

## Characterization of Carbon Oxidation: Increased Stability of PEM Fuel Cell Electrodes by Graphitization of Carbon Supports

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Excessive degradation of stack voltage is well recognized as a possible failure mode for fuel cell systems. Carbon corrosion and platinum dissolution/sintering of carbon-supported platinum catalysts are primarily responsible for degradation of stack voltage when stack operation is interrupted/discontinued. Oxidation of carbon support can lead to changes in carbon surface properties and electrode structure that can lead to high transport losses. Excessive carbon oxidation also causes platinum particles to grow resulting in loss of platinum dispersion/surface area.

It is well known that carbon can thermodynamically corrode above 0.207V to carbon dioxide and corrosion currents reach significant levels around 1V and above. Carbon support on the hydrogen-fed anode side is generally very stable, except during voltage reversal due to fuel starvation. On the other hand, cathode is generally operated in a potential window (0.6-1V) that is thermodynamically susceptible to carbon corrosion. To make situations worse, start-up and shutdown of fuel cell systems can result in local cathode potential as high as 1.5V<sup>1,2</sup>. Also, after shutdown, the anode and cathode compartments may be filled with air, setting the electrode potential to around 1.2V. Such high voltages during start-up and shutdown of a fuel cell dramatically enhance carbon corrosion. Although a large body of corrosion data on platinized carbon support is available under PAFC operating conditions<sup>3</sup>, only limited work has been published on corrosion of carbon support under PEM operating conditions<sup>4</sup>.

An attempt will be made to quantify electrochemical carbon oxidation as a function of temperature, voltage and support type using electrochemical methods and carbon dioxide/carbon monoxide measurements in the cathode air exhaust under PEM fuel cell conditions. Possibility of platinum acting as a catalyst for carbon oxidation is also considered<sup>4</sup>. Figure 1 shows carbon corrosion current measured at 95°C, 1.2V (vs. RHE) in 0.5M H<sub>2</sub>SO<sub>4</sub> for Vulcan supported carbon (Pt/Vulcan). Platinizing the carbon support increases corrosion current by a factor of two. At this rate, 25% of the platinized carbon support will be lost in approx. 500 hours.

Patterson<sup>5</sup> and Kinoshita<sup>6</sup> have shown that cycling between certain voltage regimes can lead to enhanced loss of platinum surface area. Similar experiments are performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> using button electrodes to explore the use of carbon supports that have been graphitized at high temperatures. Figure 2 shows the loss of platinum surface area when the electrode is cycled at 20 mV/s between 0 and 1.2V (vs. RHE) at 25°C. Loss of platinum dispersion due to carbon corrosion is reduced in the case where a graphitized electrode is employed. More data will be presented to stress the need for supports that are stable under conditions when cathode voltage exceeds 1.0V, i.e. in the range of 1.2-1.5V.

In Summary, in order to develop stack technology that is robust towards possible start/stop related degradation mechanisms, catalyst support materials with improved corrosion resistance are required. These may be high surface area graphitized supports for maximized Pt dispersion or alternative support materials. In addition, fundamental studies need to be conducted to understand detailed corrosion and pt-stability mechanisms.

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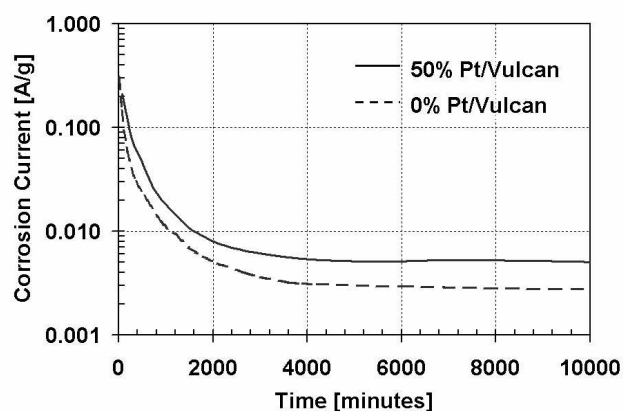


Figure 1: Carbon oxidation current measured at 95°C, 1.2V in 0.5M H<sub>2</sub>SO<sub>4</sub> showing enhanced corrosion for platinized electrodes

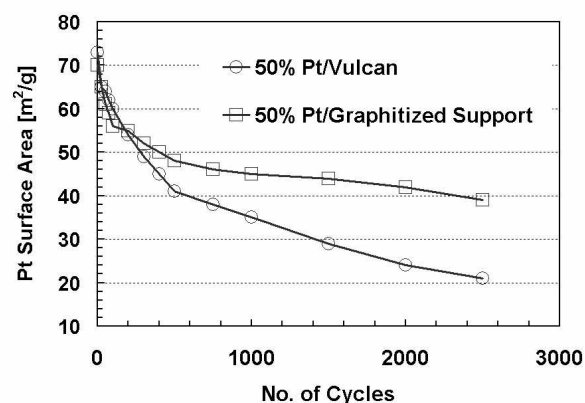


Figure 2: Graphitized carbon support demonstrating reduced corrosion leading to lower platinum surface area loss for electrodes cycled between 0 V and 1.2V (vs. RHE) at 25°C in 0.5M H<sub>2</sub>SO<sub>4</sub>

## References