

V.D.12 High-Activity Dealloyed Catalysts

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Contract Number: DE-EE0000458

Subcontractors:

- George Washington University (GWU), Washington, D.C.
- Johnson Matthey Fuel Cells (JMFC),
Sonning Common, UK
- Massachusetts Institute of Technology (MIT),
Cambridge, MA
- Northeastern University (NEU), Boston, MA
- Technical University Berlin (TUB), Berlin, Germany

Project Start Date: August 1, 2010

Project End Date: November 30, 2013

Technical Barriers

This project addresses the following technical barriers from the Technical Plan--Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Cost
- (A) Durability
- (C) Performance

Technical Targets

TABLE 1. Progress towards Meeting Technical Targets for Electrocatalysts for Transportation Applications (first 4) or for MEAs (last 2)

Characteristic	Units	2017 DOE StackTargets	Project 2012 Status (50 cm ² at GM)
Mass activity	A/mg _{PtGM} @ 900 mV _{IR-free}	≥0.44	0.52 (PtNi ₃) 0.46 (PtCo ₃)
Loss in catalytic (mass) activity	% lost after 30k cycles 0.6-1.0 V	≤40%	28%(PtCo ₃) 69% (PtNi ₃)
PGM Total Content	g _{PGM} /kW _{rated}	≤0.125	0.16 (PtNi ₃) @1.5 A/cm ² in H ₂ /air
PGM Total Loading	mg _{PGM} /cm ² _{geo}	≤0.125	0.15 (0.05 on anode)
Performance @ rated power	mW/cm ²	1,000	940
Performance @ 0.8 V	mA/cm ²	300	200

PGM - Platinum group metal

Fiscal Year (FY) 2012 Objectives

- Demonstrate, in 50-cm² membrane electrode assemblies (MEAs) in fuel cells, a dealloyed catalyst both (1) giving an initial oxygen reduction activity ≥0.44 A/mg_{PGM} and (2) losing less than 40% of that activity after 30,000 voltage cycles from 0.6 to 1.0 V.
- Optimize manufacturable procedures for precursor synthesis and dealloying of the catalyst powders.
- Demonstrate electrodes made from dealloyed catalysts that give good high current density performance using air as the oxidant: >570 mV at 1.5 A/cm² when tested with the DOE-targeted cathode loadings ≤0.1 mg_{PGM}/cm².
- Improve understanding of where alloying-element atoms should reside with respect to the surface of the catalyst particle for simultaneously good activity, durability, and high-current-density performance in air.

FY 2012 Accomplishments

- Developed catalysts achieving initial mass activities of 0.52 (dealloyed PtNi₃) and 0.46 A/mg_{PGM} (D-PtCo₃), exceeding the target of ≥0.44, with better durability and high-current-density performance than the D-PtCu₃ reported last year.
- The small-batch GM D-PtCo₃ lost only 38% percent of its initial activity after 30,000 cycles 0.6-1.0 V, bettering the target of <40% loss and giving more than a 2-fold improvement vs. last year's D-PtCu₃. The durability of the dealloyed large-batch JMFC PtNi₃ tested to date, while better than that of D-PtCu₃, still needs improvement.
- MEAs made with large-batch D-PtNi₃ at 0.1 mg_{PGM}/cm² matched or bettered, at all current densities on H₂/air, the initial performance of those made with baseline Pt/carbon at 0.4 mg_{PGM}/cm². They thereby demonstrate a pathway to the Pt-cost reduction needed for mass

production of fuel cells, if the durability limitations seen to date with this material can be overcome.



Introduction

The amount of expensive platinum used as the oxygen reduction catalyst in fuel cells must be reduced about 4-fold to make proton exchange membrane fuel cells (PEMFCs) cost-competitive with other power sources. Pt-alloy catalysts, typically prepared with a composition of Pt_3M (M being a non-precious metal) have historically provided about half of the necessary activity gain vs. state-of-the-art pure-Pt/carbon catalysts. Prior to this project, team member Peter Strasser's group had shown, in small-scale laboratory experiments, that additional activity gains could be obtained by first synthesizing alloys with excess M and then removing most of the M by an electrochemical treatment [1]. They hypothesized that this treatment leaves the surface Pt atoms closer to one another than they are in pure Pt, causing electronic structure changes that accelerate the reduction of oxygen [2]. This project has developed manufacturable means of scaling up these dealloyed catalysts, confirming that most of the activity gains seen in ex situ laboratory experiments can also be achieved in practical fuel cells at GM which satisfy the DOE catalyst activity target. However, we identified severe problems: (1) lack of durability and (2) poor performance in hydrogen/air fuel cells at high current density, associated with the use of the alloying element, copper, which had seemed most attractive in ex situ experiments. In FY 2012 we have successfully shifted to other alloying elements, cobalt and nickel, which avoid one of the mechanisms whereby copper caused problems. Made in small batches, several dealloyed PtCo catalysts satisfied DOE catalyst targets for both activity and durability in GM fuel cells. Larger-scale dealloyed $PtNi_3$ catalysts have to date satisfied the DOE activity target and the project milestone for high current density performance in GM fuel cells. We continue to pursue ideas to solve the durability shortfall that we have seen to date for the large-scale dealloyed $PtNi_3$ materials.

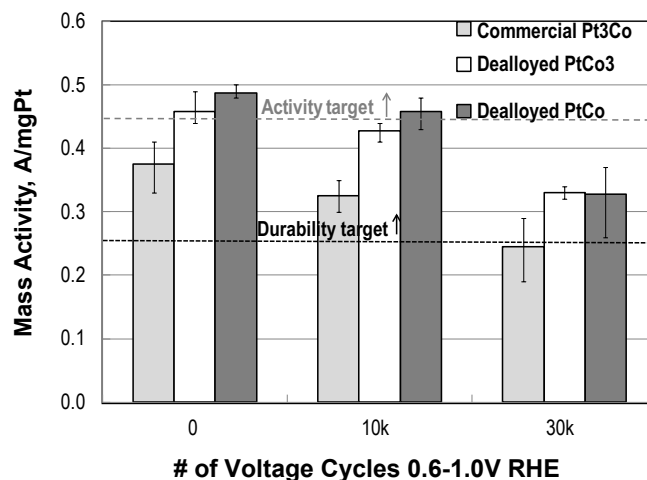
Approach

Project member Peter Strasser's group had demonstrated, in ex situ experiments prior to this project, that electrochemical removal of most of the non-noble alloying element M from Pt-alloy precursors with initial composition of PtM_3 could give higher oxygen reduction activities than the ~2-3-fold improvement vs. Pt alone that had historically been seen for Pt-alloy catalysts directly prepared at a composition of Pt_3M . Last year, this project demonstrated that this improved activity could be achieved in MEAs tested in fuel cells with $PtCu_3$ dealloyed as a catalyst powder using manufacturable chemical methods. However, GM

found the durability of the $D-PtCu_3$ to be very poor. Also, amounts of Cu (remaining after dealloying) sufficient to give good initial kinetic activity gave very poor performance in H_2 /air fuel cells at high current density. The latter effect was due in part to Cu^{2+} crossing from the cathode through the membrane to the anode, where it plated out as Cu metal and blocked the H_2 oxidation reaction. This year extensive work was done, optimizing manufacturable methods, to generate dealloyed catalysts and cathode electrodes using two alloying elements, Co and Ni, which do not plate out as the metals at the hydrogen potential in the acidic electrolyte of a PEMFC. Advanced electron microscopy and synchrotron X-ray techniques were applied to aged electrodes to correlate atomic-scale structure and composition with differences in activity and durability between individual catalysts, thereby guiding the further development of durably active catalysts.

Results

Figure 1 shows that GM-made small-batch $D-PtCo_3$ and $D-PtCo$ catalysts met, in 50-cm^2 fuel cells at GM, both the initial activity and the durability DOE 2017 targets shown in Table 1, as well as outperforming a commercial Pt_3Co catalyst subjected to the same test procedures. These results show that a dealloyed catalyst can simultaneously meet the DOE numerical targets for kinetic activity and durability. However, insufficient quantities of these catalysts could be prepared to allow testing in multiple laboratories and at different loadings. The intention of this project is for JMFC, as an established catalyst manufacturer, to generate the primary materials for investigation so as to facilitate eventual commercial availability of the advanced catalysts developed.



RHE - reference hydrogen electrode

FIGURE 1. ORR Pt mass activities measured in GM 50-cm^2 H_2/O_2 fuel cells at standard conditions for three catalysts, at $0.2\text{ mg}_{Pt}/\text{cm}^2$ loadings, as a function of the number of 0.6-1.0 V triangle-wave potential cycles at 50 mV/s in fully-humidified H_2/N_2 at 80°C . "Activity target" (see Table 1) is judged at 0 cycles; "Durability target" is judged at 30,000 cycles. Error bars show range of 3 MEAs/point.

Based on some preliminary data from TUB suggesting that the Pt-Ni system could be superior to the Pt-Co, JMFC generated several large (~100 g) batches of PtNi₃ precursors. GM chemically dealloyed this material in 1 M HNO₃ for different times and temperatures, yielding catalyst powders with the compositions labeled for individual sets of points in Figure 2. GM fabricated 50-cm² MEAs from these powders, giving the initial (after break-in) activities shown in Figure 2. While the initial oxygen reduction reaction (ORR) activity dropped as more Ni was removed from the precursor with more aggressive dealloying, the activity remained above the DOE target for a wide range of final catalyst compositions. This provides us with the freedom to optimize for other properties such as durability and high-current-density performance.

Figure 3 shows that the durability against voltage cycling of the large-batch D-PtNi₃ catalyst dealloyed for 1 day at 70°C did not meet the DOE target. Transmission electron microscopy of the fresh and cycled MEAs showed that this catalyst had a spongy, hole-riddled structure in all sizes of particles, and extended X-ray absorption fine structure (EXAFS) of these electrodes showed little evidence of Pt-Ni bonding, though a fair amount of Ni remained in the catalyst. In contrast, the more durable small-batch D-PtCo₃ catalyst had shown much more Pt-M binding in EXAFS, and detailed atomic-scale elemental mapping with electron energy loss spectroscopy had shown Pt-Co cores within Pt shells, as well as some pores, in all particle sizes [3]. We hypothesize that the alloy cores of this D-PtCo₃ catalyst improved its durability vs. the more porous, percolated structure of this

D-PtNi₃ (Ni and Co have similar corrosion chemistry); and we are trying a range of different dealloying conditions to promote more of a core-shell structure as a means of improving durability in the PtNi system.

While the durability of the kinetic activity of the large-batch D-PtNi₃ has so far been disappointing, its initial performance at high current density in air has been quite good, particularly in light of the lack of optimization of cathode electrode structure to date. Figure 4 shows that the 50-cm² MEA performance in H₂/air of 0.1 mg_{PGM}/cm² D-PtNi₃,

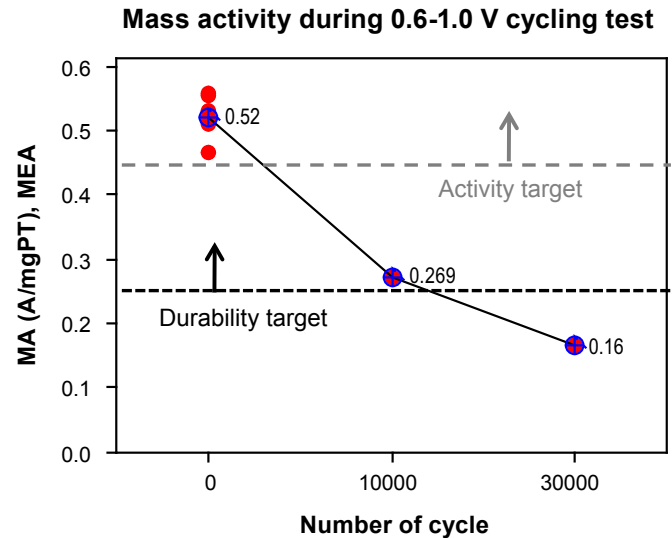


FIGURE 3. ORR Pt mass activities for JMFC large-batch PtNi₃/Ketjen dealloyed by GM for 24 h at 70°C as a function of the number of H₂/N₂ voltage cycles 0.6-1.0 V at the conditions of Figure 1.

Acid leaching conditions on mass activity

95% CI for the Mean

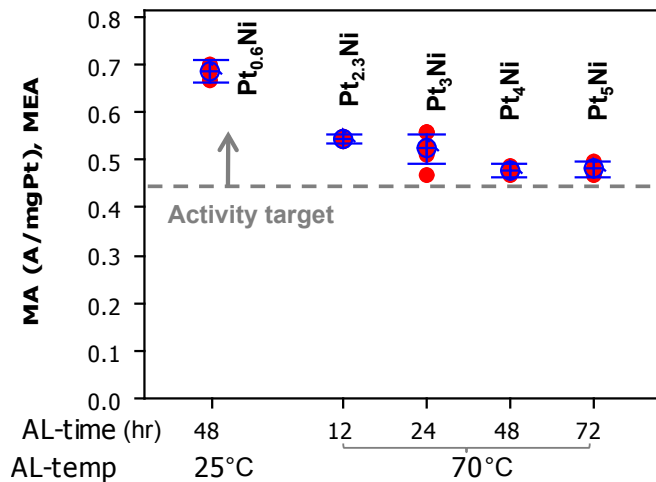


FIGURE 2. Initial ORR Pt mass activities measured in GM 50-cm² H₂/O₂ fuel cells at standard conditions for JMFC large-batch PtNi₃/Ketjen dealloyed (in the powder form) by GM in 1 M HNO₃ for the temperatures and times shown. Error bars are 95% confidence intervals for 4-7 MEAs for each type. Compositions shown are for the dealloyed catalyst powders prior to fabrication of the MEAs.

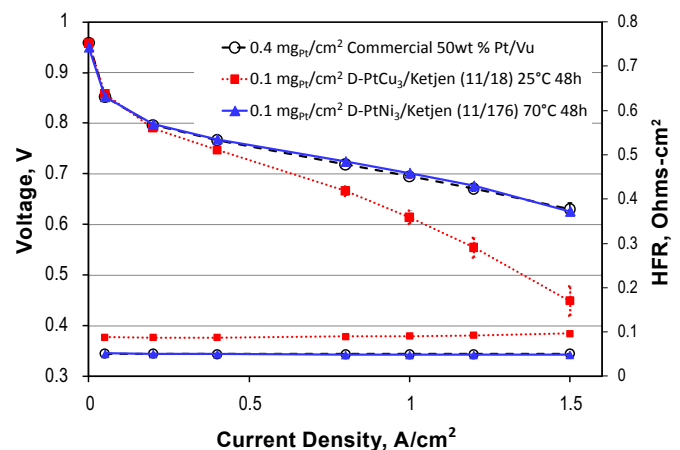


FIGURE 4. Comparison of GM 50-cm² H₂/air polarization curves for 0.4 mg_{Pt}/cm² loadings of commercial Pt/V and for 0.1 mg_{Pt}/cm² loadings of JMFC PtCu₃/Ketjen and JMFC PtNi₃/Ketjen dealloyed by GM to give initial activities >0.44 A/mg_{Pt}. 80°C, 170 kPa_{abs}, relative humidity 100%/100%, stoichiometries 1.5/2. High-Frequency Resistances measured at 1 kHz. Error bars show the standard errors of 3-4 MEAs of each type.

dealloyed to a point that still satisfies the initial activity target, matches or exceeds that of MEAs with a $0.4 \text{ mg}_{\text{PGM}}/\text{cm}^2$ loading of a conventional Pt/Vulcan carbon catalyst at all points of the polarization curve. In contrast, D-PtCu₃ with enough Cu left to give good kinetic activity gave very poor performance in air at high current density. The benefits of the shift from Cu to a less-noble alloying element are clear. Detailed alternating-current impedance studies have shown that the higher high-frequency resistance values for the PtCu electrode were due to an additional impedance loop caused by the poisoning of most of the anode surface with metallic copper. The D-PtNi₃ data in Figure 4 satisfy the project milestone for the initial high-current-density performance, but we still need to further optimize the electrodes to fully comply with the more recent DOE electrode performance targets shown in the last two lines of Table 1.

Conclusions and Future Directions

- D-PtNi₃ is looking good for initial kinetic activity and high-current-density performance.
- Working to improve durability of D-PtNi₃ by:
 - Modifying dealloying conditions to promote core/shell vs. percolated structure.
 - JMFC is running diverse precursor preparation techniques to improve particle-size uniformity.
 - Adding third components to control dealloying process.
 - TUB is controlling facet exposure, adding third components to limit activity loss.
- MIT is investigating how relative positions in electrochemical series and metal-Pt binding strengths influence dealloying.
- Once durability of kinetic activity is under control, will scale up to full-active-area fuel cells to test durability of high-current-density performance.

FY 2012 Publications/Presentations

1. Liu, Z.Y.; Xin, H.L.; Yu, Z.Q.; Zhu, Y.; Zhang, J.L.; Mundy, J.A.; Muller, D. and Wagner, F.T., “Atomic-Scale Compositional Mapping and 3-Dimensional Electron Microscopy of Dealloyed PtCo₃ Catalyst Nanoparticles with Spongy Multi-Core/Shell Structures”, *J. Electrochem. Soc.*, in press (likely V. 159, no. 9, 2012).
2. Jia, Q.; Halder, A.; Ramaker, D.E.; Ziegelbauer, J.M. and Mukerjee, S., “Investigation of Cathodic Underpotential Deposition of Cu onto Pt/C Electrocatalysts and its Influence on the Oxygen Reduction Reaction”, *The Electrochemical Society*, 9–14 October 2011, Boston, MA.; Abstract # 930, manuscript in preparation.
3. Jia, J.Q.; Trahan, M.; Ramaker, D.E.; Ziegelbauer, J.M. and S. Mukerjee, “X-ray Absorption Spectroscopy Investigations on the Activity and Durability of a Dealloyed PtCo₃ Electrocatalyst”, *The Electrochemical Society*, 9–14 October 2011, Boston, MA.; Abstract #770, manuscript in preparation.

4. Caldwell, K.; Mukerjee, S.; Qingying, J.; Ziegelbauer, J.M. and Ramaker, D.E., “X-ray Absorption Spectroscopy Investigation on a High Activity Dealloyed PtCo₃ Cathodic Catalyst”, *The Electrochemical Society*, 9–14 October 2011, Boston, MA.; Abstract #860, manuscript in preparation.
5. Wagner, F.T.; Lakshmanan, B.; Gu, W.; Greszler, T.A. and Mathias, M.F., “Electrons to Go: Electrochemistry and the Future of the Automobile”, invited plenary-session talk at the 220th national meeting of The Electrochemical Society, Boston, MA, October 9–14, 2011. Included short section on dealloyed catalysts. Abstract #770 and *Electrochemical Society Transactions* 41 (2011) 13-26.
6. Wagner, F.T., “Reduction of Platinum Usage in Automotive Fuel Cells, *Acta Materiala Materials and Society Award Forum: Vehicle Electrification Honoring Dr. Alan Taub*, Boston, MA, November 27, 2011. Section on dealloyed catalysts.
7. Wagner, F.T., “Near-Surface Science and Oxygen Reduction Electrocatalysis”, *Fuel Cell Seminar at Yamanashi Univ., Kofu, Japan*, December 9, 2011. Section on dealloyed catalysts.
8. Wagner, F.T. “Surface Science towards the Electrification of the Automobile”, *International Symposium on Surface Science and Nanotechnology*, Tokyo, Japan, December 14, 2011. Section on dealloyed catalysts.
9. Strasser, P., “Materials for Fuel Cell Catalysts”, *American Chemical Society*, San Diego, CA, March 26, 2012.
10. Strasser, P., “Core-Shell Nanoparticle Catalyst Concepts for High Performance Polymer Electrolyte Membrane Fuel Cells”, keynote presentation at the *Grove Fuel Cells 2012 Science & Technology Conference*, Berlin, Germany, April 11, 2012.
11. Kongkanand, A.; Gu, W. and Wagner, F.T., “Electrocatalyst Design in Proton Exchange Membrane Fuel Cells for Automotive Application”. In “*Heterogeneous Catalysis at the Nanoscale for Energy Applications*.”; Tao, F.; Schneider, W. and Kamat, P. eds.; Wiley-VCH (2012) submitted. Section on dealloyed catalysts.
12. Ramaker, D.E.; Caldwell, K.; Mukerjee, S.; Jia, Q. and Ziegelbauer, J.M. “Investigations on High Activity De-alloyed Pt₃Co Cathodic Catalysts using XAS”, *63rd Annual Meeting of the International Society of Electrochemistry*, Aug. 19–20, 2012, Prague, Cz; ISE#120638; manuscript in preparation.

References

1. Koh, S.; Strasser, P., “Electrocatalysis on Bimetallic Surfaces: Modifying Catalytic Reactivity for Oxygen Reduction by Voltammetric Surface Dealloying”, *J. Am. Chem. Soc.*, Vol. 129, pp. 12624-12625, 2007.
2. Strasser, P.; Koh, S.; Anniyev, T.; Greeley, J.; More, K.; Yu, C.; Liu, Z., Kaya, S.; Nordlund, D.; Ogasawara, H.; Toney, M.F. and Nilsson, A., “Lattice-Strain Control of the Activity in Dealloyed Core-Shell Fuel Cell Catalysts”, *Nature Chemistry*, Vol. 2, pp. 454-460, 2010.
3. Liu, Z.Y.; Xin, H.L.; Yu, Z.Q.; Zhu, Y.; Zhang, J.L.; Mundy, J.A.; Muller, D. and Wagner, F.T., “Atomic-Scale Compositional Mapping and 3-Dimensional Electron Microscopy of Dealloyed PtCo₃ Catalyst Nanoparticles with Spongy Multi-Core/Shell Structures”, *J. Electrochem. Soc.*, in press (likely V. 159, no. 9, 2012).