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

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05/17/2006

CABOT

Project ID #: FC16

This presentation does not contain any proprietary or confidential information

Overview

Timeline:

• **Project Start Date: 9/2001**

• **Project End Date: 9/2006**

• **Percent complete: 95 %**

Budget:

• **Project Total:** $5.21 M

DOE share: $4.17 M Contractor share: $1.04 M

• **Funding Received in FY05:** $ 0.9 M

• **Funding for FY06:** $ 0.4 M

Barriers addressed:

• **Barrier O.** Stack Material and Manufacturing Cost

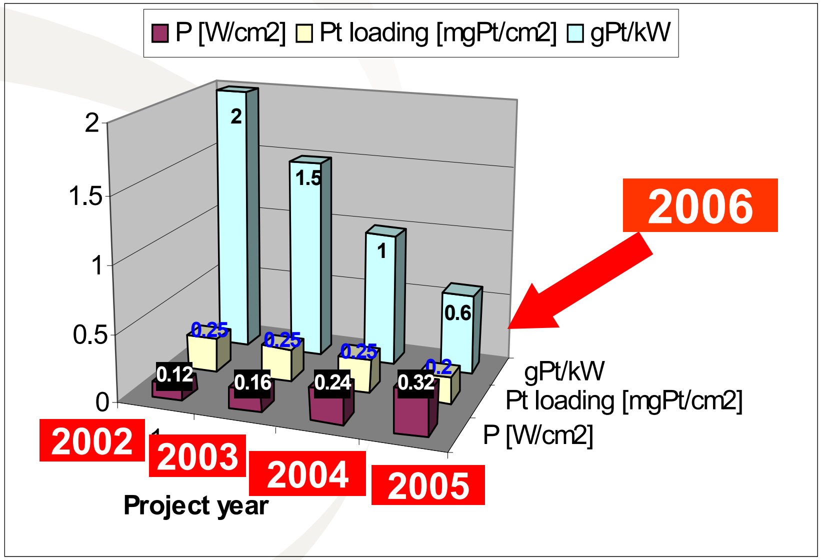
• **Barrier Q.** Electrode Performance

• **Barrier P.** Durability

Technical targets for 2010:

• **Precious metal loading:** 0.1 mgPt/cm^2; 0.2gPt/kW

• **Durability:** 5000 h



Partners: DuPont Fuel Cells

Hydrogenics – Stack testing

GM – Testing criteria

University of Illinois at Chicago - TEM

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Project Objectives

- ## Overall Project Objectives

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

- ## FY 05/06 Objectives
  - Scale up Pt alloy compositions discovered from high throughput synthesis and screening
  - Develop synthetic route for making high weight loading Pt alloys on high surface area carbon
  - Investigate post processing effect on alloys dispersion
  - Study long term durability of Pt alloys using cycling protocols
  - Integrate rapid GDE deposition equipment with rapid MEA screening unit at CSMP
  - Complete stack testing of MEA containing alloy compositions

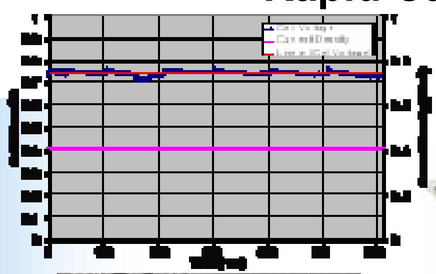
Technical Approach

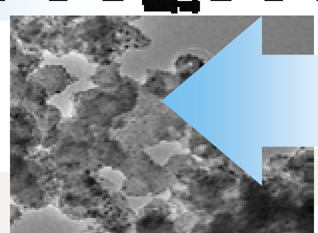
High Throughput Catalyst Discovery Platform

High Throughput Synthesis

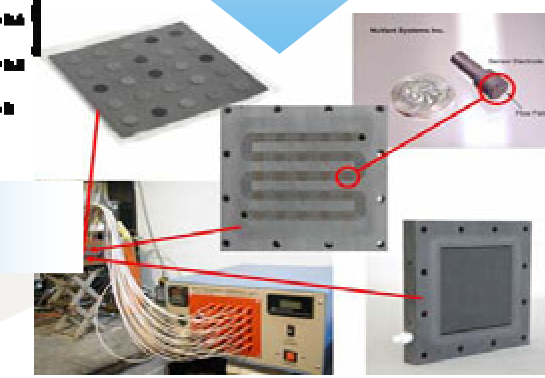
Rapid Cathode Layer Fabrication

High Volume Production





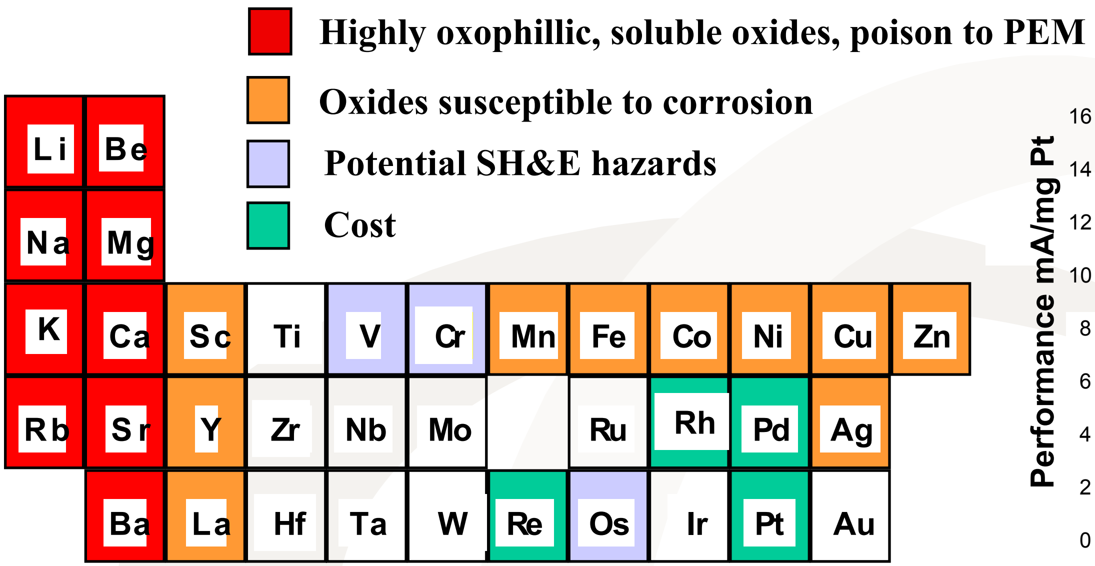
Electrochemical and Physical Characterization

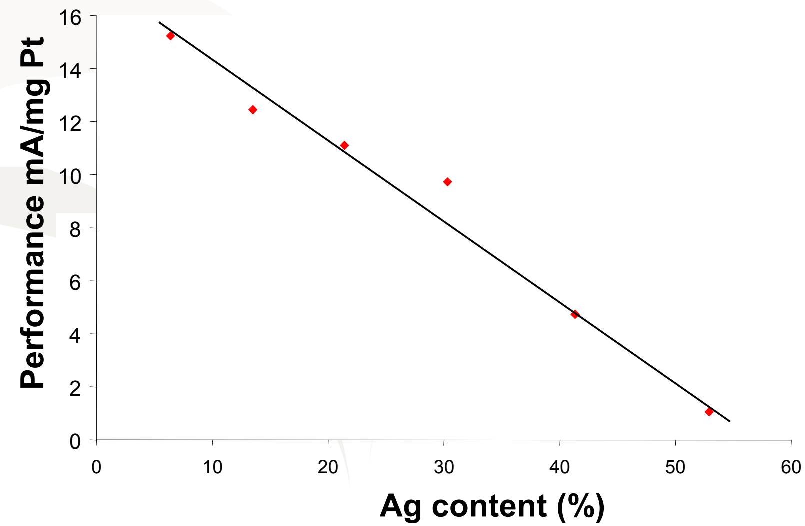


Rapid Screening in MEA Configuration

Technical Approach

Selection of Composition Targets





- Group A: Similar $E_{M\text{-}O}$ and similar atomic radius compared to Pt
  - {Ag, Rh, Pd, Ir}
- Group B: Higher $E_{M\text{-}O}$ and similar atomic radius compared to Pt
  - {Mn, Ru, Re, Mo, W, Zn}
- Group C: Higher $E_{M\text{-}O}$ and smaller atomic radius compared to Pt
  - {Co, Ni, Cu, Fe}

- Catalytic activity decreases along with Ag content for PtAg binary systems
- Ag eliminated from future explorations

7 metals in addition to Pt: Co, Ni, Pd, Fe, Mn, Cu, Ag

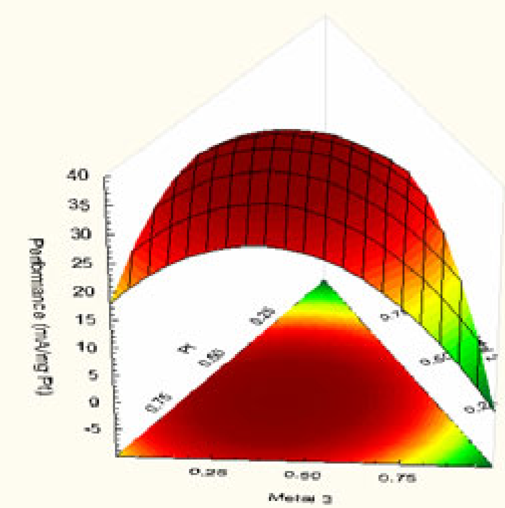
$$C_7^2 = \frac{7!}{2!\cdot(7-2)!} = 21$$

FY05/FY06 Accomplishments

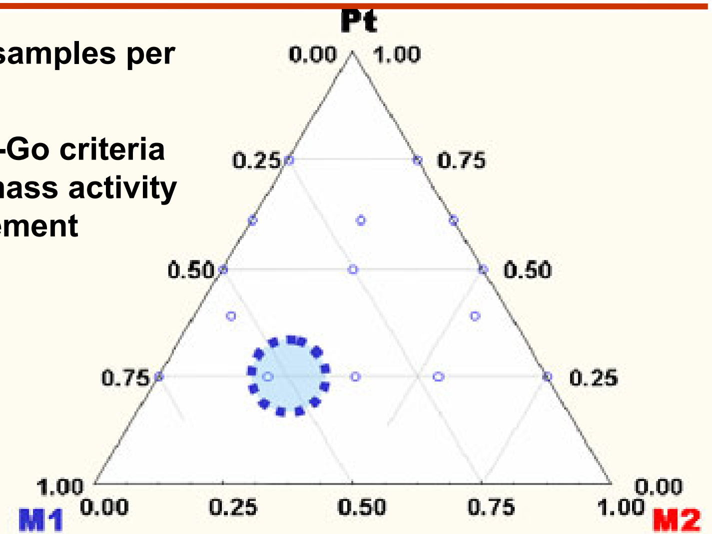
Ternary and Quaternary Alloy Libraries Completed

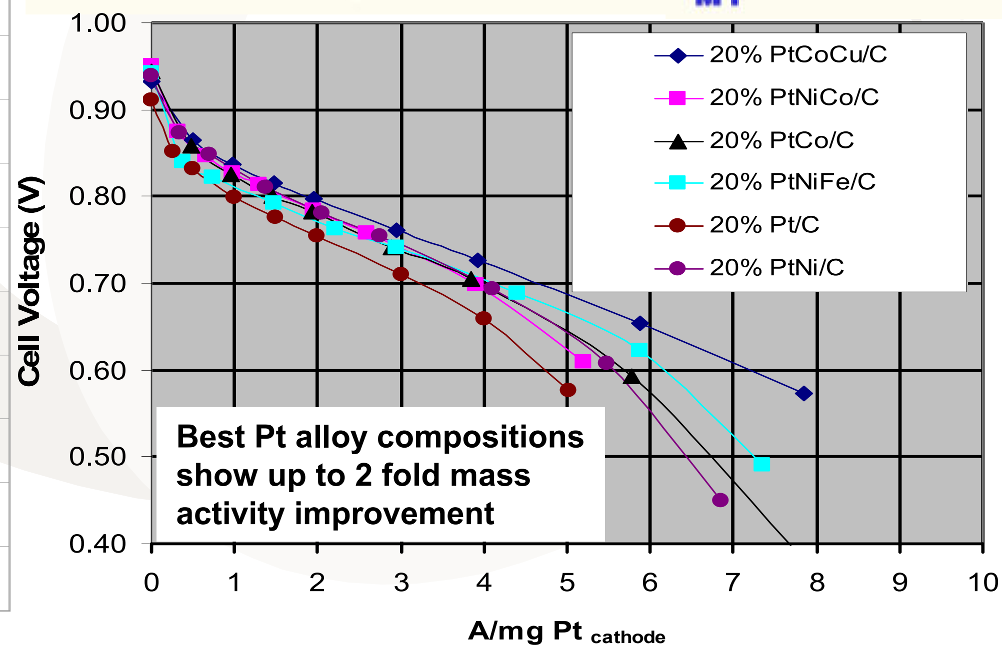
Pt Alloy Libraries

1	**PtCoCu**
2	**PtCoFe**
3	**PtFeCu**
4	**PtNiCu**
5	**PtNiFe**
6	**PtPdCu**
7	**PtPdCo**
8	PtPdFe
9	PtMnFe
10	PtPdMn
11	**PtNiCo**
12	PtCoAg
13	PtFeAg
14	PtNiAg
15	**PtPdNiCo**



- **25-75 samples per library**
- **Go/No-Go criteria >70 % mass activity improvement**



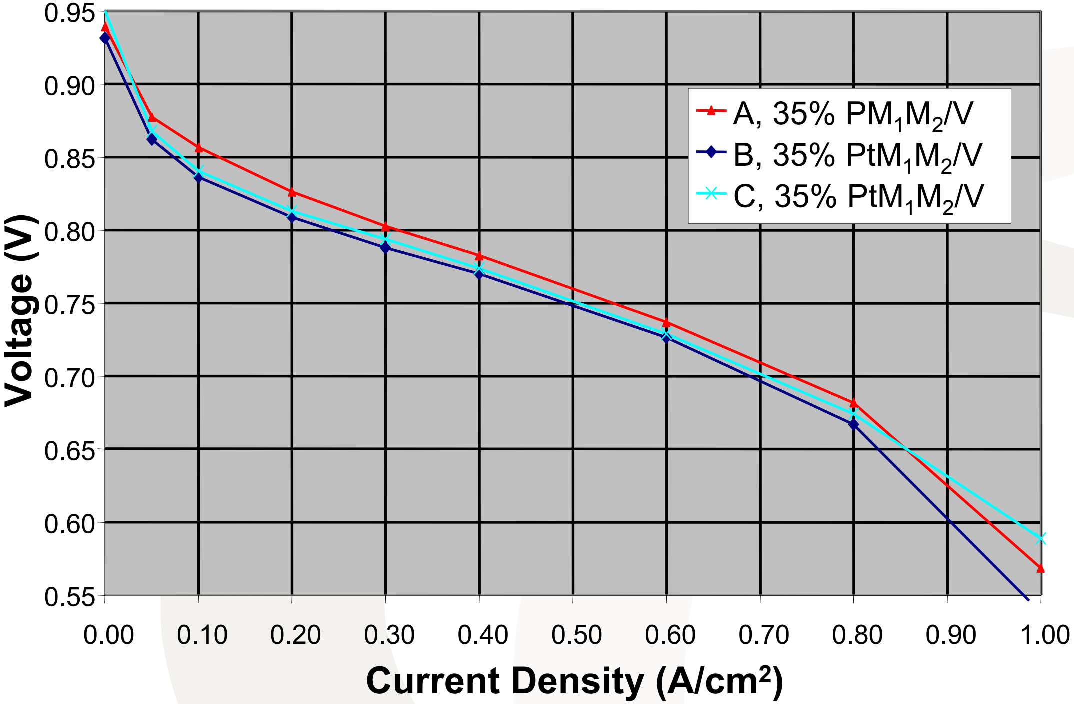


Test Conditions:

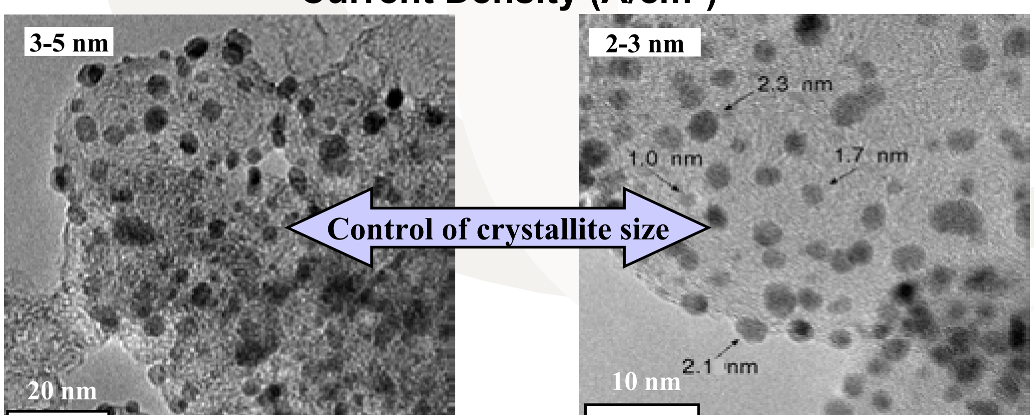
- **50 cm^2 MEA**
- **Nafion™ 112**
- **Cathode: 0.2 mgM/cm^2**
- **Anode: 0.05 mgPt/cm^2**
- **80°C, 1.5 H_2/2.5 air at 1A/cm^2, 100% RH, 30 psig, 10min/point,**
- **Non IR corrected**

FY06 Accomplishments:

Scale Up and Optimization of Best Alloy Compositions



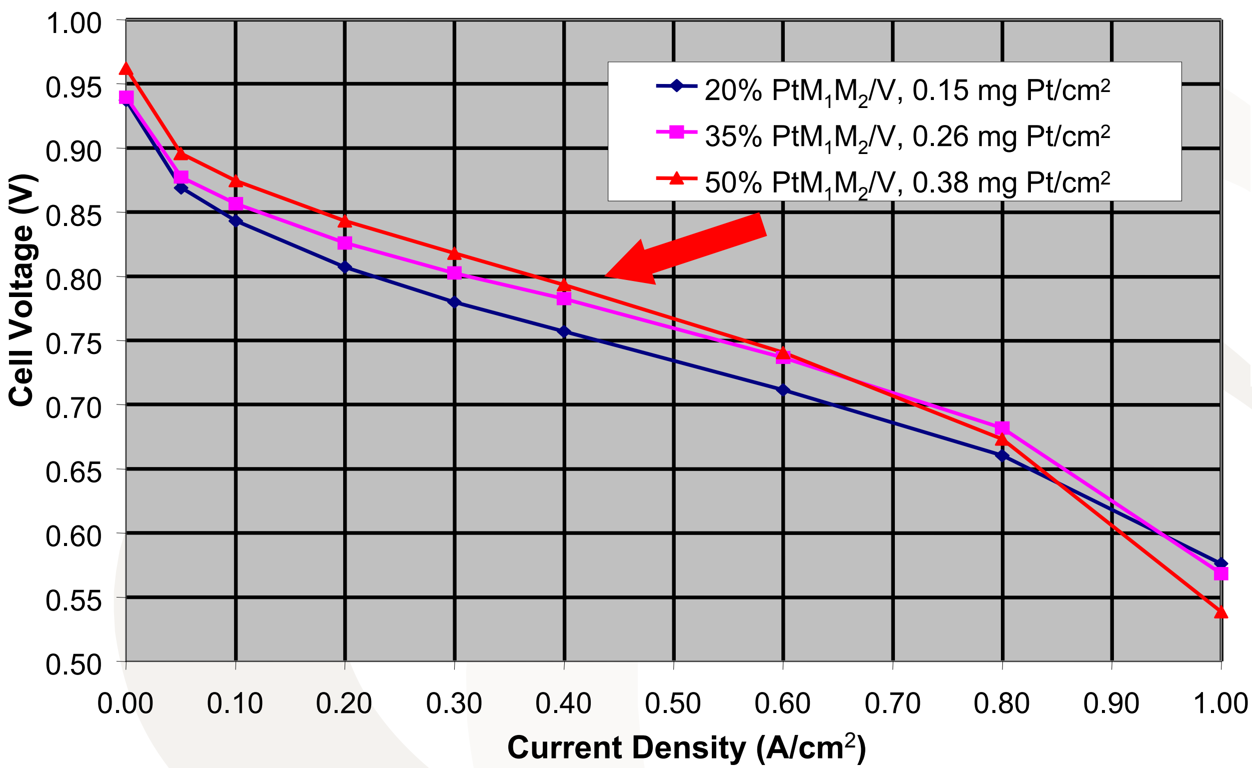
- Systematically investigated production conditions on physical and electrochemical properties of alloy.
- Characterization of crystallite particle size and degree of alloying by XRD, TEM and ECA (m^2/gPt), BET and porosity of catalyst particles
- Correlate physical properties to performance in MEA



	Average metal crystalline size	BET (m^2/g)
Sample A	3.7	108
Sample B	4.4	103
Sample C	4.3	98

FY06 Accomplishments:

Scale Up of Best Alloy Compositions



Test Conditions:

- **50 cm² MEA, Nafion™ 112 cathode: as listed anode: 0.05 mgPt/cm²**
- **80°C, 1.5 H_2/2.5 air at 1A/cm², 100% RH, 30 psig, 10 min/point,**
- **Non IR corrected**

- **Catalysts with 20-50 wt.% metal loading made on a production unit.**
- **Scale up demonstrated for several alloy compositions.**
- **Production unit has a capacity of 6-8 kg per day.**
- **Further scale up feasible.**

FY05/FY06 Accomplishments:
Mass Activity for 20-50% Pt Alloy Catalysts

Catalyst Composition	Mass Activity at 0.9V (A/mg Pt)
CSMP 20% Pt/V	0.07
CSMP 50% Pt/KB	0.13
Commercial 20% Pt/V	0.07
CSMP 20% PtNiCo/V	0.13
CSMP 20% PtCoCu/V	0.25
CSMP 50% PtNiCo/V	0.09
CSMP 50% PtNiCo/KB	0.23
CSMP 50% PtCoCu/KB	0.22

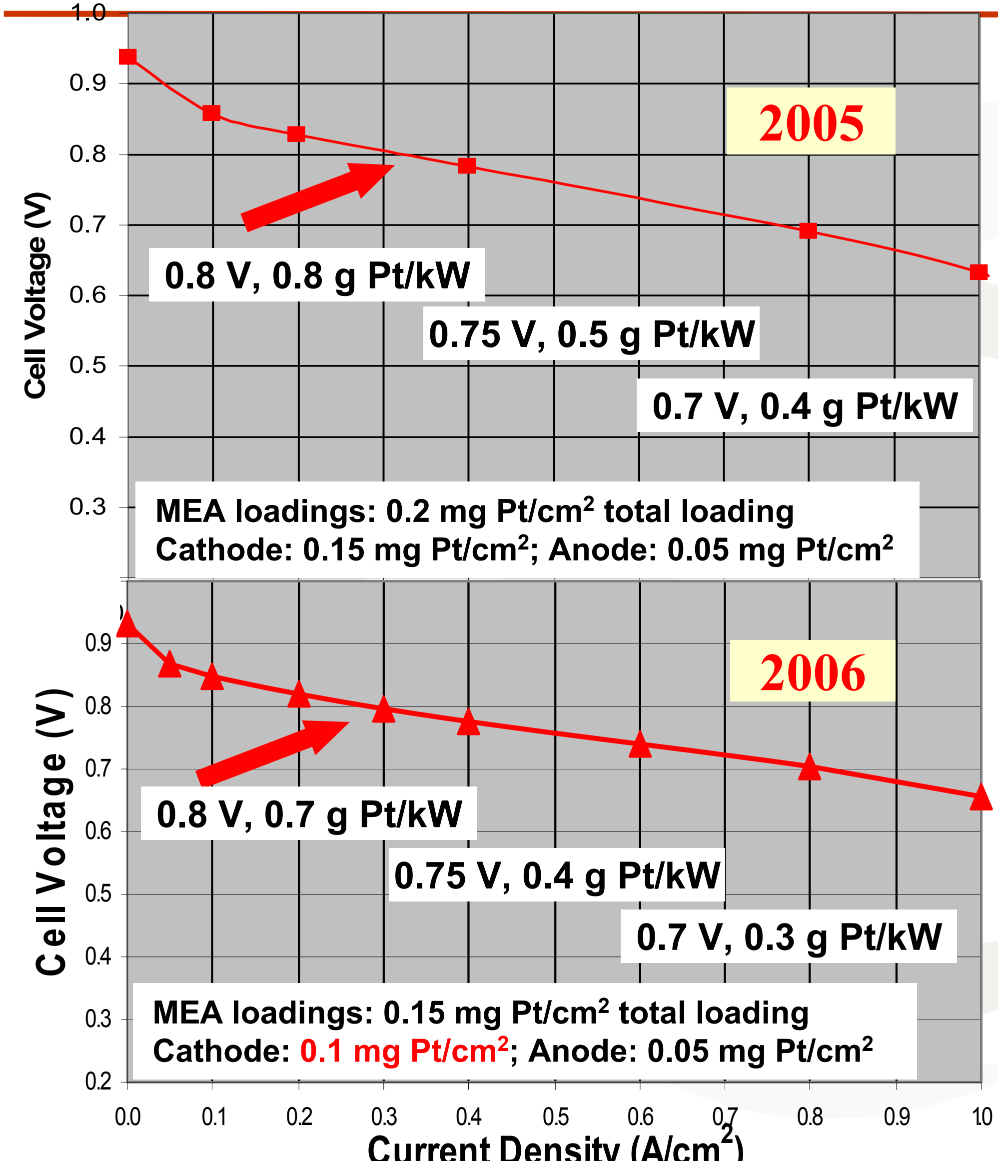
- Effect of metal loading, type of support and processing conditions on mass activity.
- Layer structure (loading, Nafion/C ratio) might have an effect on mass activity measurement.

Test Conditions:

- **80°C cell, Nafion™ 112, 100% humidification, 9 psi backpressure, H_2/O_2 (2/9.5)**
- **20 wt.% M/C: Cathode: 0.2 mg Metal/cm^2, anode: 0.05 mgPt/cm^2**
- **50 wt.% M/C: Cathode: 0.5 mg Metalcm^2, anode: 0.05 mgPt/cm^2**

FY05/FY06 Accomplishments:

Single MEA Performance vs. Project Targets

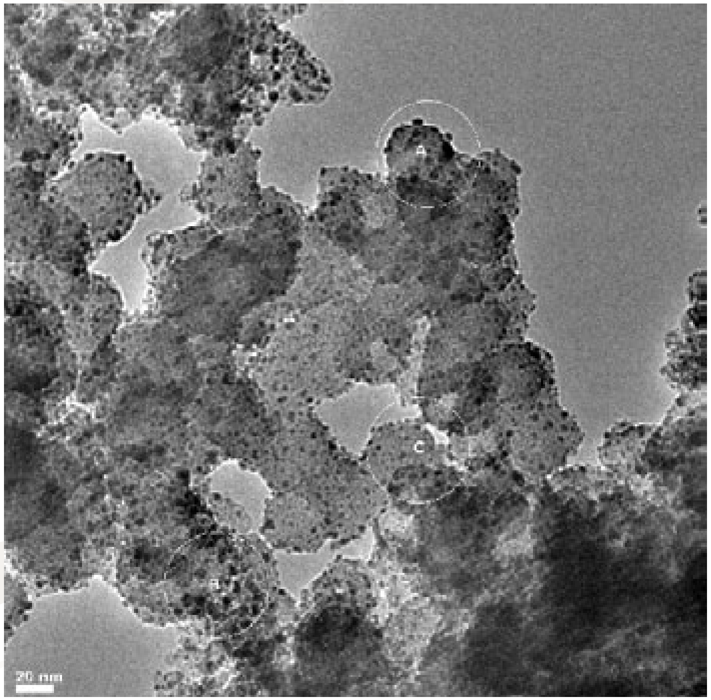


MEA Test Conditions:

- 50 cm^2, Nafion™ 112
- 80°C, 1.5 H_2/2.5 air at 1A/cm^2, 100% RH, 30 psig

10 min/point, Non IR corrected

Pt (111): 40.36 (2θ); a: 3.87 Å
Particle size (XRD): 2.4 nm



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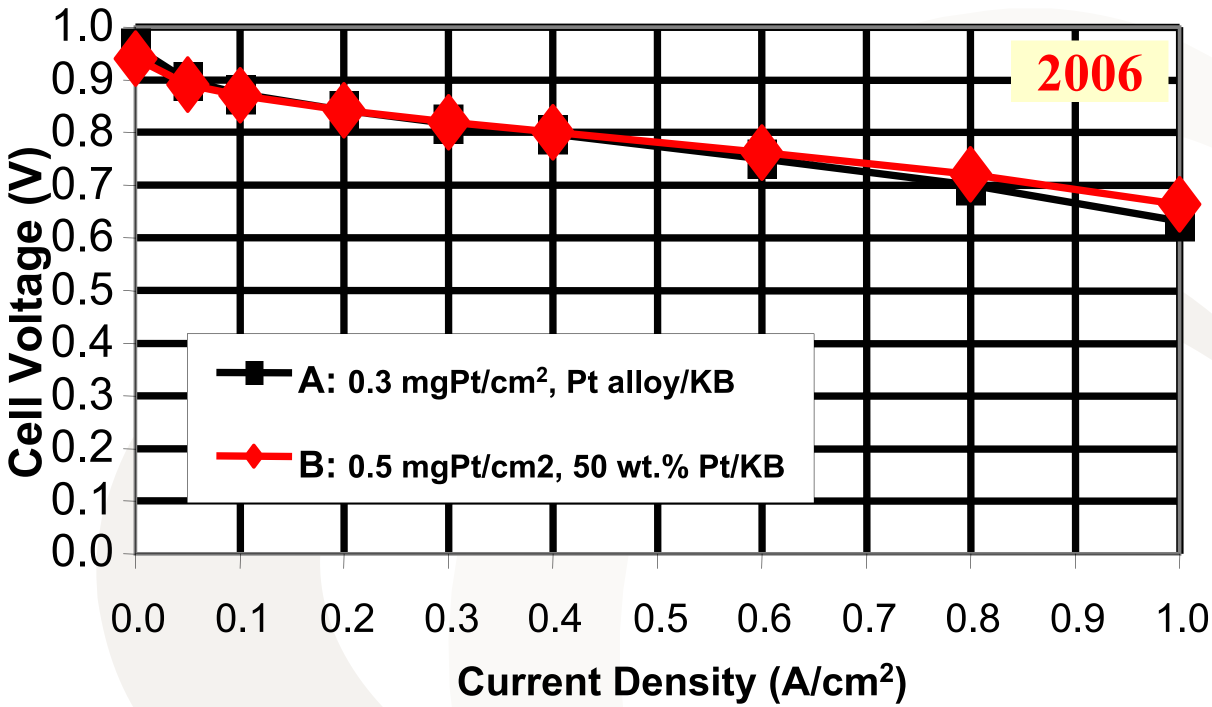
FY06 Accomplishments:
Single MEA Performance vs. Project Targets



- ***High Metal Loading Catalyst on High Surface Area Carbon Support***
- ***Identical performance at approximately half of the Pt content***

MEA Test Conditions:

- **50 cm^2, Nafion™ 112, cathode: as listed; 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,**
- **Non IR corrected**

- **At 0.8 V a power density of 0.32 W/cm^2 was achieved**
- **At 0.7 V approximately 0.56 W/cm^2 (total PM loading, anode plus cathode of 0.35 mgPt/cm^2), which corresponds to approximately 0.6 gPt/kW.**
- **The corresponding value for Pt only catalyst at 0.7 V is approximately 0.9 gPt/kW.**

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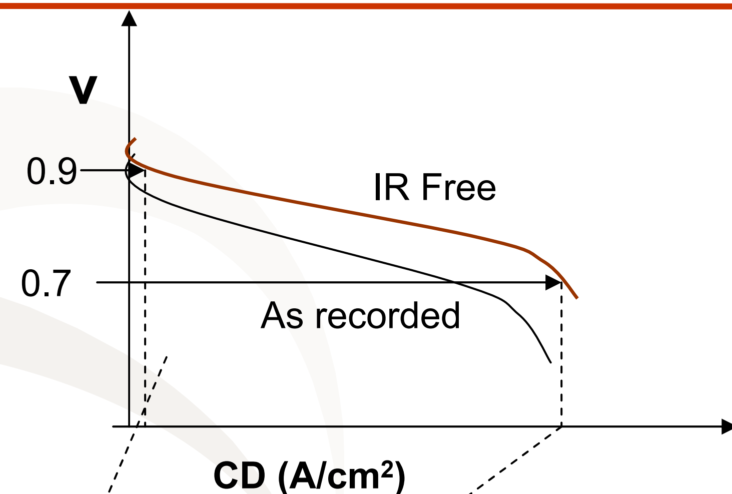
FY05/FY06 Accomplishments:

Long-Term Durability Study – Cycling Protocols

- **The test consists of cycling a 50 cm^2 MEA under H_2/air at 80°C and 100% RH between 0.7 and 0.9 V IR-free voltage (30 s hold at each potential) combined with periodical evaluation of the Pt surface area using cyclic voltammetry and performance.**

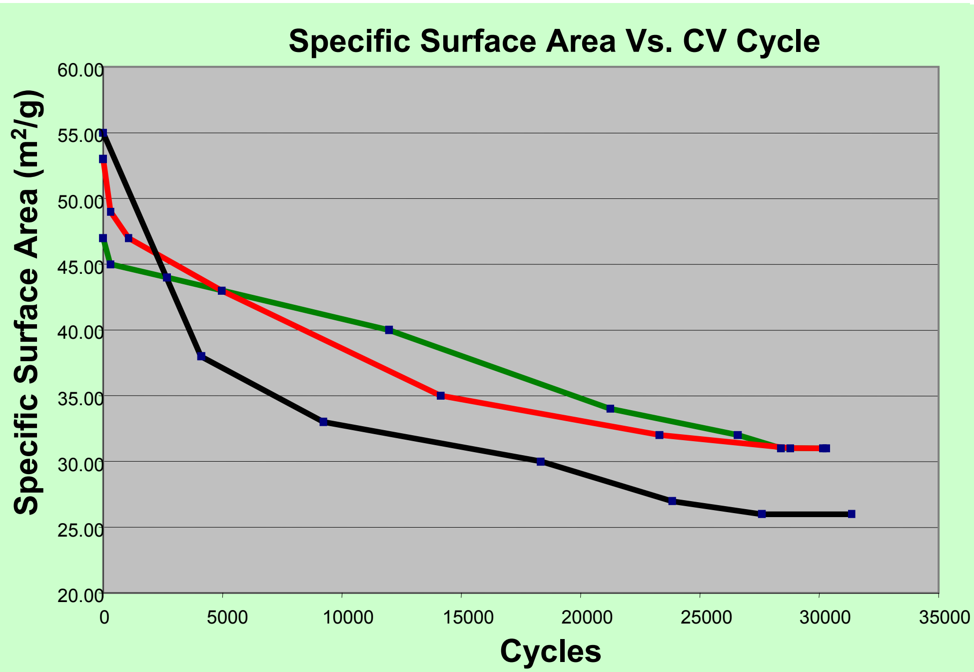


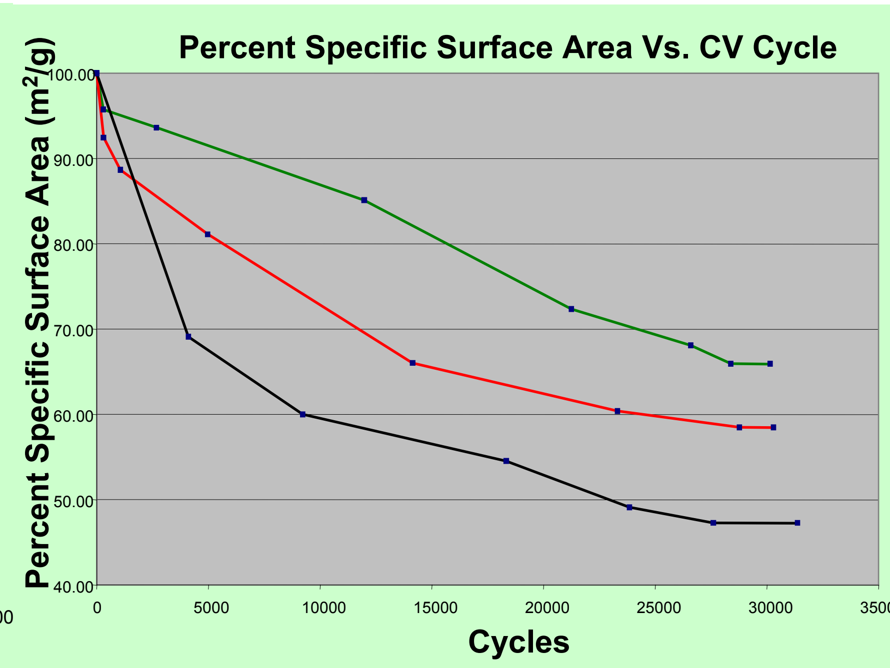
- **CV Cycling Experiment**
  - **Test Conditions**
    - Stoich (Anode/Cathode) : 2/2
    - Anode: Hydrogen, flow rate; Cathode: Air, flow rate
    - Cell Temperature: 80ºC
    - Inlet Anode and Cathode pressure - 0 psig
    - Inlet Anode and Cathode RH - 100% RH
  - **Potential Cycling (used by constant current)**
    - Square wave
    - Lower potential: 0.7V IR Free (~*1.3* A/cm², extracted from IR Free Pol. curve)
    - Upper potential: 0.9V IR Free (~*20* mA/cm² extracted from IR Free Pol. curve)
    - Time Interval: 30 sec at each step

Sequence of testing
Step 0 Conditioning
Step 1 ECA (Initial)
Step 2 CV Pol (Initial)
Step 3 CV Cycle
Every Friday Step 1
Every Monday Step 2
Continue Step 3 rest of the time
Repeat until 30K cycles
Final ECA
Final CV Pol
Final O2 IV

FY05/FY06 Accomplishments:

Long-Term Durability Study – Cycling Protocols





- **Three standard Pt/C containing MEAs were tested as baseline.**
- **All baseline samples show high initial drop and level off after ~20K cycles.**
- **On average, samples show ~35-55% reduction of initial Pt specific surface area after 30K cycles.**
- **Active area loss correlates well with performance loss at low current densities.**

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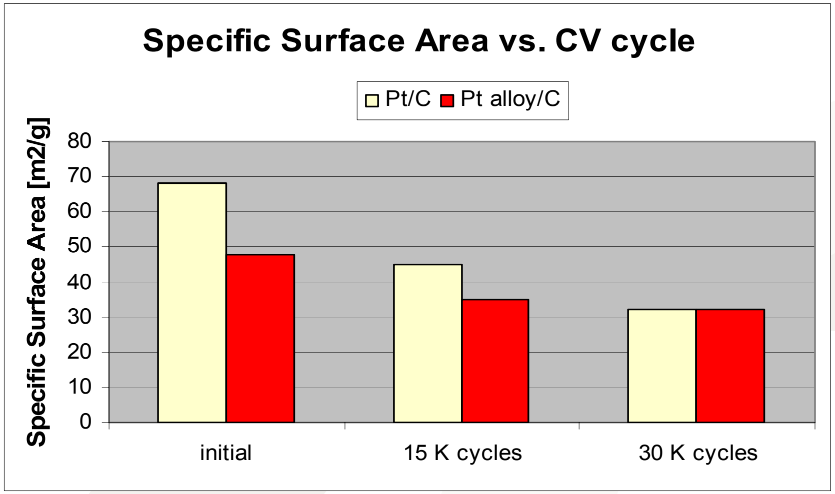
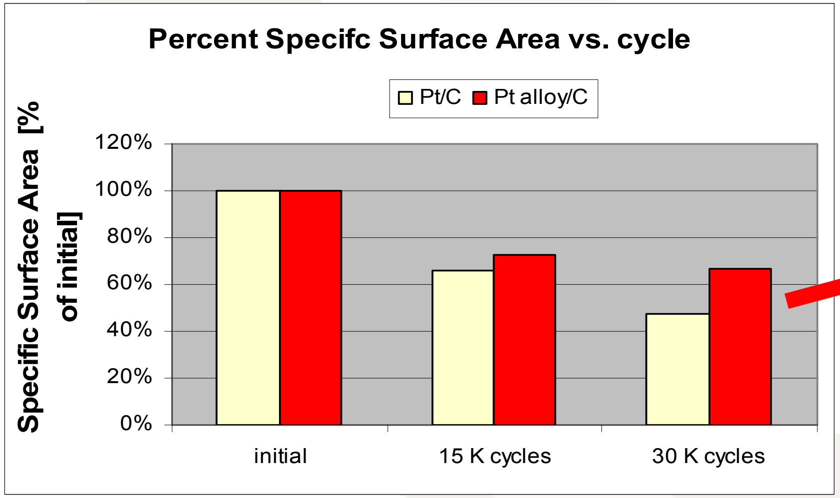
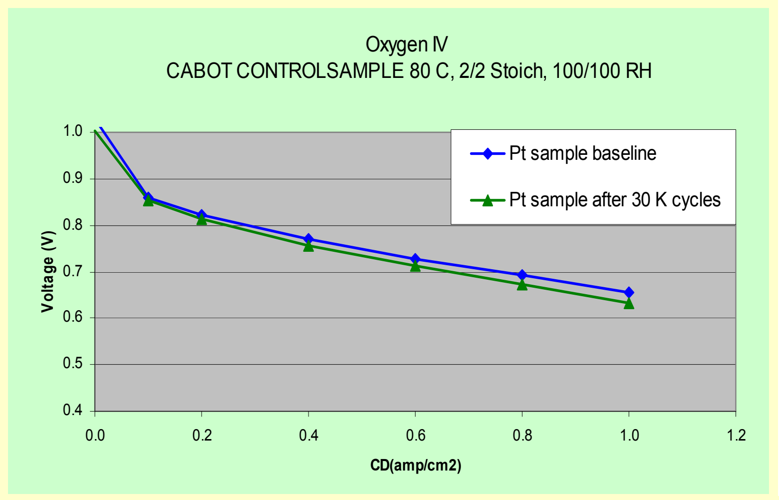
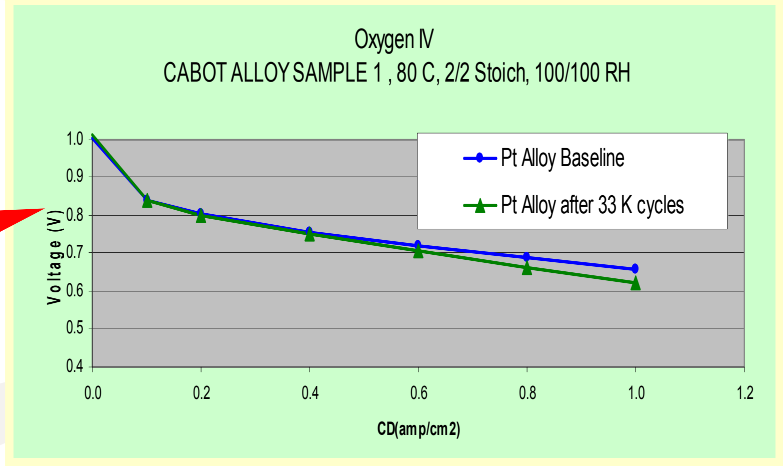
FY05/FY06 Accomplishments:

Long-Term Durability Study – Cycling Protocols





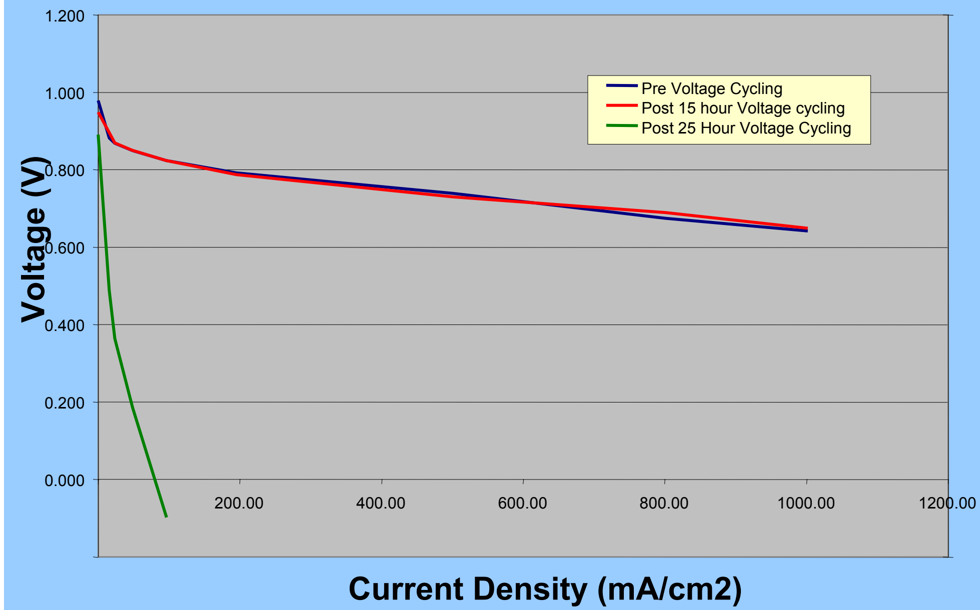




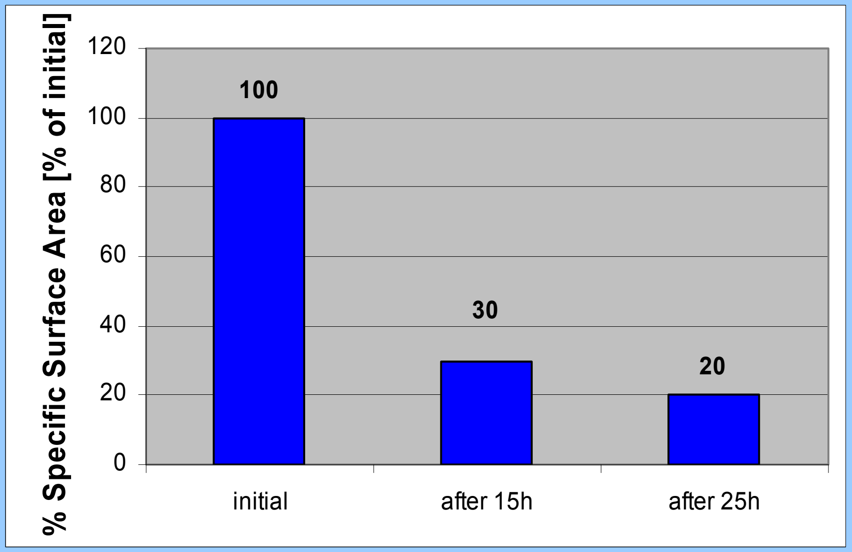
- **Two CSMP Pt/C and two Pt alloy MEAs tested.**
- **Further analysis of the alloys durability with post mortem analysis of structural changes in progress.**
- **Additional testing to separate catalyst durability from MEA morphology changes.**

FY05/FY06 Accomplishments:
Carbon Corrosion Test

Carbon Corrosion



Specific Surface Area Change Per Voltage Hold Time



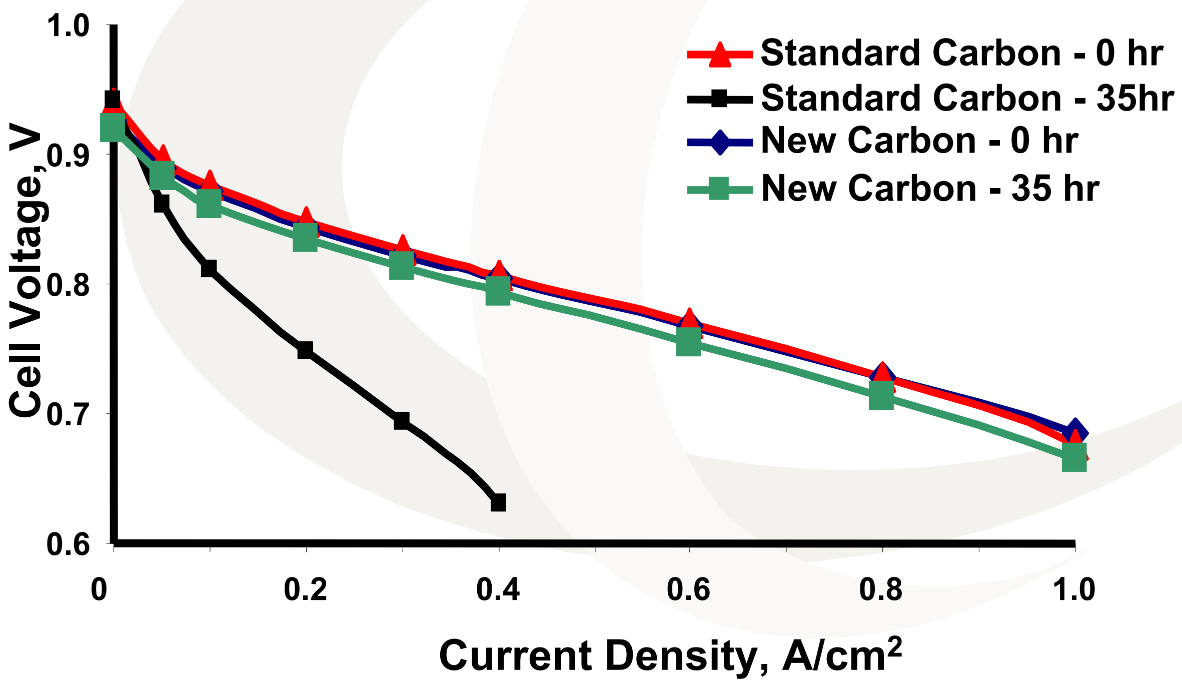
- **Constant Voltage Hold Experiment**
  - **Test Conditions**
    - Anode: Hydrogen, 500cc/min; Cathode: Nitrogen, 500cc/min
    - Cell Temperature: 80ºC
    - Inlet Cathode and Anode pressure - 7 psig
    - Inlet Cathode and Anode RH - 100% RH
    - **Constant Voltage - 1.2V**

Summary of 2006 Accomplishments

- Scaled up best Pt alloy compositions in production unit, and achieved same level of performance improvement.
- Produced high weight loading Pt alloy on high surface area carbon, with high absolute performance at significantly lower Pt content – exceeding the target of 0.6 mgPt/kW in single MEA.
- Extensively investigated catalyst morphology as function of processing conditions, carbon support and metal loading.
- Started long term durability testing using cycling protocols.
- Successfully installed rapid GDE deposition equipment at CSMP, full commissioning in progress.
- Started MEA preparation for short stack testing by Hydrogenics

Future Work

- Continue durability testing under cycling protocols:
  - Alloy compositions
  - Corrosion resistant carbons
- Combine alloys with corrosion resistant carbon.
- Preliminary results on Pt supported on new carbon support.



Constant Voltage 1.2 V Hold Experiment

- Anode: Hydrogen, 500cc/min; Cathode: Nitrogen, 500cc/min
- Cell Temperature: 80ºC
- Inlet Cathode and Anode RH - 100% RH

MEA Test Conditions:

- 50 cm^2, Nafion™ 112,
- Cathode: 0.6 mg Pt/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
- Non IR corrected

Acknowledgements

- DOE Hydrogen Program, Award DE-FC0402AL67620, Topic 1A1
- DOE Program Managers: Amy Manheim, Walter Podolski, Reg Taylor
- CSMP, DuPont Fuel Cells and CFDRC for cost share funding
- The whole CSMP team and especially: Yvette Herrera, Leonard Perez, Jim Brewster
- DuPont Fuel Cells: Todd Fountain, Gowri Nagarajan, Dennis Kountz

CSMP's Facility in Albuquerque

2005 DOE Yearly Review Comments and Recommendations

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- ***Comment:*** "Combinatorial approach might yield new information that would allow lower Pt loading".
- ***Comment:*** "Good approach in that it is a unique process/fabrication method that provides an alternative to the standard methods for making dispersed catalysts. Combinatorial capability makes a lot of sense".
- ***Comment:*** "Excellent progress in ternary selection and demonstration of performance in MEA. Good advances in pretreatment and characterization".
- ***Comment:*** "Focusing on ternaries is also good focus point given the known literature results".
- ***Comment:*** "The interaction with DuPont is good and obviously beneficial".
- ***Comment:*** "Performance, catalyst utilization and durability still needs improvement".
- ***Comment:*** "Approach does not appear to be influenced by theoretical considerations".

Responses to Previous Year Comments

- ***Comment:*** "Must include repeated potential cycling testing to assess durability."
  - ***Initiated potential cycling protocols.***
- ***Comment:*** "Must show activity normalized per mass of total noble metal, not just Pt mass. This is essential since the identity of the alloying elements is not disclosed (i.e., no way to assess ultimate material costs of compounds)."
  - ***For best performing compositions, activity normalized per mass of total noble metal is the same normalized per mass of Pt.***
- ***Comment:*** "Opportunities to alter or modify the carbon support materials in the CSMP process should be part of of any catalyst durability studies"
  - ***Work on corrosion resistant carbon initiated with promising preliminary results.***
- ***Comment:*** " Why not repeat library with a different support, i.e. electronically conducting oxide"
  - ***Spray method is not limited to carbon supports, possible in future work.***