

V.D.12 High-Activity Dealloyed Catalysts

Frederick T. Wagner
 General Motors, LLC (GM)
 10 Carriage St.
 Honeoye Falls, NY 14472
 Phone: (585) 624-6726
 E-mail: frederick.t.wagner@gm.com

DOE Managers
 HQ: Dimitrios Papageorgopoulos
 Phone: (202) 586-5463
 E-mail: Dimitrios.Papageorgopoulos@ee.doe.gov
 GO: Gregory Kleen
 Phone: (720) 356-1672
 E-mail: Greg.Kleen@go.doe.gov

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- 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

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Objectives

- Prepare, characterize, and test dealloyed catalysts with initial oxygen reduction mass activities exceeding the DOE 2015 target of 0.44 A/mg_{Pt} at 900 mV reversible hydrogen electrode in 50 cm² fuel cells.
- Demonstrate, for these materials, loss of no more than 40% of the catalytic (mass) activity after the DOE-specified voltage-cycling test in 50 cm² fuel cells.
- Develop and demonstrate, with these catalysts, electrodes giving high current density performance in air adequate to meet the DOE platinum group metal (PGM) loading targets of <0.125 g_{PGM}/kW_{rated} and <0.125 mg_{Pt}/cm²_{geo}.
- Demonstrate durability of the high current density performance in air in full-active-area fuel cells.
- Determine, at the atomic scale, 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.

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:

- Durability
- Cost
- Performance

Technical Targets

TABLE 1. Progress towards Meeting Technical Targets for Electrocatalysts for Transportation Applications

Characteristic	Units	2015 DOE StackTargets	Project 2011 Status (50 cm ²)
Mass activity	A/mg _{PGM} @ 900 mV _{R-free}	≥0.44	0.58 (PtCu ₃) 0.37 (PtCo ₃)
Loss in catalytic (mass) activity	% lost after 30k cycles 0.6-1.0 V	≤40%	38% (PtCo ₃) 83% (PtCu ₃)
PGM total content	g _{PGM} /kW _{rated}	≤0.125	0.19 @ 1.5 A/cm ² in H ₂ /air
PGM total loading	mg _{PGM} /cm ² _{geo}	≤0.125	0.15
Specific activity	μA/cm ² _{PGM}	720	860

} For more highly dealloyed PtCu₃

PGM - platinum group metal

Fiscal Year (FY) 2011 Accomplishments

- Demonstrated in 50 cm² fuel cells a dealloyed PtCu₃ catalyst with initial mass activity of 0.58 A/mg_{Pt}, exceeding the DOE 2015 target of 0.44 A/mg_{Pt}.
- Demonstrated in 50 cm² fuel cells a dealloyed PtCo₃ catalyst with a loss of 38% of its initial mass activity after 30,000 cycles 0.6-1.0 V in H₂/N₂, (slightly) bettering the DOE 2015 target of <40% loss. The initial activity of this PtCo₃ catalyst, at 0.37 A/mg_{Pt}, tested slightly below the DOE target for initial activity.
- Developed methods to scale up the production of relevant catalyst precursors from <0.5 g to 100 g.
- Derived similar ~3 monolayer Pt shell/PtCu_{1.8} core structures from transmission electron microscopy (TEM) and extended X-ray absorption fine structure for a dealloyed PtCu₃ catalyst.



Introduction

The amount of expensive platinum used in the air electrode of fuel cells must be reduced at least 4-fold to make fuel cells cost-competitive with internal combustion powertrains, requiring a compensating increase in the oxygen reduction activity per gram of Pt used. Pt-alloy catalysts have historically given a ~2-fold increase in activity vs. pure Pt, leaving a 2-fold gap remaining. However, prior to this project the group of project team member Peter Strasser (now at TUB) had found in laboratory experiments that if one started with a large excess of the inexpensive non-noble alloying element and then removed most of that element with an electrochemical voltage-cycling “dealloying” treatment, significantly enhanced activities exceeding the DOE 2015 target of 0.44 A/mg_{Pt} could be achieved [1]. This project seeks to develop and scale up new catalysts that take advantage of this activity gain from dealloying while also achieving the durability and high current density performance needed for production fuel cells.

Approach

Catalyst precursors with the general formulation PtM₃ are being prepared on carbon-black supports, with the choices of M including Cu, Co, Ni, and possibly Fe and V. Electrochemical and chemical processes have been developed to partially dealloy the precursor powders down to a composition of ~Pt₂M. This must be done prior to incorporation of the catalysts into a membrane electrode assembly (MEA) to prevent excessive displacement of hydrogen ions from the ion-exchange sites of the ionomer by M^{x+} ions. This project has scaled up the production of relevant catalyst precursors from a <0.5 g level to the >100 g needed for durability and integration studies. Dealloying methods more suitable to eventual mass production have been developed and are being further optimized.

The catalysts are then tested for oxygen reduction kinetic activity on rotating-disk electrodes (RDEs) and for both activity and durability in 50 cm² fuel cells. Advanced TEM and X-ray absorption spectroscopy (XAS) techniques are being applied to fresh and used catalyst samples to determine atomic-scale composition and structure. Iterative cycles of synthesis, testing, and characterization are being used to optimize the dealloyed catalysts. We plan to achieve durability by leaving just the right number of M atoms, and no more, at just the right places in the catalyst particles. At the end of the project, downselected catalysts will be fabricated into full-active-area fuel cell short stacks to test the durability of high current density performance while operating with hydrogen/air.

Results

Figure 1 shows that in 50 cm² MEAs in H₂/O₂ fuel cells under standard conditions, GM has obtained initial mass activities of 0.58 A/mg_{Pt} at 900 mV for catalysts prepared

from PtCu₃/HSC precursors from the Strasser group using a readily manufacturable chemical dealloying process applied to the precursor powder. This value exceeds the DOE target of 0.44 A/mg_{Pt}. A scaleable, though still less convenient, electrochemical dealloying procedure applied to the powder gave 0.32 A/mg_{Pt}. While the initial activity target has been reached with the chemically-dealloyed material, the Strasser group had been able to prepare precursors to highly active dealloyed catalysts only in batches of ≤0.5 g (with thermal annealing being the scale-limiting step), severely limiting the amount of fuel cell testing that could be done. JMFC’s initial attempts to scale up (to >80 g) the annealing of PtCu₃ precursors under this project led to materials with badly diminished surface areas. After intense study of preparation techniques, including thermal gravimetric analysis, JMFC developed modified preparation procedures at the 100-g scale that can reproduce the physical properties of Strasser’s small batches. GM applied its chemical dealloying procedures to this large-batch PtCu₃/Ketjen precursor, generating catalysts that show a laboratory RDE activity of 0.52 A/mg_{Pt}, in good agreement with RDE results from the Strasser small batches. However, the first 50 cm² MEAs made from the large JMFC batch of PtCu₃ have given mass activities of only 0.26 A/mg_{Pt}. While it is unfortunately common to measure lower activities for a catalyst in real fuel cells than in RDE, that had not been the case for the Strasser small batches. The dealloyed JMFC PtCu₃ has a higher electrochemical surface area (93 m²/g_{Pt}) than the Strasser small batch (67 m²/g_{Pt}), so it may prove useful for JMFC to slightly raise their annealing temperature.

While the dealloyed PtCu₃ gave very good initial oxygen reduction reaction activity, Figure 2 shows that it lost 82% of its initial activity after 10,000 potential cycles 0.6-1.0 V

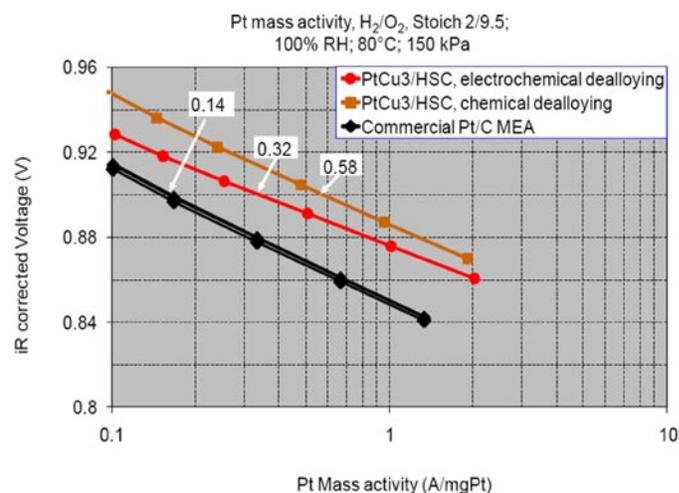


FIGURE 1. Oxygen reduction activity in 50 cm² fuel cells (targets at 0.90 V) for Strasser-group PtCu₃ precursor dealloyed by chemical or electrochemical methods at GM, plus pure-Pt-catalyzed commercial MEAs for comparison, at the standard conditions shown. X-axis is the current density (A/cm²_{geo}) divided by the Pt loading (mg_{Pt}/cm²_{geo}).

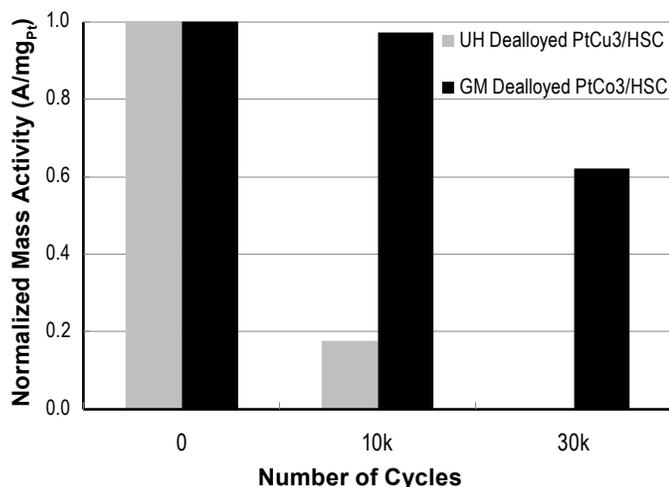


FIGURE 2. Mass activities for dealloyed PtCu₃ and dealloyed PtCo₃ catalysts, normalized to initial values, after indicated number of potential cycles 0.60-1.00 V in H₂/N₂ 50 cm² fuel cells. Activities measured in H₂/O₂ under conditions of Figure 1.

in 50 cm² H₂/N₂ fuel cells. In contrast, Figure 2 also shows that a GM-prepared dealloyed PtCo₃/HSC catalyst lost only 38% of its initial activity after 30,000 cycles, meeting the DOE target of a <40% loss. Since the initial activity of the dealloyed PtCo₃, 0.37 A/mg_{Pt}, did not quite meet the initial activity target, we have one catalyst satisfying initial activity (PtCu₃) and a different one satisfying durability (PtCo₃) targets. Dealloyed PtCo (lower initial Co) has given 0.48 A/mg_{Pt} under slightly different test conditions.

Through detailed analysis by XAS and several forms of high resolution TEM, we seek to determine which atomic-scale structural and compositional structures confer high activity and which improve durability. With such knowledge in hand, we should be able to prepare catalysts simultaneously satisfying both targets. Our initial XAS and TEM work with dealloyed PtCu₃, showed a preponderance of particles with a core of a ~PtCu_{1.8} alloy surrounded by a shell of three monolayers of pure Pt. Preliminary analysis of similar data for dealloyed PtCo₃ suggests the presence of thicker Pt shells. Given that the enhanced activity of the surface Pt atoms is believed to arise from lattice-compression [2] and/or direct electronic effects of the non-Pt atoms in the cores, and that these non-Pt atoms are much more susceptible to corrosion, one might expect an increase in shell thickness activity to decrease activity and increase durability, consistent with our preliminary structural observations. However, other parameters being measured (listed below under Conclusions) may exert more direct control than shell thickness. The knowledge gained from the characterization work is guiding our synthetic efforts in an iterative process.

Pre-project work at TUB suggested that dealloyed PtNi₃ could be more stable than PtCo₃, with at least

equivalent activity. TUB and JMFC have developed independent methods to prepare a single-phase (helpful for the production of the uniform catalyst particles needed for definitive experiments) PtNi₃ precursor. Initial GM RDE experiments on JMFC small-batch dealloyed PtNi₃ have given activities of 0.33 A/mgPt, but no optimization has yet been done on this system.

Excess non-noble metal ions leached from the catalyst can suppress oxygen reduction performance at high current density [3]. We have so far observed a negative correlation between high-current-density performance and the amount of M left in the catalyst after dealloying. We are working to identify just the right number of M atoms, in just the right place in the particle, needed for maximum durable activity, and then to synthesize particles with no excess M.

Conclusions and Future Directions

- A dealloyed catalyst (PtCu₃) has met the DOE target for oxygen reduction mass activity.
- A different dealloyed catalyst (PtCo₃) has met the DOE target for retention of mass activity after voltage cycling.
- The primary goal for 2011 is to achieve both initial activity and durability targets with the same catalyst, learning from the detailed atomic-scale characterization work.
- Dealloying produces a range of structures featuring pure-Pt shells over M-rich alloy cores.
- The following parameters are being measured, and varied via synthesis, to determine which best correlate with activity and durability: lattice compression in Pt shell, shell thickness, M concentration in core, average Pt d-band vacancy population, and particle size.

FY 2011 Publications/Presentations

1. J. Zhang, Z. Yu, Z. Liu, J. Ziegelbauer, I. Dutta, Y. Liu, R. Srivastava, X. Zhu, P. Strasser and F. Wagner, "An activity and durability study on chemically dealloyed PtCu₃/C electrocatalysts for the oxygen reduction reaction in PEM fuel cells", The Electrochemical Society, 1-6 May 2011, Montreal P.Q., manuscript in preparation (mostly pre-project work).
2. J.M. Ziegelbauer, I. Dutta and J. Zhang, "Chemical and Electronic Structure of High-Activity Chemically-Dealloyed PtM-alloy Electrocatalysts", The Electrochemical Society, 1-6 May 2011, Montreal P.Q., manuscript in preparation.
3. Z. Yu, J. Zhang, Z. Liu and F. Wagner, "Activity, Durability, and Structure of a Chemically-Dealloyed Platinum-Cobalt Catalyst for PEM Fuel Cells", North American Catalysis Society, 5-10 June, 2011, manuscript in preparation.
4. F.T. Wagner, "Electrochemistry and the Future of the Automobile", Frederick S. Billig and L. Gordon Croft Lecture at Johns Hopkins University, 28 March 2011 (small section on dealloyed catalysts).

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 A. Nilsson, "Lattice-strain control of the activity in dealloyed core-shell fuel cell catalysts", *Nature Chemistry*, Vol. 2, pp. 454-460, 2010.
3. Greszler, T.A., Moylan, T.E. and Gasteiger, H.A., "Modeling the impact of cation contamination in a polymer electrolyte membrane fuel cell", in W. Vielstich, H. Yokokawa and H.A. Gasteiger, eds., "Handbook of Fuel Cells: Fundamentals, Technology and Applications", Vol. 6, Wiley, Chichester, UK, p. 728, 2009.