Application Note - Break-in Procedure for a PEM Fuel Cell

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Introduction

A pristine, unused fuel cell does not exhibit its maximum performance which is why it must be broken-in before the cell can be used. The "break-in procedure" is the initial exercising of the fuel cell that is done so that the cell is at is maximum performance before it is used further. Break-in is also called "activation". During activation, the performance of the cell increases to a maximum and then remains constant. The point where the performance stops improving is the where the cell can be considered "broken in". The time it takes to get to the break-in point is important because the faster the cell is broken in, the faster the cell can be used.

Balogun et. al. recently summarized common break-in approaches, noting the advantages and disadvantageous of each, including the time required to complete the activation process as well as the impact on durability.

Approaches to activation include voltage scanning, voltage stepping, application of high current density, and short circuiting, among others. Voltage scanning continuously changes the cell voltage without holding the voltage constant whereas voltage stepping changes the voltage in larger increments and holds the voltage constant for some period of time before stepping to another voltage. The U.S. DOE break-in protocol is based on voltage cycling while the EU protocol [Tsotridis 2015] relies on a series of step-wise RH, current and voltage cycles. Balogun and coworkers demonstrate a method based on cathode starvation (shutting of the oxygen supply while under load).

The break-in procedure is usually done under fully humidified conditions (100% RH on the anode and cathode), and may or may not be done at elevated pressure. For a hydrogen (H₂) polymer electrolyte membrane fuel cell (PEMFC), typical break-in temperature is 60-80 °C with higher temperatures accelerating the break-in procedure. Direct methanol fuel cells (DMFC) can generally be broken in with methanol or hydrogen and often at a lower temperature than a H₂ PEMFC.

Objective

The goal of this work was to compare the time it took to break-in a PEMFC with two different break-in methods and provide data for each of the examples.

Experimental

Materials

The cells used in this study were assembled using a Gore Primea 57 Series MEA with an 18 μm thick membrane and catalyst loading of 0.4 mg Pt cm $^{-2}$ for the anode and cathode. The gas diffusion layer was a SGL 25BC (SGL Carbon). For the anode the main gasket was a 152 μm polytetrafluoroethylene (PTFE)-filled fiberglass sheet (Furon) and the sub-gasket was a 51 μm perfluoroalkoxy alkane (PFA) film. For the cathode both the main gasket and the sub-gasket

were 51 μ m PFA. The target pinch was 25%. The cell was assembled to a torque of 11.30 N·m (100 in.·lbs) on each of the 8 bolts.

Break-in Procedure and Cell Performance Characterization

Each cell was assembled and connected to an 850e Fuel Cell Test System (Scribner Associates, Inc.). The temperatures of the cell, anode and cathode humidifiers were set to 70 °C and no pressure was added. The minimum flow rate of the anode (hydrogen) was 0.05 standard liter per minute (SLM) and the stoichiometry was 1.2. For the cathode (air) the minimum flow rate was 0.1 SLM and the stoichiometry was 2.5.

For both of the cells a polarization curve was done before the break-in, half way through and after the break-in was completed. The polarization curve consisted of a voltage step-stair experiment from open circuit to 0.3 V and then back to open circuit, with 120 sec/step and a 0.05 V step size.

The first break-in method consisted of rapid voltage steps according to a procedure developed by W.L. Gore & Associates [Murthy 2006]. The cell was held at a constant voltage of 0.6 V, 0.3 V and open circuit for 60 sec each. This was repeated 20 times and the data was recorded at 1 sec/pt. This voltage step sequence was then repeated 20 more times after the intermediary polarization curve.

The break-in method for the second cell consisted of much longer voltage steps than the first break-in procedure. The cell was held at a constant voltage of 0.6 V for 15 min, open circuit for 60 sec and 0.3 V for 15 min. This was repeated 4 times and the data was recorded at 1 sec/pt. This voltage step sequence was then repeated 4 more times after the intermediary polarization curve.

Data and Results

Fuel Cell #1 - Rapid Voltage Cycling Procedure

The first part of the break-in consisted of cycles 1-20 and took 60 min to complete. The second part of the break-in consisted of cycles 21-40 and also took 60 min to complete, for a total of 120 min. Figure 1 shows the current density as a function of the break-in time. Figure 1(a) shows all of the current density points during the break-in and Figure 1(b) shows the average current density for the last 30 seconds of each voltage cycle.

For the 0.3 V step the average current density was 1312 mA/cm², 1414 mA/cm² and 1415 mA/cm² for cycles 1, 20 and 40 respectively. For the 0.6 V step the average current density was 736 mA/cm², 911 mA/cm² and 914 mA/cm² for cycles 1, 20 and 40 respectively. There was no significant increase in the current density between cycles 20 and 40 indicating that the cell was broken in by cycle 20 or after the first 60 min.

The open circuit voltage also increased slightly as a result of the break-in: it started at 0.904 V and reached 0.919 V at the end of the first part of the break-in. At the end of the second part of the break-in, the voltage had not increased and was 0.917 V.

The polarization curves in Figure 2 show the current density and power density improved as the cell was broken in. In both graphs the greatest increase between the polarization curves was a result of the first part of the break-in. There was almost no increase in the performance as a result of the second part of the break-in which indicated that the cell was broken in after the first part of the break-in. The open circuit voltage increased by 0.057 V as the cell was broken in. The starting open circuit voltage was 0.836 V and the final open circuit voltage was 0.893 V.

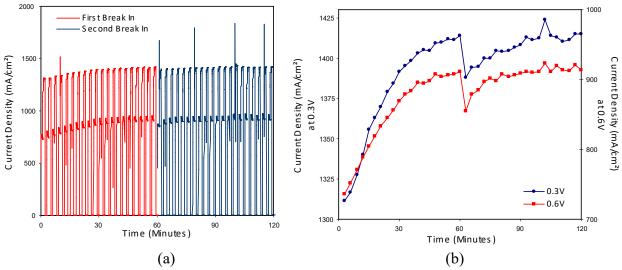


Figure 1. (a) Current density as a function of time during the break-in. The red section is the first part of the break-in, cycles 1-20 and the blue is the second part of the break-in, cycles 21-40. Each part of the break-in lasted 60 min for a total of 120 min. (b) Average current density for the last 30 seconds of each cycle as a function of time for the 0.3 V and 0.6 V step during the break-in.

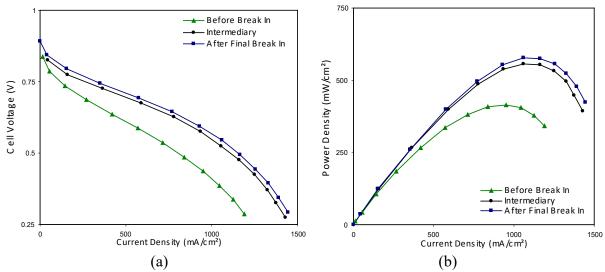


Figure 2. The polarization before the break-in is in green, the intermediary in black and the final polarization after the break-in was completed is in blue. (c) Average cell voltage as a function of current density for each polarization curve throughout the break-in.

polarization after the break-in was completed is in blue. (d) Average power density as a function of current density during each of the polarization curves.

Figure 3 shows the cell resistance during the polarization curves (a) and break-in (b). The resistance during the break-in is the average resistance for the last 30 seconds of each. In both graphs the resistance decreased overtime as the cell was broken in. The resistance during the 0.3 V step was also greater than the resistance during the 0.6 V step throughout the break-in.

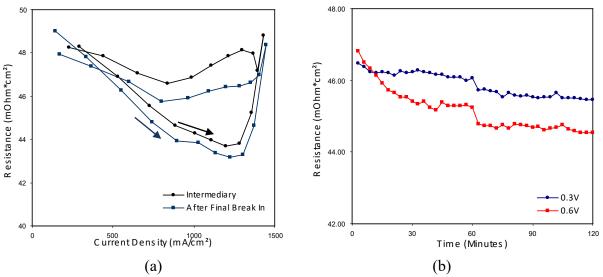


Figure 3. (a) Resistance as a function of current density during the polarization curves. The intermediary polarization is in black and the final polarization after the break-in was completed is in blue. (b) Average resistance for the last 30 seconds of the 0.3 V and 0.6 V steps during the break-in as a function of time. The 0.3 V step is in blue and the 0.6 V step is in red.

Fuel Cell #2 – Long Duration Voltage Cycling Break-in Procedure

The first part of the break-in was cycles 1-4 and took 124 min; the second part of the break-in was cycles 5-8 and also lasted 124 min. Figure 4 shows the current density throughout the break-in. Figure 4(a) shows the real-time current density during the voltage cycling and Figure 4(b) shows the average current density for the last 5 min of each cycle.

For the 0.6 V step the average current density was 746 mA/cm², 885 mA/cm² and 887 mA/cm² for cycles 1, 4 and 8 respectively. For the 0.3 V step the average current density was 1385 mA/cm², 1416 mA/cm² and 1391 mA/cm² for cycles 1, 4, and 8 respectively. The current density in the 0.6 V step did not increase significantly after the first part of the break-in and in the 0.3 V step the current density actually decreased after the first part of the break-in. The constant current in the 0.6 V step indicated the cell was broken in after the first part of the break-in at 124 min.

During the open circuit step of the break-in the voltage started at 0.910 V and reached 0.939 V at the end of the first part of the break-in. By the end of the second part of the break-in the voltage was 0.940 V. Since it did not increase significantly after the first part of the break-in, this also indicated that the cell was broken in after the first part of the break-in.

Figure 5 shows an increase in current density and power density as the cell was broken in. In both graphs the largest increase between the polarization curves was a result of the first part of the break-in and there was almost no change as a result of the second part of the break-in. The starting open circuit voltage was 0.902 V and the final open circuit voltage was 0.928 V.

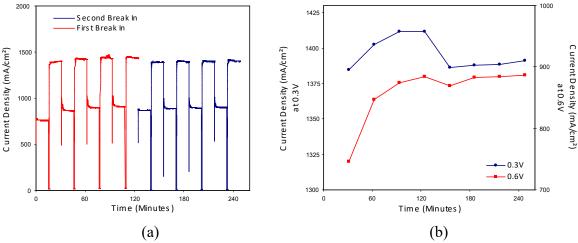


Figure 4. Current density as a function of time for the break-in. (a) The first part of the break-in is in red and the second part is in blue. The first part of the break-in was cycles 1-4 and the second part of the break-in was cycles 5-8. Each part of the break-in lasted 124 min for a total break-in time of 248 min. (b) The average current density for the last 5 min of the 0.3 V and 0.6 V steps during the break-in as a function of time. The blue is the current density for the 0.3 V step and the red is the current density for the 0.6 V step.

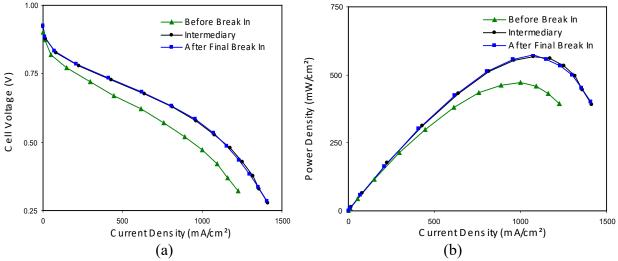


Figure 5. The polarization before the break-in is in green, the intermediary in black and the final polarization after the break-in was completed is in blue. (i) Cell voltage as a function of current density for each of the polarization curves. (j) Power density as a function of current density for each of the polarization curves.

Figure 6 shows the resistance during the polarization curves and the break-in. Figure 6(a) shows the resistance during the polarization curves. Figure 6(b) shows the average resistance of the last

5 min of each voltage cycle during the break-in. In both cases the resistance decreased as the cell was broken in. The resistance during the 0.6 V step was less than the resistance during the 0.3 V step of the break-in.

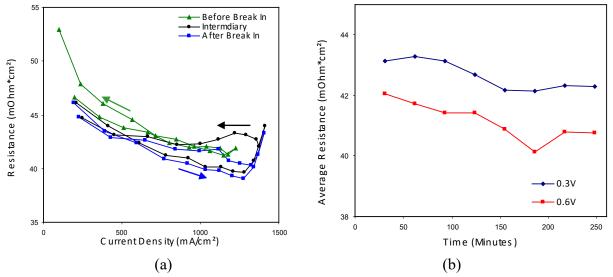


Figure 6. (a) Resistance as a function of current density for each of the polarization curves. The polarization before the break-in is in green, the intermediary in black and the final polarization after the break-in was completed is in blue. (b) Average resistance as a function of time for the last 5 min of the 0.3 V and 0.6 V steps for each cycle during the break-in.

Discussion and Conclusion

The cell was considered broken in when the current density stopped increasing as a result of the voltage cycling. This occurred in the first cell after approximately 60 min and in the second cell after approximately 124 min. The point where the cell was broken in was more evident during the 0.6 V step than during the 0.3 V step. The current density for the first cell at the break-in point for the 0.6 V step was 911 mA/cm² and the current density for the second cell at the break-in point was 885 mA/cm². For the 0.3 V step the current density was 1414 mA/cm² for the first cell and 1412 mA/cm² for the second cell.

The polarization curves also confirmed that the cells were essentially broken in after the first part of the break-in. The largest increase in cell performance was a result of the first part of the break-in and there was a much smaller increase or no increase in cell performance as a result of the second part of the break-in. The open circuit voltage also increased for each polarization curve. The first cell started at 0.836 V at the start of the first polarization curve and ended at 0.893 V. The second cell started at 0.902 V at the start of the first polarization curve and ended at 0.928 V. The voltage cycles in the first break-in method were much shorter than the voltages cycles in the second break-in method. The first break-in procedure based on rapid voltage cycling between open circuit voltage and 0.6 V and 0.3 V was a better procedure because it took less than half of the time to break-in the cell than the second method.

References

Balogun, E., Barnett, A. O., and Holdcroft, S. "Cathode starvation as an accelerated conditioning procedure for perfluorosulfonic acid ionomer fuel cells" *Journal of Power Sources*, **3**, 100012 (2020).

Tsotridis, G., Pilenga, A., Marco, G. D., and Malkow, T. (2015). "EU Harmonised Test Protocols For PEMFC MEA Testing In Single Cell Configuration For Automotive Applications." *EUR* 27632 EN, European Commission.

Murthy, Mahesh, Nicholas T. Sisofo, III, and Carole A. Baczowski. "Method and Device to Improve Operations of a Fuel Cell" U.S. Patent 0166015. 27 July 2006.

U.S. Department of Energy (2009), "Procedure for Performing PEM Single Cell Testing." Contract # DE-FC36-06G016028.