

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

Contractor: Cabot Superior MicroPowders
Duration: 4 years, 9/2001- 9/2005
Award: DE-FC0402AL67620, Topic 1A1

Subcontractors: DuPont Fuel Cells
CFDRC

Stack Testing: GM

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Project Objectives

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- Four year program to develop and apply **combinatorial powder synthesis platform based on spray pyrolysis** for discovery of high-performance low-Pt cathode electrocatalysts for PEM automotive fuel cells
 - Use the platform for **electrocatalyst composition discovery** and microstructure optimization under conditions that can be **scaled for commercial powder production**
 - Deliver high-performance cathode electrocatalysts and MEAs with **lower Pt content to meet the DOE target of 0.6 gPt/kW in 2005**
- **FY 03/04 objectives**
 - Complete the development of rapid testing equipment –DuPont Fuel Cells
 - Start high throughput synthesis of ternary alloy compositions in a discovery mode
 - Further optimize MEA electrode structure
 - Test long term stability of new electrocatalysts
 - Deliver electrocatalysts and test MEAs to stack manufacturers



Relevance to DOE Technical Barriers and Targets

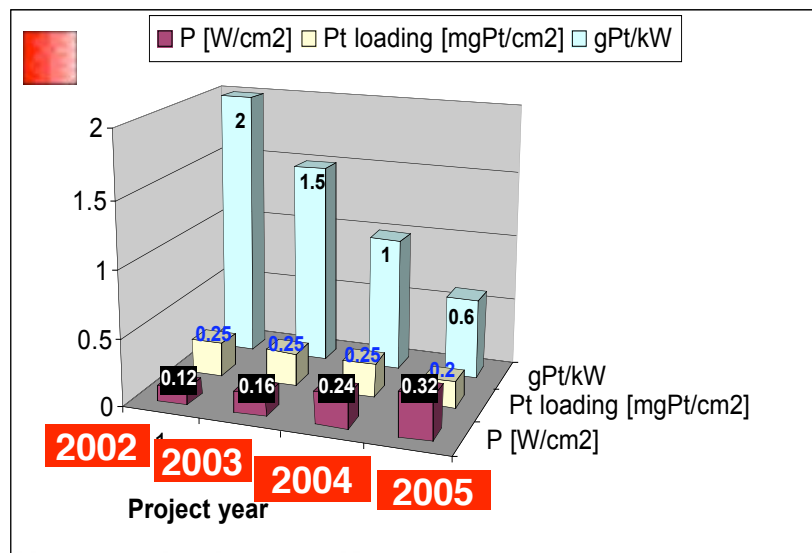
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■ Technical barriers for FC components:

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

■ Technical targets for 2010:

- Precious metal loading – 0.1 mgPt/cm²; 0.2 gPt/kW
- Durability - 5000 h



■ Test conditions:

- Single MEA 50 cm² test cell, Nafion 112
- Cell temperature 80C
- 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, 80C dew points
- Galvanostatic, mode, 15 min per point



Budget

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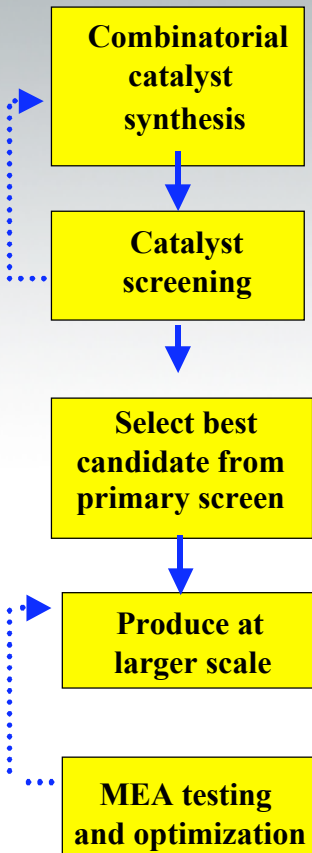
	Total	DOE	Contractor
Project Total	\$5,212,000	\$4,170,000	\$1,042,000
FY02	\$810,000	\$650,000	\$160,000
FY03	\$1,125,000	\$900,000	\$225,000
FY04	\$1,563,000	\$1,250,000	\$313,000
FY05	\$1,714,000	\$1,370,000	\$344,000

- **FY 02, FY03 and FY04 - significant part of the budget for equipment design and assembly**
- **FY04 and FY05 – high throughput synthesis and screening of novel compositions and stack testing**

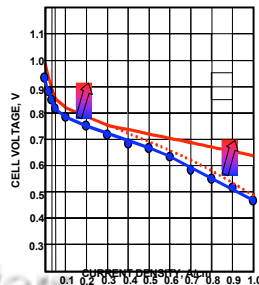
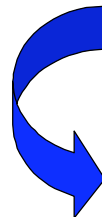
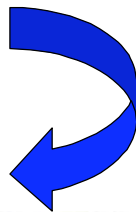
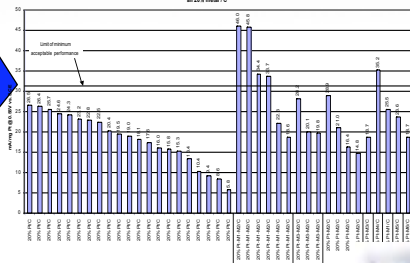


Technical Approach

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100 mg



1000's kg

- **CSMP:** build a **combinatorial powder synthesis platform** and use it for screening large variety of compositions for oxygen reduction electrocatalysts
- **DuPont Fuel Cells:** use rapid screening method for electrocatalysts and develop **rapid electrode fabrication method**
- **CSMP:** characterize structure, scale up best performing alloy electrocatalyst, test and optimize electrode structure in hydrogen-air MEAs
- **CFDRC:** modeling of the electrode structure
- **CSMP:** Deliver electrocatalysts and test MEAs to stack manufacturers



Project Safety

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Design Features for Safe use of H₂ and CO in Fuel Cell Testing

- Minimize Potential Exposure
 - Gas manifold room to minimize number of cylinders
 - Premixed, low concentration CO (<10%)
 - Flow restrictors at cylinder outlet, sized to allow maximum of 50% H₂ LEL, 50 ppm CO
- 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
- Pre-Startup Safety Review
 - Formal signoff on proper implementation of design
 - Operation of emergency shutdown systems, leak testing, electrical grounding, labeling, ...

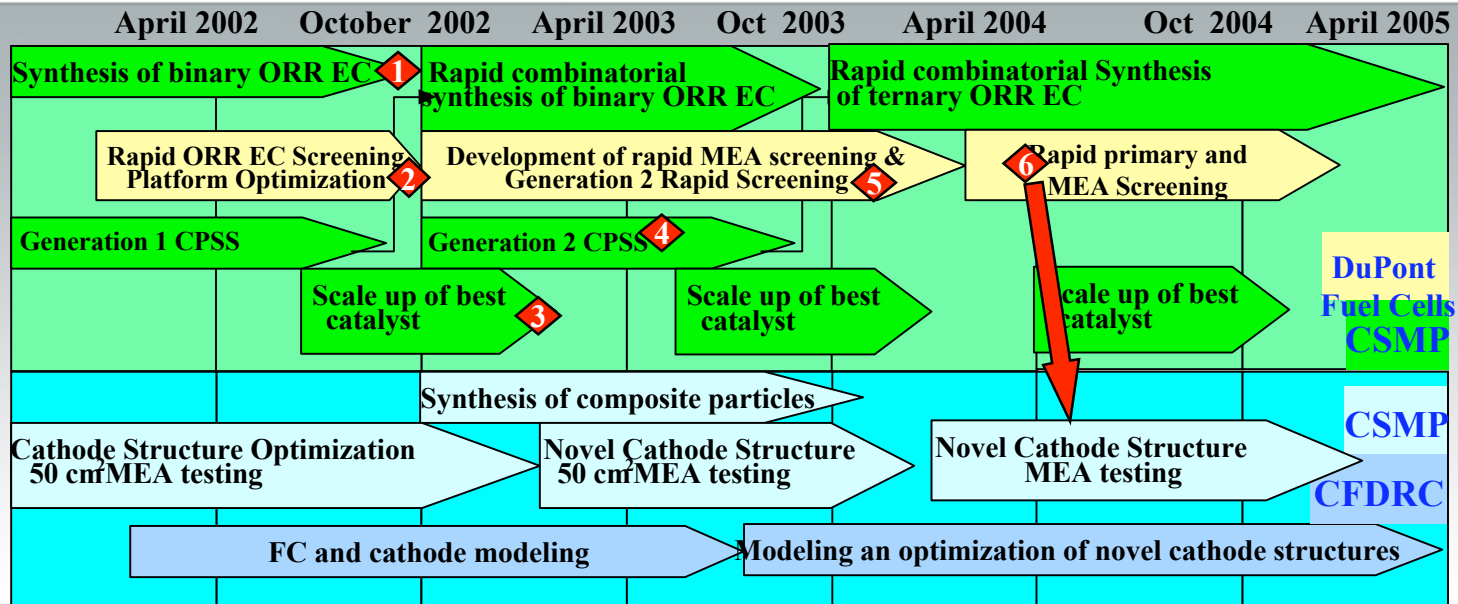


Project Timeline and Milestones

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Effort 1

Effort 2



Milestone	Description	Achievement	Timing	Status
3	Scale up of best performing catalysts	High surface area Pt/carbon and Pt ternary alloy/carbon catalysts scaled up	January 2003	Performance of scaled up materials at least equal to small scale ones
4	Complete assembly of Combinatorial Powder Synthesis System (CPSS) and optimize parameters	System fully integrated and automated, target production rates achieved, Pt/C catalysts benchmarked	March 2003	100 samples per week at 0.25 g achievable, start to investigate broad number of alloy compositions and microstructures
5	Complete assembly of rapid ink formulation equipment at DuPont	System assembled, testing of baseline catalysts in progress	May 2003	75-150 samples per week testing rate achievable



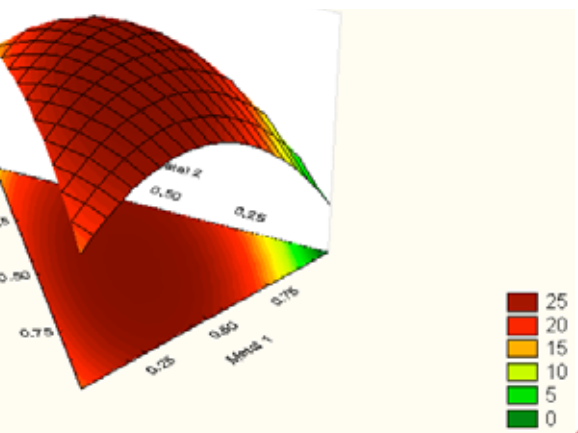
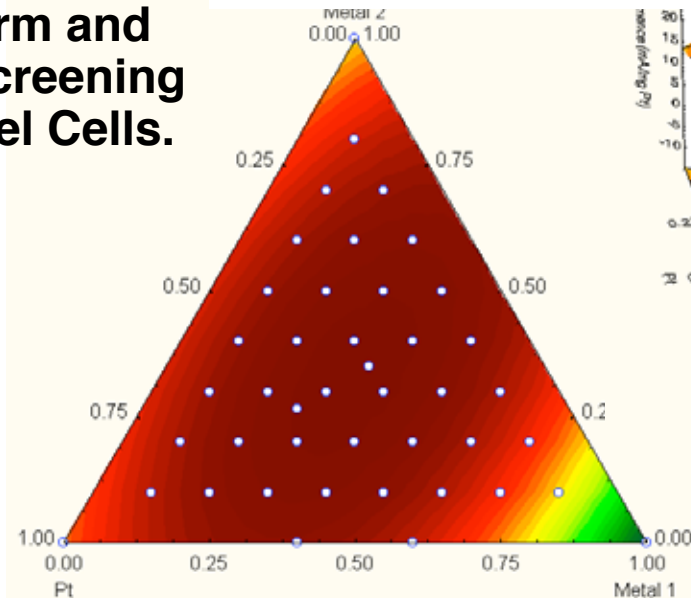
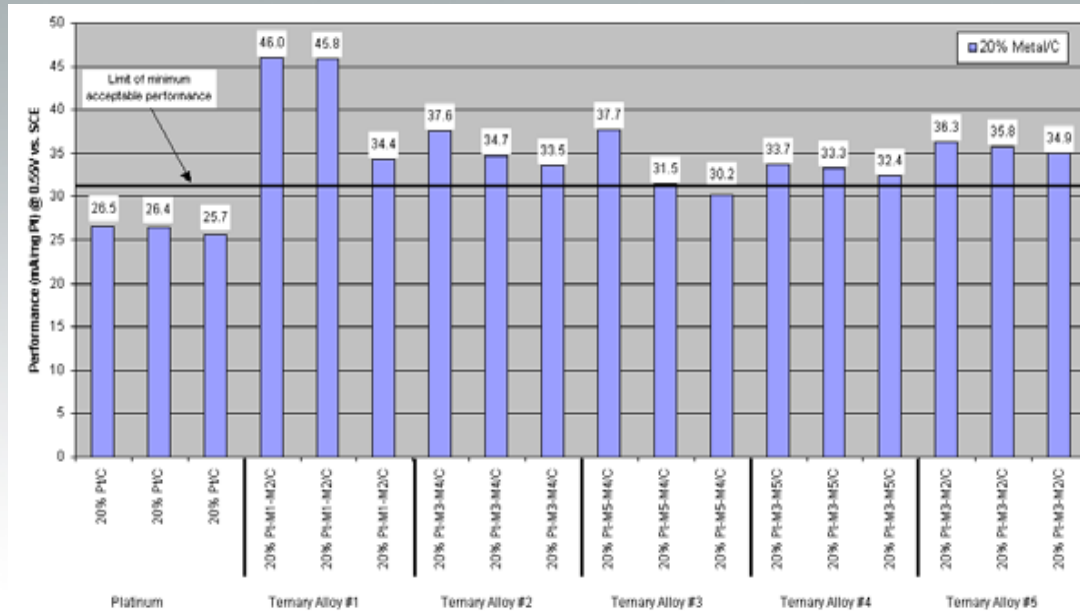
FY 03/04 Progress: Combinatorial Powder Synthesis – Milestone #4 met

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- 2004 rates
 - 0.25 grams per sample
 - 24 samples per day
 - 8 hour day
- 120 samples per week
- 480 samples a month
- 5 new ternary compositions

were synthesized on CSMP's combinatorial platform and tested in the rapid screening device at DuPont Fuel Cells.

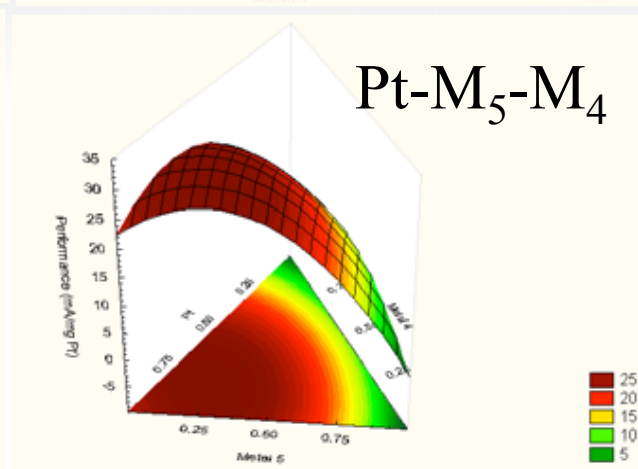
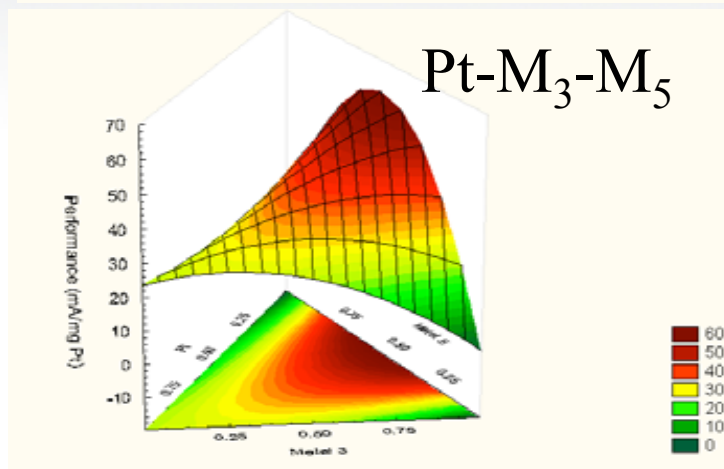
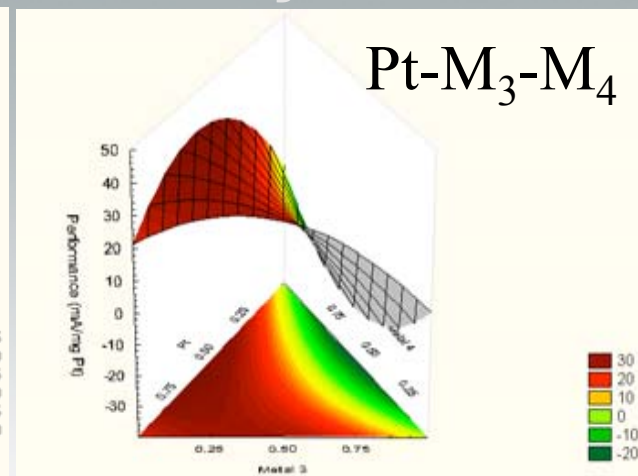
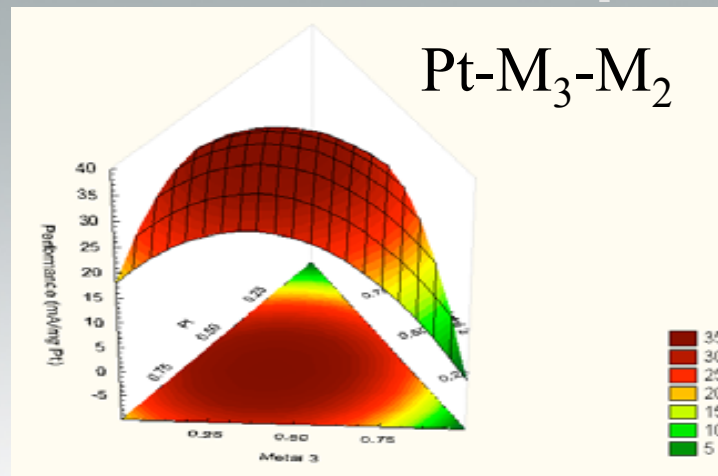
- Pt-M₁-M₂
- Pt-M₃-M₄
- Pt-M₅-M₄
- Pt-M₃-M₅
- Pt-M₃-M₂





FY 03/04 Progress: Performance Maps – Activity in ORR

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Currently Ternary Alloys Combinatorial Synthesis:
9 metals in addition to Pt

- ◆ **Develop a method for rapid ink formulation and electrode preparation to increase throughput of rapid screening device to be able to test 75-150 samples per week.**
- ◆ **Excellent reproducibility for ink preparation and electrode coating (stdev/Ave)% <10%.**
- ◆ **Variation between duplicates/same ink (dev/avg)% <<10%**
- ◆ **Capacity exceeds requirement of 75-150 catalysts per week.**
- ◆ **Half cell measurement kinetics correlate well with CSMP MEA data.**

Automatic System

Robot

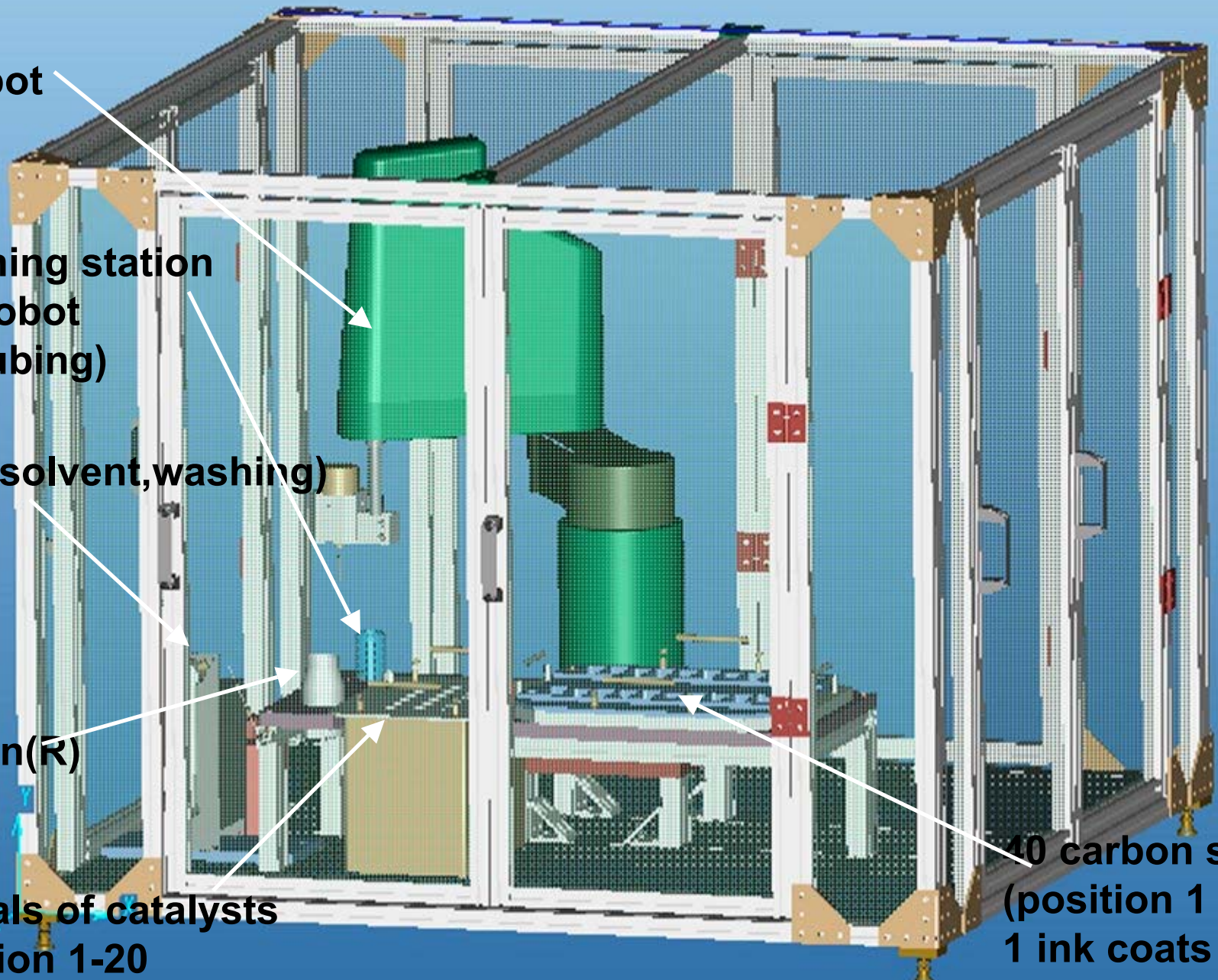
Cleaning station
(for robot
tip, tubing)

H₂O (solvent, washing)

Nafion(R)

20 vials of catalysts
position 1-20

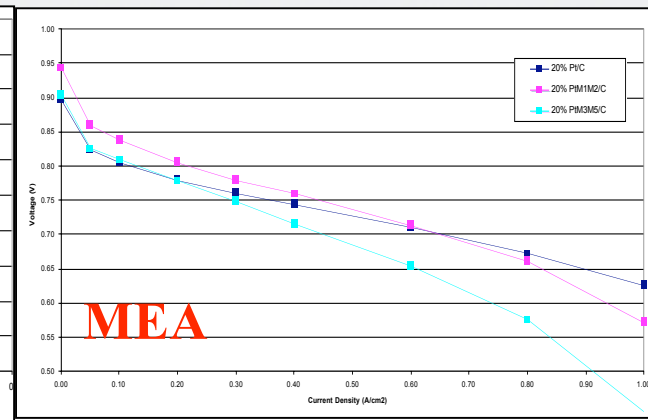
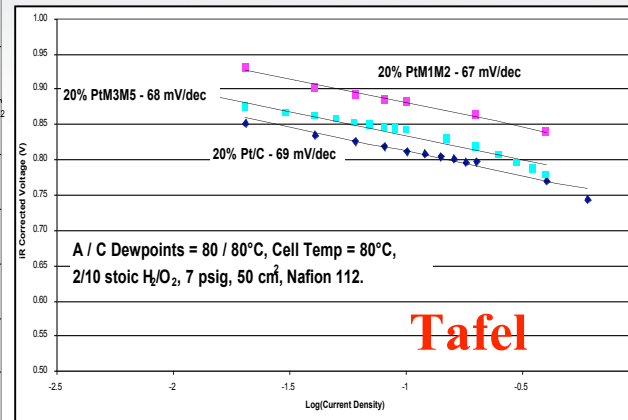
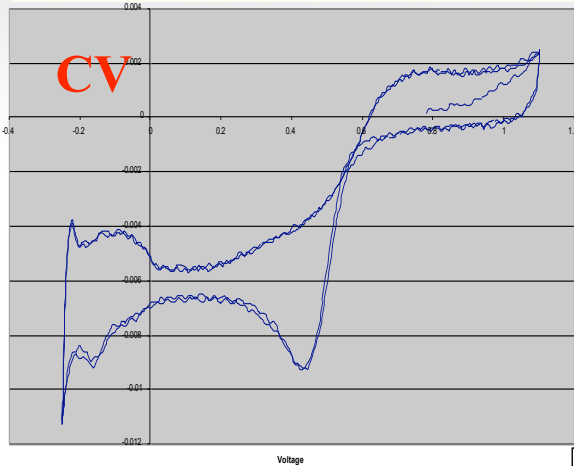
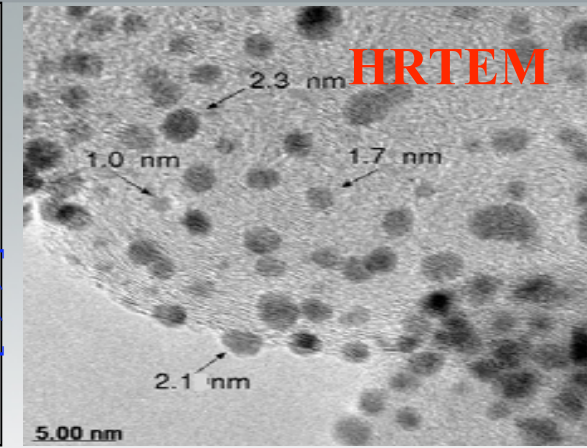
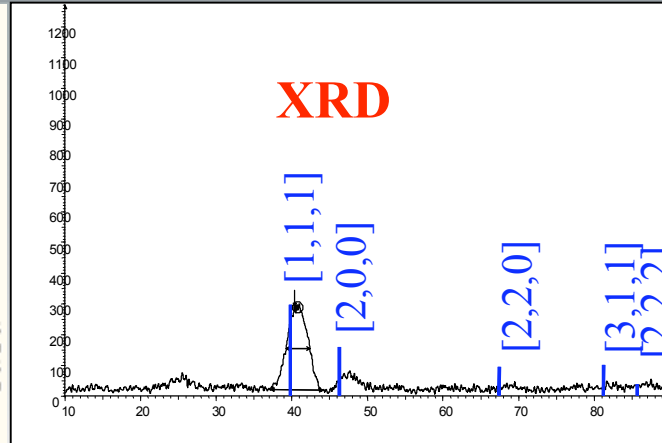
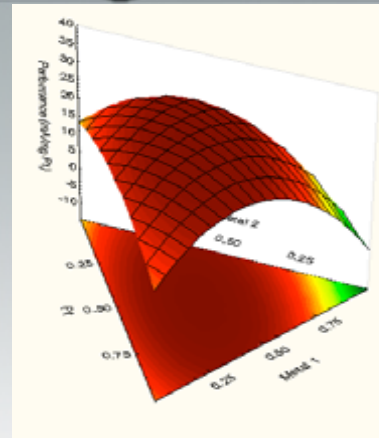
40 carbon strips
(position 1 - 40)
1 ink coats strips



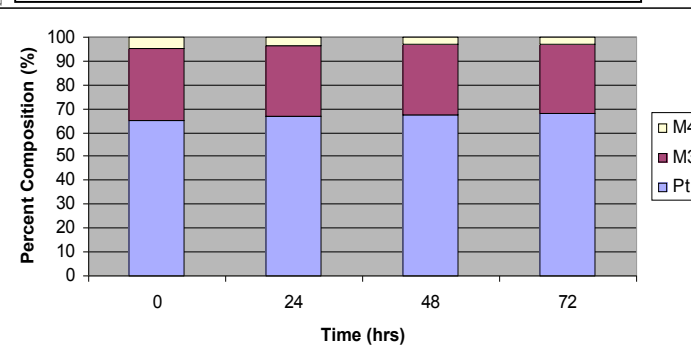
- ◆ **Work in progress**
- ◆ **Build on rapid catalyst screening platform.**
- ◆ **Focus is on rapid GDE fabrication that can be utilized with other rapid MEA testing equipment.**
- ◆ **GDL surface properties can vary, coating uniformity is challenging.**
- ◆ **First stage is to demonstrate process uniformity at 25 cm².**
- ◆ **Second stage will be to integrate capability with rapid MEA testing equipment working with GDE at 1 cm²**



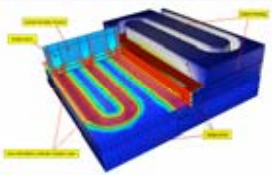
FY 03/04 Progress: Structural and Electrochemical Characterization



Stability of alloys in acid



Long term performance of MEA

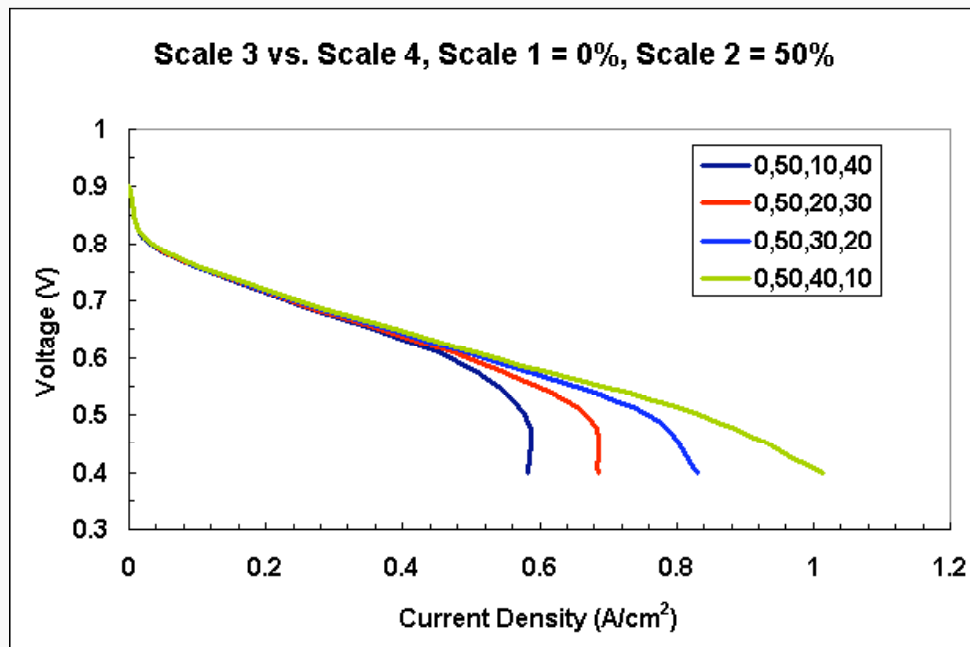


Optimization of PEM Fuel Cell Catalyst Layers Through Modeling and Simulation

- Identify microscale parameters that affect transport and reaction within catalyst structures

- **Pore Size Distribution** (Scale 1: Large ; Scale 2: Medium; Scale 3: Small ; Scale 4: Sub nm)

- **Fraction of catalyst placed in each pore size “bin”**



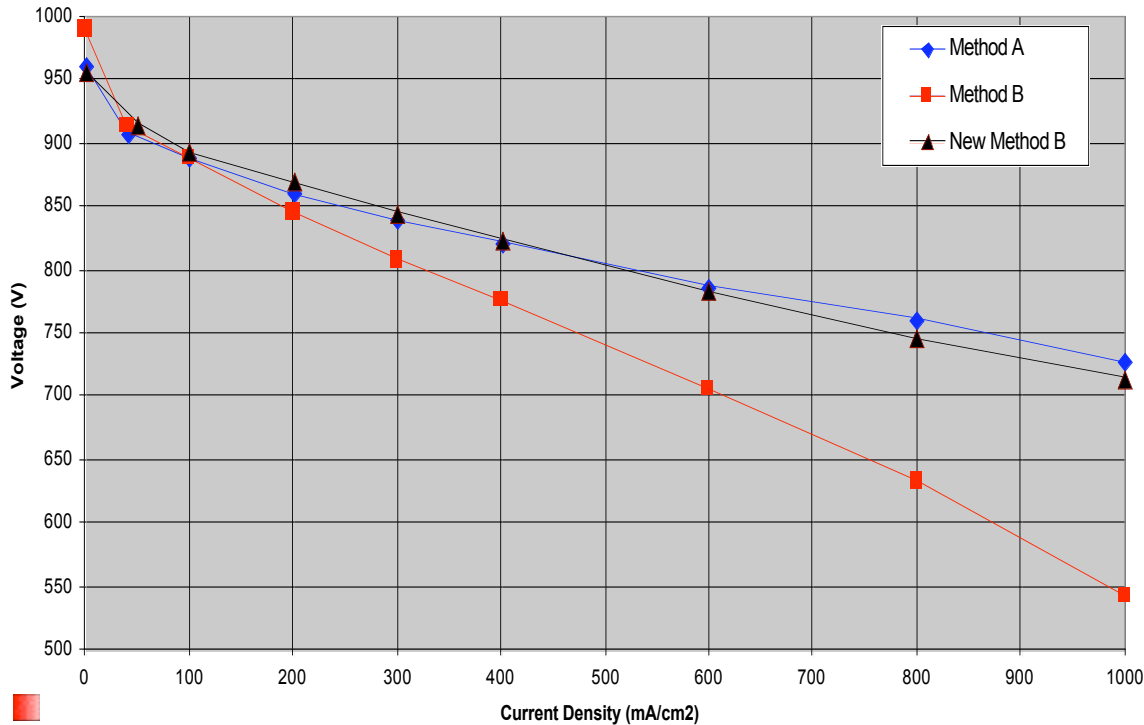
- Studies were performed to systematically move the catalyst between these various scales, i.e., given a certain catalyst loading, what happens if the relative amounts at the various scales are changed?

- These studies were conducted for various operating temperatures and pressures, and for various catalyst layer porosity.



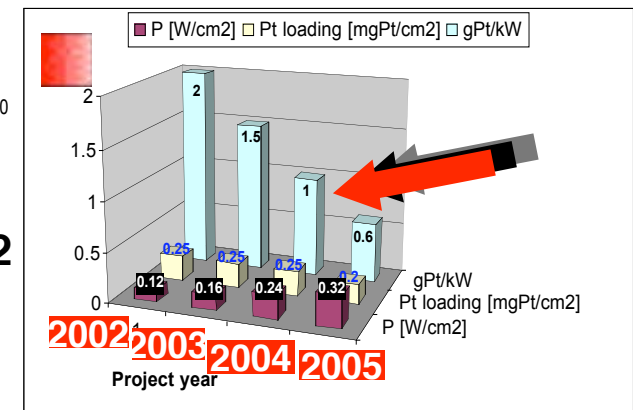
FY 03/04 Progress: MEA Optimization

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- Method A: 1.5 gPt/kW Method B: 2.6 gPt/kW
- 0.55 mg Pt/cm² total loading, 50wt.%Pt/C, Nafion 112
- New Method B: 0.4 mg Pt/cm² total loading
- 1 gPt/kW at 0.8 V; 0.7 gPt/kW at 0.75 V
- 0.6 gPt/kW at 0.7 V

- Design of experiments involving 5 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 while maintaining the anode loading around its minimum value





Summary of Accomplishments

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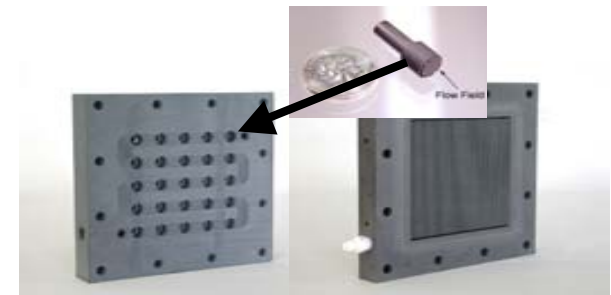
- Unique combinatorial platform for supported electrocatalyst in place (synthesis and screening)
- Focused approach in combination with structure characterization
- Initial targets for throughput met and potential for significant increase – milestones #3-5 met or exceeded
- **Shift from alloys benchmarking and optimization mode to a discovery mode !**
- Optimization of MEA structure led to a significant performance improvement
- Performance targets met in a single MEA
- Long term stability testing in progress



Future Work

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- Execute detail plan on ternary alloy systems synthesis and testing
- Strong emphasis on long term stability of electrocatalysts and MEAs
 - Stability in acidic media
 - Stability to active phase agglomeration
 - Optimal MEA structure
- Testing in Stacks
- Execute path forward identified for rapid MEA screening tool
- Rapid Testing in MEA configuration
 - Evaluate NuVant Systems Rapid Testing Device
25 mini fuel cells, referenced against the same counter electrode





Interactions and Collaborations

- General Motors, Fuel Cell Activities
 - Testing criteria
 - Validation testing
- Confidential discussions and sampling to several MEA developers
- Confidential discussions and sampling to FC stack developers and FC OEMs
- To supply MEAs for stack testing to a FC stack developer
- Production platform scale up validation through parallel product activities



Responses to Previous Year Comments

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- **Comment:** *“Appears to be catching up where others are, not clear that the processing costs are being reduced”*
 - First years focus was on building the combinatorial synthesis and screening equipment to enable the discovery mode.
 - Combinatorial approach does not guarantee success but significantly increases probability for getting to the next generation materials.
 - Product cost is driven by scaled up production cost, not just R&D scale production method cost. Spray – based process is a continuous non-batch process and the discovery is done on a consistent platform, one that has already been scaled up.
- **Comment:** *“Not clear who is going to benefit, SMP is not going to produce MEAs and fuel cells”*
 - The entire industry will benefit from improvements in these areas. Partnerships at all levels are necessary for fuel cell technology to succeed. Today, CSMP’s focus is on next generation electrocatalyst development and production, and MEA structure optimization.
 - Large volume MEA and automotive FC manufacturers are examples of potential users of CSMP materials to achieve high performance, low cost targets needed for broad market adoption.



Acknowledgements

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- DOE OTT, Award DE-FC0402AL67620, Topic 1A1
- DOE Program Manager: Valri Lightner
- CSMP, DuPont Fuel Cells and CFDRRC for cost share funding
- The whole CSMP team and especially:
Bogdan Gurau, Jim Brewster, Paul Napolitano, Jenny Plakio, Heath Quiggle, Tomas Wood, Bryan Apodaca, Henry Romero, Roya Cone
- DuPont Fuel Cells: Lin Wang, Keith Tomey, Jung Chae, Jo-Ann Schwartz, Dennis Kountz
- CFDRRC: Sandip Mazumder, Ashok Gidwani



CSMP's New Facility in Albuquerque