Development of High-Performance, Low-Pt Cathodes Containing New Catalysts and Layer Structure

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05/23/2005

Project ID #: FC19

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Overview

Timeline:
• Project Start Date: 9/2001
• Project End Date: 9/2005 (3/2006)
• Percent complete: 75 %

Budget:
• Project Total: $5.21 M
  DOE share: $4.17 M
  Contractor share: $1.04 M
• Funding Received in FY04: $1.2 M
• Funding for FY05: $1.0 M

Barriers addressed:
• Barrier O. Stack Material and Manufacturing Cost
• Barrier Q. Electrode Performance
• Barrier P. Durability

Technical targets for 2010:
• Precious metal loading:
  0.1 mg Pt/cm²; 0.2 g Pt/kW
• Durability - 5000 h

Partners: DuPont Fuel Cells
CFDRC
GM – Testing criteria
Project Objectives

Overall Project Objectives

Develop and apply high throughput powder synthesis platform based on spray pyrolysis for discovery of high-performance low-Pt cathode electrocatalysts for PEM automotive fuel cells, target precious metal loading – 0.6 gPt/kW for FY05

FY 04/05 Objectives

- Perform high throughput synthesis of ternary Pt alloy compositions in a discovery mode, test electrochemical performance, rank
- Test best compositions in MEAs and optimize Pt alloy based cathode structure.
- Extensively characterize Pt alloy composition and microstructure.
- Initiate long term stability study for alloy electrocatalysts.
- Develop rapid GDE fabrication equipment – DuPont Fuel Cells.
- Evaluate rapid MEA testing approach – NuVant’s device.
Technical Approach

- Unique high throughput platform for supported electrocatalyst in place (synthesis and screening)
- CSMP: build high throughput powder synthesis platform and screen large variety of compositions for oxygen reduction electrocatalysts: 75-120 samples per week
- DuPont Fuel Cells: use rapid screening method for electrocatalysts and develop rapid electrode fabrication method: >75-150 electrodes per week
- CSMP: characterize structure, scale up best performing alloy electrocatalyst, test and optimize electrode structure in hydrogen-air MEAs
- CSMP: Deliver electrocatalysts and test MEAs to stack manufacturers

Combinatorial catalyst synthesis

Catalyst screening

Select best candidate from primary screen

Produce at larger scale

MEA testing and optimization

100 mg

1000’s kg

Limit of minimum acceptable performance

CURRENT DENSITY, A/cm²

CELL VOLTAGE, V

Current Density: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0

Cell Voltage: 10, 15, 20, 25, 30, 35, 40, 45

Combinatorial catalyst synthesis

Catalyst screening

Select best candidate from primary screen

Produce at larger scale

MEA testing and optimization
FY04/FY05 Accomplishments: High Throughput Discovery of Advanced Cathode Catalysts

- Completed synthesis and screening of 15 ternary Pt alloy libraries, 25 - 75 samples per library
- Selection was based on fundamental properties of elements as well as available modeling and theoretical data for binary systems.
- Mass activity normalized by Pt amount of best Pt alloy compositions show 70-100% improvement compared to that of pure Pt electrocatalyst in the liquid electrolyte rapid testing performed by DuPont Fuel Cells.
FY04/FY05 Accomplishments:
Advanced Cathode Catalysts Tested in MEA Configuration

- Most active compositions, higher than the go-no-go criteria of >70 % improvement, identified by the rapid screening testing were tested in MEA configuration.
- Mass activity normalized by Pt amount of best Pt alloy compositions show up to 80% improvement compared to that of pure Pt electrocatalyst at 0.8 V in MEA configuration.

MEA test conditions, cathode: 0.2 mg M/cm², anode: 0.05 mgPt/cm², 80 C, 1.5 H₂/2.5 air at 1A/cm², 100% RH, 30 psig, 10 min/point
FY04/FY05 Accomplishments: Performance Improvement Through Acid Leaching

- Leaching was performed in 0.5 M sulfuric acid at 85°C.
- No significant morphology and crystalline phase change.
- Leaching improves fuel cell performance of Pt alloy catalysts.
FY04/FY05 Accomplishments:
Electrocatalyst Characterization – Composition and Uniformity by TEM and Field Emission X-Ray Analysis

µm scale

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<th></th>
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<th>B (%)</th>
<th>Pt (%)</th>
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<td>28</td>
<td>43</td>
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<tr>
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sub-µm scale

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</tr>
<tr>
<td>B</td>
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<tr>
<td>C</td>
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<tr>
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nm scale

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<tr>
<td>Expected</td>
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<td>25</td>
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FY04/FY05 Accomplishments: Electrode Layer Structure Development with 20 wt.% Pt Alloy Catalyst

MEA loadings: 0.2 mg Pt/cm² total loading (Cathode: 0.15 mg Pt/cm²; Anode: 0.05 mg Pt/cm²)

- Design of Experiments involving 3 variables in MEA preparation performed
- The response variables were the single cell current densities at 0.8V and 0.7V.
- Goal: to maximize the value of the response function.

Test conditions:
- Single MEA 50 cm² test cell, Nafion 112
- Cell temperature 80°C
- Anode/cathode constant flow rates = 510/2060 mL/min H₂/air (1.5H₂/ 2.5 air stoich at 1 A/cm²)
- 30 psig pressure on both anode and cathode
- 100% humidification of gases, 80°C dew points
- Galvanostatic mode, 10 min per point
FY04/FY05 Accomplishments:
Long-Term MEA Stability Study

- Evaluation of Pt alloy/C long term stability in progress:
  decay rates ~ 30 - 60µV/h in a constant current mode.

- Recent DOE testing protocol implementation in progress.

- Long-term stability study with periodic diagnostic testing is on-going.
FY 04/05 Accomplishments:
Rapid Screening and GDE Fabrication Equipment

◆ Continue rapid screening of electrocatalysts - over 500 samples tested
◆ Complete rapid GDE fabrication equipment employing robot
◆ Procedure:
  ■ Up to 20 catalysts are pre-weighed into a vials (6 ml)
  ■ Catalyst, solvent and ionomer mixture prepared in the vial
  ■ Ink deposited onto substrate
◆ Capability:
  ■ Fabricate catalyst electrodes for half-cell testing, can handle 20 different catalysts to make 40 electrodes at a single run within two hours.
  ■ Capacity exceeds requirement of 75-150 catalysts per week.
  ■ Excellent reproducibility for ink preparation and electrode coating (stdev/Ave)% <10%.
  ■ Fabricate 20 different catalysts into twenty 25 cm² GDEs within three hours.
FY 04/05 Accomplishments:
GDE Fabrication Equipment – Coating Uniformity

◆ Achieve acceptable GDE coating uniformity:
  - Demonstrate process uniformity at 25 cm² – XRF tests
  - Demonstrate process uniformity at 1 cm²

<table>
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<th>mg/cm²</th>
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<tr>
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<td>S3</td>
<td>0.2457</td>
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Target loading 0.235 mg Pt/cm²
25cm² GDE, 20% Pt/C

Target | 0.235
Average | 0.2419
STD | 0.0077
STD/Average | 3.20%
FY 04/05 Accomplishments:
MEA Performance of GDEs evaluated at CSMP

- Three identical GDEs made by DuPont Robotic Equipment (cathode: 0.235 mg/cm², anode: 0.05 mg/cm²)
- GDE-based MEA performance identical and closely matching CCM-based MEA performance
- Preparing equipment transfer to CSMP.

![Graph showing voltage versus current density for samples A, B, and C.](attachment://graph.png)
FY04/FY05 Accomplishments:
Rapid Testing in MEA Configuration

• Evaluate NuVant Systems Rapid Testing Device for ability to rank oxygen reduction catalysts in MEA configuration
  – 25 mini fuel cells (1 cm²) referenced against the same counter electrode.
  – Three sets of catalyst arrays submitted by CSMP.
  – Testing was done at cell temperatures of 50°C, 60°C, 70°C, Reference side - H₂, Array side - Air/Oxygen.

• The purpose of these experiments was to evaluate the NuVant’s testing device for:
  – Row or column effects, standard deviations for identical catalysts.
    • Row and column effects not observed, < 10% STD/average at potentials of interest.
  – Ability to rank the catalyst with different activities.
    • Device can reasonably rank catalysts for their ORR activity.
  – Integration with Rapid GDE equipment feasible.
Responses to Previous Year Comments

- **Comment:** “Development of rapid MEA screening system and combination with rapid-throughput catalyst preparation will be a significant accomplishment”
  - Rapid-throughput catalyst preparation, GDE fabrication equipment have been completed and performed as expected. Integration with rapid testing MEA device planned.

- **Comment:** “No national labs or universities were mentioned”, “Increase effort in characterizing what is synthesized”
  - National Lab contacted for further characterization and validation of performance for selected alloy catalysts.

- **Comment:** “Need to investigate durability of catalyst alloys”
  - Testing started, development of accelerated methods planned.

- **Comments:** “Role of DuPont unclear.”
  - DuPont designed and completed rapid ink formulation and electrode deposition device, which has been exclusively used for screening the electrocatalyst compositions.
  - DuPont developed rapid GDE fabrication approach that can be utilized with rapid MEA testing equipment, and demonstrated process uniformity at 25 cm².

- **Comment:** “Not clear how general spray pyrolysis method is used for catalyst preparation”
Summary of Accomplishments and Future Work

• Major Accomplishments:
  • Single cell performance of 0.8 g Pt/kW at 0.8 V and 0.5 gPt/kW at 0.75 V demonstrated for 20 wt.% Pt/alloy electrocatalyst.
  • High throughput screening in MEA configuration feasibility demonstrated, milestone # 6 met.

• Future Work:
  • Optimize and scale up best performing Pt-alloy compositions identified.
  • Testing in stack – CSMP to deliver electrocatalysts or test MEAs.
  • Transfer and integrate rapid DuPont GDE fabrication equipment with NuVant rapid MEA testing device at CSMP.
  • Execute a detailed plan to study long-term stability of Pt alloy electrocatalyst.
  • DuPont Fuel Cells:
    • Develop an accelerated fuel cell test method to screen MEAs for automotive applications. The objectives of this test are to include acceleration of the primary deactivation modes: Pt sintering, Pt dissolution, and carbon corrosion.
Acknowledgements

- DOE Hydrogen Program, Award DE-FC0402AL67620, Topic 1A1
- DOE Program Managers: Amy Manheim, Walter Podolski, Valri Lightner
- CSMP, DuPont Fuel Cells and CFDRC for cost share funding
- DuPont Fuel Cells: Lin Wang, Keith Tomey, Jung Chae, Jo-Ann Schwartz, Dennis Kountz
Publications and Presentations


The most significant hydrogen hazard associated with this project is use of H₂ in Fuel Cell Testing

- Hydrogen leaks in gas lines, test stations.
- Hydrogen leaks due to poor sealing of MEA.
Hydrogen Safety

Our approach to deal with this hazard is:

- **Minimize Potential Exposure**
  - Gas manifold room to minimize number of cylinders.
  - Flow restrictors at cylinder outlet, sized to allow maximum of 50% H₂ LEL.

- **Safe Shutdown**
  - Manual and PLC-based automatic shutdown systems.
  - Shutdown sequence linked to gas detection, test station stop, lab emergency stop, ventilation flow switch.
    - Automatic gas cutoff at cylinders.
    - Elimination of static H₂ through automatic N₂ purging of test stations and common vent stack.
    - Multi-hydrogen leak detectors.

- **Pre-Startup Safety Review**
  - Formal signoff on proper implementation of design.
  - Operation of emergency shutdown systems, leak testing, electrical grounding, labeling.