Formic Acid Oxidation at Pd Electrodes

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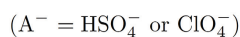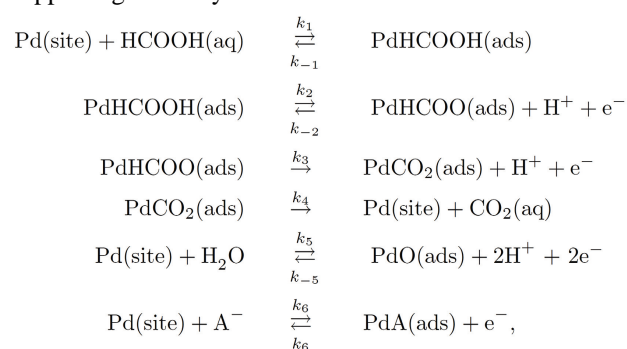Victoria, BC, Canada V8W 3V6

Direct liquid fuel cells have advantages of simpler fuelling infrastructure than hydrogen fuel cells. The Direct Formic Acid Fuel Cell also has the additional advantages that formic acid can be produced from biomass sources, and that the two-electron reaction to CO_2 means that catalysis should be simpler than for methanol or ethanol oxidation. Pd is currently the best developed electrocatalyst for this system, but the mechanism for oxidation of formic acid at Pd is still under investigation. In particular, the deactivation of the catalyst over time has been controversial, and there is a significant dependence on the electrolyte anion that needs to be better understood.

We have investigated this system on polycrystalline wire electrodes using cyclic voltammetry, potential step, and dynamic electrochemical impedance spectroscopy (dEIS) measurements. The species responsible for deactivation has been investigated by deliberate additions of various organic additives.

The classic poison CO(ads) is seen on carbon-supported Pd nanoparticle catalysts after long times[1], but not by SEIRAS on polycrystalline macroelectrodes[2]. We also found that addition of CO to the solution blocks the HCOOH oxidation and shows a new sharp peak near 1 V, implying that CO is not the deactivating process. Holding the potential for varying times leads to deactivation, but only a small amount of subsequent anodic charge at potentials higher than is characteristic for CO oxidation.

Contaminants in the formic acid have been suggested[3], especially methyl formate, but addition of this increased the current, consistent with its hydrolysis to formic acid and methanol. Methanol itself is unreactive (and non-blocking) on Pd, so the increased current comes from the formic acid hydrolysis product. However, methanol is known to dissociate to CO on nanoparticles, which likely explains the observed poisoning from methyl formate in nanoparticle systems. Formaldehyde is a poison, since its addition passivates the surface and leads to a CO oxidation peak; it is known to oxidize to CO.

A reaction model was developed to explain the differences in behavior in sulfuric acid and perchloric acid supporting electrolytes.

$$\text{Pd(site)} + \text{HCOOH(aq)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{PdHCOOH(ads)}$$

$$\text{PdHCOOH(ads)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{PdHCOO(ads)} + \text{H}^+ + \text{e}^-$$

$$\text{PdHCOO(ads)} \overset{k_3}{\rightarrow} \text{PdCO}_2\text{(ads)} + \text{H}^+ + \text{e}^-$$

$$\text{PdCO}_2\text{(ads)} \overset{k_4}{\rightarrow} \text{Pd(site)} + \text{CO}_2\text{(aq)}$$

$$\text{Pd(site)} + \text{H}_2\text{O} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \text{PdO(ads)} + 2\text{H}^+ + 2\text{e}^-$$

$$\text{Pd(site)} + \text{A}^- \underset{k_6}{\overset{k_6}{\rightleftharpoons}} \text{PdA(ads)} + \text{e}^-,$$

$$(\text{A}^- = \text{HSO}_4^- \text{ or } \text{ClO}_4^-)$$

The appropriate differential equations were set up, and solved to find the voltammograms and the coverages of various species. We made some simplifying assumptions: fast mass transport in solution; no charge transfer for the anion adsorption; CO_2(ads) assumed for the "bicarbonate" species seen in SEIRAS[1]; an empirical equation for oxide formation was applicable also in the presence of formic acid; interactions between adsorbed formate and anions were modeled by the Frumkin isotherm.

The voltammograms and SEIRAS coverages were well approximated by having step 4 fast in sulfuric acid but rate determining in perchloric acid. This is consistent with the observed binding order ClO_4^- < "bicarbonate" <HSO_4^-. The adsorbed formate and (bi)sulfate are interacting strongly, and their adsorption beginning at around 0.6 V vs RHE is the cause of the decreasing oxidation current in this region.

The dEIS spectra were measured around the voltammogram. Except in the oxide reduction region, the low-frequency data were consistent with the prediction from the slope of the voltammogram, showing that there were not missing features at unmeasured lower frequencies. In the early stages of the oxidation, the data fitted to equivalent circuits with two time constants, one associated with the double-layer charging and the other with a single adsorbed species, corresponding to formate in the case of sulfuric acid electrolyte and the "bicarbonate" species (of uncertain structure) in the case of perchloric acid electrolyte.

An additional time constant was found in the region where the current is decreasing, in agreement with the model, where the interaction of the formate with the sulfate anion is implicated.

The concentration and sweep rate dependence of the circuit parameters was consistent with the concentration and sweep rate dependence observed in the voltammetry.

References
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2. X. Yu and P.G. Pickup, *J. Power Sources*, **182**, 124 (2008).
3. W.L. Law, A.M. Platt, P.D.C.Wimalaratne, and S.L. Blair, **156**, B553 (2009).