

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

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Objectives

- To demonstrate the possibility of synthesizing novel electrocatalysts for O₂ reduction with monolayer-level Pt loadings
- To further characterize the PtRu₂₀ electrocatalyst for CO and H₂ oxidation, and conduct long-term stability tests
- To gain an understanding of the activity of Pt monolayer and PtRu₂₀ 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 PtRu₂₀ electrocatalyst with combined CO/H₂ and H₂ 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/cm² (20% Ru: 2% Pt, 3% air-bleed); small losses after 1000 h with 18 μg Pt/cm² (10% Ru: 1% Pt, 4% air-bleed); and very small losses in a 600 h test with 19 μg Pt/cm² (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 O₂ reduction.
 - The Pt mass-specific activity of Pt/Pd/C is 5-8 times higher than that of Pt (10%)/C. The (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

- H₂ oxidation
 - Deposit Pt sub-monolayers on non-noble-metal alloy nanoparticles,
 - and study their activity.
- O₂ 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 H₂/CO oxidation that comprises a submonolayer of Pt on carbon-supported Ru nanoparticles (PtRu₂₀) 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 O₂ 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

H₂/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 H₂ 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 O₂ 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 O₂ reduction was comparable to that of Pt.

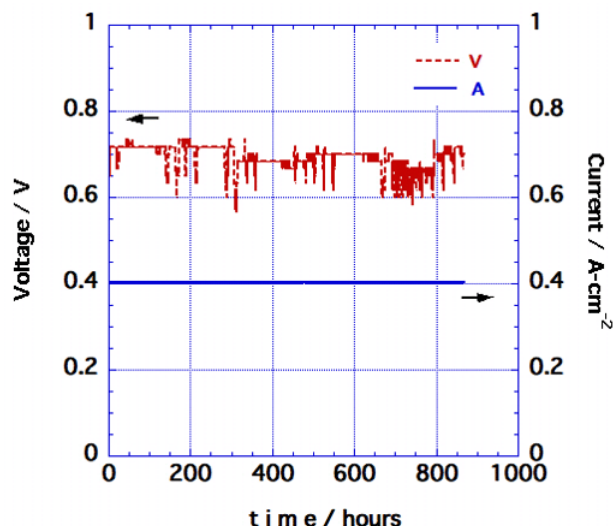


Figure 1. Long-term test of the performance stability of the PtRu₂₀ electrocatalyst in an operating fuel cell using clean H₂ and H₂ + 50 ppm CO + 3% air bleed. Anode: 0.09 mg total metal/cm² (20% Ru, 2% Pt), 18 μg Pt/cm²; Cathode: 0.24 mg Pt (20% Pt/C, ETEK)/cm²; Electrode areas=50 cm²; T= 80°C; Pressures A/C = 30/30 psi. Total run time = 870 h at a constant current density (0.4 A/cm²).

Results

Figure 1 shows the stability in performance of the PtRu₂₀ 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/cm² using electrodes of 50 cm² with an anode catalyst Pt content of 18 μg/cm². Clean H₂ and H₂ 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 H₂ 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 O₂ 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

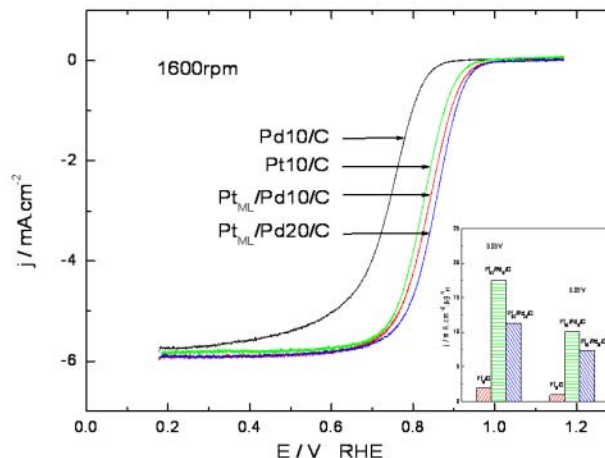


Figure 2. Comparison of polarization curves for O₂ reduction on Pd (10 nmol) and Pt (10 nmol) nanoparticles, and a Pt monolayer on Pd nanoparticles (10 and 20 nmol Pd) in 0.1 M HClO₄. The insert shows Pt mass-specific activities of the three electrodes expressed as a current divided by the Pt mass at 0.8 and 0.85 V.

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 0.85 and 0.80 V (RHE). The electrodes having a Pt monolayer show 5-8 times higher activity than that with Pt nanoparticles.

Comparing the polarization curves for O₂ reduction on Pd(111), Pt(111), and Pt/Pd(111) confirms that a very active O₂ 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 O₂ 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

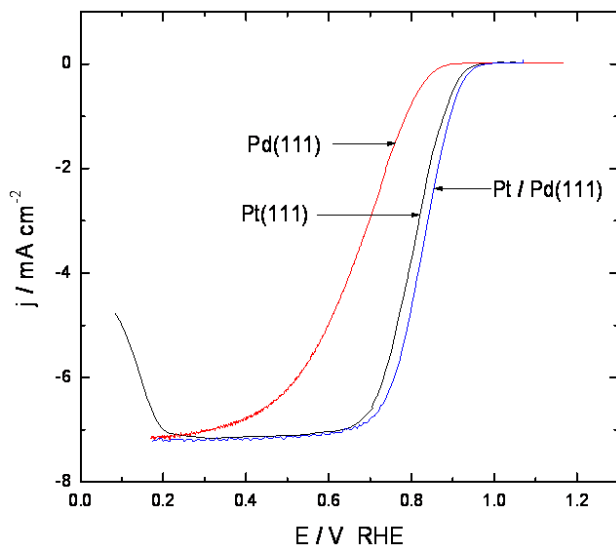


Figure 3. Comparison of the polarization curves for O_2 reduction kinetics on Pd(111), Pt(111) and Pt/Pd(111) in a 0.1 M $HClO_4$ solution. The sweep rate for Pd(111) and Pt/Pd(111) is 20 mV/s, while for Pt(111) it is 50 mV/s.

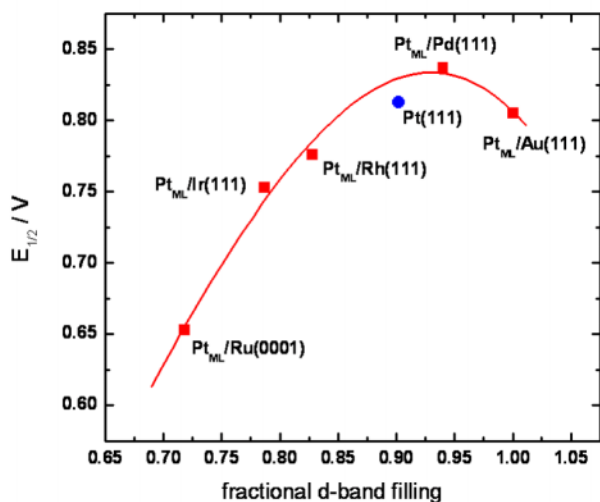


Figure 4. O_2 reduction activities of Pt monolayers on different substrate metals plotted as a function of the fractional d-band filling of the substrates. The data for Pt(111) are given for comparison.

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

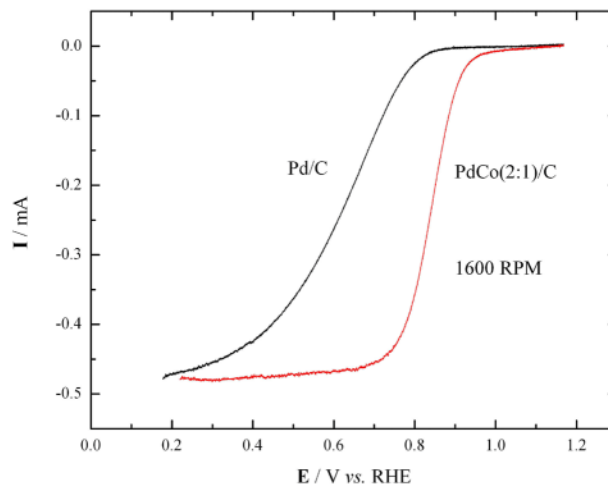


Figure 5. Comparison of polarization curves for O_2 reduction on Pd/C and PdCo(2:1)/C nanoparticles in 0.1 M $HClO_4$.

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.

Conclusions

- The PtRu₂₀ 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 $\mu\text{g Pt}/\text{cm}^2$ 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

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2. K. Sasaki, Y. Mo, J.X. Wang, M. Balasubramanian, F. Uribe, J. McBreen, R.R. Adzic, Pt submonolayers on metal nanoparticles - novel electrocatalysts for H₂ oxidation and O₂ reduction, *Electrochim. Acta*, 48 (2003) 3841.
3. J.X. Wang, N.M. Markovic, R.R. Adzic, Kinetic simulation of O₂ reduction on Pt(111) in acid solutions: Intrinsic kinetic parameters and anion adsorption effects, *J. Phys. Chem. B*, 108 (2004) 4127.
4. K. Sasaki, J.X. Wang, M. Balasubramanian, J. McBreen, F. Uribe, R.R. Adzic, Ultra-low platinum content fuel cell anode electrocatalyst with a long-term performance stability, *Electrochim. Acta*, in press.
5. J. Zhang, Y. Mo, M.B. Vukmirovic, R. Kile, K. Sasaki, R.R. Adzic, Platinum monolayer electrocatalysts for O₂ reduction: Pt monolayer on Pd(111) and on carbon-supported Pd nanoparticles, *J. Phys. Chem. B*, in press.

Presentations

1. R.R. Adzic, K. Sasaki, Y. Mo, F. Uribe, Pt submonolayer electrocatalysts for H₂ oxidation and O₂ reduction, 54th annual meeting of ISE, August 31-September 5, Sao Pedro, Brazil, 2003.
2. R.R. Adzic, K. Sasaki, J.X. Wang, Y. Mo, M.B. Vukmirovic, M. Balasubramanian, Structural, electronic and catalytic properties of Pt monolayers on single crystal and nanoparticles surfaces, 54th annual meeting of ISE, August 31-September 5, Sao Pedro, Brazil, 2003.
3. K. Sasaki, Y. Mo, J.X. Wang, M. Balasubramanian, F. Uribe, J. McBreen, R.R. Adzic, Catalytic and electronic properties of Pt monolayer electrocatalysts for H₂/CO oxidation and O₂ reduction, 204th ECS meeting, October 12-16, Orlando, Florida, 2003.

Patents

1. R.R. Adzic, S.R. Brankovic, J.X. Wang, Carbon Monoxide Tolerant Electrocatalyst with Low Platinum Loading and a Process for Its Preparation. United States Patent No.: US 6,670,301 B2 December 30, 2003.