
V.C.5 Development of High-Performance, Low-Pt Cathodes Containing New Catalysts and Layer Structure

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CFDRC, Huntsville, AL
Hydrogenics Corporation, Ontario, Canada

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Hydrogen, Fuel Cells and Infrastructure Technologies
Program Multi-Year Research, Development and
Demonstration Plan:

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

Technical Targets

This project is conducting research for the discovery of high performance, low-Pt cathodes incorporating alloy electrocatalysts towards the following DOE 2010 transportation fuel cell stacks targets:

- Precious metal loading: 0.1 mg Pt/cm²; 0.3 g Pt/kW_e
- Mass activity: 0.44 A/mg_{Pt} @900 mV_{IRfree}
- Durability: 5,000 h

Accomplishments

- Scaled up best Pt alloy compositions in production unit, and achieved same level of performance improvement.
- Produced high weight percent loading Pt alloy on high surface area carbon, which demonstrate high absolute performance at significantly lower Pt content.
- Extensively investigated catalyst morphology as a function of processing conditions, carbon support and metal loading.
- Finished long term durability testing using cycling protocols, for more than 30,000 cycles, and demonstrated that Pt alloy catalysts have better durability than Pt/C.
- Successfully installed rapid ink formulation and gas diffusion electrode (GDE) deposition equipment at CSMP, full commissioning in progress.
- Delivered two sets of catalyst coated membranes (CCM) incorporating baseline catalyst and new alloy composition with 200 cm² active area to Hydrogenics for short stack testing.

Objectives

- Develop and apply combinatorial powder synthesis platform based on spray pyrolysis for discovery of high performance, low-Pt cathode electrocatalysts for proton exchange membrane (PEM) automotive fuel cells.
- Develop engineered cathode layer structures containing the new electrocatalysts.
- Demonstrate enhanced performance of membrane electrode assemblies (MEAs) with low Pt content towards the DOE goals of 0.6 g Pt/kW in automotive applications for the year 2005.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the

Introduction

The overall project goals as stated previously are to significantly improve both the kinetic performance of the electrocatalyst powder at low noble metal loadings (Effort 1: *Combinatorial discovery of low-Pt compositions with microstructure optimization using*

spray-based catalyst manufacturing) and its utilization in the cathode layers through layer structure development (Effort 2: Development of engineered particles and layers).

Approach

The approach relies on the integration of combinatorial synthesis of oxidation reduction reaction (ORR) electrocatalysts by spray conversion and optimized electrode structures enabled by the unique morphology of these electrocatalysts. Further, the effort is focused on building an integrated rapid synthesis and testing approach. In addition, the CSMP combinatorial platform is built upon commercially scaled spray-based processing technology, therefore removing the scale-up issues normally associated with newly discovered electrocatalyst compositions or microstructures.

Results

During the past year, CSMP scaled up the best Pt alloy compositions identified through combinatorial discovery in production-scale unit. Systematic investigation of the effect of production conditions on the physical and electrochemical properties of Pt alloy electrocatalysts led to improved understanding of the critical performance drivers and to the demonstration of identical performance compared to those made on the combinatorial discovery unit. An extensive structural characterization of alloy catalysts at different production steps was carried out to understand the alloy formation mechanism. As a result of a unique spray process combined with low temperature reduction, highly dispersed Pt alloy with 2-4 nm average particle size can be formed with a high degree of alloying and uniformity at micron, sub-micron and nanometer scales.

Extensive alloy catalysts and cathode layer structure optimization led to further single cell performance improvements. The best catalyst shows a performance equivalent to 0.7 g Pt/kW at 0.8 V; 0.4 g Pt/kW at 0.75 V and 0.3 g Pt/kW at 0.7 V with a total loading of 0.15 mg Pt/cm². This is a significant improvement compared to the 2005 best single cell performance of 0.8 g Pt/kW at 0.8 V; 0.5 g Pt/kW at 0.75 V and 0.4g Pt/kW at 0.7 V with a total loading of 0.2 mg Pt/cm² and exceeds the project goals for single cell testing (Figure 1).

Selected active compositions were further deposited on a high surface area carbon support with high weight percent loading, and demonstrated to deliver identical performance as the high weight ratio Pt/C with roughly half of the Pt content (Figure 2). The mass activity of the alloy catalysts was tested in a single MEA at 80°C using fully humidified H₂/O₂ (S=2/9.5) and a total outlet pressure of 150 kPa. Best alloy compositions demonstrated mass activity of 0.23-0.25 A/mg_{Pt} at 0.9 V IR-free. Compared to a mass activity of the best Cabot

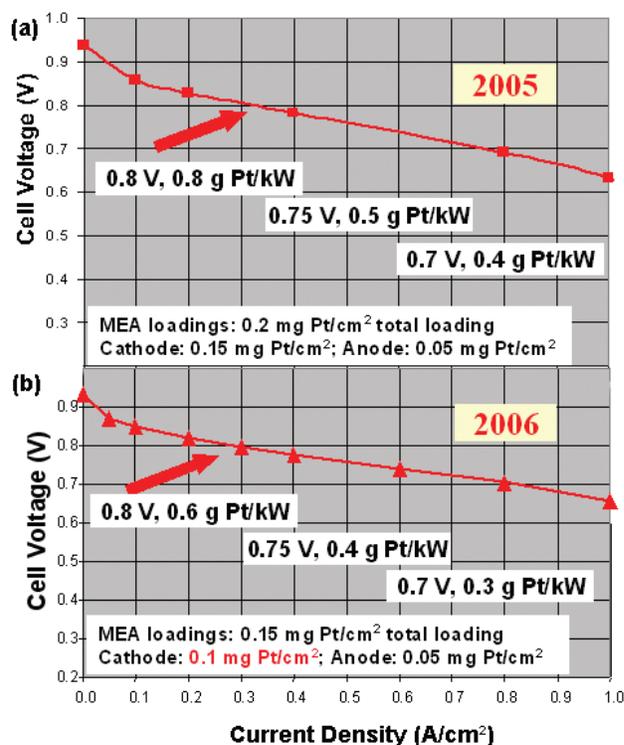


FIGURE 1. Fuel Cell Performance using Pt alloy/C as Cathode
(a) Cathode loading, 0.15 mg Pt/cm²; anode loading, 0.05 mg Pt/cm²
(b) Cathode loading, 0.10 mg Pt/cm²; anode loading, 0.05 mg Pt/cm².
The MEAs were tested at 80°C, with flows corresponding to 1 A/cm² at 1.5 stoichiometry for hydrogen and 2.5 stoichiometry for air on the anode and cathode, respectively. H₂ and air (100% humidified) were used at 30 psig pressure on both the anode and cathode.

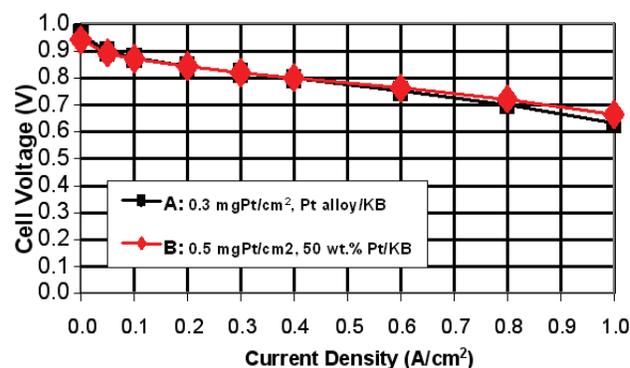


FIGURE 2. Fuel cell performance using high weight percent loading of Pt alloy/C and Pt/C as cathode. Cathode loading is indicated in the figure; anode loading, 0.05 mg Pt/cm². Testing condition is the same as in Figure 1.

Pt/C catalyst (0.13 A/mg_{Pt}) and other commercial Pt/C catalysts (0.11 A/mg_{Pt}), these novel alloy-based catalysts show close to a two-fold improvement.

DuPont Fuel Cells performed durability studies under potential cycling, for over 30,000 cycles.

The durability cycling protocol is similar to one described in a General Motors paper published in The Electrochemical Society Interface, fall of 2005. The test consists of cycling a 25 cm² MEA under H₂/air at 80°C and 100% relative humidity (RH) between 0.7 and 0.9 V iR-free voltage (30 s hold at each potential) combined with periodical evaluation of performance and Pt surface area. Three standard Pt/C containing MEAs were tested as a baseline. All three samples show high initial drop of Pt surface area which is leveled off after approximately 20,000 cycles. On average, the baseline samples show approximately 50-65% reduction of Pt surface area after 30,000 cycles. In addition to the baseline samples, two Cabot Pt/C and two Cabot Pt alloy/C containing MEAs were tested. Figure 3 represents the changes of specific surface area over 30,000 cycles. Pt/C-based MEA demonstrates higher initial specific surface area compared to Pt alloy/C. For both types of MEA a decline of the specific surface area is observed as a function of the number of cycles. The decline of the specific surface area is faster for the Pt/C sample as expressed in Figure 3(b). After 30,000 cycles more than 55% loss of the initial surface area was observed for Pt/C-based MEA, while the loss of surface area for the Pt-alloy based MEA is approximately 35%. This result confirms that Pt alloy-based catalysts have better durability under cycling protocols compared to Pt/C.

The performance of the MEAs before and after cycling was evaluated. Pt alloy-based MEA shows

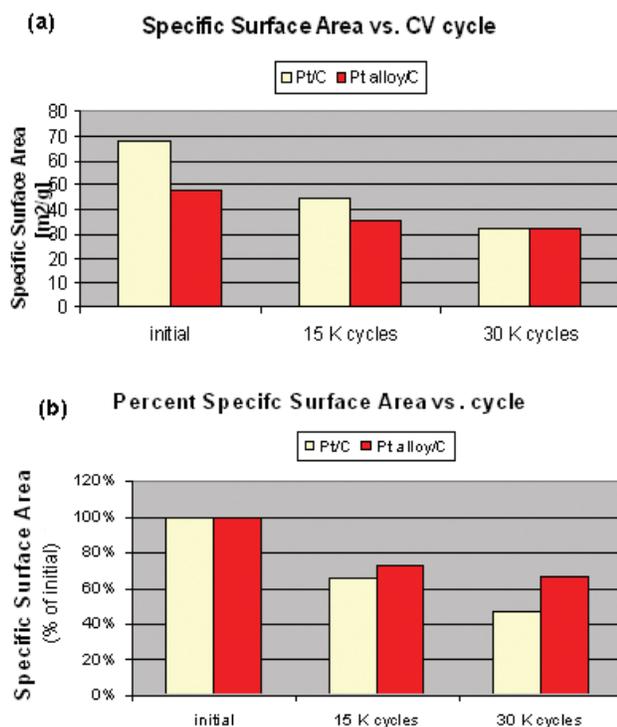


FIGURE 3. Absolute (a) and Normalized (b) Specific Surface Area Change during 30,000 Cycles for Pt/C and Pt-alloy based MEAs

minimal activity decay in the kinetic region, and slightly larger decay in the mass transport region (Figure 4). On the other hand, Pt/C MEA shows same level of activity decay in the mass transport region, and higher decay in the kinetic region. Further investigation of the Pt/C and Pt alloy/C MEA with post mortem analysis of structural changes is in progress.

Conclusions and Future Directions

- Demonstrated effectiveness of combinatorial discovery platform based on spray conversion, which lead to identification of several highly active compositions that have been scaled up to commercial volumes.
- Demonstrated better durability of Pt alloy/C catalyst compared Pt/C under cycling protocols for over 30,000 cycles.
- Need to complete short stack testing at Hydrogenics.

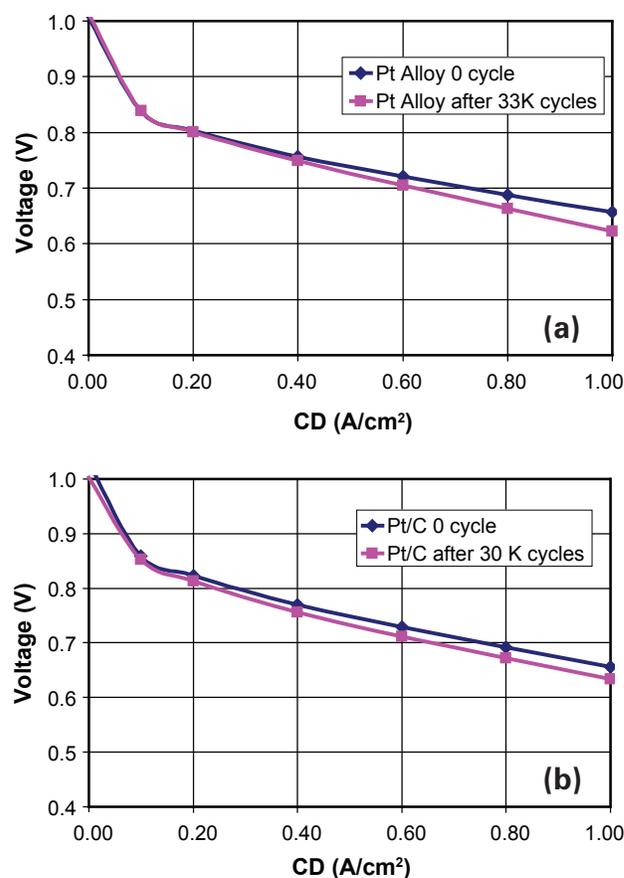


FIGURE 4. Comparison of oxygen IV curves at beginning and end of 30,000 cycles for Pt alloy/C (0.27 mg Pt/cm² cathode loading) (a) and Pt/C (0.5 mg Pt/cm² cathode loading) (b) MEAs; the MEAs were tested at 80°C using fully humidified H₂/O₂ (S=2/2) and ambient pressure.

- Need to fully commission DuPont rapid ink formulation and GDE deposition equipment.

FY 2006 Publications/Presentations

1. Paolina Atanassova, Yipeng Sun, Dennis Kountz, Jo-Ann Schwartz and Lin Wang, DOE Hydrogen Program, FY 2005 Progress Report.
2. Paolina Atanassova, Yipeng Sun, Presentation at 2006 DOE Annual Review, May 15-19, 2006, Washington, D.C.