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CONTINUED STUDY OF THE EFFECTS OF HEAT
TREATMENT AND MICROSTRUCTURE ON
ELECTROCATALYST PERFORMANCE

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ABSTRACT

Platinum and platinum-chromium bulk electrodes were analyzed in 100 wt.% H_3PO_4 at 200°C to evaluate the kinetics for the oxygen reduction reaction (ORR) in the phosphoric acid fuel cell (PAFC) operating environment. Dispersed platinum and platinum-chromium catalyst electrodes were operated potentiostatically under simulated PAFC operating conditions (0.7 V vs. RHE in 100 wt.% H_3PO_4 at 200°C) using the submerged mode to evaluate the degradation mechanism.

Differences observed between the hanging meniscus rotating disk (HMRD) electrode and the rotating disk electrode (RDE) method were related to the different hydrodynamics present in the hanging meniscus. The boundary conditions applicable to an infinite rotating disk are no longer present. The most probable cause for the observed differences is that the surface of the HMRD electrode is no longer uniformly accessible with respect to the diffusing species. Therefore, the kinetic data extracted from the mixed control conditions are altered sufficiently so that precise potential-current curves cannot be obtained. However, the data obtained are highly reproducible. Therefore, the method appears suitable for determining comparative kinetic data for platinum and platinum-chromium at 200°C in 100 wt.% H_3PO_4 , where RDE designs will not function.

Cyclic voltammetry conducted on platinum and platinum-chromium electrodes in 100 wt.% H_3PO_4 at 200°C were similar qualitatively to those obtained at room temperature. Comparison of the double layer currents demonstrated that an approximately two-fold increase in surface area, due to dissolution of chromium from the electrode surface, occurred during typical cycling durations; extensive chromium dissolution was observed during long-term cycling. Comparison of the

current densities, after correction for actual surface area, demonstrated that lower current densities were obtained from platinum-chromium throughout the cycle.

Lower oxygen reduction current densities were obtained from bulk platinum-chromium than for bulk platinum held potentiostatically at 0.9 V versus RHE in 100 wt.% H_3PO_4 at 200°C for short periods. This indicates that the kinetics for oxygen reduction are slower for platinum-chromium than for platinum, as was found by a similar comparison at room temperature in dilute phosphoric acid. These results are opposite to the relationship observed for dispersed catalysts employed in gas diffusion electrodes in PAFC's at elevated temperature, pressure, and electrolyte concentration.

The ORR polarization scans in 100 wt.% H_3PO_4 at 200°C did not possess a sigmoidal shape for either the platinum or platinum-chromium electrodes; pseudo-ohmic behavior was observed over a wide range of potentials (from 0.9 to 0 V vs. RHE). A dependence of the measured resistance on rotation rate was observed for platinum but not platinum-chromium. The data support the presence of an adsorbed layer, probably composed of polyphosphoric acid, as the controlling mechanism responsible for the observed potential-current response. While not affecting the hydrogen evolution reaction, the Tafel slope for hydrogen oxidation, occurring in the same potential range as oxygen reduction, was increased substantially relative to the calculated value. Electrochemical impedance spectroscopy showed that the capacitance increased proportionally to the resistance decrease with increasing rotation rate, indicative of a thinning layer.

The current densities obtained from platinum-chromium were lower than for platinum for similar operating conditions, in part due to the greater stability of the proposed layer on the roughened platinum-chromium surface. However, for the cases where similar resistances were observed, the reduced current densities from

the platinum-chromium electrode indicate that the activity for oxygen reduction is lower than for platinum. This is consistent with the results obtained from the stationary electrodes.

Analysis of the platinum catalyst microstructure as a function of operation using the submerged mode with 100 wt.% H_3PO_4 at 200°C revealed a linear catalyst size increase with operating time. A dissolution-deposition mechanism has been proposed, in which a platinum-ligand complex is formed on dissolution of platinum under these conditions. A potential gradient, present due to the non-compensated resistance of the electrolyte within the pores of the electrode, establishes the conditions necessary for simultaneous dissolution and deposition within the electrode.

Extensive dissolution of the platinum-chromium dispersed catalyst was observed. After 2000 hours operation, no chromium was detected in the electrode. This demonstrates that, even without anodic potentials being applied to the catalyst as occurred during cyclic voltammetry, chromium does not stabilize the catalyst. In fact, for comparable operating times, the increase in catalyst size was approximately twice that observed for platinum.

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