

## SURFACE OXIDATION EFFECTS IN PEM FUEL CELL ELECTRODES

T. D. Jarvi

UTC Fuel Cells, 195 Governors Highway,  
South Windsor CT

Surface oxidation phenomena are fundamentally intertwined with the oxygen reduction process occurring in the PEM cathode. Environmental conditions within the cathode, including the presence of oxygen, high potential and high water concentration promote oxidation. Furthermore, electrocatalytic oxygen reduction requires the platinum surface to partially oxidize to produce water. High surface area carbon, generally present as a catalyst support, also undergoes oxidation at cathode potentials. Hence the surface states of both catalyst (Pt/C) constituents are necessarily dynamic in an operating PEM cathode. In this paper, recent work will be summarized that highlights the dynamic and reactive nature of the PEM cathode catalyst surface.

Surface oxidation of platinum has been related to significant, recoverable performance loss in PEM fuel cells [1-3]. Recently, platinum surface oxidation in the presence of gas phase oxygen has been characterized [4]. Fig. 1 shows that the extent of surface oxidation increases with increasing exposure to oxygen at +0.85 V<sub>RHE</sub>. No dependence on oxygen exposure was found at +0.95 V<sub>RHE</sub>. The extent of oxidation plateaus at about 1 ML. These results will be compared and contrasted to the well-characterized electrochemical oxidation of platinum by water.

In high-performance PEM fuel cells, platinum is supported on high surface area carbon (up to 1500 m<sup>2</sup>/g). Carbon is unstable under cathode conditions and undergoes oxidation, although the kinetics can be slow. While carbon surface oxidation was studied widely under conditions similar to those in phosphoric acid cells, little research has been conducted under conditions similar to those found in PEM fuel cells [5]. The extent of surface oxidation of Vulcan XC-72 as a function of time at 1.2 V<sub>RHE</sub> was measured by several different methods. Fig. 2 shows a summary of the results that indicates significant surface oxidation occurs in relatively short oxidation periods.

The results in Figs. 1 and 2 taken together suggest that surface species formed on either carbon or platinum may interact with one another. This could be important, for example if platinum plays a role in destabilizing the carbon to oxidation. Carbon corrosion was measured by monitoring CO<sub>2</sub> during cyclic voltammograms for carbon and Pt/C at different mass fractions of platinum [6]. The results in Fig. 3 show that the onset of CO<sub>2</sub> detection shifts to lower potential as the platinum content increases.

The results presented here demonstrate that the cathode catalyst surface is dynamic and interactive. Both platinum and carbon oxidize significantly under PEM cathode conditions, and evidence has been obtained that the oxidative behavior of Pt/C catalysts is not a linear combination of platinum and carbon behavior.

### REFERENCES

1. T. Jarvi, T. Patterson, N. Cipollini, J. Hertzberg, and M. Perry, Abstract 1211, 203<sup>rd</sup> Electrochemical Society Meeting, Paris, France (2003).
2. F. A. Uribe, T. A. Zawodzinski, Jr., *Electrochimica Acta*, **47** (2002) 3799.
3. P. Zelenay, presented at the 203<sup>rd</sup> Electrochemical

Society Meeting, Paris, France (2003).

4. C. H. Paik, T. D. Jarvi, and W. E. O'Grady, *Electrochem. Solid State Lett.*, **7** (2004) A82.
5. K. H. Kangasniemi, D. A. Condit, and T. D. Jarvi, *J. Electrochem. Soc.*, **151** (2004) E125.
6. L. M. Roen, C. H. Paik, and T. D. Jarvi, *Electrochem. Solid State Lett.*, **7** (2004) A19.

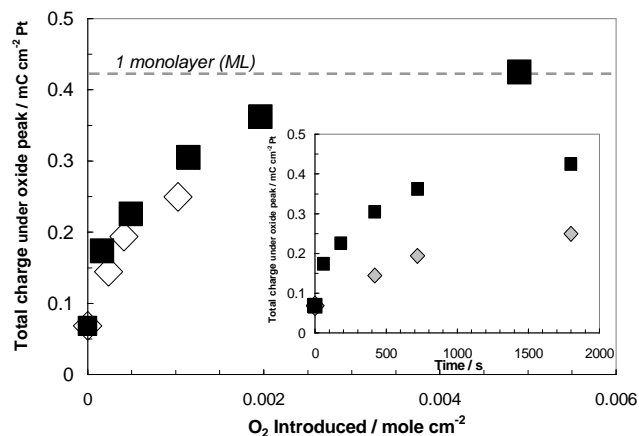


Figure 1. Cumulative reduction charge passed after exposure to oxygen (■) and 21% O<sub>2</sub> (◇) at 0.85 V<sub>RHE</sub> at 25 C. The total time of the potential hold at +0.85V was 3 hours; the gas exposure period varied from 1-30 min.

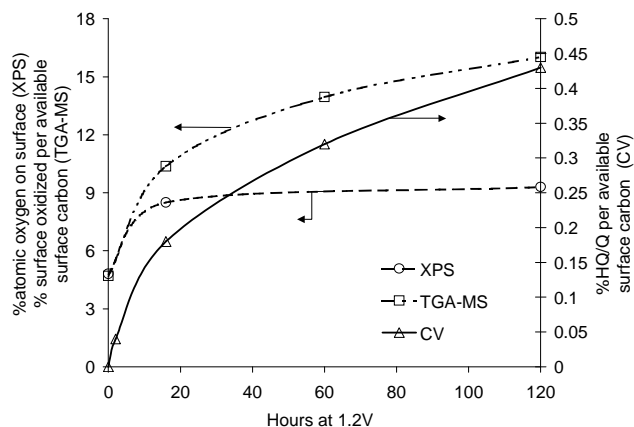


Figure 2. Surface oxygen concentration of Vulcan XC-72 as a function of time at 1.2 V at 25 C as determined by CV, XPS, and TGA-MS. The CV data were quantified based on the hydroquinone-quinone feature.

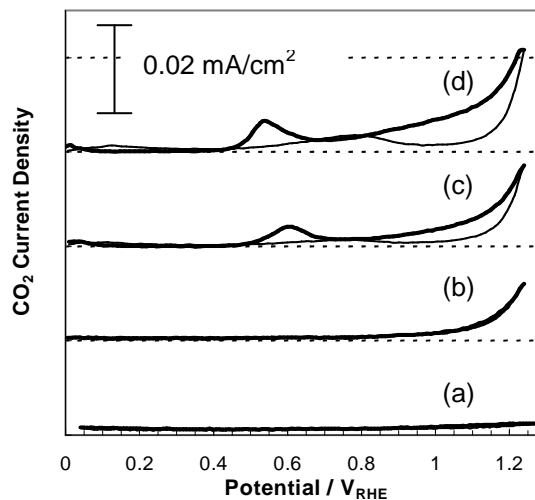


Figure 3. Comparison of CO<sub>2</sub> emission versus potential for (a) no electrode, (b) 0% Pt (Vulcan only) (c) 10 % Pt and (d) 39% Pt all on Nafion 112. The electrochemical cycles were performed at 2 mV/s, 50°C.