Damage in specific areas caused by frequent starting and stopping of proton exchange membrane fuel cells

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Abstract

One of the primary objectives to increase the durability of Proton Exchange Membrane Fuel Cells (PEMFC), particularly for transportation applications, is to reduce the circumstances known to accelerate degradations during start-up and shut-down. These kinds of extreme situations are often mimicked with the use of accelerated stress tests like cyclic voltammetry cycles. The findings provided in this study imply that the degradations induced by this approach do not correlate to those observed under actual operating circumstances, despite the fact that it is simple to apply.

Introduction

While the power density of PEMFC has increased to the point that they may be employed in automotive systems, their limited durability prevents them from being widely used. The fuel cell's anode chamber must be maintained empty at all times for safety reasons. While it is possible to perform a fuel cell shutdown (SD) without injecting air into the anode compartment (by, for example, sealing the inlet and outlet until hydrogen crosses the membrane spontaneously), it is extremely challenging to do so during a fuel cell startup (SU), and the presence of oxygen in the anode is known to severely damage the Membrane Electrode Assembly (MEA) [1, 2]. While some writers have investigated the degradations brought on by start-up and shutdown first-hand [3-5], Accelerated Stress Tests (AST) are often chosen due to their ease of use and the speed with which they provide data [6, 7]. The goal of this work is to look at how cyclic voltammetry (CV, a basic AST technique) deterioration stacks up against SU-induced degradation. To track changes on a global and microscopic level, the studies were carried out in a cell that had been sectioned. Timely measurements of polarization and estimates of local electrochemical surface areas (LECSAs) are made.

Experimental Conditions

Segmented fuel cell

The segmented cell measuring 1 x 30 cm2 was used for these experiments (see references [8], [9]). Nafion 212 membrane, 0.6 mgPt/cm2 cathode (0.2 mgPt/cm2 anode), and 190 m thick gas diffusion layers (Toray paper) compressed to 150 m using Teflon gaskets made up the MEAs supplied by Johnson Matthey. Five parallel passages measuring 0.7 mm 1 mm allow for the passage of air and hydrogen. Four 15 mm long, 1 mm thick gold plated brass strips gather electricity from 20 electrically isolated segments, while the cathode compartment itself is carved into a polycarbonate plate. The current is averaged throughout the width of the MEA by connecting the four strips electrically outside the cell. Aluminum with a gold plating serves as the anode flow field plate. It is not segmented, and a cooling circuit and thermostated bath are utilized to regulate the temperature within the cell. In the current studies, hydrogen and air were fed into the cell in a counterflow arrangement, and water vapor was added to all gases through bubbling. Local current densities up to 2 A/segment were measured using 20 5 m shunt resistors and recorded using a data processing and acquisition system while the cell was operating normally. Hall current sensors (CT 0.1-P - LEM - 200mA) were used to detect current densities of up to 20 mA/segment during the recording of the voltammograms. A power source (3A-20V) is connected in parallel with the cell and the load in cyclic voltammetry.

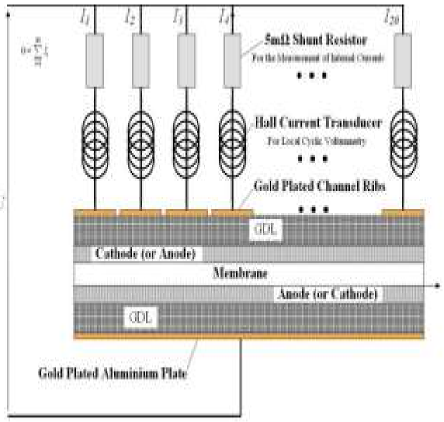

Fig. 1. Segmented cell electrical connections

Test bench Aging protocols

Starting and stopping the fuel cell, as well as performing local characterization sequences (electrochemical impedance spectroscopy -EIS-, CV, polarization curves), all need the use of various gases at the fuel cell's anode and cathode.

An automated test bench was employed for the task at hand. It has seven mass flow controllers and seven three-way solenoid valves, so you may choose from a wide variety of flow rates. To enhance the responsiveness of the mass flow controllers, each gas was sent via a discharge tube before entering the cell. The mass flow of the various gases, valve operation, load, power supply, and data collecting may all be managed by means of a Labview application. Galvanostatically, at frequencies between 0.05 and 800 Hz, and with an amplitude of the (total) current oscillation equal to 5% of the steady state adjusted to 0.5 A/cm2, local EIS recordings were made using a National Instrument USB 6221 load controller.

Experimental protocols

Initial conditioning of the fresh MEA lasted for about 24 hours. The conditioning process included increasing the current density up to 1.2 A/cm2 and then twice depriving the tissue of oxygen by cutting off the airflow while keeping the current density at 0.5 A/cm2. In the past, aging procedures included repeatedly performing the same cyclic voltammetry or power-on/power-off cycles: x the first method relied on 272 voltammetry cycles in rapid succession. Two linear potential scans at a sweep rate of 50 mV/s between 0.1 V and 1.2 V made up each cycle. Saturated hydrogen was delivered to the anode, while saturated nitrogen (no flow) was introduced to the cathode. After every 17 cycles, a series of defining characteristics was created. Start-up protocols were executed with low (2 slph - 8 cm/s*) and high (10 slph - 42 cm/s*) hydrogen flow rate, and included the following steps: o Operating the fuel cell at constant current density (0.5 A/cm2 for 300 s); o Measuring the local EIS spectrum for each segment; o Measuring the global and local fuel cell polarization curve. The cell was run at 0.5A/cm2 for 300 seconds in between each start and stop. Every 17 sequences, we did a cyclic voltammetry and the characterization procedure we just went through. For example, during the start-up and cyclic voltammetry protocols, shutdowns were performed with 20 slph (87 cm/s) of air or hydrogen, and starts-ups were performed with 20 slph (87 cm/s) of air or hydrogen to reduce degradations as much as possible.

Results and discussion

Fuel cell voltage at 0.5 A/cm2 with time and number of startup/CV cycles is shown in Fig. 2. The fuel cell's performance does not degrade during cyclic voltammetry; in fact, the voltage improves slightly (from 0.725 to 0.736 V). Insulation Resistance High frequency resistance was found to decrease from 7.9.10-2.cm2 at the start of the treatment to 7.5-10-2.cm2 by its conclusion, as measured by spectroscopy. The latter is responsible for much of the voltage boost; a reduction in high frequency resistance of 4.10.cm2 results in an increase in voltage of 8.10.3 V at 0.5A/cm2. In contrast, the fuel cell voltage decreases due to start-up aging processes, and this decrease is more significant as the hydrogen flow rate decreases, from -30 mV (-100 V/Start-up) at a rate of 10 slph (42 cm/s) to -190 mV (-700 V/Start-up) at a rate of 2 slph (8 cm/s).

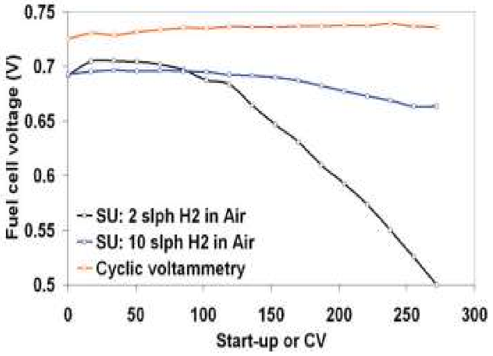

Fig. 2. Evolution of the fuel cell voltage during cyclic voltammetry and start-up aging protocols.

A first quantitative distinction between wear caused by cyclic voltammetry and wear caused by start-up and shut-down operations is shown in Fig. 2. The global and regional changes in the platinum ECSA provide complementary data (Fig. 3). While repeated voltammetry cycles have no effect on the fuel cell voltage, the ECSA decreases by about 25%. This decline is consistent throughout the cell. Previous research [10, 12] has related the ECSA loss to the emergence of platinum particles in the membrane and the coarsening of particles in the catalyst layer, both of which are effects of (long and short range) Ostwald ripening. Due to the large platinum loading of the MEAs used here, the loss of ECSA has no noticeable impact on cell performance. After 272 consecutive voltammetry readings at 0.8 A/cm2, it was found that the fuel cell voltage had begun to drop under the identical experimental circumstances. Comparable (-25%) ECSA decline was seen after 306 CV. While the ECSA drops of the first segment are similar regardless of the aging protocol (on the order of 30% with CV or SU with various hydrogen velocity - Fig. 3b), that of segment #20 depends clearly on the protocol applied (Fig. 3c) due to the nonhomogeneous nature of the MEA surface and the low hydrogen flow rate. ECSA loss at 272 SU is around 90% when the hydrogen velocity is low, 80% when the hydrogen velocity is high, and 25% when the hydrogen velocity is very low (272 CV). The second through nineteenth segments show a declining profile of ECSA from the anode compartment's intake to its outflow, indicating a degradation level somewhere in the middle. In fact, Pt and carbon oxidation produced by reverse currents in the passive section of the cell during SU and SD account for the vast majority of degradations experienced during startup [13]. Air (oxygen) and hydrogen residence times in the anode compartment were shown to be positively associated [8, 14]. Potential cycling produced by start-up and shut-down operations may also contribute to these degradations, but to a considerably smaller level. Postmortem analyses performed on MEA that had been subjected to SU aging protocols corroborated these findings: we observed a thinning of the cathode near the hydrogen outlet and the presence of a Pt-band characteristic of long range Ostwald ripening within the MEA (Fig. 4), but neither of these features was present near the hydrogen inlet.

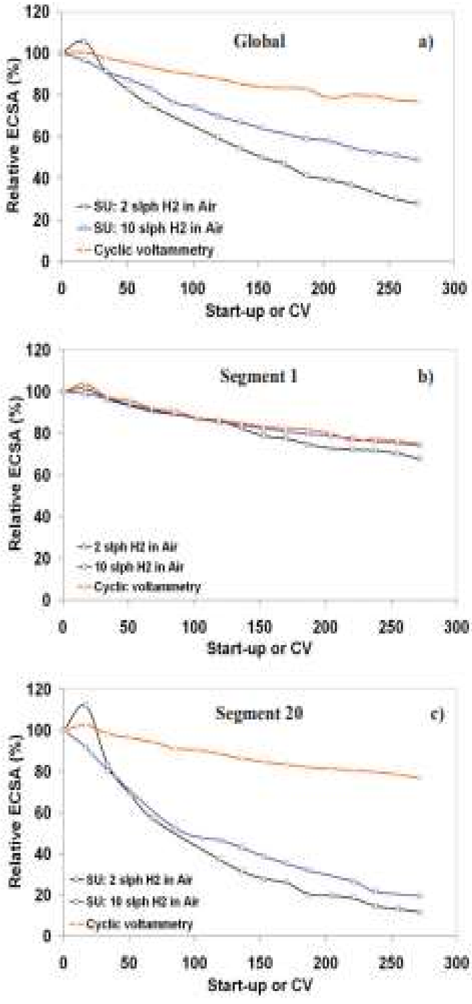

Fig. 3. Evolution of the platinum ECSA during the different aging protocols: a) mean value over the whole cell, b) values measured in segment #1, and c) #20.

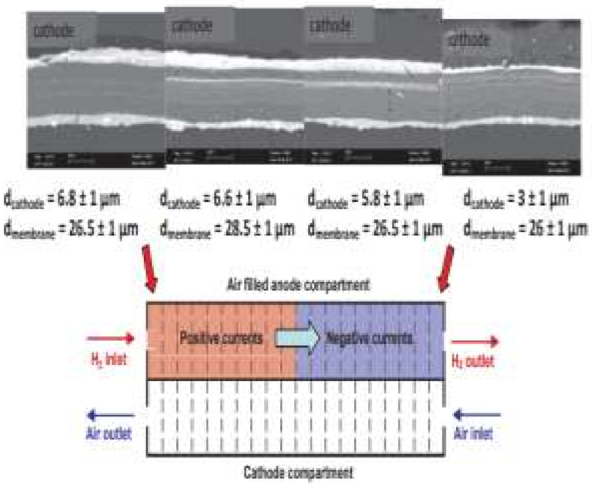

Fig. 4: SEM images in back-scattered mode of a MEA aged under repeated start-up cycles (136 start-up performed at 2 slph hydrogen flow rate for different segments along the cell

Conclusions

This article demonstrates that start-up and shut-down operations cause different types of damage than repetitive voltammetry cycles. The ECSA is reduced in a uniform fashion by repeated CV, and this has a considerably less effect on fuel cell performance than SU. According to SU (and SD), the anode compartment contains oxygen and hydrogen at the same time, for a period of time proportional to the gas velocity. The ECSA drops far more unevenly and a lot of carbon is burned up in the process. Therefore, it would seem that repeated cyclic voltammetry sequences are not a suitable AST for investigating the impacts of start-up and shut-down operations.

References

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