

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

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Contract Number: DE-FC0402AL67620

Subcontractor:

DuPont Fuel Cells, Wilmington, DE

Start Date: September 2001

Projected End Date: March 2006

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 goal 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 of the 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 oxygen reduction electrocatalysts and cathode structures towards the following DOE 2010 transportation fuel cell stacks targets:

- Precious metal loading: 0.1 mg Pt/cm²; 0.2 g Pt/kW_e
- Durability: 5,000 h

Approach

- Apply Combinatorial Powder Synthesis System (CPSS) for synthesis of a large number of electrocatalyst powders with variable composition and microstructure.
- Apply rapid ink formulation and electrode deposition equipment to screen electrocatalysts generated by CPSS for their activity in oxygen reduction reaction (ORR) in half-cell configuration.
- Develop rapid MEA screening approach, consisting of a rapid MEA printing device and a rapid MEA testing device, to enable testing and optimization of the cathode structure and long-term stability in MEA configuration.
- Optimize MEA structure through design of experiments using electrocatalysts identified through high throughput discovery.
- Deliver electrocatalysts and MEAs to stack manufacturers for testing.

Accomplishments

- Completed high throughput synthesis and screening of 15 Pt-containing ternary libraries. Identified 6 Pt-alloy compositions that show up to two-fold improvement in mass activity normalized by Pt amount compared to that of pure Pt electrocatalyst in liquid electrolyte rapid testing.
- Tested the most active compositions identified by the rapid screening in MEA configuration. Mass activity normalized by Pt amount of best Pt-alloy composition shows up to two-fold improvement compared to that of pure Pt electrocatalyst at 0.8 V tested in hydrogen-air pressurized conditions in single cell.
- Further improved the performance of Pt-alloy containing cathodes through leaching the catalysts in acid.
- Optimization of layer structure through design of experiments using Pt-alloy as cathode led to significant MEA performance improvement. Performance of 0.8 gPt/kW at 0.8 V and 0.5 gPt/kW at 0.75 V was demonstrated in a single cell.
- Demonstrated long-term durability of a single cell MEA with Pt-alloy cathode of over 900 hours with decay rate of 6 $\mu\text{V/hr}$.
- Completed development of rapid gas diffusion electrode (GDE) fabrication equipment and demonstrated good GDE uniformity.
- Completed evaluation of NuVant rapid MEA screening device.

Future Directions

- Optimize and scale-up best performing Pt-alloy compositions identified.
- Testing of Cabot Superior MicroPowders (CSMP) electrocatalysts or MEAs in stack.
- Integrate rapid DuPont GDE fabrication equipment with NuVant rapid MEA testing device at CSMP.
- Continue long-term durability study of Pt-alloy electrocatalyst using cycling protocols.

Introduction

The overall project goals 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 ORR electrocatalysts by spray conversion and optimized electrode structures enabled by the unique morphology of these electrocatalysts. Further, the effort is focused on building a rapid testing approach in MEA configuration, consisting of automated electrode deposition equipment, designed and developed by

DuPont Fuel Cells, and its integration with a rapid MEA testing device developed by NuVant.

Results

During past year, CSMP and DuPont Fuel Cells initiated high throughput synthesis and screening of Pt-alloys in a discovery mode. Among 15 Pt-containing ternary libraries studied, 6 compositions were identified that show up to two-fold improvement in mass activity normalized by Pt amount compared to that of pure Pt electrocatalyst in liquid electrolyte rapid testing (Figure 1). These active compositions were then tested in a single cell MEA configuration; MEA testing results confirm the high throughput discovery results. Mass activity normalized by Pt amount of best Pt-alloy composition shows up to two-fold improvement compared to that of pure Pt electrocatalyst at 0.8 V (Figure 2).

The performance of the Pt-alloy containing cathodes was further improved through leaching of the electrocatalyst in acid (Figure 3). Physical characterization indicates no significant morphology and crystalline phase changes of the alloy electrocatalyst as a result of the treatment. The possible reason for performance improvement could be the removal of un-alloyed base metals bonded to the carbon support surface, which might otherwise leach out and contaminate the Nafion[®] membrane during fuel cell operation and/or because of modification of the carbon surface hydrophilic/hydrophobic properties. Further experiments are in progress in order to better understand the effect.

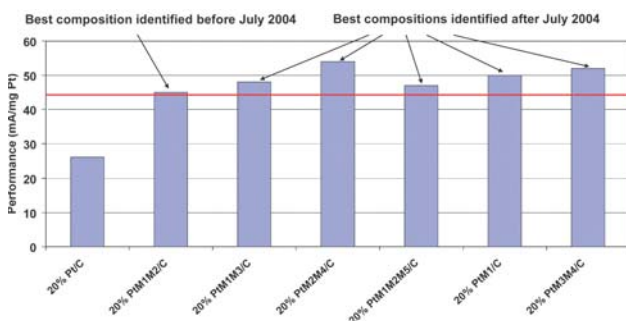


Figure 1. Half-Cell Test Results for Active Compositions Identified Through High Throughput Discovery Effort

In a parallel effort, layer structure development focusing on optimization of the electrode deposition method as well as ink formulation was carried out using 20 percent Pt-alloy as cathode electrocatalyst. Design of experiment involving three variables in MEA preparation was performed. The response variables were the single cell current densities at 0.8V and 0.7V. The performance obtained under the

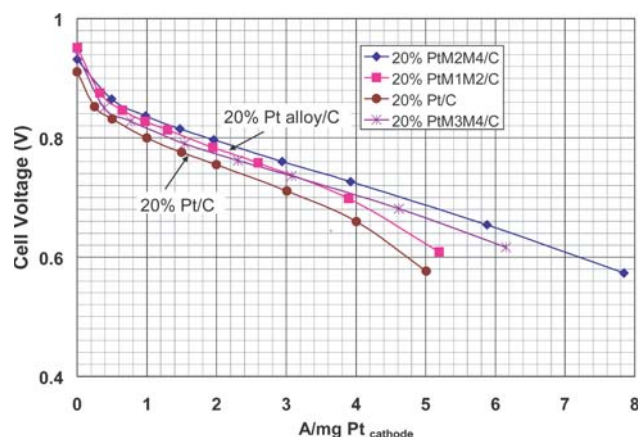


Figure 2. Fuel Cell Performance Using Pt-alloy/C and Pt/C as Cathode (Cathode loading, 0.2 mg metal/cm²; anode loading, 0.05 mg Pt/cm². The MEAs were tested at 80°C, with flows corresponding to 1 A/cm² at 1.5 stoichiometry for hydrogen and 2.5 stoichiometry for air on the anode and cathode, respectively. H₂ and air (100% humidified) were used at 30 psig pressure on both the anode and cathode.)

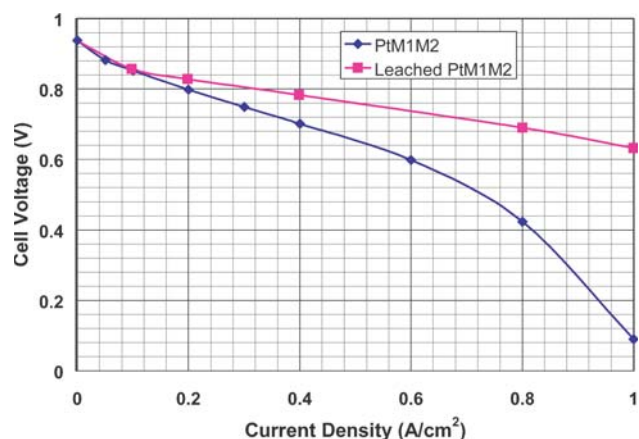


Figure 3. Effect of Acid Leaching on the Performance of Pt-alloy Containing Electrodes. Testing conditions were the same as in Figure 2.

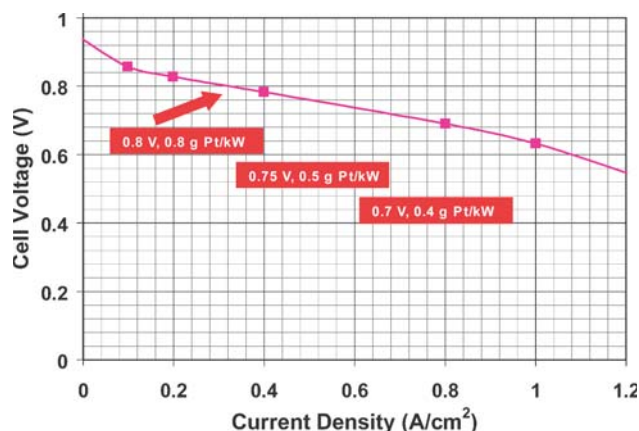


Figure 4. Single Cell Performance of Pt-alloy/C with Optimized Electrode Identified from Design of Experiments Cathode loading, 0.15 mg Pt/cm^2 ; anode loading, 0.05 mg Pt/cm^2 . Testing conditions were the same as in Figure 2.

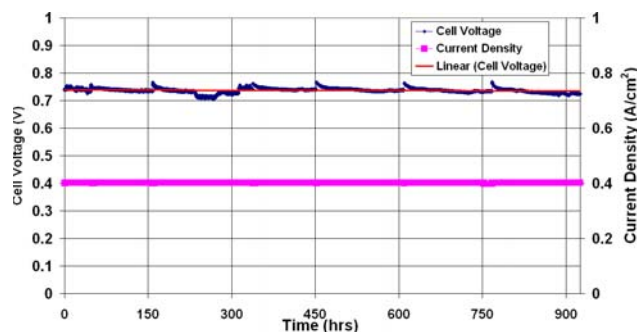


Figure 5. Durability of Pt-alloy/C Tested Under Constant Current Density in H_2 -Air at 80°C , 30 psi Back Pressure with Anode and Cathode Reactant Gases at Relative Humidification of 100%

optimized conditions translates to 0.8 g Pt/kW at 0.8 V , 0.5 g Pt/kW at 0.75 V and 0.4 g/kW at 0.7 V (Figure 4).

Long-term durability is a key challenge for the Pt-alloy electrocatalysts. Figure 5 shows the durability of Pt-alloy/C MEAs tested under H_2 -Air at 80°C , 30 psi back pressure with anode and cathode reactant gases relative humidification of 100 percent. Periodic diagnostic measurements were taken every 150 hr. The degradation rate is ca. $6 \mu\text{V/hr}$ and electrochemical surface area loss is less than 20 percent during the entire period. The long-term durability experiment was stopped due to membrane failure as evidenced from a significant increase of hydrogen crossover current.

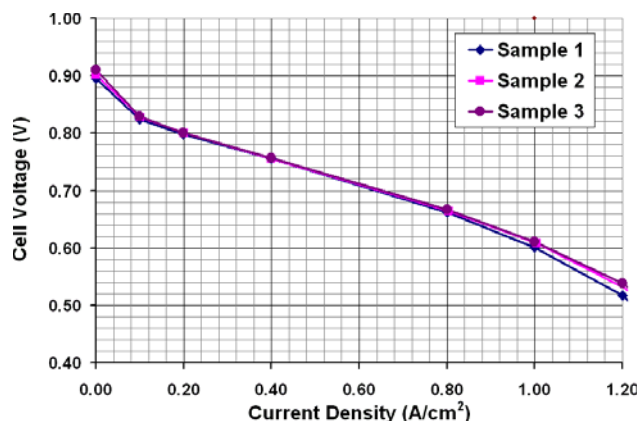


Figure 6. Fuel Cell Performance of MEAs Using Three Identical GDEs Made by DuPont GDE Equipment Cathode loading (0.25 mg Pt/cm^2), anode loading, 0.05 mg Pt/cm^2 made by CSMP. Testing conditions were the same as in Figure 2.

At DuPont Fuel Cells, the development of rapid GDE deposition equipment was completed and the ability to print electrodes with controlled composition and uniformity was demonstrated. Electrodes printed with the rapid deposition tool were evaluated at CSMP for loading uniformity by X-ray diffraction measurements and their electrochemical performance tested in MEA configuration (Figure 6). The results confirm that good reproducibility and uniformity was achieved for optimal ink formulations and deposition profiles.

As part of evaluation of NuVant Systems' rapid MEA testing device, CSMP submitted to NuVant electrode discs and counter electrodes for three array MEAs. The purpose of the tests performed was to evaluate the capability of NuVant's MEA testing unit for ranking catalyst with different activities, the spread of the data from electrodes with identical composition, as well as any possible systematic errors (row or column effect). Analysis of the screening results shows that the device can reasonably rank ORR activity of catalysts in MEA configuration.

Conclusions

During the fourth year of the project, several significant accomplishments were achieved and milestones met. CSMP and DuPont's high throughput synthesis and screening systems have been extensively used in a discovery effort of high

performance, low-Pt electrocatalyst compositions. As result of the exploration, several new compositions that show superior performance in both half-cell configuration and fuel cell configuration have been identified. The durability of CSMP Pt-alloy catalysts is comparable to literature reports for pure Pt/C catalysts with less loss of electrochemical surface area.

Progress was also made in the development of rapid GDE fabrication and MEA screening approach. Combination of these two pieces of equipment will

provide CSMP with the capability of rapid screening of catalyst compositions in a fuel cell configuration.

FY 2005 Publications/Presentations

1. P. Atanassova, B. Gurau, Y. Sun, J. Brewster, D. Kountz, J. Schwartz, L. Wang, A. Gidwani, DOE Hydrogen Program, FY 2004 Progress Report.
2. Y. Sun, G. Rice, P. Atanassova, "High Throughput Synthesis, Performance and Stability of Electrocatalysts for Hydrogen-Air Fuel Cells", Fuel Cell Seminar, Nov. 2-5, 2004, San Antonio, TX.