IV.C.3 Low Platinum Loading Catalysts for Fuel Cells

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Objectives

- To demonstrate the possibility of synthesizing novel electrocatalysts for O\textsubscript{2} reduction with monolayer-level Pt loadings
- To further characterize the PtRu\textsubscript{20} electrocatalyst for CO and H\textsubscript{2} oxidation, and conduct long-term stability tests
- To gain an understanding of the activity of Pt monolayer and PtRu\textsubscript{20} electrocatalysts

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells Section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Q. Electrode Performance

Approach

- Develop low-Pt-loading electrocatalysts by placing a submonolayer-to-monolayer of Pt on nanoparticles of suitable metals or alloys to obtain electrocatalysts with the following characteristics:
  - Ultimately reduced Pt loading
  - Enhanced Pt activity
  - Complete utilization of Pt
- Two methods were developed for depositing a Pt monolayer:
  - Electroless (spontaneous) Pt deposition on Ru
  - Pt deposition by replacing an underpotential deposition (UPD) metal adlayer

Accomplishments

- ANODE
  - Stability tests of the PtRu\textsubscript{20} electrocatalyst with combined CO/H\textsubscript{2} and H\textsubscript{2} operation, conducted by F. Uribe and coworkers at Los Alamos National Laboratory (LANL), showed the following: no loss of voltage after 870 h with 18 µg Pt/cm\textsuperscript{2} (20% Ru: 2% Pt, 3% air-bleed); small losses after 1000 h with 18 µg Pt/cm\textsuperscript{2} (10% Ru: 1% Pt, 4% air-bleed); and very small losses in a 600 h test with 19 µg Pt/cm\textsuperscript{2} (2% air-bleed).
  - This electrocatalyst can reach the DOE’s durability target of 2000 h by 2005.
  - The DOE’s target for 2005 for noble metals of 0.6 g/kW (0.3 g/kW for anode) is met for Pt: only 0.063 g Pt/kW is necessary. If Ru is counted, 0.630 g total metal is needed.
• **CATHODE**
  − A Pt monolayer on carbon-supported metal or on metal-alloy nanoparticles can be an active catalyst for \( \text{O}_2 \) reduction.
  − The Pt mass-specific activity of Pt/Pd/C is 5-8 times higher than that of Pt (10%)/C. The \( (\text{Pt + Pd}) \) mass activity is 2.5 times higher. The fuel-cell tests (F. Uribe, LANL) are quite promising.
  − A PdCo/C electrocatalyst was synthesized with activity comparable to that of Pt.
  − A Pt/AuNi/C electrocatalyst was synthesized with activity similar to that of Pt.

**Future Directions**

• **\( \text{H}_2 \) oxidation**
  − Deposit Pt sub-monolayers on non-noble-metal alloy nanoparticles,
  − and study their activity.

• **\( \text{O}_2 \) reduction**
  − Develop the Pt/Pd/C electrocatalyst further, and test it at LANL.
  − Develop nanoparticles of immiscible Au-non-noble-metal alloys as supports for Pt.
  − Investigate the abilities of multi-metal monolayers to reduce PtOH coverage and to modify the electronic properties of Pt.
  − Explore non-noble metals as supports for Pt.

**Introduction**

We continued developing a highly active electrocatalyst for \( \text{H}_2/\text{CO} \) oxidation that comprises a submonolayer of Pt on carbon-supported Ru nanoparticles (PtRu\(_{20}\)) with the goal of improving its properties and further understanding the origins of its activity. F. Uribe and coworkers (LANL) tested its long-term stability in a membrane electrode assembly (MEA). Their measurements demonstrated an excellent long-term performance in fuel-cell operation (870 h without loss in activity). Its Pt loading met the DOE’s target for 2005.

The possibility was demonstrated of synthesizing active catalysts for \( \text{O}_2 \) reduction consisting of Pt monolayers on carbon-supported metal nanoparticles or metal alloy nanoparticles. The Pt mass-specific activity of Pt/Pd/C is several times higher than that of Pt/C, indicating excellent promise of our approach for obtaining highly active cathode electrocatalysts.

**Approach**

Two new Pt deposition methods were employed for preparing catalysts. One method involved the electroless deposition of Pt on Ru nanoparticles for \( \text{H}_2/\text{CO} \) oxidation. All the Pt atoms in this catalyst are available for the reaction. The interaction of the Pt atoms with Ru, and the state of the Ru surface, are of utmost importance for the catalyst’s activity. The activity for \( \text{H}_2 \) oxidation and CO tolerance was determined by a thin-film rotating disk electrode. Another new method that opened the possibility of reducing Pt loading involved the galvanic displacement by Pt of a UPD Cu monolayer from a substrate, such as Pd. It also promised to improve the activity of the catalysts. The rotating ring-disk electrode measurements obtained with a Pt monolayer deposited on Pd nanoparticles and Pd (111) showed the high activity of such surfaces for \( \text{O}_2 \) reduction. The deposition of the Pt monolayer on the Pd(111) surface was verified by voltammetry and by scanning tunneling microscopy. The structural and electronic properties of the electrocatalysts were investigated by an in-situ x-ray absorption spectroscopy at the National Synchrotron Light Source.

PdCo nanoparticles were deposited on carbon using an impregnation method in which the metal ions on the carbon particles were reduced to a metallic state. The activity of PdCo for \( \text{O}_2 \) reduction was comparable to that of Pt.
Figure 1. Long-term test of the performance stability of the PtRu$_{20}$ electrocatalyst in an operating fuel cell using clean H$_2$ and H$_2$ + 50 ppm CO + 3% air bleed. Anode: 0.09 mg total metal/cm$^2$ (20% Ru, 2% Pt), 18 µg Pt/cm$^2$; Cathode: 0.24 mg Pt (20% Pt/C, ETEK)/cm$^2$; Electrode areas=50 cm$^2$; T= 80°C; Pressures A/C = 30/30 psi. Total run time = 870 h at a constant current density (0.4 A/cm$^2$).

Results

Figure 1 shows the stability in performance of the PtRu$_{20}$ electrocatalyst (20% Ru, 2% Pt) during a long-term test in an MEA under real operating conditions. The test was run at a constant current density of 0.4 A/cm$^2$ using electrodes of 50 cm$^2$ with an anode catalyst Pt content of 18 µg/cm$^2$. Clean H$_2$ and H$_2$ with 50 ppm of CO and 3% air bleed were used as fuel. No voltage losses were seen after 870 hours. This result clearly demonstrates that Pt sub-monolayers on Ru nanoparticles are stable during the fuel-cell operation and that this system represents a real catalyst. In addition to the high activity for H$_2$ oxidation and the weak CO bonding, the strong segregation of Pt and Ru is a key factor determining this catalyst’s stability.

Figure 2 illustrates O$_2$ reduction on Pd and Pt nanoparticles, and on Pt monolayers on Pd nanoparticles (two different loadings). The activity of the Pt monolayer on Pd nanoparticles (10 nmol) is much higher than that of the Pd nanoparticles (10 nmol), and, more importantly, is somewhat higher than that of the Pt nanoparticles (10 nmol). The higher activity of the Pt monolayer on Pd nanoparticles compared with those of Pt and Pd alone indicates that there is a synergetic relation between them. Consequently, Pt loadings can be significantly reduced. The insert of Figure 2 shows Pt mass-specific activities from the three electrodes expressed as a current divided by the Pt mass at 0.8 and 0.85 V.

Comparing the polarization curves for O$_2$ reduction on Pd(111), Pt(111), and Pt/Pd(111) confirms that a very active O$_2$ reduction catalyst can be obtained with only one monolayer of Pt on a suitable substrate (Figure 3).

Figure 4 illustrates the effect of metal substrates on the activity of Pt monolayers. The half-wave potentials for O$_2$ reduction for Pt monolayers are plotted as a function of the fractional d-band filling of the substrates. The data for Pt(111) are given for comparison. The plot shows a volcano shape; the Pt monolayer on Pd(111) exhibits the highest activity while other systems show similar or much lower activities compared with Pt(111). This quasi-volcano
Figure 3. Comparison of the polarization curves for $O_2$ reduction kinetics on Pd(111), Pt(111) and Pt/Pd(111) in a 0.1 M HClO$_4$ solution. The sweep rate for Pd(111) and Pt/Pd(111) is 20 mV/s, while for Pt(111) it is 50 mV/s.

Figure 4. $O_2$ reduction activities of Pt monolayers on different substrate metals plotted as a function of the fractional d-band filling of the substrates. The data for Pt(111) are given for comparison. The plot also indicates that, in terms of $O_2$ reduction, metals with low d-band filling are not suitable support materials for Pt monolayer electrocatalysts.

To make the catalytic properties of another metal close to those of Pt for $O_2$ reduction, we synthesized PdCo nanoparticles on carbon using the impregnation method (PdCo(2:1)/C) inspired by our Density Functional Theory (DFT) calculations of the activity of Pd monolayers on several substrates. Figure 5 shows the preliminary results that compare the kinetics of $O_2$ reduction on Pd/C and PdCo/C. Adding Co to Pd has a pronounced catalytic effect, which makes its activity comparable to that of Pt.

Figure 5. Comparison of polarization curves for $O_2$ reduction on Pd/C and PdCo(2:1)/C nanoparticles in 0.1 M HClO$_4$.

Conclusions

- The PtRu$_{20}$ anode electrocatalyst was demonstrated to exhibit excellent long-term performance stability in an operating fuel cell. No voltage losses were seen after 870 h testing with 18 µg Pt/cm$^2$ using H$_2$ with 50 ppm of CO and 3% air bleed. The electrocatalyst met the DOE’s target for 2005 for Pt loading (Ru not counted).
- The new cathode electrocatalysts comprising Pt monolayers deposited on Pd (111) and on carbon-supported Pd nanoparticles were very active in reducing $O_2$. The Pt mass-specific activity of the Pt/Pd/C electrode is 5-8 times higher than that of the Pt/C electrocatalyst.
- A new PdCo/C electrocatalyst for $O_2$ reduction was synthesized whose activity is comparable to that of Pt.
**Publications**


**Presentations**


**Patents**