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

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CABOT

Project ID #: FC19

This presentation does not contain any proprietary or confidential information

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/cm^2; 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

Combinatorial catalyst synthesis

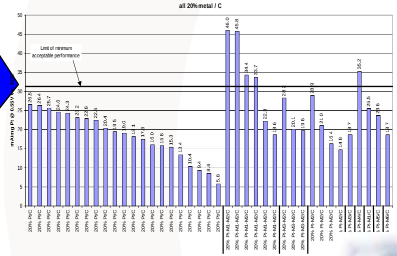
Catalyst screening

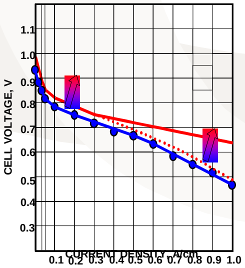
Select best candidate from primary screen

Produce at larger scale

MEA testing and optimization

100 mg



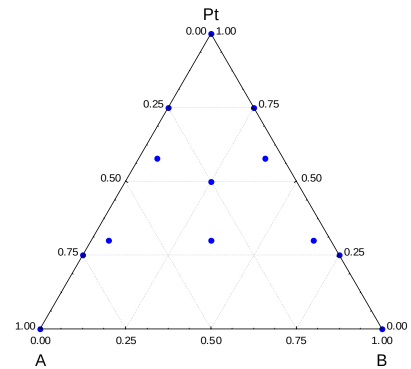


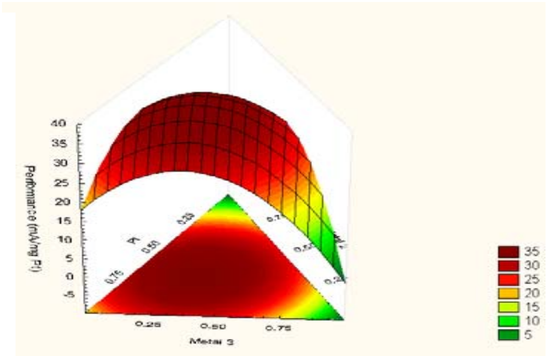
1000's kg

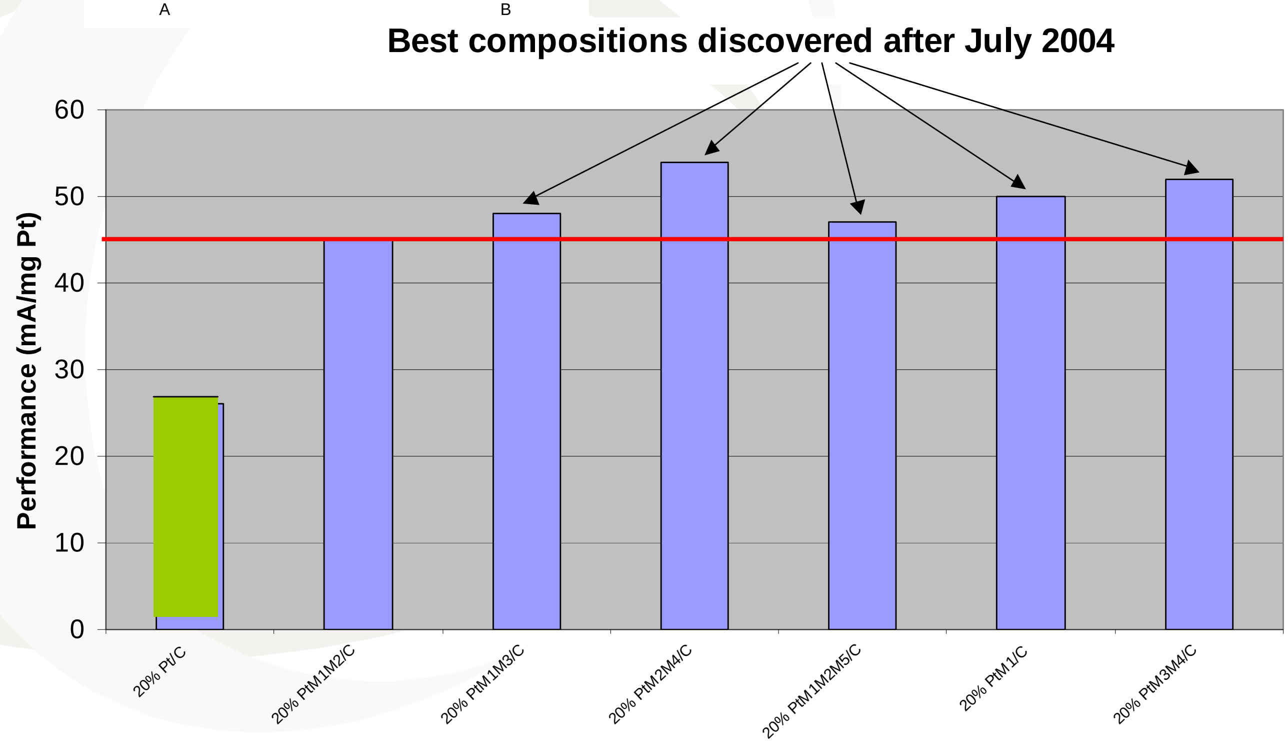
- **Unique high throughput platform for supported electrocatalyst in place (synthesis and screening)**
- **CSMP: build high throughput powder synthesis platform and screen large variety of compositions for oxygen reduction electrocatalysts: 75-120 samples per week**
- **DuPont Fuel Cells: use rapid screening 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**

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.



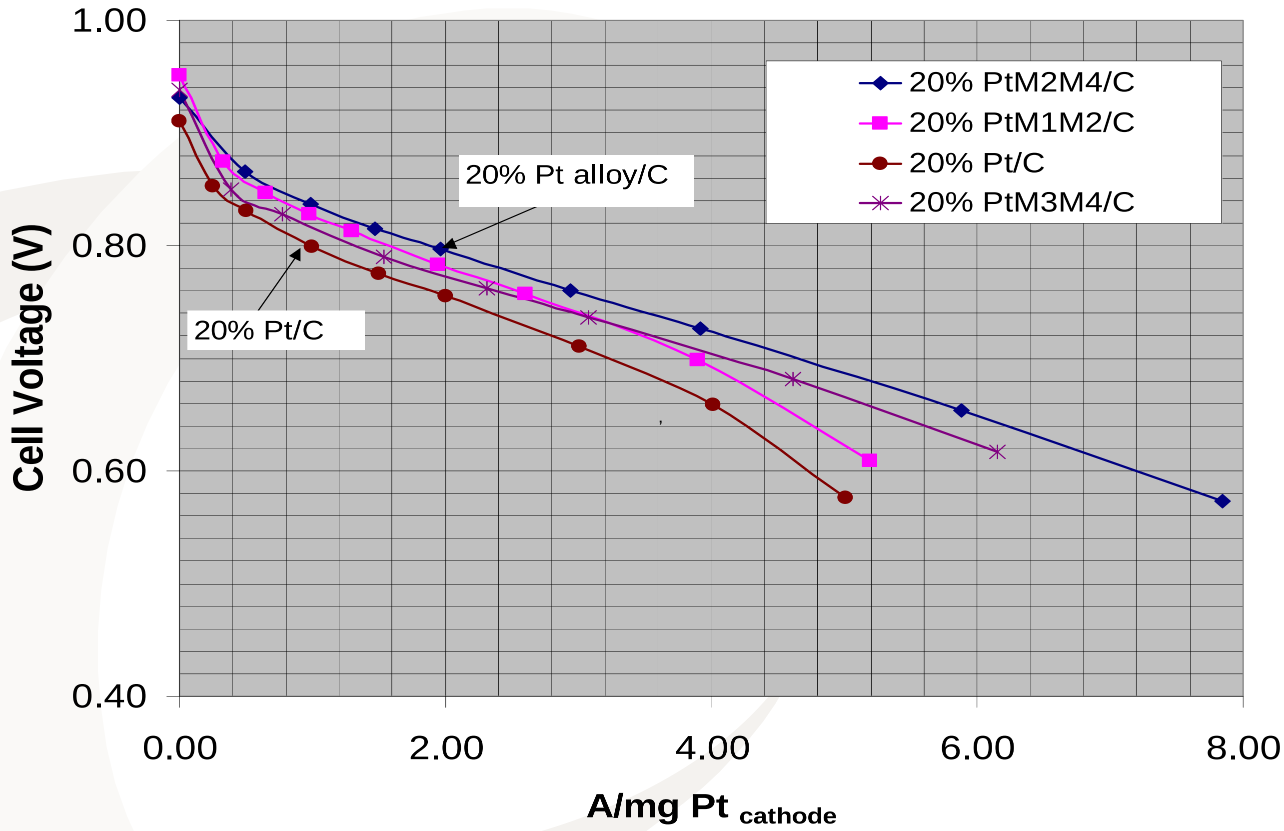




FY04/FY05 Accomplishments: Advanced Cathode Catalysts Tested in MEA Configuration

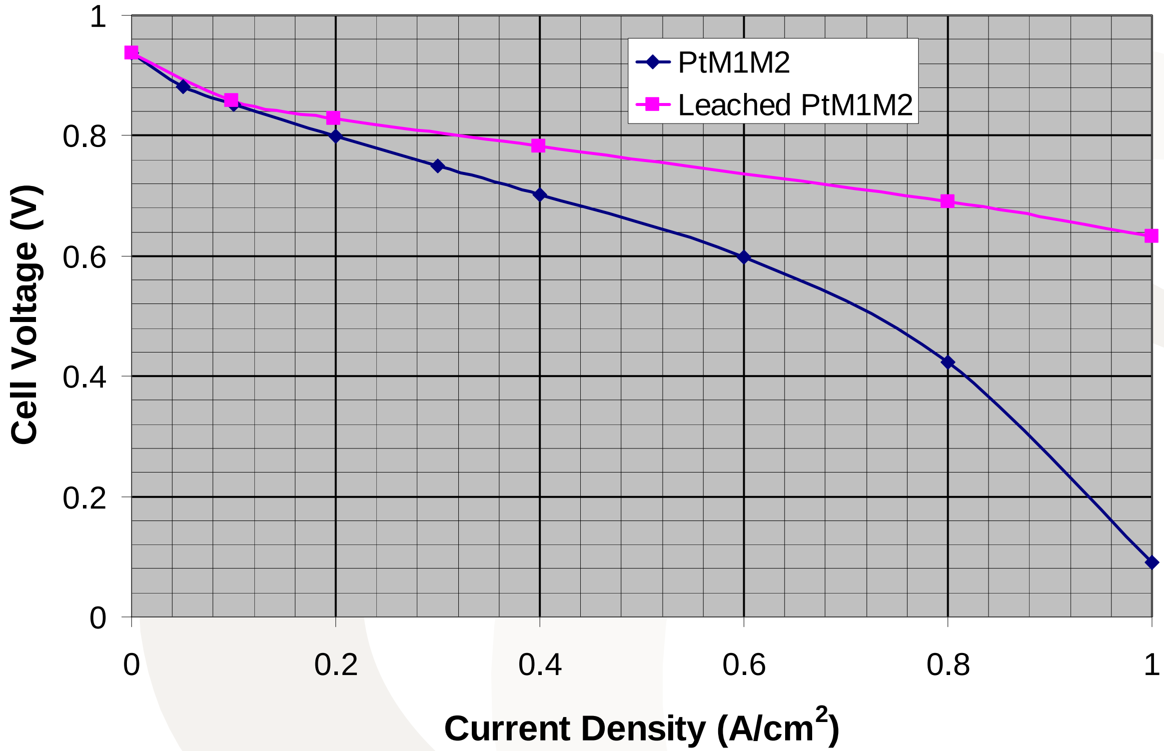
- Most active compositions, higher than the go-no-go criteria of >70 % improvement, identified by the rapid screening testing were tested in MEA configuration.

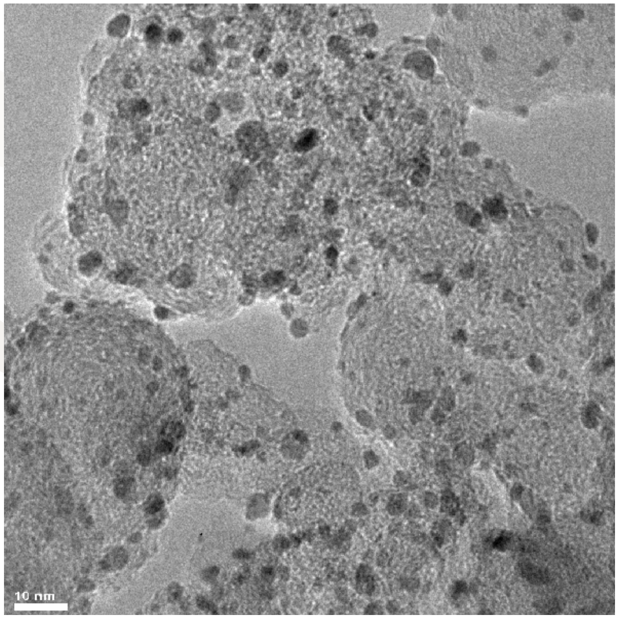
- Mass activity normalized by Pt amount of best Pt alloy compositions show up to 80% improvement compared to that of pure Pt electrocatalyst at 0.8 V in MEA configuration.



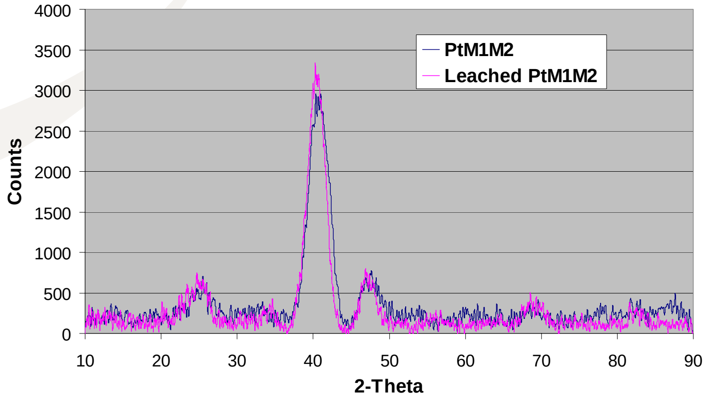
MEA test conditions, cathode: 0.2 mg M/cm^2, anode: 0.05 mgPt/cm^2
80 C, 1.5 H_2/2.5 air at 1A/cm^2, 100% RH, 30 psig, 10 min/point

FY04/FY05 Accomplishments: Performance Improvement Through Acid Leaching



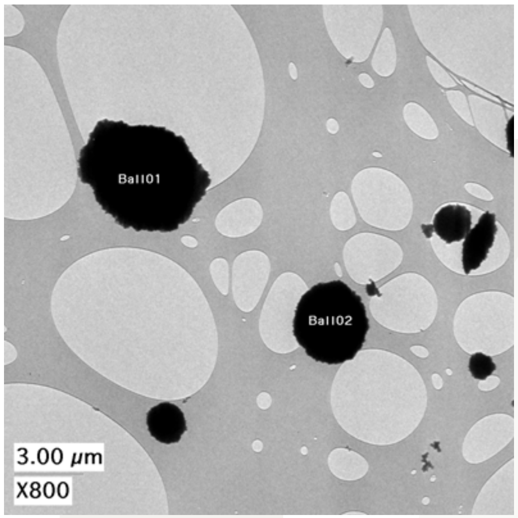


- Leaching was preformed in 0.5 M sulfuric acid at 85°C.
- No significant morphology and crystalline phase change.
- Leaching improves fuel cell performance of Pt alloy catalysts.

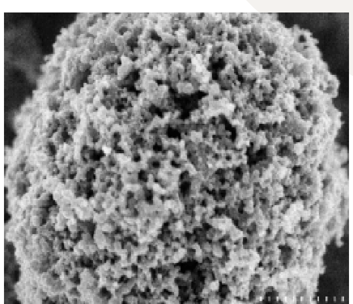


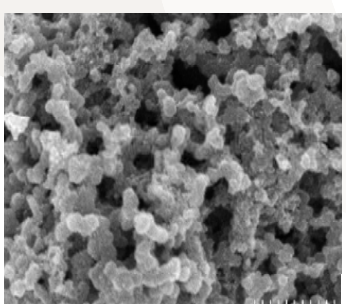
FY04/FY05 Accomplishments:
Electrocatalyst Characterization – Composition and Uniformity by TEM and Field Emission X-Ray Analysis

µm scale

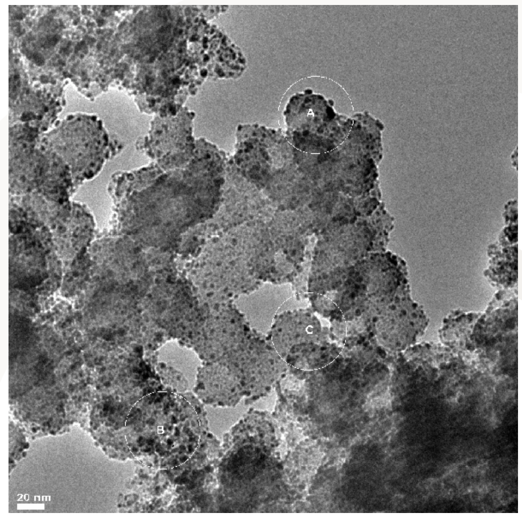


	A (%)	B (%)	Pt (%)
Ball02	29	28	43
Ball01	30	28	42
Expected	25	25	50



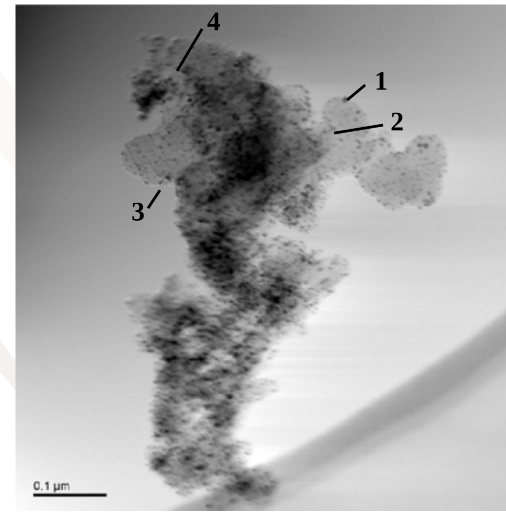


sub-µm scale



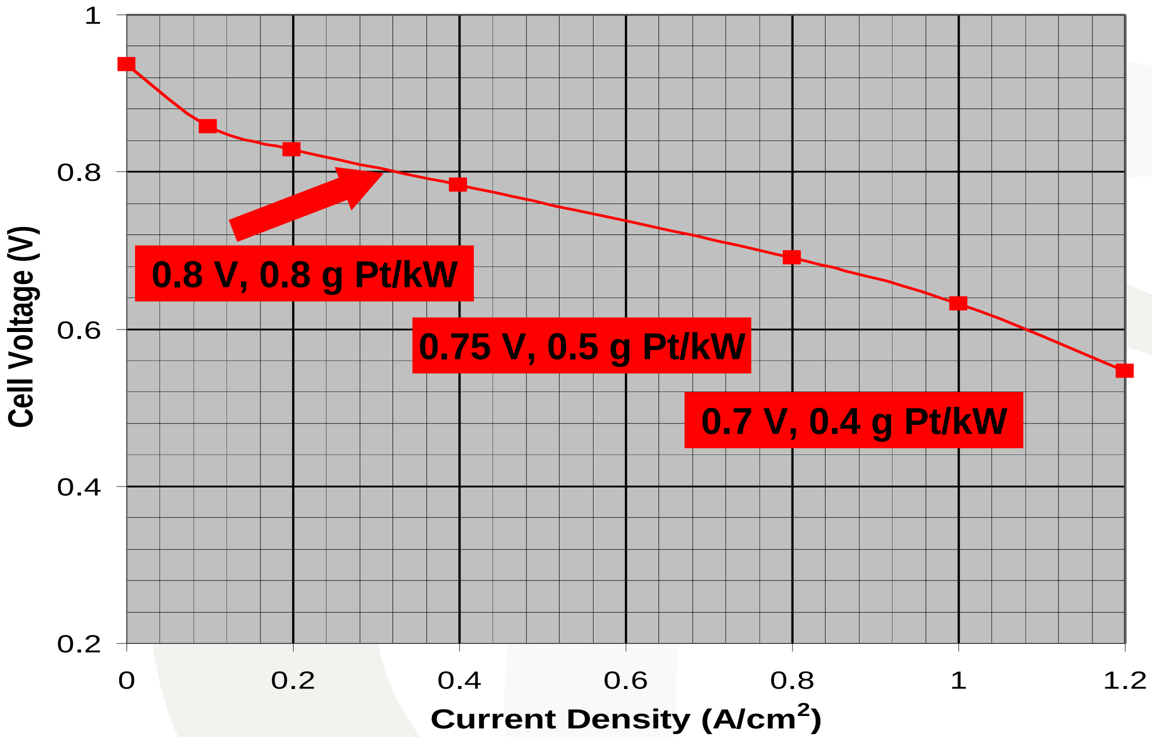
	A(%)	B (%)	Pt (%)
A	33	23	44
B	29	25	46
C	30	27	43
Whole area	31	20	49
Expected	25	25	50

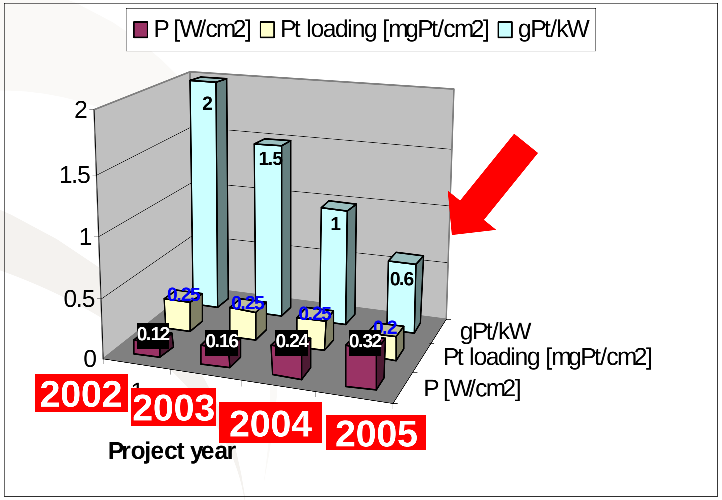
nm scale



	A (%)	B (%)	Pt (%)
1	22	22	56
2	17	11	72
3	16	11	73
4	22	18	60
Expected	25	25	50

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)

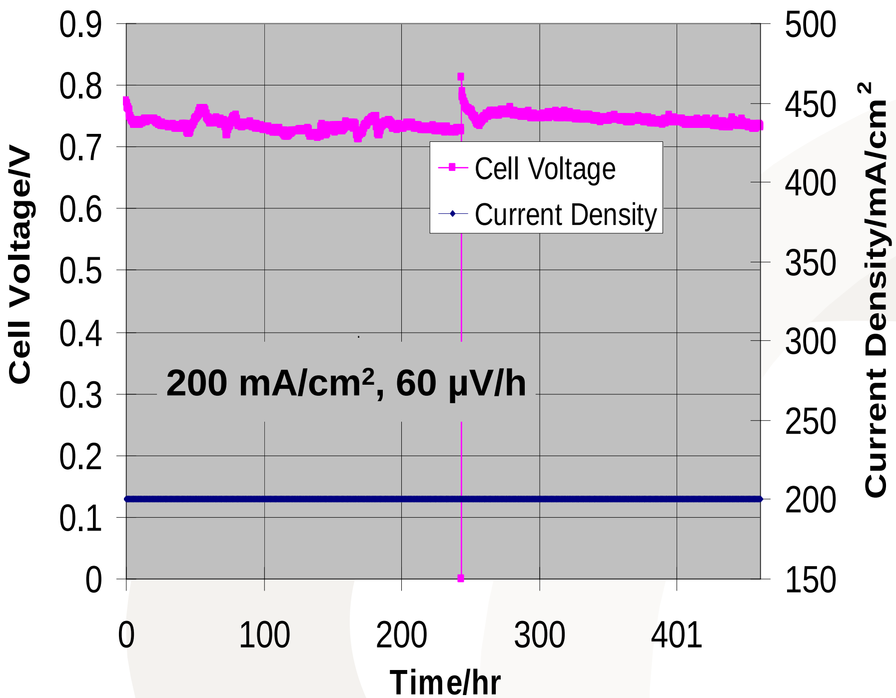
- **Design of Experiments involving 3 variables in MEA preparation performed**
- **The response variables were the single cell current densities at 0.8V and 0.7V.**
- **Goal: to maximize the value of the response function.**

Test conditions:

- **Single MEA 50 cm² test cell, Nafion 112**
- **Cell temperature 80C**
- **Anode/cathode constant flow rates = 510/2060 mL/min H_2/air (1.5H_2/ 2.5 air stoich at 1 A/cm²)**
- **30 psig pressure on both anode and cathode**
- **100% humidification of gases, 80C dew points**
- **Galvanostatic mode, 10 min per point**

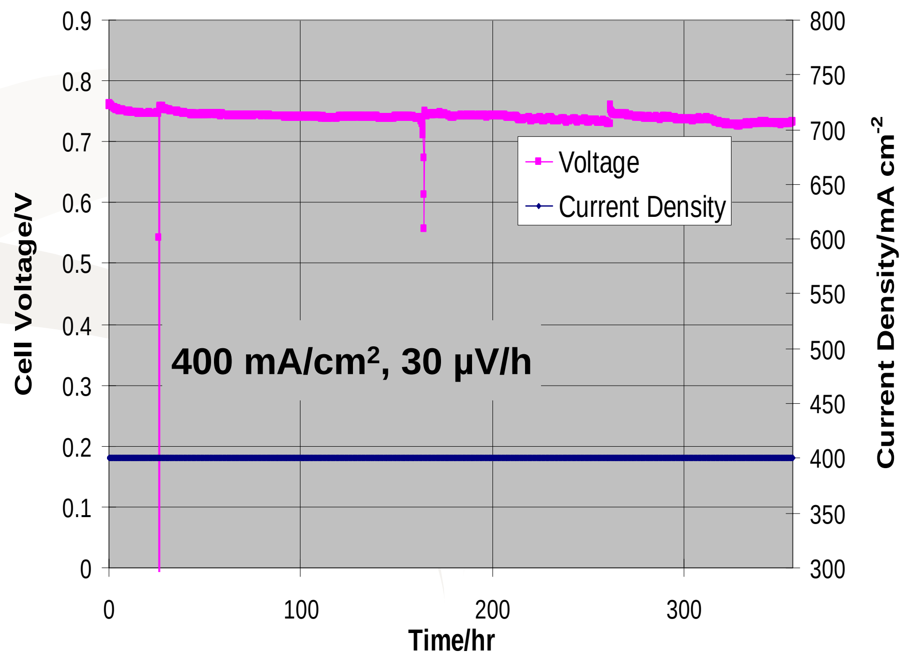
FY04/FY05 Accomplishments:

Long-Term MEA Stability Study



Cathode: **20% Pt Alloy/C**, 0.15 mg Pt/cm^2

Anode: 10% Pt/C, 0.05 mg Pt/cm^2



Cathode: **20% Pt Alloy/C**, 0.20 mg Pt/cm^2

Anode: 10% Pt/C, 0.05 mg Pt/cm^2

- Evaluation of Pt alloy/C long term stability in progress:

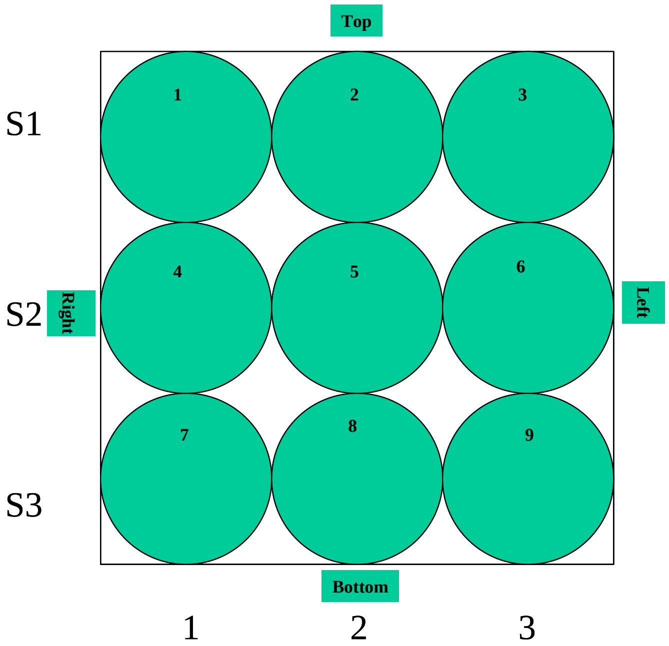
  decay rates ~ 30 - 60μV/h in a constant current mode.
- Recent DOE testing protocol implementation in progress.
- Long-term stability study with periodic diagnostic testing is on-going.

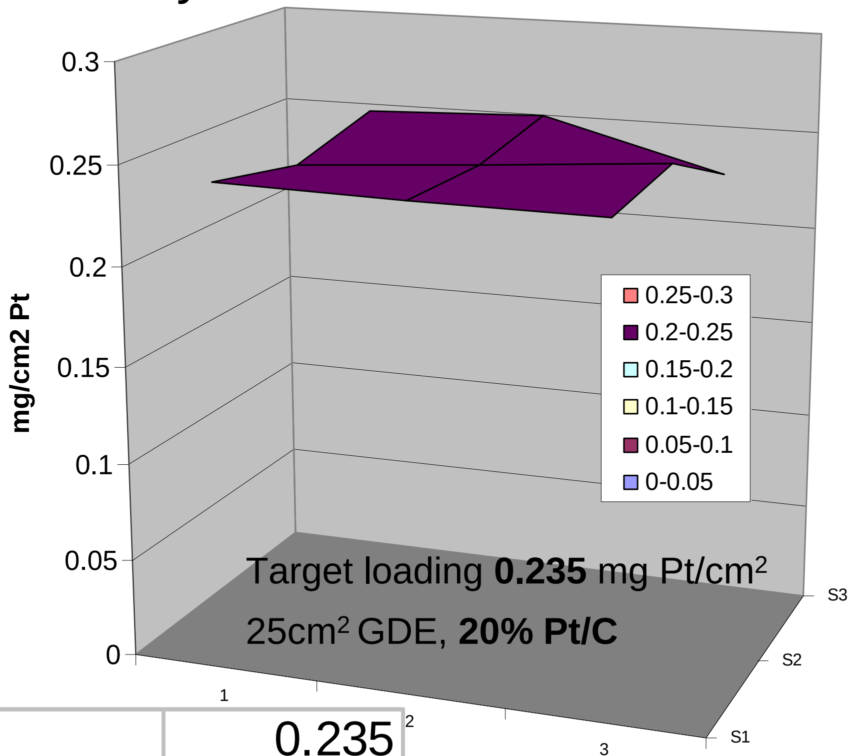
FY 04/05 Accomplishments:
Rapid Screening and GDE Fabrication Equipment

- **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 cm^2 GDEs within three hours.

FY 04/05 Accomplishments:
GDE Fabrication Equipment – Coating Uniformity

- **Achieve acceptable GDE coating uniformity:**
  - Demonstrate process uniformity at 25 cm^2 – XRF tests
  - Demonstrate process uniformity at 1 cm^2



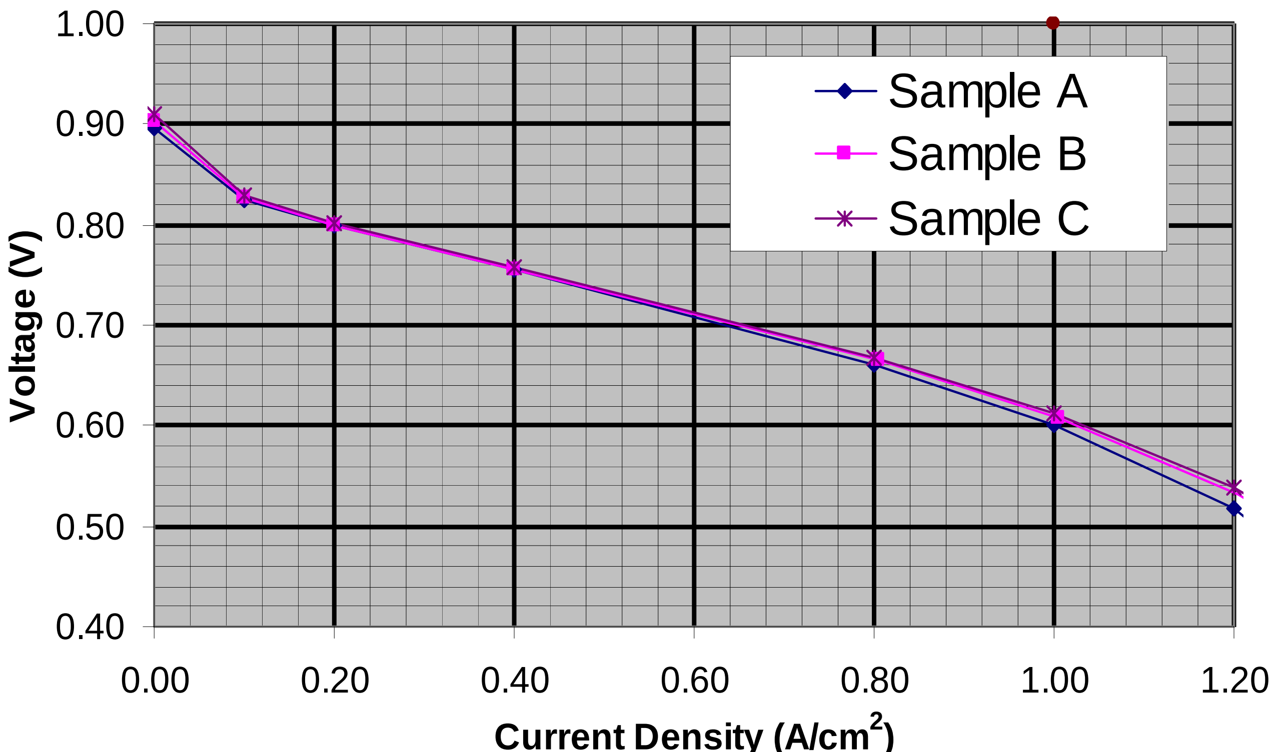


mg/cm^2	1	2	3
S1	0.2453	0.2432	0.2426
S2	0.2347	0.2412	0.2492
S3	0.2457	0.2499	0.2253

Target	0.235
Average	0.2419
STD	0.0077
STD/Average	3.20%

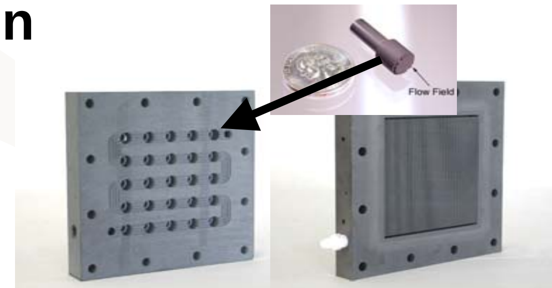
FY 04/05 Accomplishments:
MEA Performance of GDEs evaluated at CSMP

- **Three identical GDEs made by DuPont Robotic Equipment (cathode:0.235 mg/cm^2, anode: 0.05 mg/cm^2)**
- **GDE-based MEA performance identical and closely matching CCM-based MEA performance**
- **Preparing equipment transfer to CSMP.**



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 cm^2) 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 - H_2, 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 cm^2.***
- ***Comment:* "Not clear how general spray pyrolysis method is used for catalyst preparation"**
  - ***Mark Hampden-Smith et all,"Manufacture of Electrocatalyst Powders by a Spray-Based production platform", in Handbook of Fuel Cells: Fundamentals Technology and Applications, Wiley Ltd., 2003, Volume 4, Part 2, pg. 497 – 508.***

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
- The whole CSMP team and especially:

  Yvette Herrera, Victoria Gonzales, Leonard Perez, Jim Brewster, Jenny Plakio, Tomas Wood, Bryan Apodaca, Henry Romero, Roya Cone
- DuPont Fuel Cells: Lin Wang, Keith Tomey, Jung Chae, Jo-Ann Schwartz, Dennis Kountz

CSMP's Facility in Albuquerque

Publications and Presentations

1. 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

2. Yipeng Sun, Gordon Rice, Paolina Atanassova, “High Throughput Synthesis, Performance and Stability of Electrocatalysts for Hydrogen-Air Fuel Cells”, Fuel Cell Seminar, Nov. 2-5, 2004, San Antonio, TX.

Hydrogen Safety

The most significant hydrogen hazard associated with this project is use of H_2 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% H_2 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 H_2 through automatic N_2 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.