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Project Title: Novel Intermetallic Catalysts to Enhance PEM Membrane Durability

PI: Prof. Francis J. DiSalvo

Cornell University

Ithaca, NY 14853

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Summary of Accomplishments

Introduction

Rotating disk electrode chronoamperometry (constant-potential electrolysis) was used for the long term testing of catalysts for the hydrogen oxidation reaction (HOR). Surprisingly, this reaction had been found by researchers at United Technologies Research Center (UTRC) to result in Pt dissolution and re-precipitation and other side reactions that lead to decreasing fuel cell performance in polymer membrane fuel cells (PEMFC). The observation is surprising, since the potentials at which hydrogen is oxidized (just above 0.0 V) in a PEMFC are well below the standard reduction potential for Pt ($E^{\circ} = 1.2$ V).

Methodology

In collaboration with scientists at UTRC we designed an electrochemical method to explore this phenomenon. A considerable hurdle in this research is the need to maintain a clean environment for electrochemical testing. The main challenge is that we are using large volume (20 ml) aqueous electrolytes which are saturated with hydrogen gas and the total catalyst surface area is rather small, so very low levels of impurities in the electrolyte or gas can poison the Pt surface, masking other degradation mechanisms.

We used rotating disk electrodes to control the diffusion conditions. In a real fuel cell, the electrolyte is largely trapped in the polymer membrane and has, relative to the Pt surface area, a very low volume. Yet the idea was to explore degradation mechanisms *ex situ* in the laboratory, to see if the degradation observed in PEMFCs was universal.

Ultrapure conditions are required given the proclivity for platinum poisoning, conditions which are far beyond those originally anticipated by us. In this work, ultrahigh purity

hydrogen was used as fuel and special gas filters were used to remove the organic contaminants from hydrogen. In our early work, a sodium chloride saturated Ag/AgCl was used as reference electrode (RE). Since the effect of Cl⁻ poisoning eventually becomes visible in long term test, a reversible hydrogen electrode (RHE) was used as RE in this work. By testing bulk Pt electrodes and commercial carbon supported Pt nanoparticles (coated on glassy carbon electrode), the protocol for long term testing, including cleaning and ink deposition, was established.

In order to make sure the whole electrochemical testing system is clean enough for long term testing, a Pt bulk electrode (diameter 5mm) was tested first. As shown in Figure 1, the activity of Pt bulk was affected seriously by the condition of the hydrogen filter. By maintaining the conditions as clean as current technology allows, a chronoamperometric study of Pt bulk still showed remarkable decrease in catalytic activity. However, under the same conditions, commercial carbon supported Pt nanoparticles (50 wt% Pt/C, E-Tek) shows relatively low loss over 16 hours (Figure 2). At first we concluded that Pt/C is much more stable than Pt bulk. However, after further investigation, we determined that this was due to the much larger surface area of the Pt nano-particles.

By comparing Figure 1 and Figure 2, it is apparent that the initial currents of HOR on Pt bulk and Pt/C were similar. The potential of the current-time measurement was set at 100mV (vs. RHE). At that potential, the current has already reached the diffusion limit. For the rotating disk electrode, the diffusion limiting current is determined only by geometrical radius of the electrode (r , $i_d = 0.62\pi r^2 nFD^{2/3} \nu^{-1/6} \omega^{1/2} C$). For both the Pt bulk electrode and Pt/C coated glassy carbon electrode, the diameters are 5mm. So the diffusion limiting current should be same at the initial process of the current-time measurement.

Then why is the current of HOR on Pt/C stable while that on Pt bulk decreases fast? For Pt/C, since the active surface area (electrochemical surface) is very large, the electron transfer is much faster than the mass transport. Likely Pt/C loses part of activity by poisoning during the long term measurement, but the electron transfer is still faster than the mass transport, since the initial surface area is so large. In that case the whole reaction is only controlled by the

mass transport and the current measured is always the diffusion limiting current. For Pt bulk, the electrochemical surface is orders of magnitude smaller than the Pt/C. At the start of the measurement, the reaction rate (current) is controlled only by the mass transport. As the measurement proceeds, the activity of bulk Pt decreases due to surface poisoning and the electron transfer rate becomes slower than the mass transport rate. Consequently, the measured current decreases relatively rapidly. The surface area of the catalyst is not sufficient to adsorb all the impurities without becoming completely blocked by those impurities. The Pt/c on the other hand has sufficient surface area to adsorb most or all of the impurities and still have uncontaminated surface remaining to allow hydrogen oxidation.

However, we can show that Pt/C is in fact also poisoned, as we discuss next. At our experimental conditions, the change of Pt/C activity can't be shown because the current we measured is always diffusion limiting current. In order to detect a change in the catalytic activity, we must decrease the polarization potential to decrease the electrochemical current, or increase the rotation rate to accelerate the mass transport. Then the reaction will not be controlled by the mass transport and the change of Pt/C activity will be visible. As shown in Fig. 3, Pt/C showed a decrease in activity as we expected when we decreased the polarization potential or increase the rotating rate, as we expected.

The long term activity of PtPb bulk was also tested by using rotating disk electrode chronoamperometry. As seen in Fig. 4, even though the surface area of our PtPb bulk electrode is smaller than the Pt bulk electrode, the PtPb bulk electrode still showed a better stability for the catalysis of HOR than Pt bulk electrode (Fig. 1). This result proves that PtPb is more stable than Pt as a catalyst for HOR. The reason for the good stability is worth further exploration.

Experimental

For Pt/C, a suspension of the nanoparticle catalyst was prepared as follows: to 8 mg of Pt/C nanoparticle sample (50 wt%, E-Tek), 3.98 mL of distilled water and 1 mL of isopropyl alcohol (Aldrich) were added. Additionally, 20 μ L of a 5% w/w Nafion solution in alcohols

and water (EW: 1100, Aldrich) was added to this mixture. The resulting mixture was sonicated in a bath type ultrasonicator for 1 hr. Then, this suspension was coated onto a 5mm diameter glassy carbon electrode. The electrode has been previously polished with diamond paste (METADI-Buehler, ϕ 1 μ m) and ultrasonicated in Millipore water (18 MW cm, Millipore Milli-Q) for 10 mins. The electrode was then rinsed with Millipore water and allowed to dry in air. 80 μ g cm⁻² of Pt (20 μ L of the suspension) was coated onto the clean GC electrode and dried in air. Both Pt bulk electrode and commercial carbon supported Pt nanoparticles (on glassy carbon electrode) were examined in a three-electrode electrochemical cell. The reference electrode was a reversible hydrogen electrode (RHE), and the counter electrode was a Pt wire. All electrochemical experiments were carried out at room temperature with a Pine Instrument Company AFRDE2 potentiostat and MSR rotator. All solutions were prepared with Millipore water.

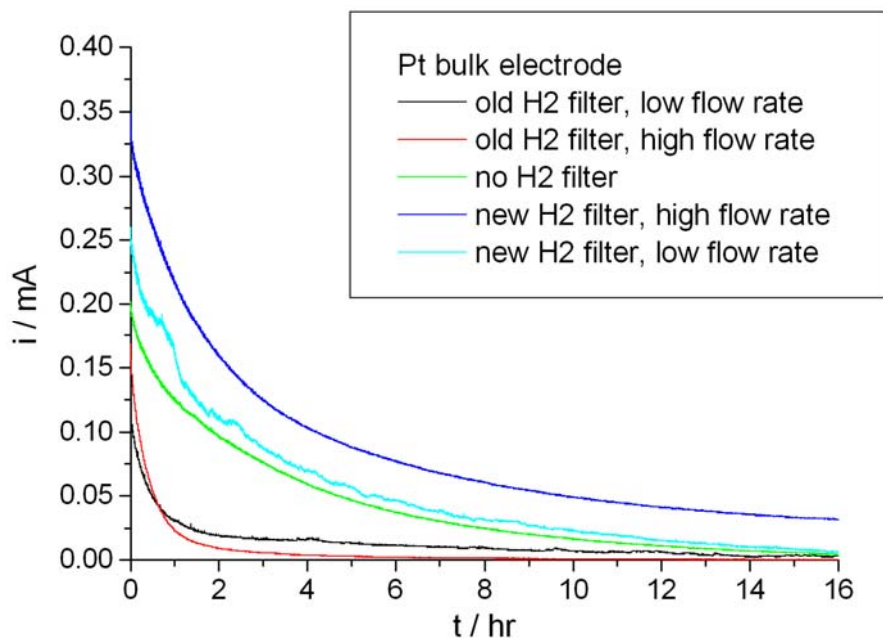


Figure 1 Chronoamperometry scan of hydrogen oxidation on Pt bulk electrode in 0.1M H₂SO₄ (100mV vs.RHE, 900rpm, room temperature).

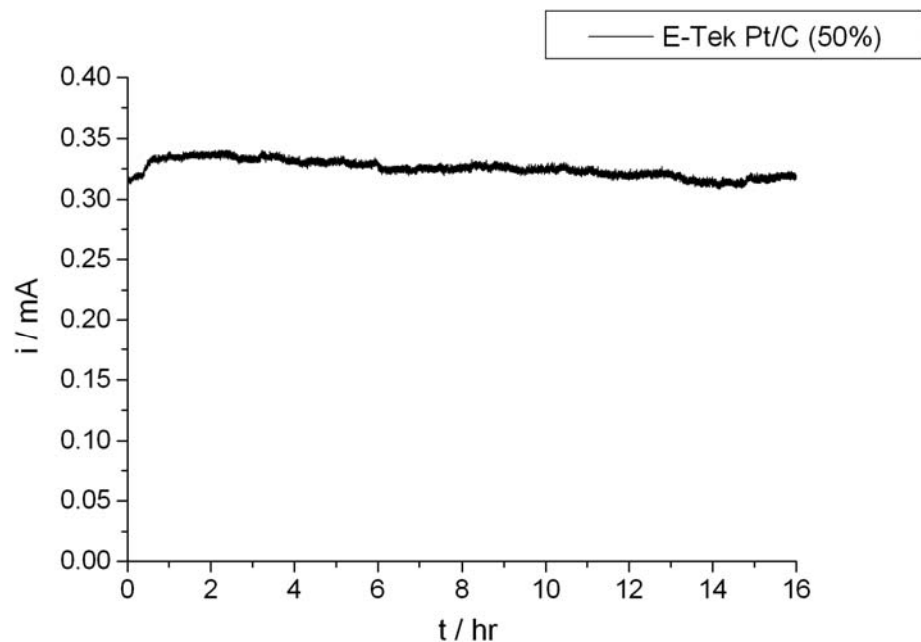


Figure 2 Chronoamperometry scan of hydrogen oxidation on Pt/C coated glassy carbon electrode in 0.1M H_2SO_4 (100mV vs.RHE, 900rpm, room temperature).

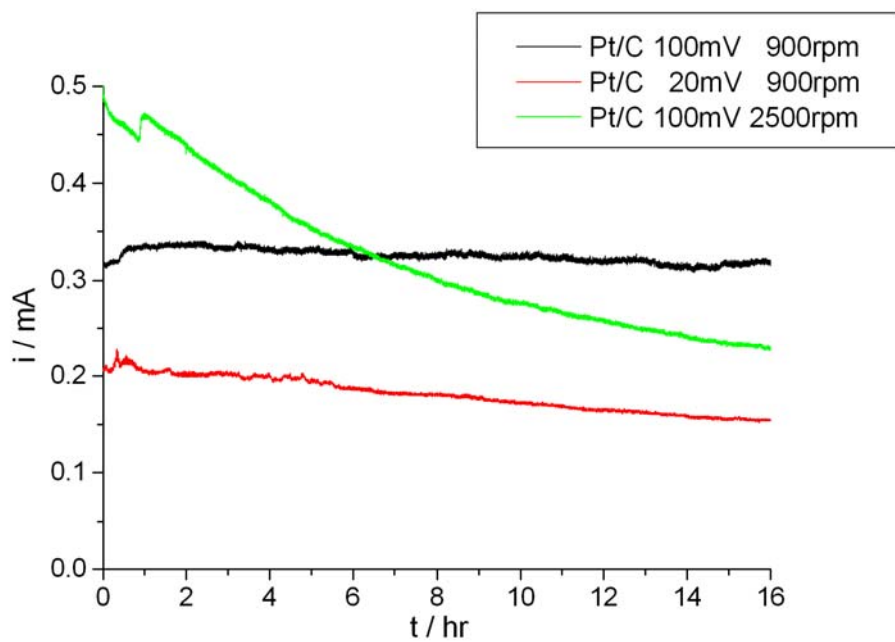


Figure 3 Chronoamperometry scan of hydrogen oxidation on Pt/C coated glassy carbon electrode in 0.1M H_2SO_4 (different potential and different rotating rate).

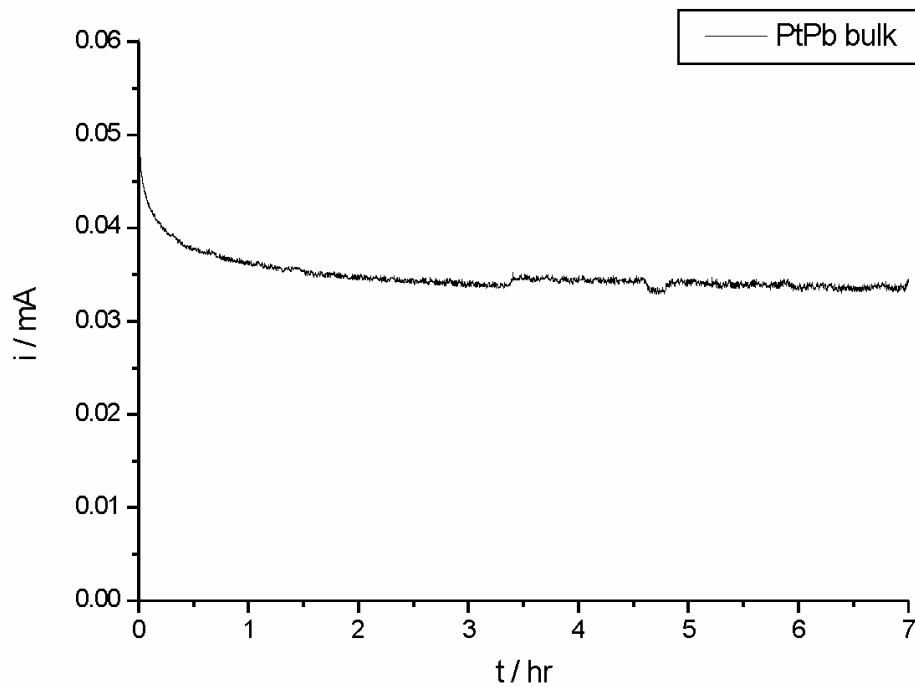


Figure 4 Chronoamperometry scan of hydrogen oxidation on PtPb bulk electrode (diameter 1~2mm) in 0.1M H₂SO₄ (100mV vs.RHE, 900rpm, room temperature).

Training of Graduate Students and Postdocs

During the term of this grant (3 years), two graduate students and three post-doctoral students worked on this project.

Publications or Patents

Since this project was unable to elucidate any mechanisms of degradation beyond that caused by impurities left in even the cleanest of electrolyte solutions, as discussed above, no publications have resulted from this project.