Ex-situ and in-situ stability studies of PEM fuel cell catalysts: the effect of carbon type and humidification on the thermal degradation of carbon supported catalysts.

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Introduction

Proton exchange membrane fuel cells are poised to change the landscape of power generation over the next ten years. For this to be realized, however, considerable technical challenges must be overcome. One of the most significant challenges for stationary systems is lifetime, where 40,000 hours of operation with less than 10% decay in performance is desired. There are several different membrane electrode assembly (MEA) associated degradation mechanisms inhibiting MEAs from obtaining their desired lifetime targets. The focus of this research is on the loss of cathode surface area over time, which results in MEA performance losses, since MEA performance is proportional to cathode catalyst surface area. Two proposed mechanisms – support oxidation and platinum dissolution are studied using different accelerated tests. These results are compared to cathode catalyst surface area loss data from real-time fuel cell tests in order to decouple the two degradation mechanisms.

Approach

Two accelerated test methods were used to study the phenomena of cathode catalyst surface area loss – ex-situ thermal treatments and in-situ electrochemical tests. The ex-situ methods were developed at Dalhousie University [1] and consist of thermal treatments (125°C and 150°C) at various gas humidification levels where the mass loss of the catalyst was measured at different time intervals during a 1,000 hour test. BET and XRD techniques were also employed to measure changes in the nature of the catalyst after the accelerated test was completed.

Two in-situ electrochemical tests were applied to look at the cathode catalyst/support stability. In both cases, the predominance of work was done at 80ºC cell temperatures with symmetric $50cm^2$ active area MEAs under H_2/N_2 at 200/500sccm with fully saturated gas streams and ambient outlet pressure. The first method involved aging the cathode catalyst at 1.2 V (vs. SHE) in five hour increments. At the beginning of the test and between each five hour increment, the catalyst surface area was measured using cyclic voltammetry (CV) [2]. The 1.2 V method is best thought to probe the support stability and shows excellent agreement with the ex-situ method. The second electrochemical method consists of cycling the voltage between 0.6 V – 1.0 V at 25 mV/s for 500 cycles. The cell operating conditions are the same as the 1.2 V test method. The surface area was measured by CV at the beginning and after each set of 500 0.6 V – 1.0 V cycles. The 0.6 V – 1.0 V cycle method is thought to best probe the platinum dissolution.

Commercially available carbon supported catalysts were used in these experiments. The catalysts studied varied in catalyst surface area, support surface area, platinum crystallite size, and metal weight percent. Inks were made from the catalysts using Nafion® ionomer and were subsequently coated onto a gas diffusion layer (GDL) to yield an electrode with a Pt loading of 0.4 mg Pt/cm^2. The electrodes were then bonded to a polymer electrolyte membrane. Variables explored for each of these accelerated tests include cathode relative humidity (RH) and cell temperature.

Fuel cell tests are ongoing using a 50% Pt catalyst on a high surface area carbon at a loading of 0.4 mg Pt/cm^2 in a $50cm^2$ cell. Two test scripts were employed for the fuel cell tests. The first held the cell voltage at 750 mV throughout the test. The second continuously cycled the cell voltage between 740 mV to 875 mV. For both tests, H_2/air was supplied at 250/680 sccm. Surface area measurements were taken at room temperature. Different samples were tested at cell temperatures between 80ºC and 130ºC under 100% RH to obtain an activation energy for the degradation mechanism.

Results

The results of the ex-situ thermal and in-situ 1.2 V tests indicate that catalyst support stability is dependent on temperature, RH, carbon type, and to a lesser extent the platinum weight percent on the support. One set of samples explored the effect of carbon surface area with a fixed metals percentage of 50% and a fixed particle size of about 2.2nm. The results of this study can be seen in Figure 1. In general, the higher the surface area of the carbon support, the more susceptible it is to oxidation. The exception to this trend is the graphitized carbon support with a surface area of 266 m^2/g. While the graphitized carbon is similar to the 220 m^2/g carbon, the surface area of the 220 m^2/g carbon decreased by 16%, while the 266 m^2/g graphitized carbon is basically unchanged. Figure shows the

effect of metal weight percent. For the same carbon support, decreasing the Pt metal weight percent reduces the carbon support area loss. From these findings, one can conclude that the carbon support corrosion is a result of the Pt catalyzing the carbon combustion.

The loss of surface area has a strong effect on fuel cell performance. Figure 3 shows fuel cell performance and catalyst surface area change under the accelerated 1.2 V protocol. The fuel cell performance was measured at 70ºC cell temperature at 100% RH under H_2/air at 800/1800 sccm and ambient outlet pressure. The loss in cathode surface area and subsequent loss performance in the kinetic region is also observed in real-time fuel cell tests operating for thousands of hours.

Comparing the CVs from the fixed and cycling accelerated tests provides insight into the different degradation pathways. Figure 4 compares the CVs. The first observable is the difference in the width of the double layer region of the CV between the two methods. The peak associated with carbon oxidation is best observed with the steady state scans. Figure 5 summarizes the changes in double layer with time of test and loss of surface area of the catalyst.

Summary

Accelerated electrochemical tests have been used to understand fuel cell cathode catalyst surface area loss due to carbon oxidation and platinum dissolution as a function of relative humidity, carbon type and metals loading. Analysis of the double layer capacitance yields insight into the different degradation mechanisms between the two methods. These results will be compared against fuel cell durability testing observations.

Acknowledgements

References

[1] D.A. Stevens and J.R. Dahn, "Degradation of the carbon support in carbon-supported electrocatalysts for PEM fuel cells," 204th Meeting of the Electrochemical Society, October 2003.

[2]   J. Xie, D.L. Wood III, K.L. Moore, P. Atanassov and R.L. Borup, "Microstructural changes of membrane electrode assemblies during PEFC durability testing at high humidity conditions," *J. Electrochem. Soc*. **152** (5) A1011-A1020 (2005).
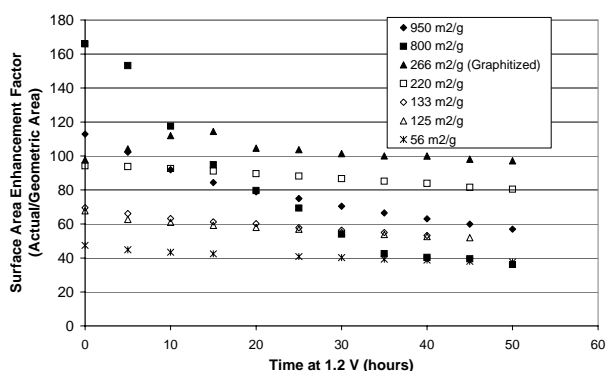
Figure 1. Effect of carbon support surface area on carbon support stability for 50% Pt metal loading.
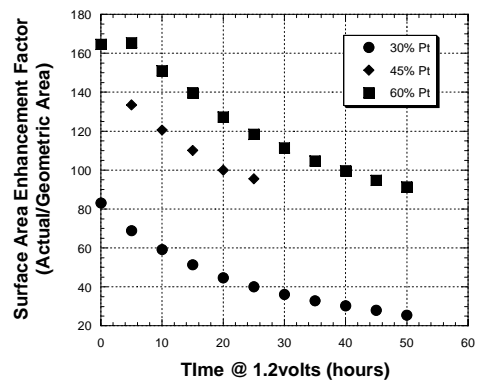
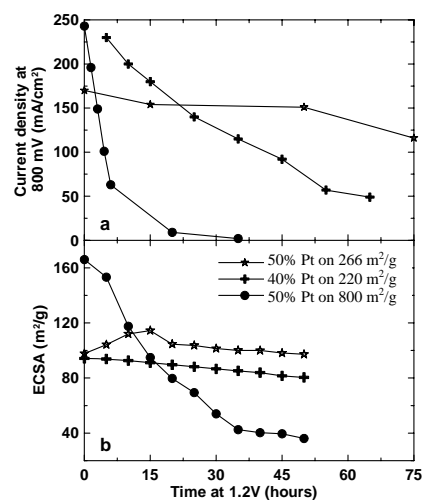Figure 2. Effect of metal weight percent on carbon support stability.

Figure 3. Relationship between carbon support stability and fuel cell
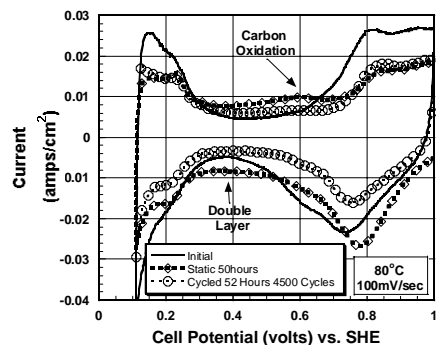   performance.

Figure 4. Cyclic voltammagrams of electrochemically aged catalyst:
          initial, 50 hours at 1.2 V and 52 hours of cycling between
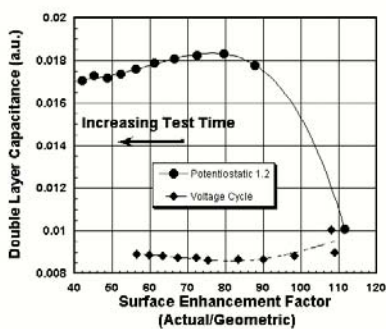   0.6V – 1.0 V at 25mV/s.

Figure 5. The different relationships between the Surface Enhancement
Factor and Double Layer Capacitance between the steady
state and voltage cycle accelerated tests.