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.
- 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 R,D&D Plan:

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

Approach

- Design and build a Combinatorial Powder Synthesis System (CPSS) capable of generation of large numbers of electrocatalyst powders with variable composition and microstructure.
- Design and build rapid ink formulation and electrode deposition equipment to screen electrocatalysts generated by the CPSS for their activity in oxygen reduction reaction (ORR) in half-cell configuration.
- Establish baseline for performance of Pt electrocatalysts in ORR based on rapid screening; establish go/no-go criteria for binary and ternary alloy electrocatalysts synthesized in the combinatorial system.
- Continue optimization of the MEA structure with benchmark Pt-based supported catalysts with various Pt loadings in the catalysts and in the cathode layer.
- Model the electrode structure to reveal effects of layer porosity and gas humidification levels at different fuel cell operating conditions (temperature and pressure).

Accomplishments

- The assembly of the CPSS was completed, fully automated and integrated to achieve the initial planned rates of electrocatalyst samples production (between 100 and 150 samples per week).

- The assembly of the rapid ink formulation and electrode deposition equipment was completed, and testing rates are compatible with electrocatalyst production rates.
- Baseline performance of Pt electrocatalysts was evaluated for a broad range of Pt loadings. Go/no-go criteria were established for newly synthesized alloy electrocatalysts. The half-cell rapid screening technique is exclusively used for screening electrocatalysts for their ORR activity.
- Combination of the best ternary alloy catalyst (Effort 1) and the best MEA structure/printing approach (Effort 2) delivers single MEA performance of less than 1 g Pt/kW at 0.8 V (100% improvement compared to best results of 2002, 2 g Pt/kW), see Figure 1.
- Modeling of cathode layer porosity and pore size distribution provides guidance for electrocatalyst structure modification.

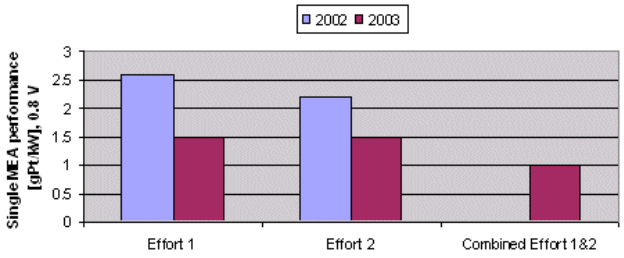

Figure 1. Summary of Performance Achievements in FY 2003 Compared to FY 2002

Future Directions

- Apply the CPSS and rapid screening equipment to the production and screening of a large number of electrocatalyst powders with variable compositions and microstructures.
- Characterize electrocatalysts by structural and electrochemical techniques to provide further focus of the combinatorial workflow and choice of compositions.
- Perform single MEA testing at various fuel cell operating conditions (gas utilization, humidification and pressure).
- Perform long-term testing.
- Demonstrate performance of best-performing electrocatalyst and the optimal MEA structure in a short stack fuel cell.
- Design and start assembly of rapid screening equipment in MEA configuration.
- Complete modeling of ionomer distribution within the cathode layer structure.

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 second year's effort was focused on the design, assembly and benchmarking of the combinatorial equipment for electrocatalyst synthesis and the high-throughput equipment for testing in half-cell configuration.

These equipment additions will allow for a significant increase in the number of compositional and micro-structural electrocatalyst variations that can be screened during Year 3 of the project. In parallel, the correlation between rapid half-cell screening test data and MEA performance for multi-component (alloys and mixed oxides) electrocatalysts was addressed.

The combined progress of both Effort 1 and Effort 2 were demonstrated 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 in the MEA configuration was expanded to cover broader variations of the operating conditions recommended by the fuel cell manufacturers in addition to the standard testing conditions.

Results

Combinatorial Synthesis. The assembly and testing of the Combinatorial Powder Synthesis System (CPSS) was completed in March 2003, and the CPSS is currently being used for combinatorial electrocatalyst synthesis (Figure 2). The CPSS was designed based on an R&D platform that leverages SMP's knowledge base of system scale-up, which ensures a pathway to high-volume manufacturing once promising candidates have been identified from an experimental campaign. The CPSS system is highly automated; an operator is required only to prepare feedstock precursor solutions (which are combined on-the-fly in controlled amounts) and to respond to operating excursions. To execute a run, the CPSS reads a database containing the physical data of the precursor solutions and the critical operating parameters (including processing temperature, gas flow rates, precursor feed rates and elemental composition of the target materials). For each individual run, the CPSS maintains and monitors the set points for all critical parameters. Graphical, numerical and statistical data for each run are presented in real-time charts and spreadsheets. Individual powder samples are isolated in the collection system to prevent cross-contamination and losses. The powders can be easily removed from the collection system and packaged for characterization, storage or shipment.

Figure 2. Combinatorial Powder Synthesis System (CPSS)

The CPSS has been engineered to accommodate up to four metal sources and two carbon sources for each campaign. As a result, a wide variety of compositions can be explored with minimal downtime for system cleaning or re-configuration. Depending on testing requirements and material systems, 100 to 150 samples per week can be produced, with a potential to further increase the number of samples to 300 per week. Furthermore, the CPSS greatly reduces the volume of paperwork, man-hours and quantity of raw materials required to accomplish a rigorous study while providing a higher level of data quality. Baseline performance of the system was evaluated against the conventional unit. Specifically, physical characteristics (e.g. metal crystallite sizes, particle sizes, morphology) of test powders were examined, and it was determined that the combinatorial system can reproduce results from the scale-up units for benchmark Pt-based catalysts. Long-term testing of the system demonstrated that the CPSS operates consistently and accurately with minimal input from the operator. Data (with statistical analysis) are automatically collected and reported by the supervisory control and data acquisition (SCADA) system to ensure reproducibility and accountability.

Rapid screening of the electrochemical performance. DuPont Fuel Cells designed and completed the assembly of the rapid ink formulation and electrode deposition equipment in June 2003. The new equipment can automatically mix and deposit electrode inks with rates comparable to those

of the electrocatalyst synthesis achieved by the CPSS at Cabot Superior MicroPowders (Cabot SMP). The samples are then tested in half-cell 3-electrode configurations in parallel using a variety of electrochemical techniques. Between 75 and 150 electrocatalysts can be screened per week, and test results are presented as current density normalized by the amount of Pt in the electrocatalyst (Figure 3). In parallel, cyclic voltamograms are recorded to facilitate a more detailed understanding of the active phase structure, such as active surface area and type and uniformity of surface features formed. The preparation of electrode inks was further optimized for electrocatalysts with different Pt and alloy compositions. An excellent correlation was established between the half-cell screening data and the performance of alloy electrocatalysts in MEA configuration.

Based on extensive testing of Pt baseline catalysts supplied by Cabot SMP, a go/no-go criteria for the mass activity of the electrocatalyst was established for each group of electrocatalysts (10, 20, 30, 40, 50, 60 wt.% Pt in combination with various carbon supports). The main goal of establishing adequate go/no-go criteria for this primary screen of newly synthesized electrocatalysts was to minimize the more time-consuming testing in MEAs and the number of false negative (or marginally positive) results. Currently, in order to qualify for testing in an MEA configuration, the specific mass activity of a new multi-component electrocatalyst needs to exceed that of the best pure Pt catalyst by at least 20% (Figure 3). The go/no-go criteria could be further increased to ensure that the testing in the MEA configuration will be focused mainly on electrode layer optimization.

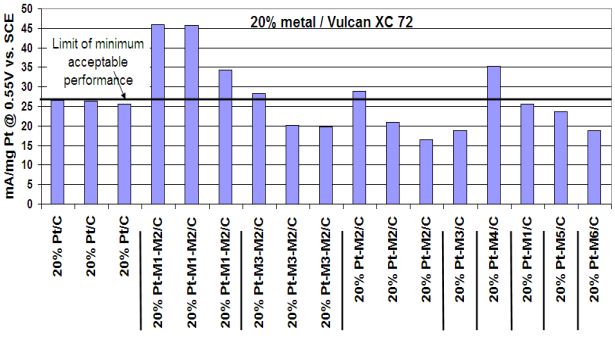

Figure 3. Test Results from Half-Cell Rapid Screening for Mass Activity of 20 wt.% Pt and Alloys Supported Electrocatalysts (SCE = saturated calomel electrode)

Binary and ternary Pt alloys. In order to establish and improve the combinatorial approach methodology, the spray pyrolysis processing of several binary and ternary compositions supported on Vulcan XC-72 was further optimized. The efforts were directed towards variations of metals loading (20, 40, 60 wt.%) and types of carbon support. The effect of spray processing and post processing conditions on the metal crystallite size and degree of alloying were also evaluated. Post processing of the electrocatalysts was further optimized, and testing of the stability of the alloys in acidic media is underway. For the best-performing 20 wt.% metal ternary alloy catalyst, an increase of the mass activity of up to 70% (in terms of mA/mg Pt) was observed when alloyed catalysts were compared to pure Pt in the rapid half-cell testing (supported alloys close to 2 times more active than pure Pt, Figure 3). Figure 4 compares the MEA performance of 20 wt.% PtM_1M_2/Vulcan XC-72 electrocatalyst compared with 20 wt.% Pt/Vulcan XC-72 at identical total Pt loadings of 0.13 mg Pt/cm^2. At 0.8 V, the performance of the ternary alloy catalyst is 220 mA/cm^2, as compared to 100 mA/cm^2 for the pure Pt electrocatalyst. If compared at constant current density of 0.2 mA/cm^2, the alloy catalyst delivers approximately 30 mV higher potential. Initial

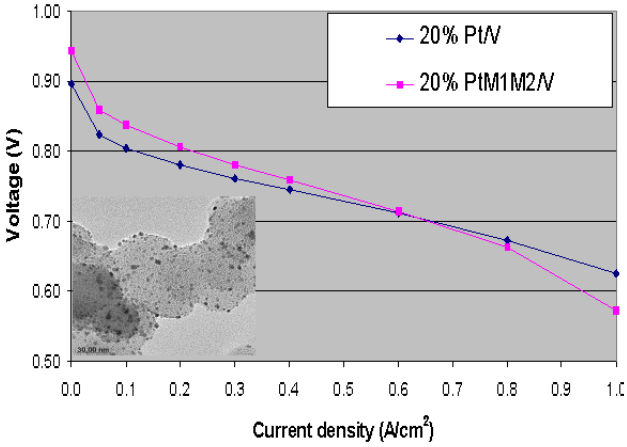

Figure 4. Polarization Curves for MEA with Total Loading of 0.13 mg Pt/cm^2 (Comparing performance of 20 wt.% PtM_1M_2 ternary alloy catalysts and 20 wt.% Pt/ Vulcan XC 72, test conditions described in the text; bottom left, TEM image of alloy catalyst.)

structural analysis of the ternary alloy electrocatalysts demonstrates excellent dispersion of the active phase (Figure 3).

MEA test conditions. Test MEAs (50 cm^2) were used for the evaluation, using Nafion 112 (DuPont) membranes. The MEAs were 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. H_2 and air (100% humidified) were used at 30 psig pressure on both the anode and cathode.

MEA structure development. The development of the electrode structure was focused on optimization of the electrode deposition method with Pt and Pt-alloy electrocatalysts that demonstrated best performance in the rapid half-cell screening. Figure 5 shows charts for the MEA performance in terms of current and power density and in g Pt/kW at 0.8 V for 50 wt.% Pt/C and 20 wt.% ternary alloy catalyst as a function of the total Pt loading in the MEA. For the 50 wt.% Pt/high surface area carbon electrocatalyst, the performance in terms of current density at 0.8 V for the whole range of Pt loadings (0.55 to 0.35 mg Pt/cm_2) is above 400 mA/cm^2, and it achieves 1 g Pt/kW for 0.35 mg Pt/cm^2 loading. The ternary alloy catalyst supported on Vulcan XC-72 demonstrates 300 mA/cm^2 at 0.8 V with 0.2 mg Pt/cm^2 total Pt loading and below 1 g Pt/kW. These results demonstrate significant improvement in the overall MEA performance compared to last year's benchmarked MEA performance of 2 g Pt/kW (over 100% improvement).

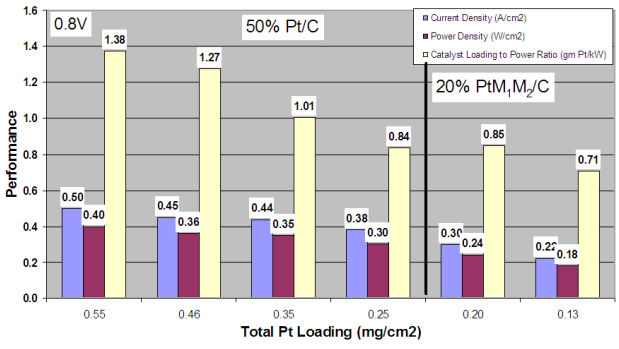

Figure 5. Summary of MEA Performance Characteristics

Modeling effort. During the past year, CFDRC developed models to address the impacts of pore size distribution and active phase placement within various pore sizes on the overall performance of the fuel cell. These models are based on detailed reaction-diffusion balance of species at various length scales and include such effects as Knudsen diffusion. The models were used for parametric studies involving variation of catalyst fractions within four different pore sizes of interest to Cabot SMP. The results clearly demonstrate the sensitivity of the MEA performance to the distribution of the active phase in various pore sizes and provide valuable guidance for modification of porosity of the electrocatalysts and electrode layer. CFDRC also performed several parametric studies to address the effects of global parameters such as temperature, pressure, relative humidity and gas stochiometries on cell performance. These studies showed good correlation to the experimentally observed trends and provided guidance on the optimization of fuel cell operating conditions and/or MEA structure.

Conclusions

During the second 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 designed and their assembly completed: Combinatorial Powder Synthesis System (Cabot SMP) and Rapid Ink Formulation and Electrode Deposition Equipment (DuPont Fuel Cells). 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. Most importantly, it was demonstrated that a combination of the best-performing ternary Pt alloy catalysts (Effort 1) and the best electrode layer structure (Effort 2) had an additive effect and delivered MEA performance of less than 1 g Pt/kW at 0.8 V, representing over 100% improvement over last year's benchmarked performance of 2 g Pt/kW (Figure 1). In addition, the synthesis of best-performing ternary Pt alloy catalyst was scaled to commercial powder production levels.

FY 2003 Publications/Presentations

1. P. Atanassova, D. Dericotte, P. Napolitano, R. Bhatia, J. Brewster, M. Hampden-Smith, C. Lundgren, L. Wang, S. Mazumder, Hydrogen, Fuel Cells and Infrastructure Technologies FY 2002 Progress Report, p.423

2. P. Napolitano, D. Dericotte, R. Bhatia, P. Atanassova, M. Hampden-Smith, T. Kodas, "Combinatorial Synthesis of Oxygen Reduction Electrocatalysts by Spray Pyrolysis", presentation, 2002 ECS Meeting, October 20-24, 2002, Salt Lake City, Utah, Meeting abstracts, p.729

3. P. Napolitano, D. Dericotte, B. Apodaca, R. Bhatia, P. Atanassova, M. Hampden-Smith, T. Kodas, "A New Focused, Scaleable Combinatorial Synthesis and Discovery Platform: Applications to Fuel Cell Electrocatalysts", presentation, 5th Annual International Symposium on Combinatorial Approaches for New Materials Discovery, February 10-21, 2003, San Jose, CA

4. M. Hampden-Smith, P. Atanassova, P. Atanassov, T. Kodas, "Manufacture of Electrocatalyst Powders by a Spray-based Production Platform", Handbook of Fuel Cells, 2003 John Wiley & Sons, Eds. W. Vielstich, H. Gasteiger, A. Lamm, Vol.3, p. 497