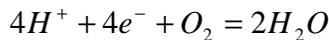


“Model of Carbon Corrosion in PEM Fuel Cells during regular operation”

Jeremy P. Meyers and Robert M. Darling
UTC Fuel Cells
195 Governor’s Highway
South Windsor, CT 06074

PEM fuel cells must be designed to be operationally robust and to withstand transient conditions without suffering degradation in performance. It is critical that cell stacks maintain a catalyst layer microstructure to maintain the catalytic and mass-transport characteristics over the lifetime of the stack. Supported platinum catalysts have enabled drastic reductions in platinum loading by increasing the specific activity of the platinum catalyst, essentially by increasing the surface-to-volume ratio of the platinum catalyst. In order for these suspended catalysts to work, however, electrical contact must be maintained between the platinum and the conductive carbon support. In this paper, we examine the mechanism of carbon corrosion and the degree to which carbon corrosion can be induced on the cathode by localized fuel starvation on the anode. This mechanism has been disclosed in several UTC patents.¹⁻²

The mathematical model is a one-dimensional representation of parallel, co-current, anode and cathode gas channels separated by a unitized electrode assembly (UEA). Three reactions may occur at either electrode:



and



The hydrogen and oxygen reactions may proceed in either the anodic or the cathodic direction, but the carbon reaction is allowed to proceed in the anodic direction only.

The average current is found by integrating the local current along the length of the channel.

$$\bar{i} = \frac{1}{L} \int_0^L i dx$$

The local current, i , may be either positive or negative. In practice, this equation is replaced by a differential equation in the numerical solver. One may specify either a total current or simulate a short by requiring that the product of cell potential and current be constant. The local current density is found by summing the partial currents of the three reactions locally at the anode:

$$i = i_{H_2,a} + i_{O_2,a} + i_{C,a}$$

The three partial currents are calculated from Butler-Volmer type equations, as described below. Ohm’s law relates the membrane phase potentials on the anode and cathode sides to the local current density. A charge balance may also be written:

$$i_{H_2,a} + i_{O_2,a} + i_{C,a} + i_{H_2,c} + i_{O_2,c} + i_{C,c} = 0$$

This equation ensures that the current densities on the anode and the cathode are the same everywhere along the length of the UEA. Hydrogen oxidation and evolution, oxygen reduction and evolution, and carbon oxidation may occur at either electrode, consistent with the local concentrations and potentials. The final equation simply states that the solid-phase potential on the cathode is constant. This assumption is made because the current collector is highly conductive.

Butler-Volmer equations are used to describe the hydrogen oxidation reaction and the oxygen reduction reactions; a Tafel expression was used to describe the carbon corrosion reaction.

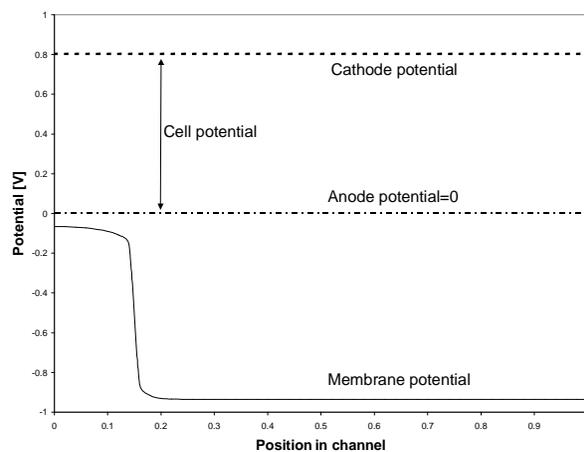
The proton concentration is assumed constant and therefore does not enter the hydrogen reaction. Similarly, the oxygen reaction is assumed to be independent of the partial pressure of water. The reference partial pressures are 1 bar, and the U values are the standard potentials. The factor of $\omega=0.1$ in the oxygen reaction was needed to fit the

experimental data.

Figure 1 shows the potential profile in a cell with a fuel-starved region; the potential difference generated in the fuel-rich region effectively sets the potential difference of the cell, because of the rapid kinetics of hydrogen oxidation. Because the solid-phase potentials are held fixed in the plane by the high conductivity of the current collectors, the overpotential in the fuel-poor region shifts to dramatically higher potentials, into the range where both oxygen evolution and carbon corrosion can occur. This interesting result demonstrates that carbon corrosion and loss of catalyst activity can occur even if cells are not driven negative. Provided that there is sufficient hydrogen delivery on average, over the planform of a cell, to meet current demand, the cell potential will remain positive, but can still inflict permanent damage on the cell.

This phenomenon demonstrates the need for uniform fuel distribution on the anode, and, in particular to minimize the likelihood of water hang-up in the anode flowfields and gas-diffusion layers. It has been demonstrated by researchers at Penn State and at NIST³ that water droplets frequently form and can be held up in solid-plate flowfields that depend upon convective flow to remove product water or condensate from the flowfields. In UTC Fuel Cells’ proprietary design, which removes water directly through the plane by active pumping through a porous bipolar plate, the flowfields and substrates can be kept free of water and ensure more uniform distribution of fuel to all points in the cell. This allows us to operate at higher fuel utilizations and overall stack efficiencies without adversely affecting lifetime of the cell stack.

Figure 1. Potential distribution for fuel rich and fuel-starved regions.



Acknowledgements

Many individuals contributed to the discovery of this mechanism. Many of those individuals are co-authors of the patents listed below, but particular credit must be given to Lawrence Bregoli for conceiving of the mechanism.

Bibliography

1. US Patent Application 20040001980, Ryan J. Balliet and Carl A. Reiser, “System and method for shutting down a fuel cell power plant.”
2. US Patent Application 20040081866, Timothy A. Bekkedahl, Lawrence J. Bregoli, Richard D. Breault, Emily Dykeman, Jeremy P. Meyers, Timothy W. Patterson, Tommy Skiba, Chris Vargas, Deilang Yang, and Jung S. Yi, “Reducing fuel cell cathode potential during startup and shutdown.”
3. R. Satija, D. L. Jacobson, M. Arif, and S. A. Werner, “In situ neutron imaging technique for evaluation of water management systems in operating PEM fuel cells,” *Journal of Power Sources*, Vol 127, 1-2, pp. 222-229 (2004).