

# 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<sup>2</sup>; 0.2 g Pt/kW**
- **Durability - 5000 h**

## Partners: DuPont Fuel Cells

**CFDRC**

**GM – Testing criteria**

# Project Objectives

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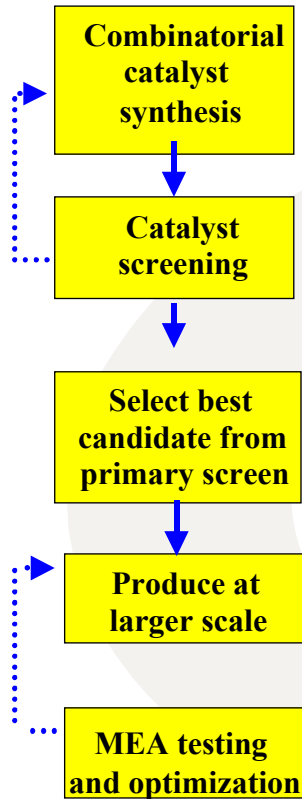
## ■ Overall Project Objectives

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

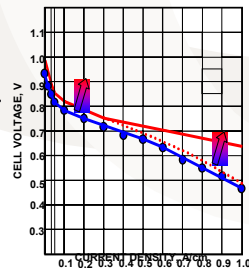
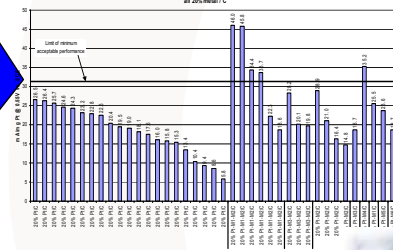
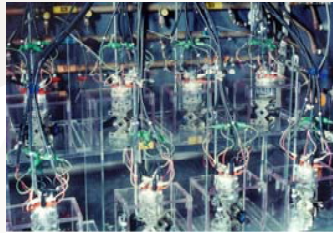
## ■ FY 04/05 Objectives

- 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



**100 mg**



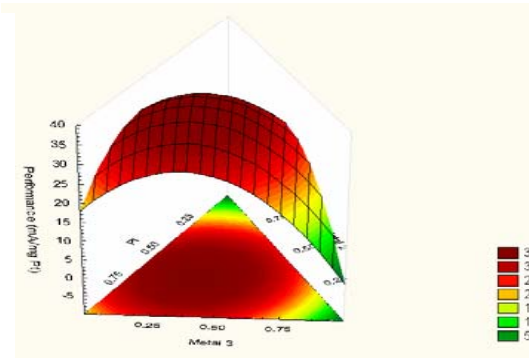
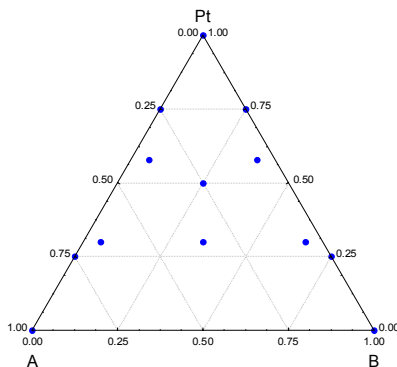
**1000's kg**



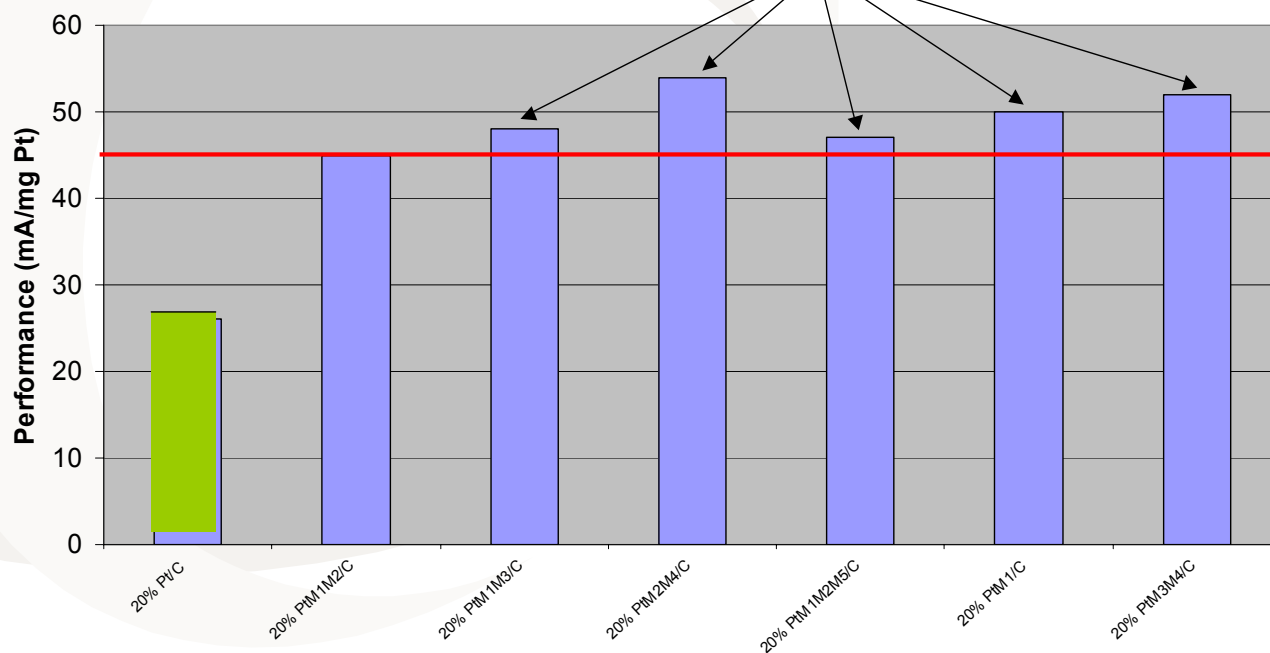
- **Unique high throughput platform for supported electrocatalyst in place (synthesis and screening)**
- **CSMP:** build high throughput powder synthesis platform and screen large variety of compositions for oxygen reduction electrocatalysts: 75-120 samples per week
- **DuPont Fuel Cells:** use rapid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

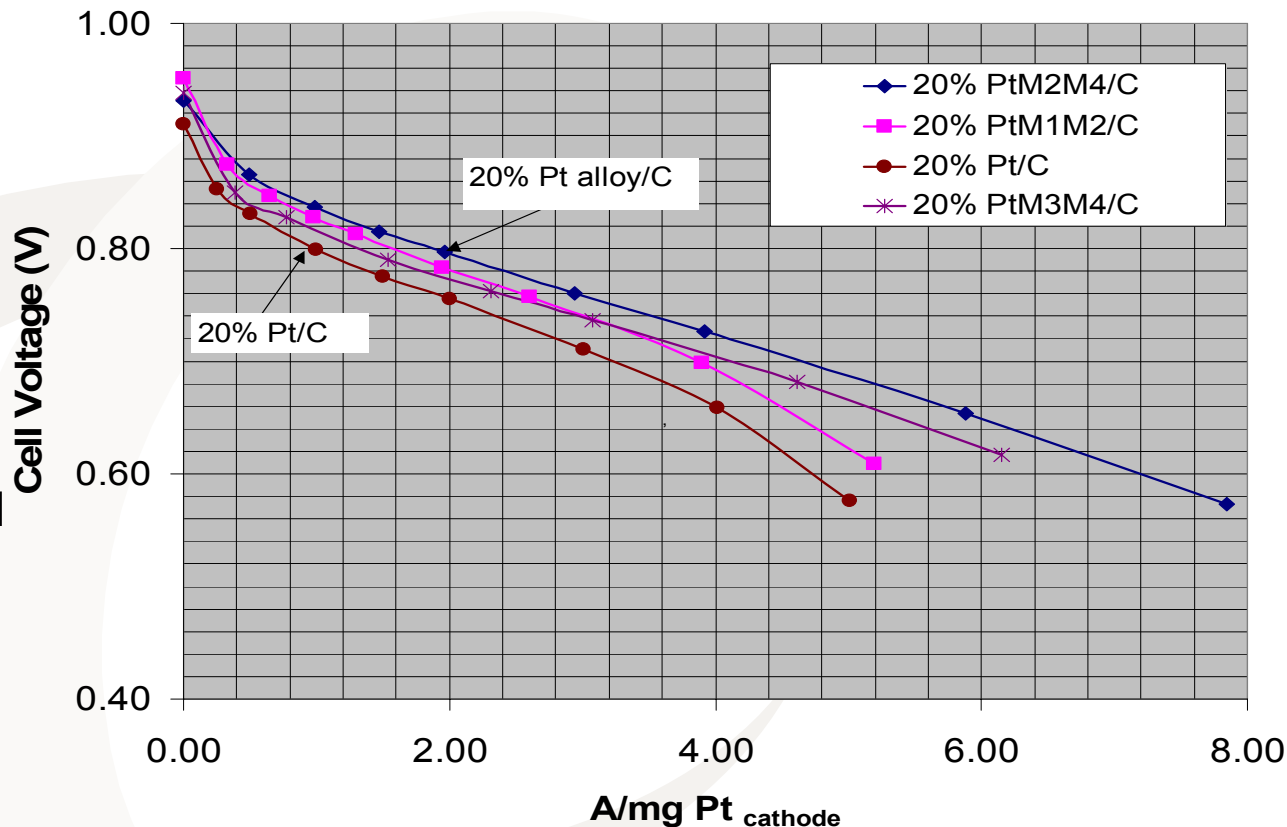


Best compositions discovered after July 2004



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

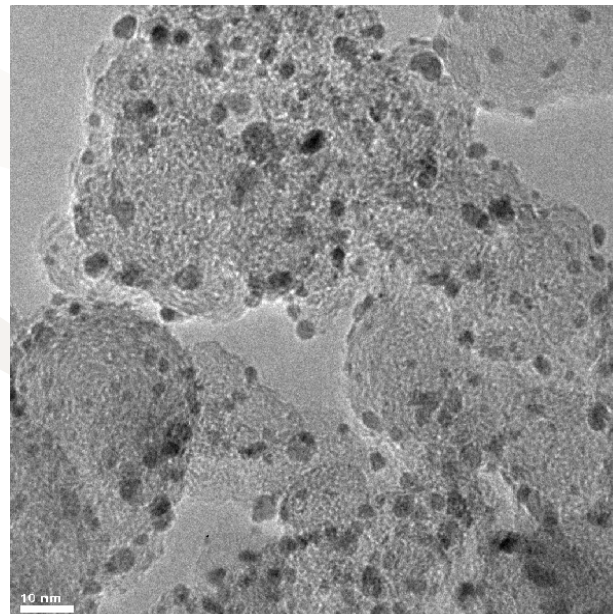
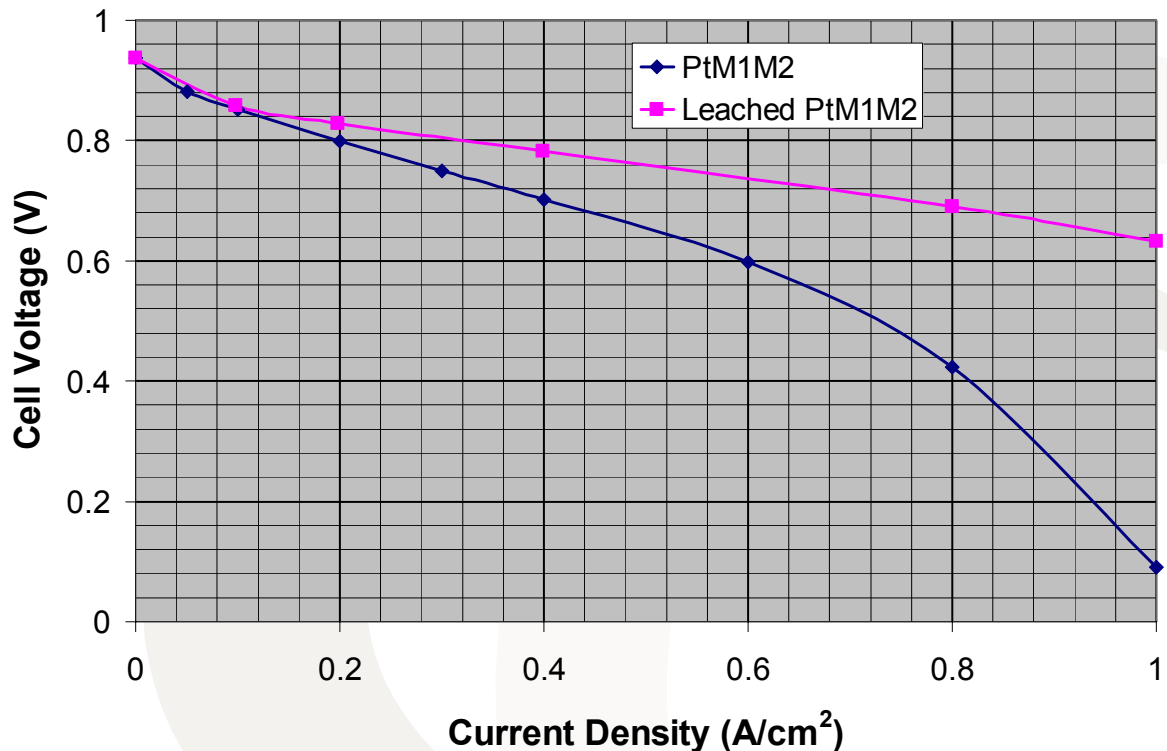
- Most active compositions, higher than the go-no-go criteria of >70 % improvement, identified by the rapid screening testing were tested in MEA configuration.
- Mass activity normalized by Pt amount of best Pt alloy compositions show up to **80% improvement** compared to that of pure Pt electrocatalyst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



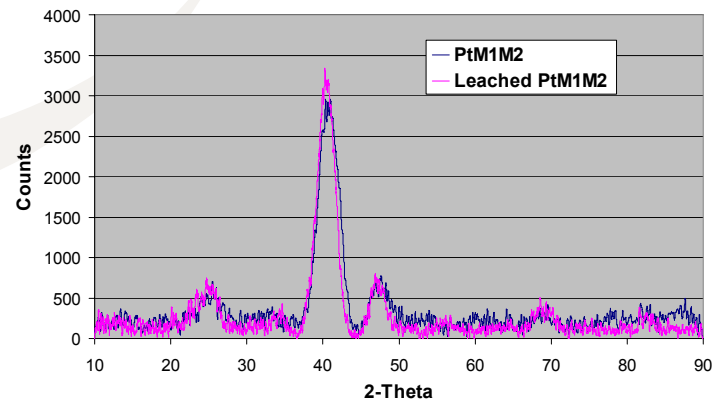
MEA test conditions, cathode: 0.2 mg M/cm<sup>2</sup>, anode: 0.05 mgPt/cm<sup>2</sup>  
80 C, 1.5 H<sub>2</sub>/2.5 air at 1A/cm<sup>2</sup>, 100% RH, 30 psig, 10 min/point



# FY04/FY05 Accomplishments: Performance Improvement Through Acid Leaching

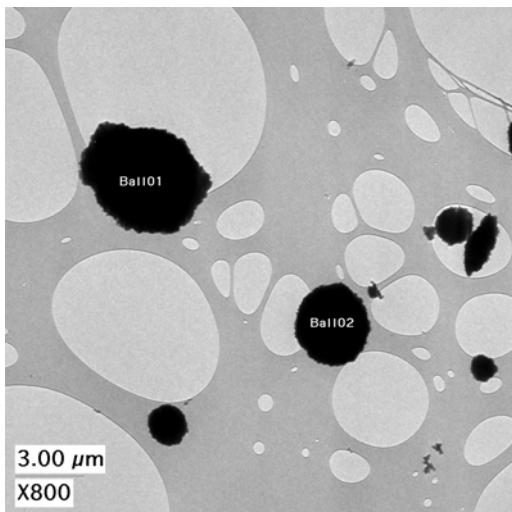


- Leaching was performed in 0.5 M sulfuric acid at 85°C.
- No significant morphology and crystalline phase change.
- Leaching improves fuel cell performance of Pt alloy catalysts.



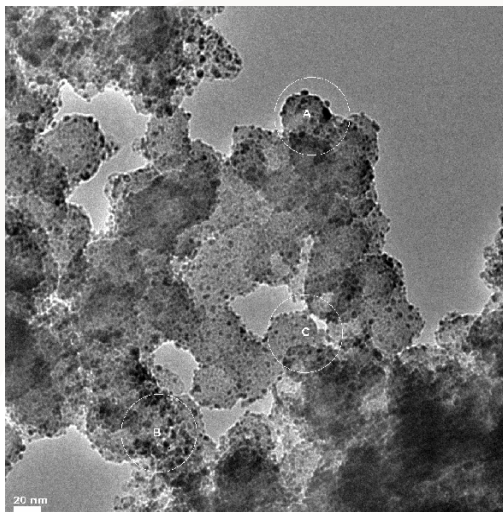
# FY04/FY05 Accomplishments: Electrocatalyst Characterization – Composition and Uniformity by TEM and Field Emission X-Ray Analysis

**μm scale**



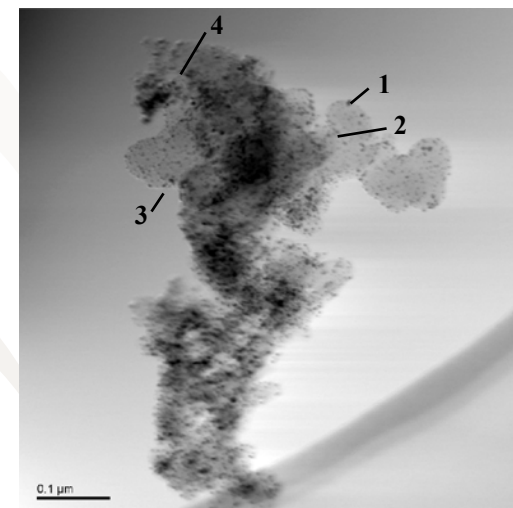
	A (%)	B (%)	Pt (%)
Ball02	29	28	43
Ball01	30	28	42
Expected	25	25	50

**sub-μm scale**

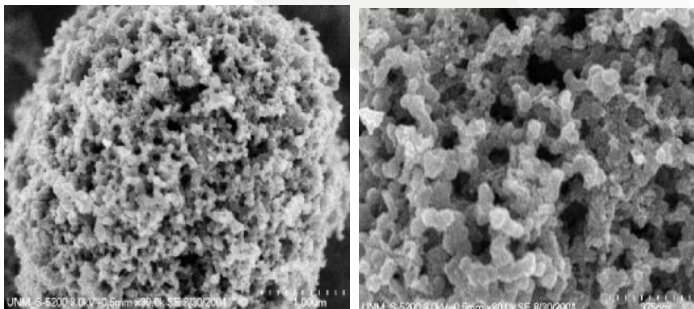


	A (%)	B (%)	Pt (%)
A	33	23	44
B	29	25	46
C	30	27	43
Whole area	31	20	49
Expected	25	25	50

**nm scale**

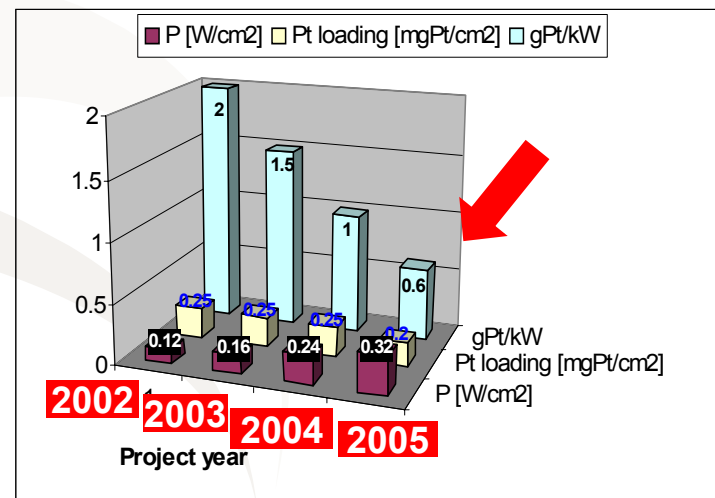
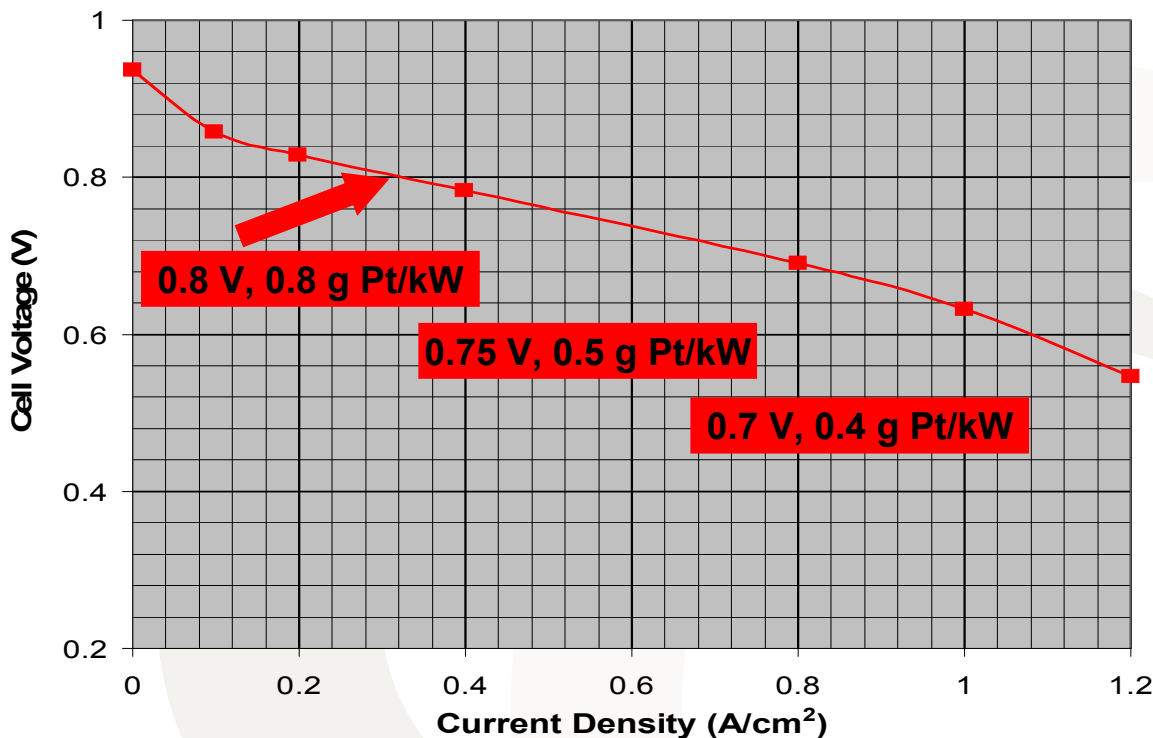


	A (%)	B (%)	Pt (%)
1	22	22	56
2	17	11	72
3	16	11	73
4	22	18	60
Expected	25	25	50





# 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)**

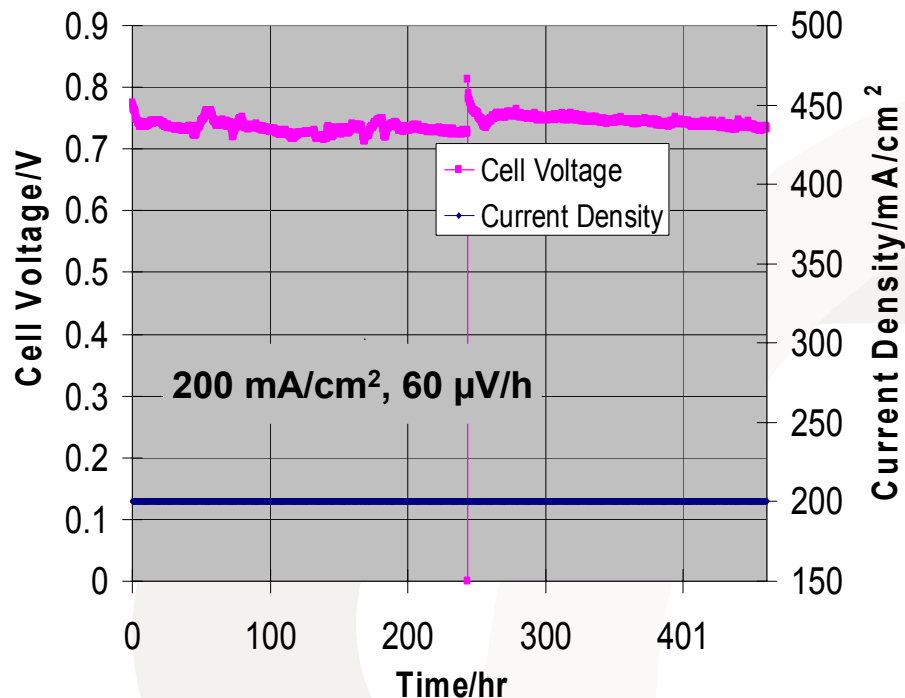
- Design of Experiments involving 3 variables in MEA preparation performed
- The response variables were the single cell current densities at 0.8V and 0.7V.
- Goal: to maximize the value of the response function.

## Test conditions:

- Single MEA 50 cm² test cell, Nafion 112
- Cell temperature 80C
- Anode/cathode constant flow rates = 510/2060 mL/min H<sub>2</sub>/air (1.5H<sub>2</sub>/ 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

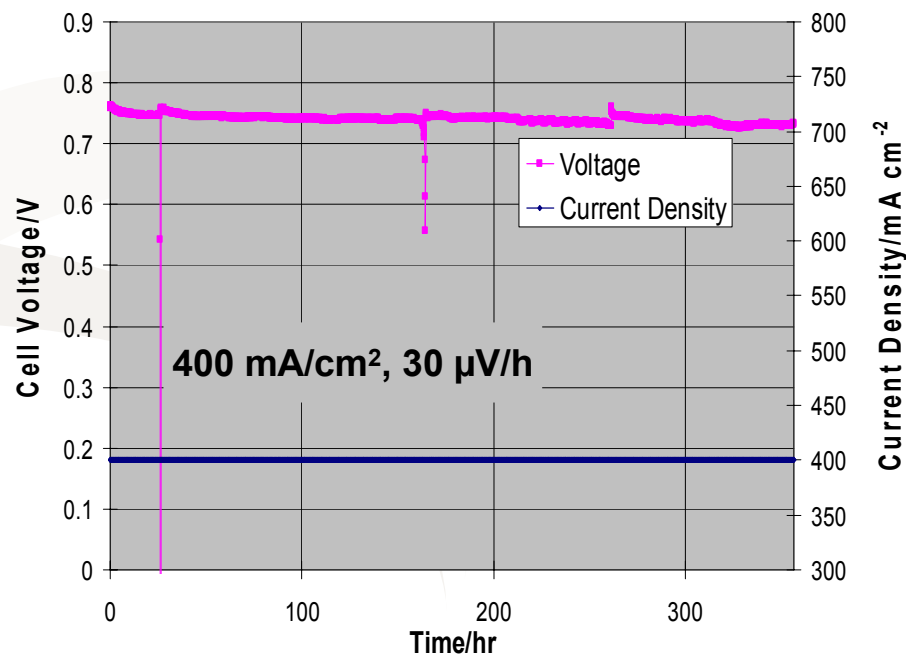
# FY04/FY05 Accomplishments:

## Long-Term MEA Stability Study



Cathode: **20% Pt Alloy/C**, 0.15 mg Pt/cm<sup>2</sup>

Anode: 10% Pt/C, 0.05 mg Pt/cm<sup>2</sup>



Cathode: **20% Pt Alloy/C**, 0.20 mg Pt/cm<sup>2</sup>

Anode: 10% Pt/C, 0.05 mg Pt/cm<sup>2</sup>

- 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.

## Rapid Screening and GDE Fabrication Equipment

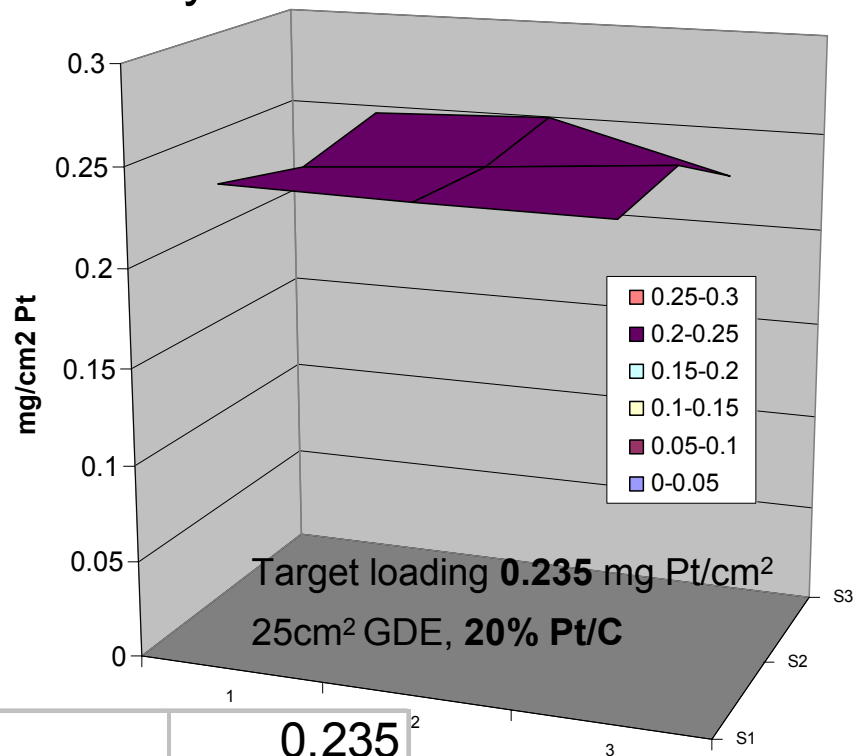
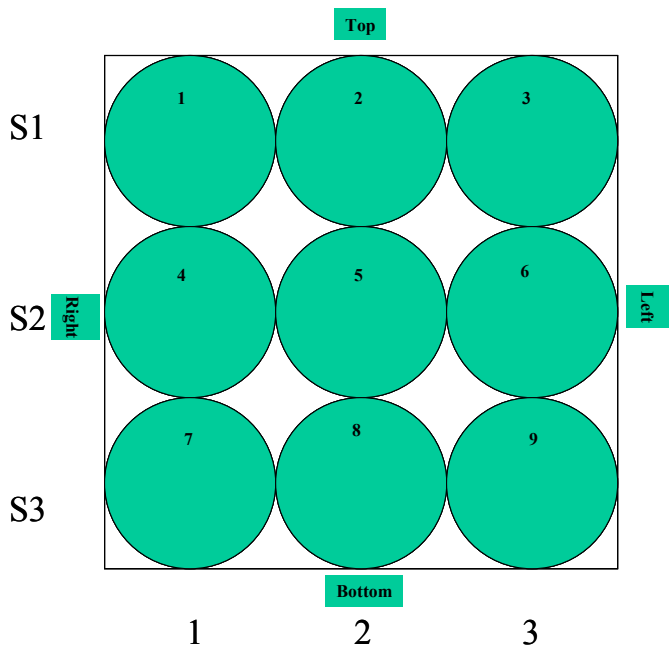
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- ◆ **Continue rapid screening of electrocatalysts - over 500 samples tested**
- ◆ **Complete rapid GDE fabrication equipment employing robot**
- ◆ **Procedure:**
  - Up to 20 catalysts are pre-weighed into a vials (6 ml)
  - Catalyst, solvent and 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<sup>2</sup> GDEs within three hours.



◆ Achieve acceptable GDE coating uniformity:

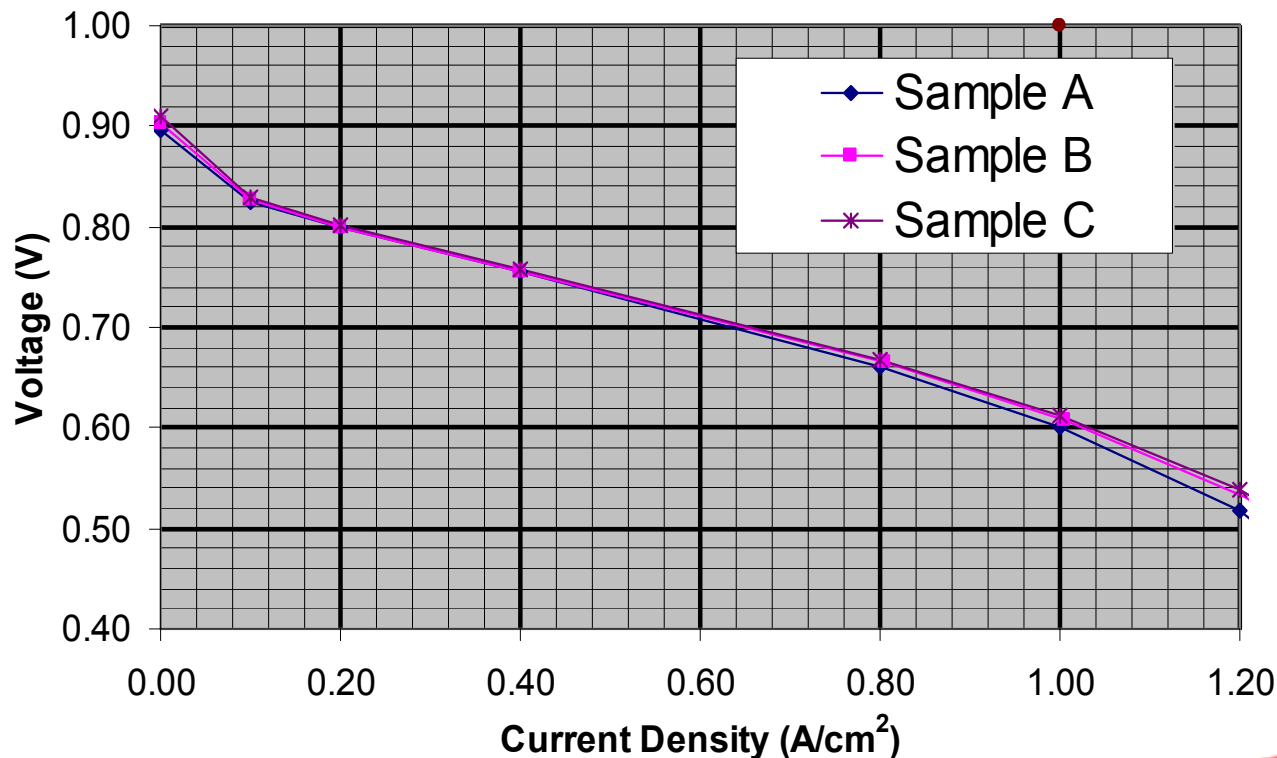
- Demonstrate process uniformity at 25 cm<sup>2</sup> – XRF tests
- Demonstrate process uniformity at 1 cm<sup>2</sup>



mg/cm <sup>2</sup>	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%

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

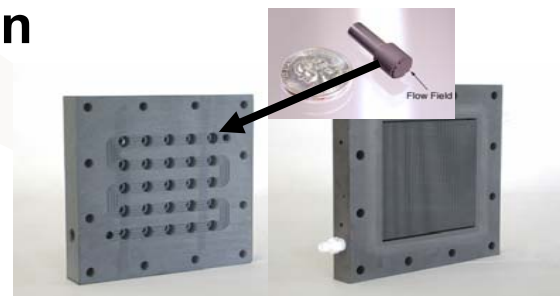


# FY04/FY05 Accomplishments:

## 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<sup>2</sup>) 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<sub>2</sub>, 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

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- **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<sup>2</sup>.*
- **Comment:** *“Not clear how general spray pyrolysis method is used for catalyst preparation”*
  - *Mark Hampden-Smith et al, “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

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## • 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



# Publications and Presentations

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1. P. Atanassova, M. Hampden-Smith, P. Napolitano, B. Gurau, "Spray Pyrolysis-based High Throughput Synthesis Platform for Discovery of Fuel Cell Electrocatalysts", 6<sup>th</sup> 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

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The most significant hydrogen hazard associated with this project is use of H<sub>2</sub> in Fuel Cell Testing

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

# Hydrogen Safety

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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<sub>2</sub> 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<sub>2</sub> through automatic N<sub>2</sub> 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.