PERFORMANCE OF HIGH TEMPERATURE PROTON EXCHANGE MEMBRANE FUEL CELLS UNDER OFF-DESIGN CONDITIONS

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ABSTRACT

Proton Exchange Membrane Fuel Cells (PEMFCs) are well suited for transportation applications by virtue of their efficiency and high power densities. Several advantages result by operating a PEMFC at elevated temperatures (above 100°C). An important factor to be considered during such operation is the effect of exposure to adverse off-design conditions on fuel cell performance. In this study, cells were built that conform to a defined baseline performance (H2/air; atmospheric pressure) at 120°C with reactant gases saturated at 90°C (38% exit relative humidity). The cells were then subject to harsh off-design conditions in a series of five increasingly challenging sequences, with temperatures going up to 150°C and reactant gas saturation temperature going down to 20°C (exit relative humidity going down to ~2%). The first and final run in each sequence were carried out at baseline conditions to determine the effect of exposure to off-design conditions on baseline performance. The results are discussed in this paper.

INTRODUCTION

Proton Exchange Membrane Fuel Cells (PEMFCs) are well suited for a variety of applications by virtue of their efficiency and high power densities. From an automotive application point of view, several advantages result by operating a PEMFC at elevated temperatures (above 100°C), such as easier and more efficient water management, higher reaction rates and better CO tolerance by the anode electrocatalyst leading to lower noble metal loadings, better system integration, higher quality waste heat and higher heat rejection rates. For other applications such as portable power and military use, the onus is on low relative humidity operation to obviate the need for saturating reactant gases – thereby reducing considerably the volume and complexity of the fuel cell system. Therefore, a significant economic incentive exists to develop and commercialize PEMFCs that operate at high temperatures and low relative humidities.

One of the most common PEMs in use today is the perfluorosulfonicacid based Nafion membrane. While this membrane performs very well in a saturated environment, its proton conductivity has a strong dependence on water content. Its water uptake, and consequently proton conductivity, decreases considerably at low relative humidities (1), leading to large resistive losses and a reduction in cell voltage. This drawback essentially means that the Nafion membrane cannot be used ‘as is’ for high temperature (>100°C) applications at ambient pressures. Nafion based organic / inorganic composite membranes with heteropolyacids additives have been shown (2, 3, 4) to maintain sufficient protonic conductivities for viable operation at temperatures above 100°C. In
overpotential at elevated temperatures. We have recently carried out the optimization of
the cathode structure for operation under these conditions (5). The objective of this work
was to determine the effect of sudden adverse changes in operating conditions such as
cell temperature and relative humidity on factors such as membrane integrity, membrane
conductivity and cathode catalytic activity, all of which have been identified as key
factors affecting long term endurance and stability of the cell (6). The results of a study
conducted to this end are discussed below.

EXPERIMENTAL

In this study, cells were built that conform to defined baseline performance of 0.45 V
or above at a current density of 400 mA/cm² for ambient pressure, H₂/air operation at a
cell temperature of 120°C with reactant gases saturated at 90°C (defined as baseline
conditions). The membrane electrode assembly (MEA) used for the experiments
consisted of a modified 0.8 mil thick recast Nafion 1100 membrane impregnated with
phosphotungstic acid, with 45% Pt/C (0.32 mg/cm² noble metal loading) and 54% Pt-
Ru/C (0.4 mg/cm² noble metal loading) on the cathode and anode respectively. The
electrolyte (Nafion 1100) loading in both catalyst layers was 25% by weight as
determined in the optimization study (3). The active area of the MEA was 5 cm².
Commercial gas diffusion layers obtained from SGL Carbon, LLC, were used in this
study. The operation of the cell was characterized by linear sweep voltammetry, cyclic
voltammetry, and cell voltage / current density performance testing.

Linear Sweep Voltammetry (LSV)

LSV experiments were performed at room temperature to evaluate and monitor fuel
crossover and to check for the presence of electronic shorts. The experiments were done
using a PAR potentiostat with a flow rate of 200 ccm of H₂ on the anode and 200 ccm of
N₂ on the cathode. A scan rate of 4 mV/s was used in the range of 0-800 mV cell voltage
with higher voltages being avoided to prevent Platinum oxidation. The experiments were
performed regularly throughout the study.

Cyclic Voltammetry (CV)

CV experiments were carried out to determine and monitor the electrochemically
active surface area (ECA) of the cathode catalyst. The experiments were done using a
PAR potentiostat with a flow rate of 50 ccm of 4% H₂ (balance N₂) on the anode and 50
ccm of N₂ on the cathode. A lower concentration of H₂ was used to reduce H₂ evolution
from the cathode at low potentials. A scan rate of 20 mV/s was used in the range of 0-800
mV cell voltage. The ECA was determined from the voltammogram using a technique
described elsewhere (7). The experiments were carried out at room temperature to avoid
uncertainties in the H₂ reference electrode potential at higher temperatures, and to
minimize the effects of gas crossover.

Cell Performance

The performance of the cell was evaluated by obtaining polarization curves at 80°C
(anode gas saturated at 80°C and cathode gas saturated at 73°C) and 120°C (both anode
and cathode gases saturated at 90°C). The data was obtained using the Fuel Cell Test System (No. 890 B) manufactured by Scribner Associates. The system was connected to a home built flow loop, and controlled by the Fuel Cell software. H₂ was used at the anode, while both O₂ and air were used at the cathode. The cell was started up by increasing the cell temperature set point to 80°C and raising the saturator temperatures to their respective values. Care was taken to maintain a temperature differential between the cell and the saturators to prevent condensation inside the cell. Similarly, the fuel and oxidant line temperatures were also maintained 10°C higher than the saturators to prevent condensation in the lines. Once the operating conditions were attained, the voltage and cell resistance were monitored at a current density of 400 mA/cm² until they attained a constant value. At this point, cell performance was measured as a function of current density with each condition held over 5 minutes. The resistance was also monitored using the current interrupt technique. In this manner, 80°C and 120°C performance data were obtained for oxygen and air, and were repeated over a period of 6 days with several shut downs and start ups. Both LSV and CV experiments were carried out prior to each start up. All experiments were carried out at ambient pressure.

Off-Design Testing

Once stable cell performance that confirmed to requirements at baseline conditions (as defined earlier) was attained, the cell was subject to harsh off-design conditions in a series of five challenging sequences with temperatures going up to 150°C and reactant gas saturation temperature going down to 23°C. The operating conditions for the runs carried out in each of the sequences are described in Table 1. At each off-design condition, the cell was equilibrated until steady state performance was attained. Performance was then measured as described earlier. The reactant gases were H₂ and air, and all runs were performed at ambient pressure. The first and final run in each sequence were carried out at baseline conditions to determine the effect of exposure to off-design conditions on baseline performance. The cell was equilibrated at 80°C between sequences. Finally, transient effects were determined by holding the cell at a current density of 400 mA/cm² and monitoring the membrane resistance and cell voltage as the exit relative humidity was first decreased and then brought back up to baseline. The voltage and resistance at each condition were noted on attaining a steady state value, which typically took about 20 minutes. The change in relative humidity was implemented both by increasing cell temperature while maintaining constant saturator temperatures, and by decreasing saturator temperatures for a given cell temperature. LSV and CV experiments were performed periodically between sequences.

Table 1

| Sequence Number | Run 1     | Run 2     | Run 3     | Run 4     | Run 5     | Run 6     |
|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1               | 120-90-90 | 120-80-80 | 120-60-60 | 120-40-40 | 120-90-90 | -         |
| 2               | 120-90-90 | 120-80-80 | 120-60-60 | 120-40-40 | 120-23-23 | 90-90     |
| 3               | 120-90-90 | 140-90-90 | 120-90-90 | -         | -         | -         |

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RESULTS AND DISCUSSION

Linear Sweep Voltammetry

The cell maintained its integrity throughout the testing program despite the use of a thin membrane, with no internal shorting and a crossover current lower than 2 mA/cm² in all cases. The results of the LSV measurements are shown in Fig. 1.

Cyclic Voltammetry

A reproducible voltammogram was obtained after 4 days of operation. The voltammogram was well resolved, with a clearly distinguishable second inflection point. From this voltammogram, the ECA was determined to be 17 m²/g-Pt by evaluating the area under the hydrogen reduction peak. The error in estimating the ECA was determined to be ± 2 m²/g-Pt. This error arose due to small uncertainties in pinpointing the exact position of the bounds of the reduction peak, namely the point of onset of hydrogen reduction and the second inflection point prior to the onset of hydrogen evolution. Fig. 2 compares the initial voltammogram to those obtained during the program. This area was lower than would be expected for this catalyst. The difference could be due to the inability to measure the entire platinum surface area using this approach and due to part of the cathode platinum being electrochemically ineffective. Little change was observed until the end of the fourth sequence. However, the hydrogen oxidation peak was observed to have shifted to a more positive potential after the final sequence, and the resolution of the voltammogram was poorer. The area under the reduction peak, and hence the ECA, were found to be nearly constant in all cases (Fig. 3). The slight reduction observed after the final sequence was within the bounds of error. This suggested that the cathode platinum catalyst retained its area even when run at off-design conditions for this period.

Stability of Cell Performance

The cell performance stabilized after an operating period of 4 days at 80°C and 120°C. This finding was in agreement with the results of the voltammetry experiments. Typical polarization curves on oxygen and air at 80°C and 120°C are shown in Fig. 4. The membrane resistance at 80°C and 120°C were found to be 0.065 and 0.165 ohm-cm² respectively. The poor limiting currents observed were attributed to mass transport limitations arising from the gas diffusion layer used, which was not optimized for high temperature operation, and the fact that that the experiments were being run with a constant flow rate of reactant gases, leading to very high utilizations (approaching 100%) even at current densities of 1300 mA/cm² on air. Notwithstanding these limitations, the performance on air at 120°C and 400 mA/cm² was found to be 489 mV, which confirmed to baseline requirements.

Off-Design Testing

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During the course of the first sequence, the cell experienced exit relative humidities of as low as 6 and 10% (down from 35% at baseline conditions) each for an hour or more. However, the performance at baseline conditions decreased only marginally from 480 mV to 450 mV at 400 mA/cm² (all subsequent references to voltages correspond to a current density of 400 mA/cm² unless otherwise stated). This drop was due to losses in the cathode layer, as the membrane resistance was found to regain its original value during the retest. It was interesting to note that during 120-80-80 operation (24% exit relative humidity), the membrane resistance contributed to 92% of the total loss in performance. This was due to the fact that the losses due to dehydration of ionomer in the catalyst layer and the resulting reduction in oxygen permeability and cathodic ionic conductivity were nearly compensated by the gains due to the increase in the partial pressure of oxygen and hydrogen. However, a further decrease in relative humidity to 10% and then down to 6% resulted in overwhelming cathodic losses. The second sequence was similar to the first, with an added run at 120-23-23, corresponding to an exit relative humidity of 2%, being the only difference. The results were found to mirror those observed in the first sequence, with a similar 25-30 mV difference in performance between the baseline test and retest. Once again, this difference was due to losses in the cathode layer, with the membrane resistance regaining its original value. Similar results were also obtained for the 120-80-80 run, and other subsequent runs. The results of the first two sequences are shown in Figs. 5 (a) and 5 (b).

Sequences 3 and 4 involved lowering relative humidity by increasing the cell temperature as opposed to the previous two sequences, where this was achieved by lowering the saturator temperatures. The results are shown in Figs. 6 (a) and 6 (b) respectively. In each case, a higher performance loss of about 40 mV between the baseline test and retest was noted. The loss was again due to the cathode layer, with the membrane resistance regaining its original value in both cases. Unlike the previous cases where a 10°C drop in saturator temperatures led to losses that were mainly due to membrane resistance, the increase in cell temperature resulted in losses due to both the membrane resistance and increased cathodic overpotential, with the split being nearly even. Besides, a near threefold increase in the magnitude of the loss occurred. While the absence of the beneficial effect of increased oxygen and hydrogen partial pressure in the latter case could account for some of the differences observed, the extent of losses incurred implied that an increase in cell temperature extracts a greater penalty from the cell when compared to a decrease in gas saturation temperature. Therefore, transients in increasing cell temperature would be expected to be particularly harmful.

Sequence 5 represented a combined approach to lowering relative humidity, with the cell temperature being increased to 140°C, and the saturator temperatures being progressively lowered all the way down to 40°C. The results are shown in Fig. 7. While the increase in temperature from 120 to 140°C produced results identical to those seen in earlier sequences, running the cell at 140°C and very low humidities during subsequent runs was found to have a detrimental effect on the activity of the cathode catalyst. A comparison between the baseline test and retest revealed a displacement of 50 - 60 mV in the Tafel region as opposed to the 15-25 mV displacement observed in earlier cases. Moreover, unlike in earlier sequences, subsequent equilibration at baseline conditions did not result in any improvement in performance. The effect of operation under such stringent conditions on the cathode was also observed in the cyclic voltammetry experiments as discussed earlier.

Finally, the transient studies yielded hysteresis curves for resistance and voltage measurements for both measurement techniques. The results are shown in Figs. 8 (a) – 8
(d). It was seen that the earlier trends in performance loss distribution were maintained to a certain extent in this experiment, with the membrane resistance contributing to approximately half the voltage loss when the cell temperature was increased with constant saturator temperatures.

CONCLUSIONS

This study revealed the ability of the MEA studied to provide reproducible performance at 120°C at a relative humidity of ~ 35% over a period of several days. Additionally, it showed that the MEA was not adversely affected by exposure to harsh off-design conditions of increased cell temperatures and greatly reduced relative humidities and displayed excellent recovery properties. While a performance loss was observed on retesting immediately at baseline conditions, this loss was recovered upon subsequent equilibration at baseline conditions and at more benign conditions. The membrane resistance at baseline conditions remained nearly constant throughout the program, and there was no evidence of crossover or internal shorting, which was commendable given the thickness of the membrane used. The cathode catalyst layer proved to be very stable, and only showed deterioration at the very end of the program after tens of hours of operation at off-design conditions. The deterioration was thought to be due to platinum recrystallization or carbon corrosion, though no conclusive evidence for either mechanism was found. The near constant ECA suggested that the contact between the ionomer and the catalyst was retained throughout the program. Overall the MEA demonstrated very good performance under testing conditions. It must be noted, however, that the entire testing sequence lasted only for a period of a few days. Even so some performance deterioration was evident towards the end. Long-term (1000s of hours) endurance of the MEA under baseline conditions remains very much a challenge, and is an issue we plan to address in our future endeavors.

FUTURE DIRECTIONS

Proposed research endeavors include a detailed study on the effect of membrane composition (additive type, concentration and size on performance under steady state and transient operation conditions at high temperature and determination of the effect of low exit relative humidities on the distribution of overpotentials using different diagnostic gases such as helium-oxygen and 4% O₂ (balance N₂) on the cathode. Endurance testing at constant current conditions for ambient pressure 120-90-90 operation is currently underway, and will be actively pursued over the next several months.

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Hydrogen crossover during test program

![Graph showing hydrogen crossover](image)

Fig. 2
Voltammetry during test program

![Graph showing voltammetry](image)

Fig. 3

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ECA after each sequence

Fig. 4
Steady State Polarization Curves on O2 and air at 80 and 120°C

Fig. 5 (a)

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Sequence 1 Data

![Graph showing iR-Free Cell Voltage (V) against Current Density (mA/cm²). The graph includes multiple lines representing different conditions such as Baseline - 120-90-90, 120-80-80, 120-60-60, 120-40-40, and Baseline retest - 120-90-90.]

Sequence 2 Data

![Graph showing iR-Free Cell Voltage (V) against Current Density (mA/cm²). The graph includes multiple lines representing different conditions such as Baseline - 120-90-90, 120-80-80, 120-60-60, 120-40-40, and Baseline retest - 120-90-90.]

Fig. 5 (b)

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Sequence 3 Data

Sequence 4 Data

Fig. 6 (b)

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Fig. 7

Sequence 5 Data

![Graph showing the relationship between current density and IR free cell voltage for different baseline and test conditions.](image-url)

- Baseline - 120-90-90
- 140-90-90
- 140-80-80
- 140-60-60
- 140-40-40
- Baseline retest - 120-90-90
Fig. 8 (a)
Transient studies

Resistance (400mA/cm²) vs Exit Relative Humidity -
Saturator Temperature constant (90°C), Cell Temperature varied (120-140°C)

Fig. 8 (b)
Transient studies

Cell Voltage (400mA/cm²) vs Exit Relative Humidity -
Saturator Temperature constant (90°C), Cell Temperature varied (120-140°C)
Fig. 8 (c)
Transient studies

Resistance (400mA/cm²) vs Exit Relative Humidity - (Cell Temperature Constant(120 C), Saturator Temperatures varied (70-90 C))

Fig. 8 (d)
Transient Studies

Cell Voltage (400mA/cm²) vs Exit Relative Humidity - (Cell Temperature Constant (120 C), Saturator Temperatures varied (70-90 C))