohm-cm², which is half of the resistance at 120/90/90°C, 0.33 Ohm-cm². The resistance here at 120/90/90°C is higher than the 0.21 Ohm-cm² mentioned previously because the membrane thickness for this cell is greater (36 μm compared to 24 μm). Corresponding to this significantly reduced membrane resistance, the cell voltage at 120/110/90°C is increased to 0.66 V. Compared to 0.56 V at 120/90/90°C, there is a 100 mV gain after the pressurization of the anode to increase the anode RH. The high RH (72%) at the anode introduces a large amount of water into the anode. However, the cathode side has much less water since its RH is only 35% RH. Due to the water concentration gradient of the anode and the cathode, the water molecules move from the anode to the cathode. The migrated water from the anode efficiently wets the whole membrane and the cathode, reducing the cell resistance. There are different mechanisms by which water can go from the anode to the cathode, such as convection, diffusion and electroosmotic drag.
Anode Pressurization at 150°C

Figure 3 shows the results using anode pressurization of the same cell to 2.7 atm at 150°C. The condition, 150/126/90°C, has a 50% RH at the anode and 15% RH at the cathode. The water partial pressure at the anode is 2.4 atm and the hydrogen partial pressure is 0.3 atm. At the cathode, the water partial pressure is still 0.7 atm and the air pressure is 0.3 atm. The membrane at 150/126/90°C is 0.28 Ohm-cm², which is also lower than 0.33 Ohm-cm² at 120/90/90°C. However, the cell voltage at 150/126/90°C is 0.44 V, which is much lower than 0.56 V at 120/90/90°C. Although anode pressurization at 150°C reduces the membrane resistance to below that of 120°C without pressurization, the cell voltage decreases 120 mV. This may first be explained by the decrease in open circuit voltage (OCV). According to the Nernst Equation, the higher temperature and the increased water partial pressure lower the theoretical OCV. At the 150/126/90°C condition, not only is the temperature higher than that at 120°C, but the water partial pressure at the anode, 2.4 atm, is also much larger than at 120/90/90°C, 0.7 atm. At 150/126/90°C, the actual OCV is only 0.86 V, which is lower than the 0.91 V at 120/90/90°C. However, the OCV only results in a 40-50 mV decrease of the cell voltage. The lower performance at 150/126/90°C may also come from a decrease in effective surface area of the electrodes, or an increase in ionic electrode resistance in the cathode at this harsh condition. To study the interface and electrode condition, linear sweep voltammetry and cyclic voltammetry were conducted, which determined the hydrogen crossover of the NTPA membrane and the ECA of the cathode.
Fig 3. Anode pressurization of PEM fuel cell at 150°C. NTPA membrane: 36µm. Anode: H₂, stoic 3; cathode: air, stoic 4. 120/90/90°C: Pₜ𝑜𝑡al =1atm, P_{H₂O}=0.7atm, P_{H₂}=0.3atm; 150/126/90°C: Pₜ𝑜𝑡al=2.7atm, P_{H₂O,anode}=2.4atm, P_{H₂}=0.3atm.

Table I shows the hydrogen crossover and partial and total pressures at four conditions: 80/80/80°C, 120/90/90°C, 120/110/90°C, and 150/126/90°C. At 80/80/80°C, the crossover is 2mA/cm²; at 120/90/90°C, the crossover is 3.1mA/cm²; at 120/110/90°C, however, the crossover is 2.1mA/cm²; and at 150/126/90°C, the crossover is 2.6mA/cm². An increase of the cell temperature increases the hydrogen crossover, as the effective diffusion coefficient of hydrogen is the membrane increases with the temperature. However, the crossover at 150/126/90°C and 120/110/90°C is lower than that at 120/90/90°C. This may be due to the high water partial pressure (P_{H₂O}=1.4atm vs. P_{H₂}=0.3atm at 120/110/90°C) and (P_{H₂O}=2.4atm vs. P_{H₂}=0.3atm at 150/126/90°C) that reduces the hydrogen concentration in the membrane. Since the hydrogen crossover lied within several mA/cm² and did not linearly increase with the voltage, no electronic shorts were present in the membrane even at 150/126/90°C, where the total pressure in the anode, 2.7atm, is much higher than that in the cathode, 1.0atm.

Table I. Hydrogen Crossover at Different Conditions

| Conditions          | 80/80/80°C | 120/90/90°C | 120/110/90°C | 150/126/90°C |
|---------------------|------------|-------------|--------------|--------------|
| Cathode            |            |             |              |              |
| P_{H₂O} (atm)      | 0.47       | 0.7         | 0.7          | 0.7          |
| P_{air} (atm)      | 0.53       | 0.3         | 0.3          | 0.3          |
| P_{Total} (atm)    | 1.0        | 1.0         | 1.0          | 1.0          |
| RH (%)             | 100        | 35          | 35           | 35           |
| Anode              |            |             |              |              |
| P_{H₂O} (atm)      | 0.47       | 0.7         | 0.3          | 0.3          |
| P_{H₂} (atm)       | 0.53       | 0.3         | 1.4          | 2.4          |
| P_{Total} (atm)    | 1.0        | 1.0         | 1.7          | 2.7          |
| RH (%)             | 100        | 35          | 72           | 50           |
| Crossover (mA/cm²) | 1.9        | 3.1         | 2.1          | 2.6          |
Figure 5 shows cyclic voltammetry curves at different temperatures and RHs. The CV curves in the range of 0.1-0.4V represent hydrogen adsorption (positive currents) and desorption (negative currents), which can be used to calculate the electrochemical area. The three conditions, 80/80/80°C, 120/90/90°C, and 120/110/90°C, display similar curves in the range of 0.1-0.4V. The calculated ECA for these three conditions is very close to each other, ~68m²/g. However, the CV for 150/126/90°C lies much below the CV curves for the other three conditions. The calculated ECA for 150/126/90°C is only 39m²/g, which is much less than the 68m²/g of the other three conditions. The low ECA at 150/126/90°C may be due to a poor electrode/membrane interface at the higher temperature and lower RH at the cathode. This may explain why at 150/110/90°C, although the membrane resistance is lower than that at 120/110/90°C, the cell voltage is lower too. Another concern is, at the harsh condition 150/126/90°C, dehydration of the electrode occurs, which results in significant ionic resistance of the cathode and cathode polarization.

**CO tolerance at Anode Pressurization**

Two conditions of anode pressurization, 120/110/90°C, and 150/110/90°C, were tested for CO tolerance at a concentration of 0.1% and 1%. Figure 5 shows the CO tolerance at 120/110/90°C. There are three cell voltage curves in the figure. For pure H₂, the cell voltage is 0.66V at 400mA/cm². For 0.1% CO, the cell voltage is reduced to 0.52V at 400mA/cm². Finally for 1% CO, the cell voltage decreases drastically with the current density, reaching 0.05V at 400mA/cm². At the base line 120/90/90°C with pure hydrogen at ambient pressure on both sides, the cell voltage was 0.56V at 400mA/cm². Therefore, for a CO concentration such as 0.1%, anode pressurization generates a cell voltage close to that at 120/90/90°C under pure hydrogen (0.52V vs. 0.56V). This is mainly due to
decreased membrane resistance at higher RH resulting from the anode pressurization. Increased RH may also improve the CO tolerance itself because some adsorbed CO is replaced with H₂O on the surface of platinum. Figure 6 also shows the resistance for pure hydrogen and different concentrations of CO. The membrane resistance at 0.1% and 1% CO is slightly higher than that for pure hydrogen. That is 0.15 Ohm-cm² for pure hydrogen, 0.18 Ohm-cm² for 0.1% CO, and 0.21 Ohm-cm² for 1% CO. This difference may be because, for pure hydrogen, most of the anode reaction occurs at the anode interface near the membrane since only a small fraction of the anode catalyst is needed; under such circumstances, any anode polarization would not contribute to the cell resistance determined using the current interruption technique even if the anode has a slight internal electronic resistance. This occurs because the ionic resistance in the anode is small due to the short distance the ions must migrate and the anode has considerable double-layer capacitance. At higher CO concentrations, the whole depth of the catalyst structure is used because of the slower reaction kinetics. Then, with a significant ionic resistance, part of the anode polarization will be included in the cell resistance determined by current interruption if some electronic resistance is present in the anode. This effect becomes more pronounced at lower RH when the ionic conductivity of the electrolyte is reduced.

Figure 6 shows the CO tolerance at 150/126/90°C. The effect of increased temperature on alleviating CO poisoning is very obvious in this case. The three curves: pure hydrogen, 0.1% and 1% CO almost coincide. For pure H₂, the cell voltage is 0.48V at 400mA/cm²; for 0.1% CO, the cell voltage is 0.47V at 400mA/cm². Even at 1% CO concentration, the cell voltage is still 0.43V at 400mA/cm². The increased CO concentration at 150°C does not poison the catalyst as much as at 120°C. The resistance also increases with the CO concentration, that is, 0.21 Ohm-cm² for pure hydrogen, 0.23 Ohm-cm² for 0.1% CO, and 0.29 Ohm-cm² for 1% CO. It is hoped that the cell performance with 1% CO at 150/126/90°C will be further improved by optimizing the cathode.
CONCLUSIONS

Anode pressurization integrated with fuel processing appears to be a promising way of running PEM fuel cells at elevated temperatures and high RH to obtain high performance with hydrogen containing carbon monoxide, without extra compression work. At 120/110/90°C, anode pressurization (1.7atm) brings significant reduction of cell resistance and results in 90mV cell voltage gain, compared to 120/90/90°C without pressurization (1atm); at 150/126/90°C, pressurization (2.7atm) decreases cell resistance, but does not increase cell voltage. Cyclic voltammetry indicates that at 150/126/90°C, the ECA is much lower than at 120/110/90°C and 120/90/90°C. The operation of PEM fuel cells at 150/126/90°C may generate high ionic and electronic resistance at the cathode and cause serious cathode polarization. Anode pressurization makes it possible to operate PEM fuel cells at higher CO levels. At 120/110/90°C, 0.56V cell voltage at 400mA/cm² is obtained for 0.1% CO in H₂; at 150/126/90°C, 0.43 V at 400mA/cm² is obtained for 1% CO in H₂. The advantage of anode pressurization was demonstrated, but the conditions selected to conduct this research are different from actual reformed gases. At 150/126/90°C, the water partial pressure at the anode is 2.4atm and the hydrogen pressure is 0.3atm. In an actual steam reforming system, the anode composition is more likely to be near 38% H₂, 16% N₂, 10% CO, 6% CO₂ and 30% H₂O. In this case, the total pressure of reformed gases must be near 10atm, to obtain 3atm of water vapor. In such a situation the large pressure difference between anode and cathode is a concern with respect to membrane strength.
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