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Design Considerations for Measuring the Kinetic Parameters of Electrocatalysts in an Operating Fuel Cell

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Differences between the surface composition of the electrocatalyst in bulk and finely divided form and the nature of porous electrodes make the measurement of electrocatalytic activity *in-situ* desireable. However, mass-transfer limitations, nonuniform potential distribution in a porous electrode, uncompensated IR-drop, and interference from counter-electrode reaction products can contribute to errors in the measurement of the electrocatalytic activity. In this paper we review some modeling techniques to help guide the design of experiments used to measure the electrocatalytic activity of an anode electrocatalyst in an operating PEM fuel cell.

In most cases of *in-situ* kinetic measurements, the working electrode is assumed to be equivalent to a planar electrode with an area equal to the total true surface area of the electrocatalyst in the porous electrode. However, the distributed nature of the porous electrode raises the possibility that the electrode can be ohmically limited or mass-transfer limited. Dimensionless parameters which describe the relative importance of mass-transfer and ohmic losses to kinetic losses are presented by Newman.[1]

An example of the use of one of these dimensionless parameters, is illustrated in Figure 1 for a PEM fuel-cell anode operating on ethanol as a fuel with different feed concentrations and different degrees of oxidation.

Even if such dimensional analysis shows that the porous working electrode is kinetically limited and can be treated as a planar electrode, errors in the measurement of electrocatalytic activity can arise from the uncompensated IR-drop. This is due to the high aspect ratio employed in most planar fuel-cell geometries. Reference electrodes are usually placed co-planar relative to the either the working or counter electrode and many electrolyte thicknesses away from the working and counter electrodes. In this case the reference senses the potential in the electrolyte far away from the working and counter electrodes.

Figure 2 shows the primary potential distribution for three different alignments of working and counter electrodes as determined by the solution of Laplace's equation using conformal mapping techniques. When the electrodes are aligned, the reference electrode picks up one-half of the potential drop between the electrodes. When the electrodes are slightly misaligned the reference electrode picks up either a larger or smaller fraction of the potential drop depending upon which electrode is offset closer to the reference electrode. If the electrodes are misaligned more than roughly one electrolyte thickness, the reference electrode picks up either almost all or only a negligible portion of the IR-drop.

In the case of PEM fuel cells, the electrolyte is somewhat permeable to various species which can transport across the electrolyte and interfere with the kinetics of the opposite electrode. One particular manifestation of this effect is that of fuel crossover in direct methanol and direct ethanol fuel cells. Another possibility arises when testing anode electrocatalysts in an operating fuel cell. If the cathode becomes mass-transfer limited due to water condensation while the cell is being driven by a potentiostat or galvanostat, its potential will continue to drop until it begins to generate hydrogen cathodically. This hydrogen can permeate across the membrane and produce artificially high currents at the anode.

It is useful to estimate the operating conditions under which liquid water will condense in the gas-diffusion layer of the cathode. Figure 3. shows the results of a very simple combined heat- and mass-transfer model of an operating cathode under conditions where the cathode is expected to become flooded.

The results of simple dimensionless analysis, simple predictions of potential distributions, and simple transport models can be used to help design *in-situ* experiments for the measurement of the electrocatalytic properties of real-world fuel cell electrocatalysts.

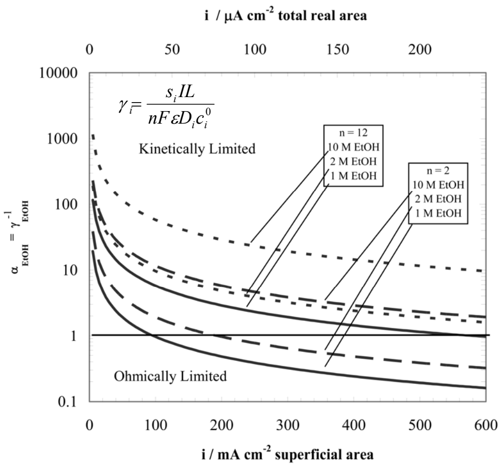

Figure 1. Operating regimes for a porous anode operating on ethanol (ε=0.5, $\langle i \rangle$=2 x 10^{-4} mA/cm^2, L=10^{-3} cm).

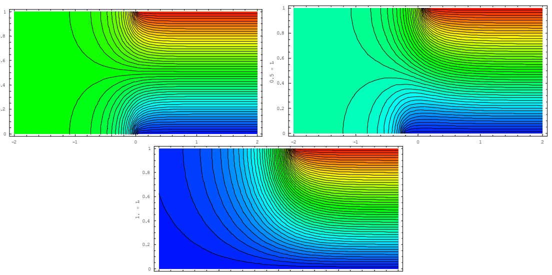

Figure 2. Primary potential distribution for different arrangement of working and counter electrodes.

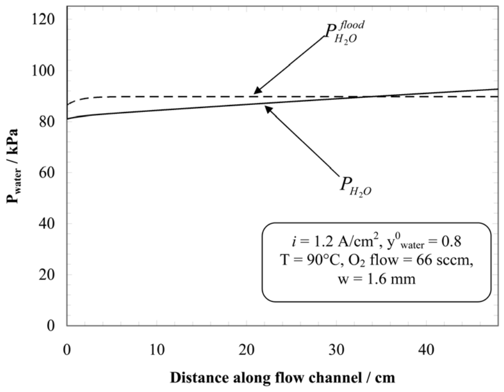

Figure 3. Conditions under which condensation of liquid water is predicted to occur in the cathode gas-diffusion layer.

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[1] Newman, J. S., *Electrochemical Systems, 2nd Edition*, Prentice-Hall, Inc. Englewood Cliffs, New Jersey, (1991), pp. 463-464, 470