IV.C.8 Development of High-Performance, Low-Pt Cathodes Containing New Catalysts and Layer Structure

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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.
- Use the platform for electrocatalyst composition discovery and microstructure optimization under conditions that can be scaled for commercial powder production.
- 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 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- O. Stack Material and Manufacturing Cost
- Q. Electrode Performance
- P. Durability

Approach

- Apply the high-throughput electrocatalyst generation Combinatorial Powder Synthesis System (CPSS) for synthesis of a large number of electrocatalyst powders with a 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.
- Continue optimization of the MEA preparation method, performing design of experiments with benchmark 50 wt.% Pt/C-supported catalyst.
- Deliver electrocatalysts and test MEAs to stack manufacturers.

Accomplishments

- The CPSS is in place and fully functional, and 5 new ternary alloy compositions were synthesized at Cabot Superior MicroPowders (CSMP) and tested in the rapid screening device at DuPont Fuel Cells: Pt-M_1-M_2, Pt-M_3-M_2, Pt-M_3-M_4, Pt-M_3-M_5, Pt-M_5-M_4.
- The capacity of the automated rapid ink formulation and electrode coating system designed and built at DuPont Fuel Cells exceeds the capacity requirement of 75-150 catalysts per week.
- The workflow of the electrocatalyst synthesis on CPSS was shifted from an alloy benchmarking and optimization to a discovery mode.
- A database management system was developed to facilitate the analysis of a large number of parameters and characterization data generated.
- Long-term stability testing of alloy electrocatalyst compositions is in progress.
- Full electrochemical and structural characterization is now being used to provide further insight into combinatorial workflow and choice of compositions.
- Modeling of ionomer distribution within the cathode layer structure was completed and provides insight on optimization of MEA performance at different operating conditions.
- The optimization of the MEA deposition method led to significant MEA performance improvement.

Future Directions

- Continue to apply the CPSS and rapid screening equipment to the production and screening of a large number of electrocatalyst powders with variable compositions and microstructures.
- Execute a detailed plan for binary and ternary alloys synthesis and testing. Nine other metals in addition to Pt were selected based on their fundamental properties, and their binary and ternary alloy combinations with Pt will be synthesized and tested.
- Strongly emphasize long-term stability of electrocatalysts and MEAs: stability in acidic media, stability to active-phase agglomeration, optimal MEA structure.
- Complete the design and assembly of the rapid ink formulation and MEA preparation equipment.
- Evaluate NuVant Systems's rapid MEA testing device with 25 mini fuel cells referenced against the same counter electrode.
- Optimize the cathode structure with selected best-performing alloy electrocatalysts and test for long-term stability in MEA configuration.
- Demonstrate performance of best-performing electrocatalyst and the optimal MEA structure in short-stack fuel cell.

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 ORR electrocatalysts by spray conversion and optimized electrode structures enabled by the unique morphology of these electrocatalysts. The majority of the last year's Effort 1 was focused on completing the benchmarking of the combinatorial equipment for electrocatalyst synthesis, and shifting toward operation of CPSS in discovery mode.

The progress of Effort 2 was demonstrated through significant improvement of performance in a single 50-cm^2 MEA. Stack testing criteria have been established and include stability testing of alloys in acidic media and long-term testing in a single MEA. Testing of the long-term stability of the MEAs has commenced, and promising results have been achieved.

Results

Combinatorial synthesis

The CPSS is currently being used for combinatorial electrocatalyst synthesis at rates of 120 samples per week, 0.25 grams per sample, which meets the milestone for rapid synthesis of samples according to the planned requirements for this system. Series of samples (ca. 100 per series) of five new ternary alloy compositions were synthesized at CSMP and tested in the rapid screening device at DuPont Fuel Cells: Pt-M_1-M_2, Pt-M_3-M_2, Pt-M_3-M_4, Pt-M_3-M_5, Pt-M_5-M_4. Figure 1 and Figure 2 illustrate the performance maps of these ternary alloy electrocatalysts in terms of mA/mg Pt as a function of the their composition. Similar performance maps were analyzed also as a function of the electrocatalyst synthesis conditions. The analysis of the performance data allowed for an improved understanding of critical parameters that affect the performance and led to improvements in the combinatorial workflow, therefore enabling an optimized approach for faster screening of multiple catalyst alloy combinations during the next year.

Rapid screening of the electrochemical performance and powder characterization

DuPont Fuel Cells completed the assembly of the rapid ink formulation and electrode deposition equipment, and this equipment is now exclusively used for testing the samples generated by the CPSS (Figure 3). The new equipment can automatically mix and deposit electrode inks at a rate of 150 samples per week, which is comparable to the rate of the electrocatalyst synthesis achieved by the CPSS at Cabot SMP. Excellent reproducibility for ink preparation and electrode loadings has been achieved, with less than 10% standard deviation. The capacity of the equipment for rapid ink

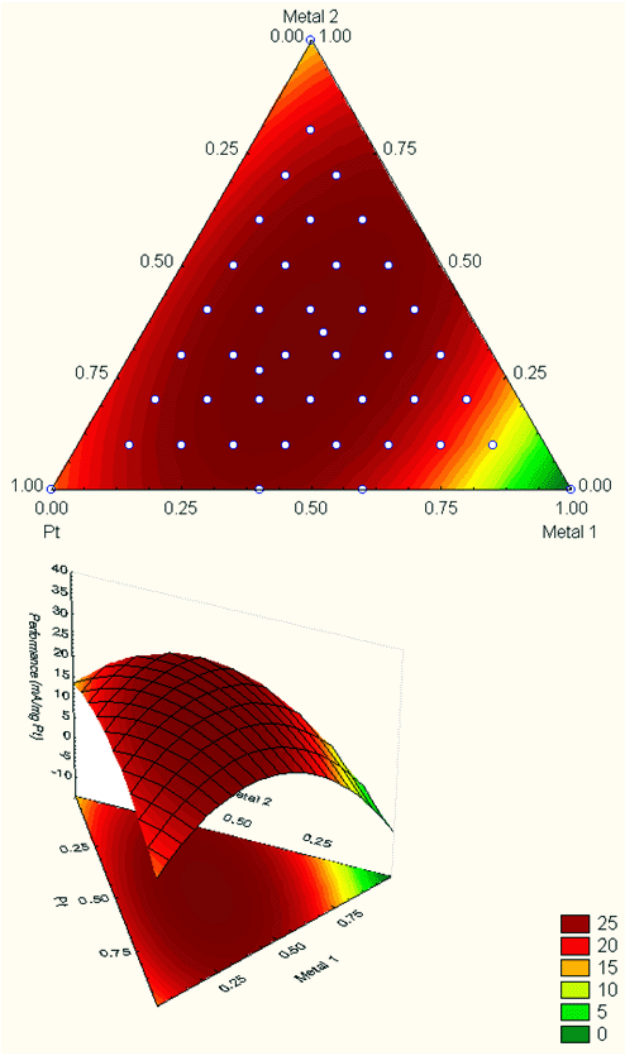

Figure 1. Electrochemical Activity Map for the Pt-M_1-M_2 Ternary Alloy

formulation and electrode preparation exceeds the requirement of 75-150 samples per week, milestone #5 in the project plan. The samples are then tested in half-cell configuration, and the test results are presented as current density normalized by the amount of Pt in the electrocatalyst.

Alloy electrocatalysts structural characterization

A full range of electrochemical and powder characterization techniques were employed to achieve superior understanding of the electrocatalysts and MEA structure. The well-performing catalysts are characterized by x-ray diffraction, and alloy particle size and degree of alloying are assessed. Tafel experiments are

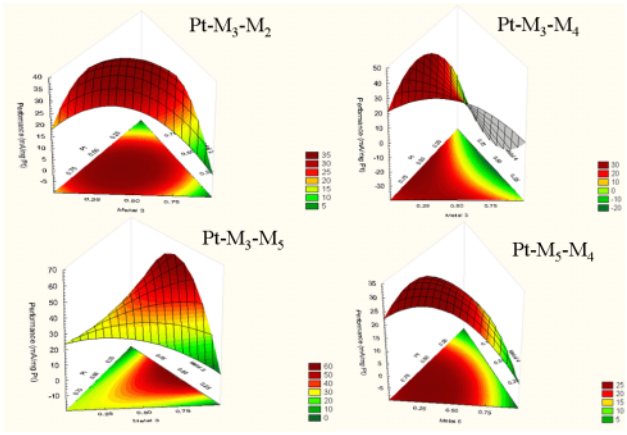

Figure 2. Electrochemical Activity Maps for the Pt-M_3-M_2, Pt-M_3-M_4, Pt-M_3-M_5, Pt-M_5-M_4 Ternary Alloys

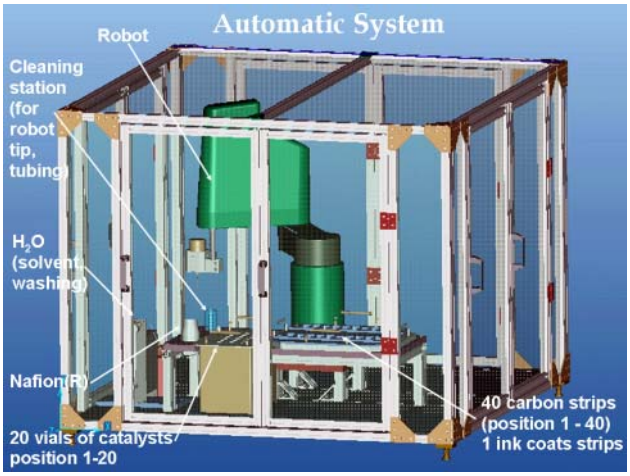

Figure 3. Rapid Ink Formulation and Electrode Deposition Equipment

performed for catalysts that demonstrate performance exceeding the go-no-go criteria in the primary screen, and the exchange current density is estimated. Under Tafel conditions, the fuel cell is operated with excess of reactant at the electrode of interest to ensure that all mass transport limitations are eliminated. By eliminating the mass transport limitations and correcting the polarization curve for the ohmic resistance, only the kinetic aspect of the electrode is represented by the polarization curve. When plotted under semilogarithmic coordinates, the Tafel plot enables the determination of the exchange current density, which is a direct measure of the electrocatalyst activity. The stability of the alloy electrocatalysts to leaching in acid is being evaluated

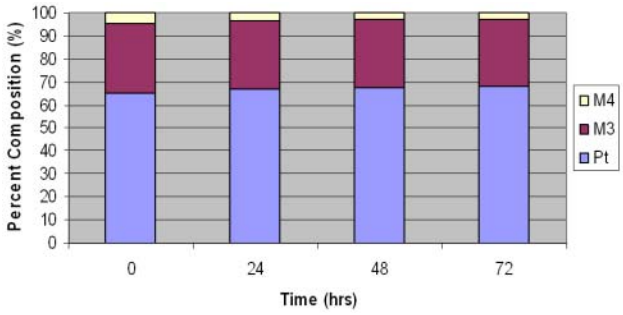

Figure 4. Catalyst Powder Characterization – Long-Term Stability of Ternary Alloy Electrocatalyst in Acid

as an ex-situ metric for the long-term stability of the alloys. An illustration of these experiments is presented as Figure 4. It has been established that both the composition and the degree of alloying have an effect on the stability of the alloy electrocatalysts.

Planned binary and ternary Pt alloys synthesis

In order to cover a relatively extensive area of potentially beneficial alloying elements, nine metals in addition to Pt were carefully selected based on fundamental principals, and their binary and ternary alloy combinations with Pt will be synthesized and tested in half-cell configuration. The best-performing compositions that exceed the new go-no-go criteria of 70% higher performance compared to pure Pt will be subjected to further characterization and MEA testing (including Tafel experiments and long-term stability in MEA under load).

Modeling of electrode structure

CFDRC has developed a model to address the impact of catalyst layer Nafion loading, and the resulting porosity and protonic conductivity, on the overall performance of the fuel cell. The model was used for parametric studies involving variation of Nafion loading for the optimum pore size distribution established from previous studies.

MEA structure development

The development of the electrode structure was focused on optimization of the electrode deposition method with Pt. Figure 5 shows the improvement in the MEA performance as a result of a design-of-experiments study that used five parameters involved

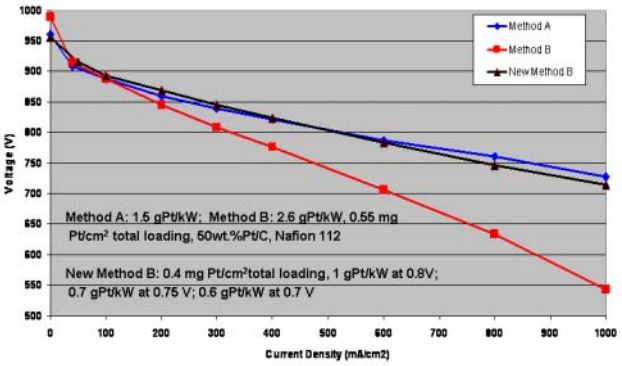

Figure 5. Progress in MEA Deposition Method Optimization (50-cm^2 test MEA was used for the evaluation, using Nafion 112 (DuPont) membrane. The MEA was tested at 80ºC, with flows corresponding to 1 A/cm^2 at 1.5 stoichiometry for hydrogen and 2.5 stoichiometry for air on the anode and cathode, respectively. 100% humidified H_2 and air were used at 30 psig pressure on both the anode and cathode.)

in MEA preparation. It can be noticed that the performance using the new method B of depositing the electrode yields the same performance as the old method A, only at lower Pt loading (0.4 mg Pt/cm^2 in case of new method B vs. 0.55 mg Pt/cm^2 in the case of method A). This performance translates to less than 1 g Pt/kW at 0.8 V, 0.7 g Pt/kW at 0.75 V and ca. 0.6 g Pt/kW at 0.7 V.

Conclusions

During the third year of the project, several significant milestones were met and progress was demonstrated on all main tasks. In Effort 1, *Combinatorial discovery of low-Pt compositions with microstructure optimization using spray-based catalyst manufacturing,* two critical tools for the combinatorial workflow were assembled and their operation optimized: Combinatorial Powder Synthesis System (Cabot SMP) and Rapid Ink Formulation and Electrode Deposition Equipment (DuPont Fuel Cells). The platform is now optimized and can be used in discovery mode, and the production of 36 ternary alloys has already started. In Effort 2, *Development of engineered particles and layers,* further improvement in the MEA performance was achieved due to optimization of the cathode structure and deposition method through design of experiments. A performance of 1 g Pt/kW was demonstrated in a single MEA at 0.8 V and 0.6 g Pt/kW at 0.7 V with 50 wt.% Pt/C electrocatalyst. Further improvements are expected when the optimal MEA structure is combined with the alloy electrocatalysts under development.

FY 2004 Publications/Presentations

1. P. Atanassova, D. Dericotte, B. Gurau, P. Napolitano, J. Brewster, R. Bhatia, B. Apodaca, M. Hampden-Smith, J. Schwartz, L. Wang, J. Gantzhorn, S. Mazumder, Hydrogen, Fuel Cells, and Infrastructure Technologies, FY 2003 Progress Report

2. P. Atanassova, D. Dericotte, P. Napolitano, B. Gurau, R. Bhatia, J. Brewster, M. Hampden-Smith, "Combinatorial Spray-Based Synthesis of PEM FC Electrocatalysts", presentation, 2003 Fuel Cell Seminar, November 2-7, 2003, Miami Beach, Florida

3. P. Atanassova, M. Hampden-Smith, P. Napolitano, B. Gurau, "Spray Pyrolysis-based High Throughput Synthesis Platform for Discovery of Fuel Cell Electrocatalysts, 6th Annual Symposium on Combinatorial Approaches for New Materials Discovery, May 4-5, 2004, Washington, DC