



2006 Fuel Cell Seminar, November 13-17, 2006, Honolulu, Hawaii
Session # 3B, Low Temperature Fuel Cells II

CABOT

Low Precious Metal Alloy Catalysts and Durable Carbon Supports

**P. Atanassova, Y. Sun, G. Rice,
J. Brewster, J. Xie, A. Kyrilidis, G. Moeser**

Cabot Fuel Cells, Albuquerque, NM



Cabot Fuel Cells

CABOT

- **New name, clear commitment to Fuel Cells commercialization**
- **Combining the expertise in carbon supports with electrocatalyst manufacturing**
- **New methods, new results!**
 - **Hydrogen-air FC & DMFC materials solutions**
- **Advanced electrocatalysts for Hydrogen Air Fuel Cells:**
 - **Low precious metal alloys**
 - **Oxidation resistant carbon supports**
 - **Modified carbon black supports for low humidity operation**



Cabot Fuel Cell Materials Development

Performance
mW/cm²

Cost
gPt/kW; \$/kW

Durability
5000 h

- **Low Precious Metal Alloy Electrocatalysts**
- **Advanced Carbon Supports**
- **Easy Handling for Inks Formulation**
- **Optimized Electrode Layers and MEA Structures**



High Throughput Catalyst Discovery Platform is Key Element for Rapid Optimization of Complex Alloy Compositions

CABOT



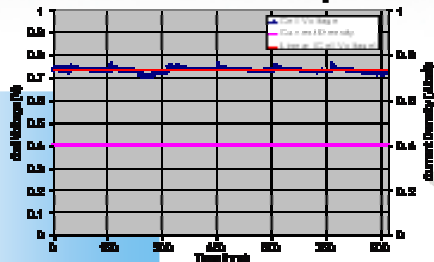
High Throughput Synthesis



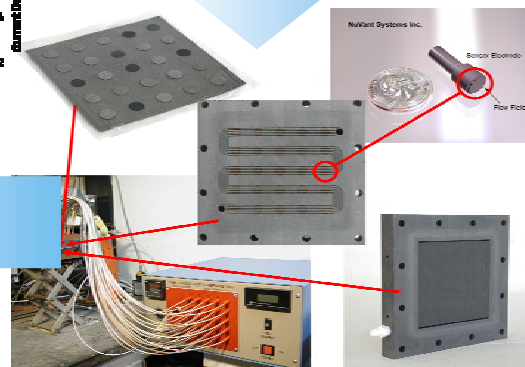
Rapid Cathode Layer Fabrication



High Volume Production



Electrochemical and Physical Characterization



Rapid Screening in MEA Configuration

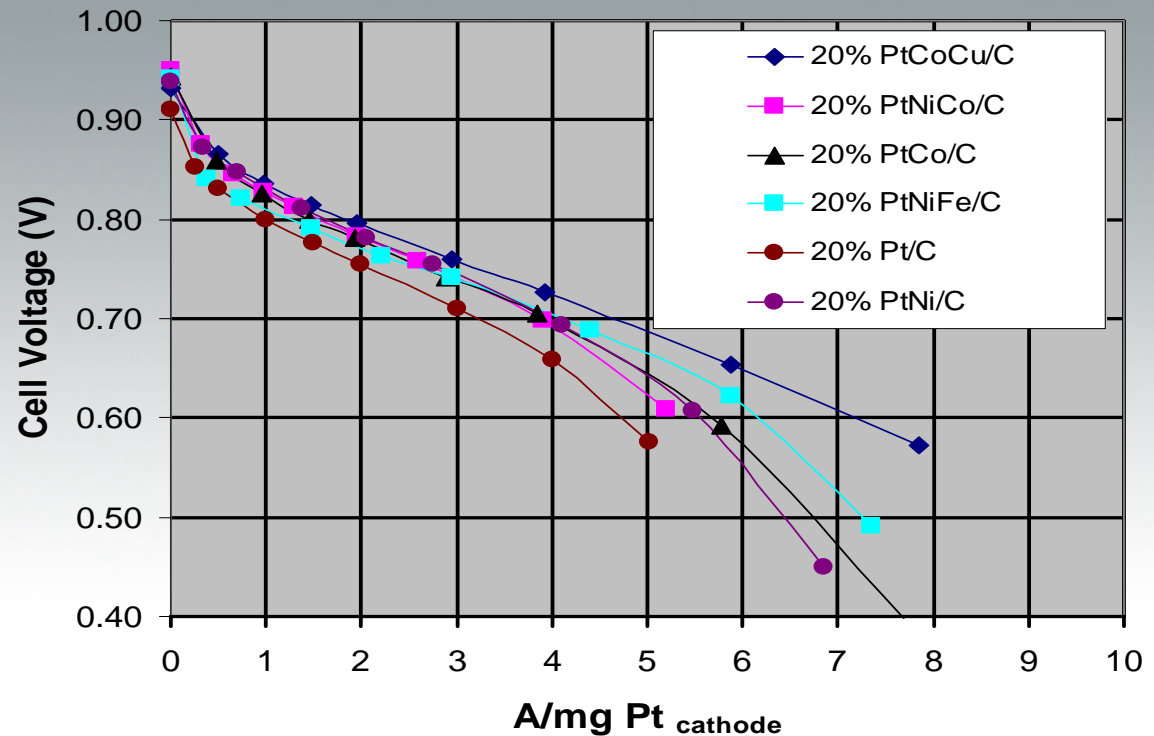
creating what matters



Two Fold Mass Activity Improvement Demonstrated by Ternary Pt- Alloy Supported Catalysts

CABOT

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



Best Pt alloy compositions show up to 2 fold mass activity improvement in hydrogen air fuel cell

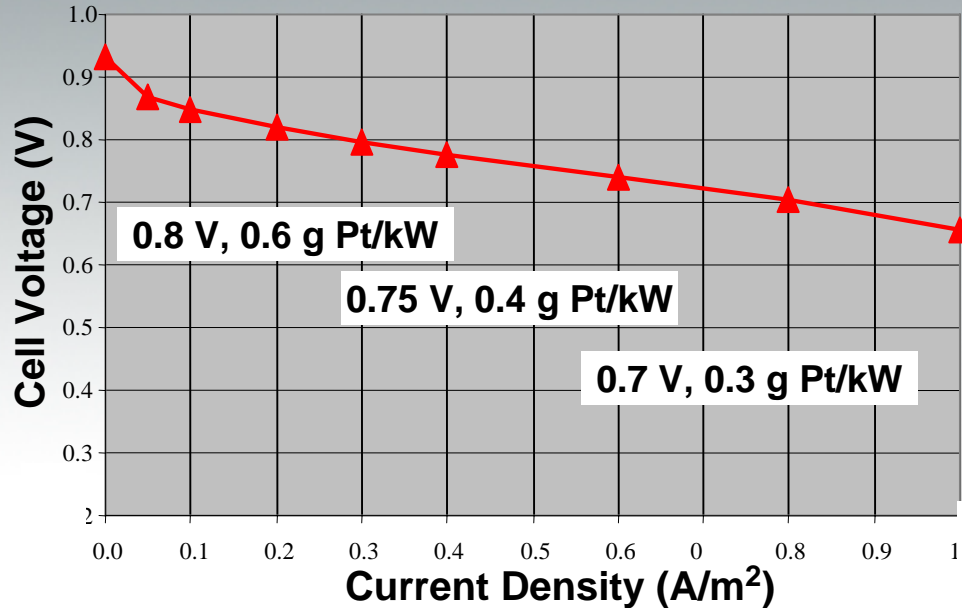
Test Conditions:

- Non IR corrected, 50 cm² MEA, Nafion™ 112
- Loadings: Cathode: 0.2 mgM/cm², Anode: 0.05 mgPt/cm²
- 80°C, 1.5 H₂/2.5 air at 1A/cm², 100% RH, 30 psig, 10min/point



Superior MEA Performance at Low Precious Metal Loadings

CABOT

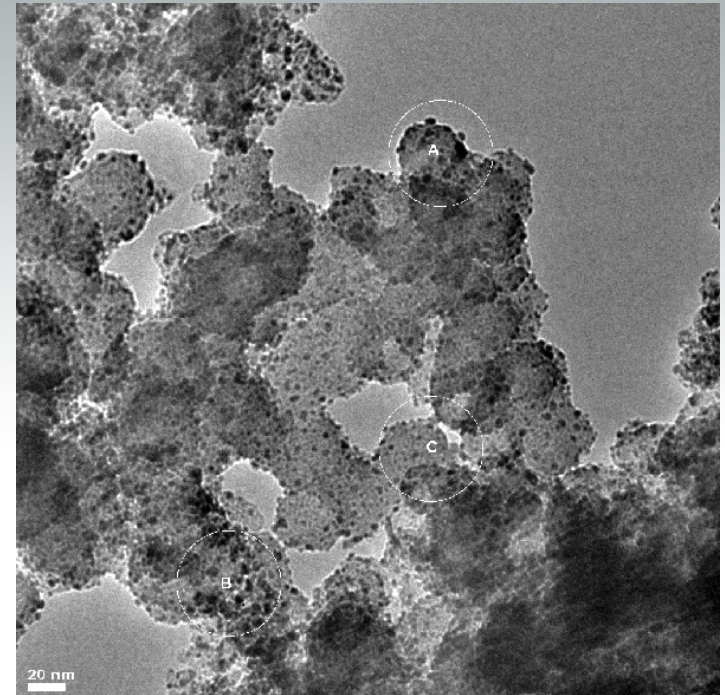


MEA loadings: **0.15 mg Pt/cm² total loading**
Cathode: **0.1 mg Pt/cm²**; Anode: 0.05 mg Pt/cm²

Test Conditions:

- 50 cm², Nafion™ 112
- 80°C, 1.5 H₂/2.5 air at 1A/cm², 100% RH, 30 psig
- 10 min/point, Non IR corrected

Highly Dispersed Alloy Catalysts

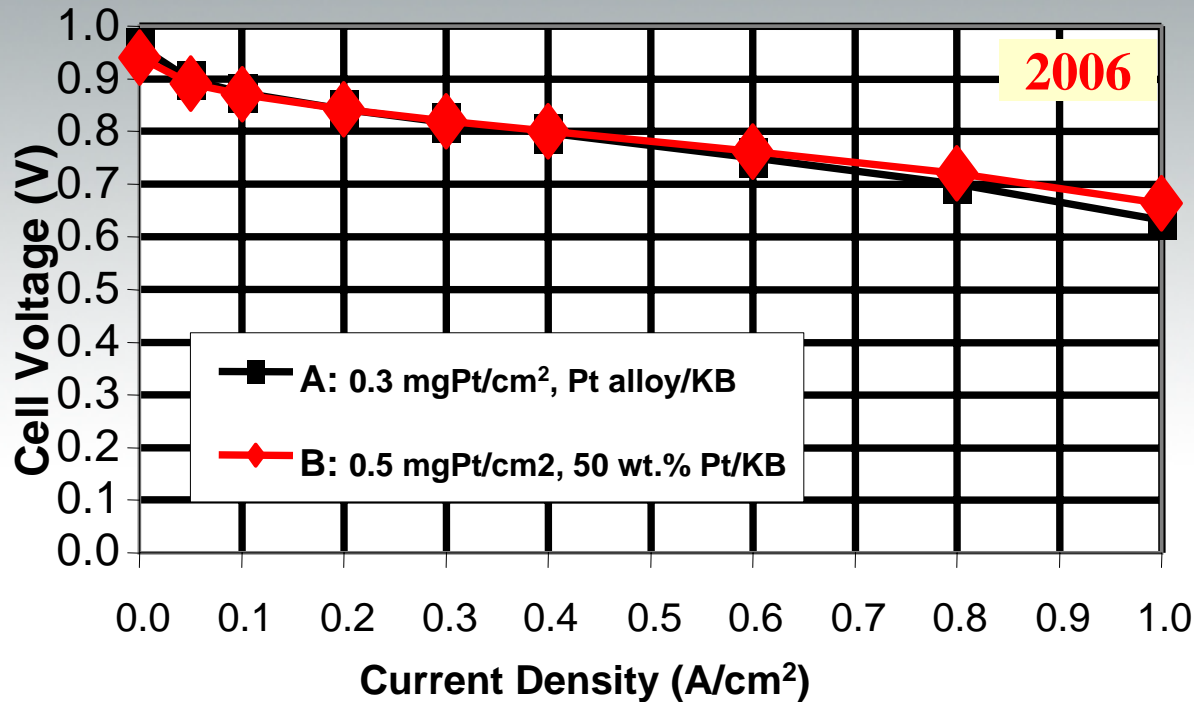


Pt (111): 40.36 (2 θ); a: 3.87 Å
Particle size (XRD): 2.4 nm



High Absolute Performance Combined with Low Precious Metal Loadings

CABOT



• *High Metal Loading Catalyst on High Surface Area Carbon Support*

• *Identical performance at approximately half of the Pt content*

Test Conditions:

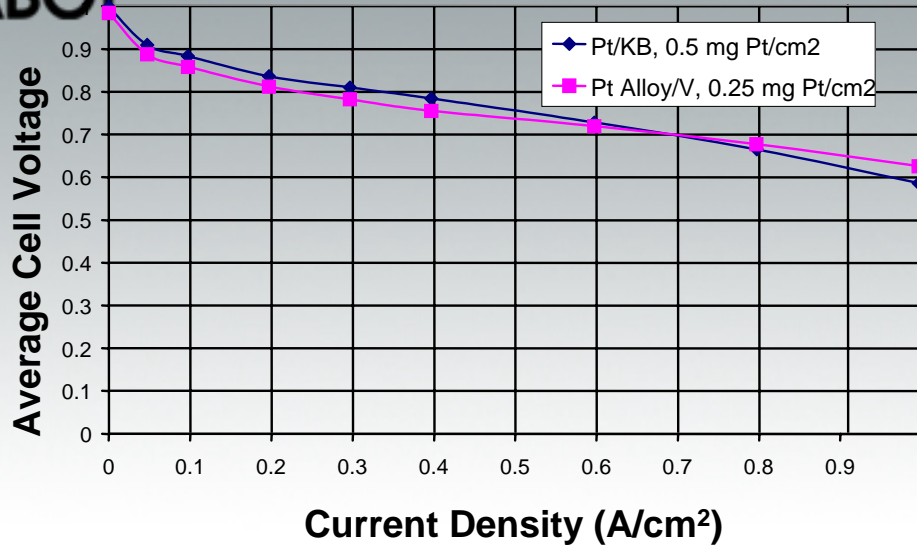
- Non IR corrected 50 cm², Nafion™ 112, cathode: as listed; anode: 0.05 mgPt/cm²,
- 80°C, 1.5 H₂/2.5 air at 1A/cm², 100% RH, 30 psig, 10 min/point

- At 0.8 V a power density of 0.32 W/cm² was achieved
- At 0.7 V approximately 0.56 W/cm² (total PM loading, anode plus cathode of 0.35 mgPt/cm²), 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



Short Stack Testing Validates Alloy Catalysts Performance

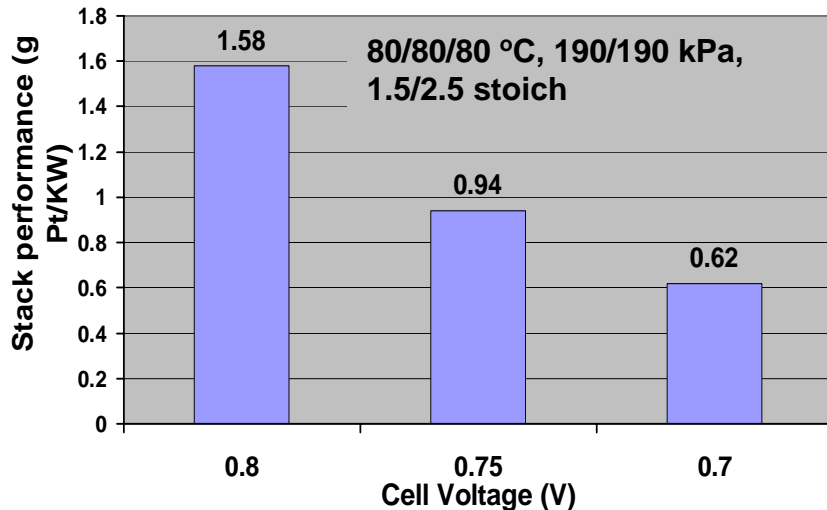
CABOT



- **Short stack evaluation completed by Hydrogenics Corporation**
- **0.6 gPt/kW demonstrated in a short stack at 0.7 V and stoich test conditions**

Stack Test Conditions:

- 5 cell, large area, Nafion™ 112 cathode: as listed; anode: 0.05 mgPt/cm²
- 80/80/80°C, 55/55 kPa, 1.5/2.5 stoich
- 80/80/80°C, 190/190 kPa, 1.5/2.5 stoich
- 80/80/64°C, 175/175 kPa, 2/2.5 stoich

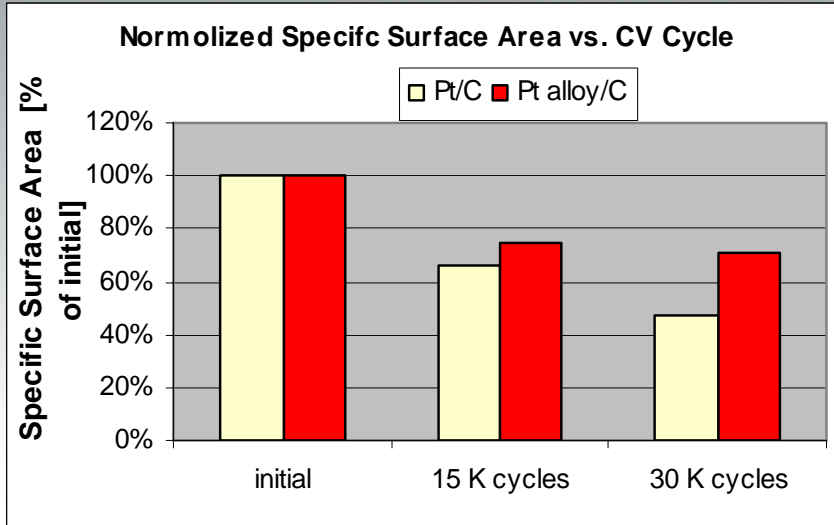


	Mass activity (A/mg Pt cathode)		Performance improvement (%)
	50% Pt/KB	Pt Alloy/V	
0.8V	0.67	0.95	42
0.75V	1.04	1.7	63
0.7V	1.37	2.75	100



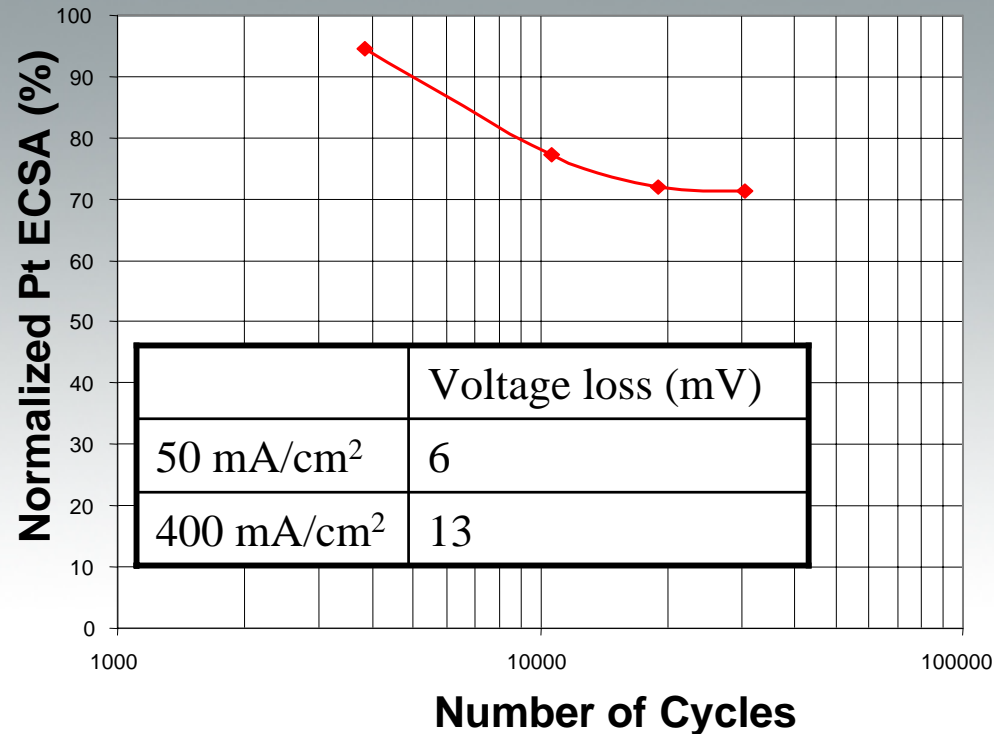
Long-Term Durability Under Cycling Protocols

CABOT



Test Conditions:

50 cm² MEA, cycling under H₂/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.



Pt alloy catalyst shows 30% loss of surface area after 20 K cycles and no further loss is observed until 30K cycles !



Long Term Performance Losses Related to Carbon Corrosion

CABOT

- **Carbon Support Durability is considered to be a major barrier for commercialization of automotive fuel cells**
- **Carbon corrosion is accelerated during start/ stop cycles and at high temperature operating conditions**
- **Type of performance losses related to carbon corrosion**
 - **Pt sintering due to loss of active phase/support interaction**
 - **Oxidation of carbon surface leads to layer flooding effects**
 - **Break down in carbon/carbon interface**
- **Conventional approaches to improving carbon durability lead to trade offs between durability, absolute performance and catalyst ink properties**



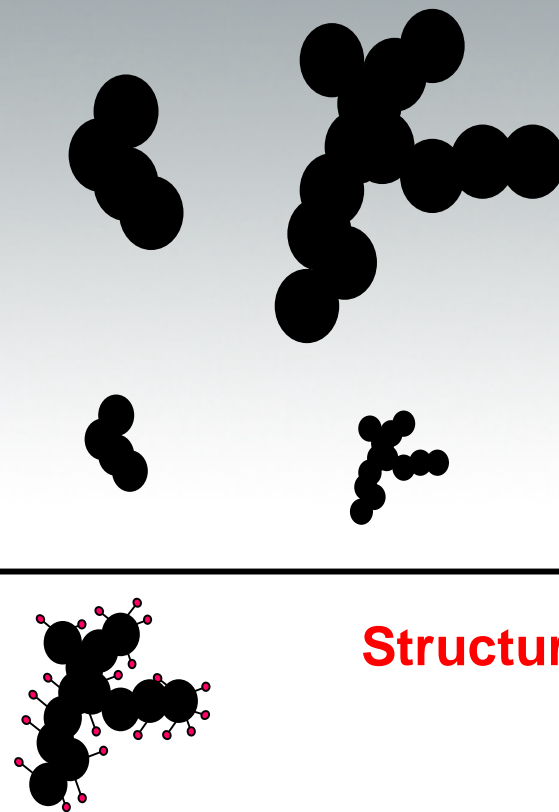
Ability to Control Carbon Support Properties

CABOT

Combination of morphology control and surface modification allows for *rational design of carbon materials*

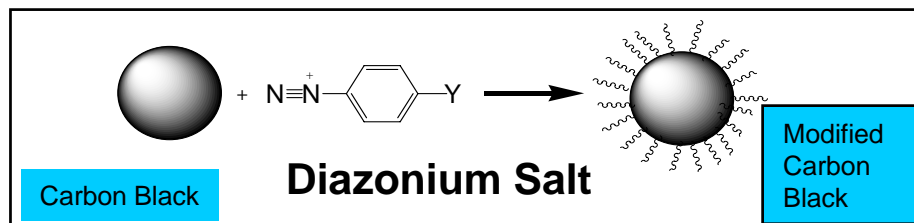
- Carbon black morphology can be controlled to design the length scale of gas and water transport channels
- Various degrees of carbon support graphitization can be achieved
- Carbon support surface chemistry can be modified

Particle Size



Structure

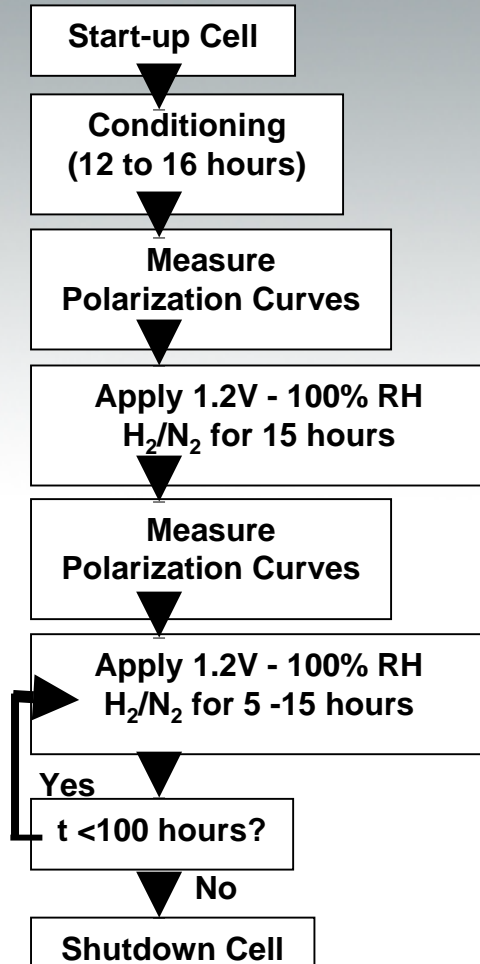
Surface Chemistry





Carbon Corrosion Analysis Approach

CABOT



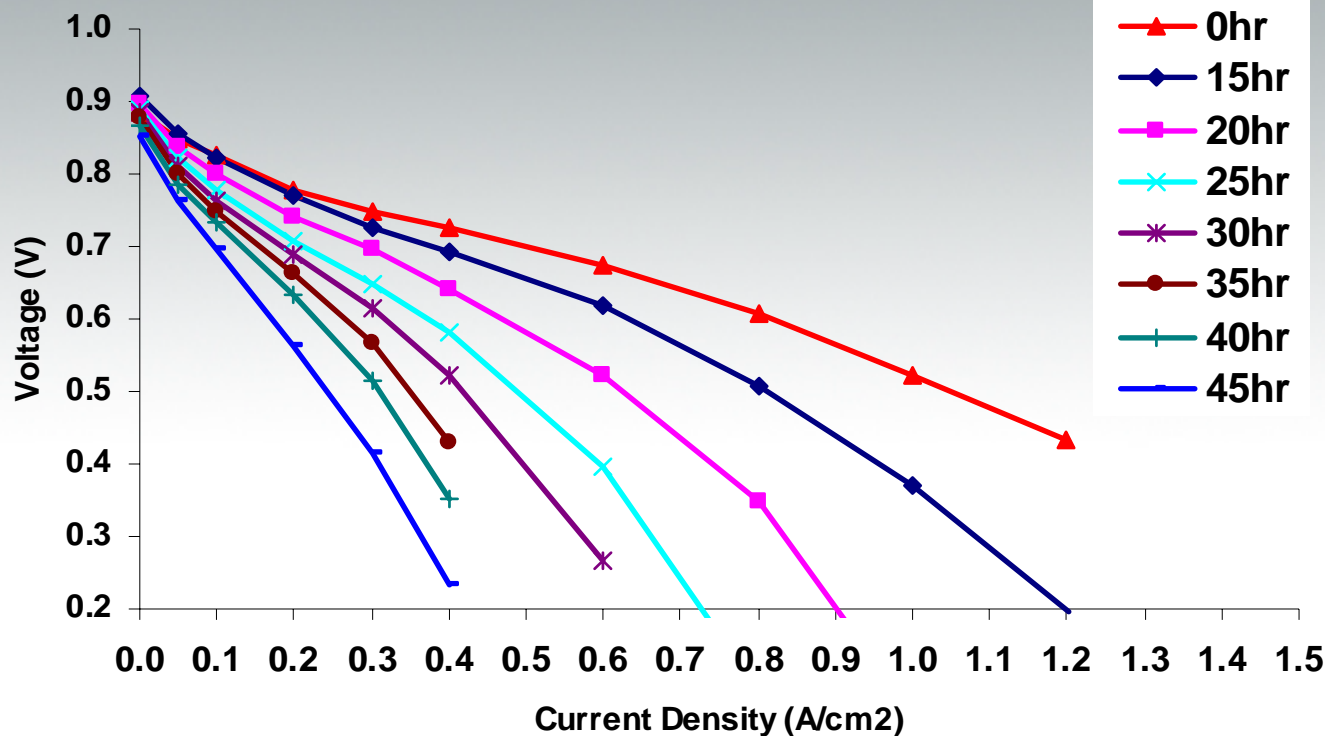
- Investigate and evaluate the corrosive behavior of dispersed carbon blacks in low temperature fuel cell environment
- Corrosion resistance evaluation protocol adopted from GM/DOE
 - Polarization curves test conditions 80°C, stoich flows A/C = 3/3, 50% RH, 7 psig
- **Study the effect of platinum loading, surface modification and morphology of the carbon blacks on the corrosive behavior of electrocatalysts.**
- Goal – less than 30 mV loss at 1 A/cm² after 100 hrs corrosion test



Severe Corrosion Losses with Standard Supports

CABOT

60% Pt / Ketjen Black



Polarization curves
test conditions:

80/80/80°C, stoich
flows A/C = 3/3,
50% RH, 7 psig

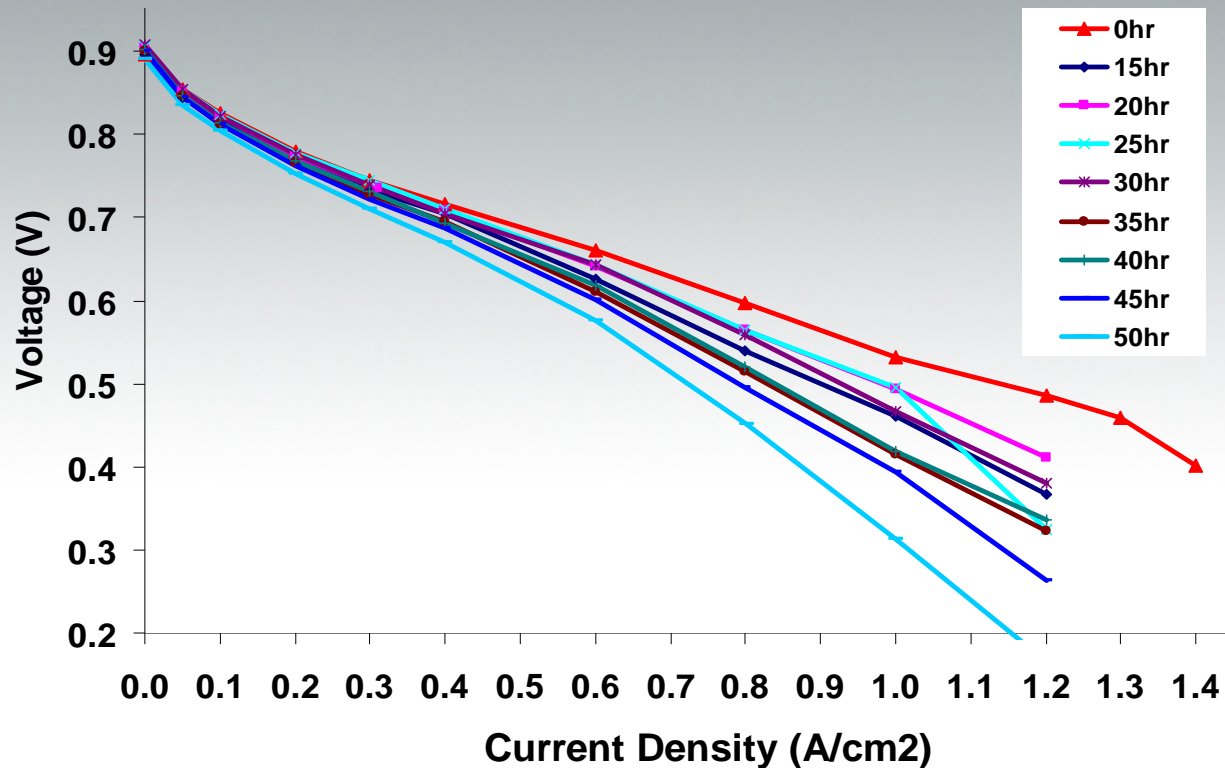
- > 100mv loss at 1A/cm² only after 15hrs
- > 53% Loss in EC area after 45hrs of standard corrosion protocol



Surface Modification Effectively Enhances Carbon Corrosion Resistance

CABOT

60% Pt / Modified Carbon Black (MCB)



Polarization curves
test conditions:

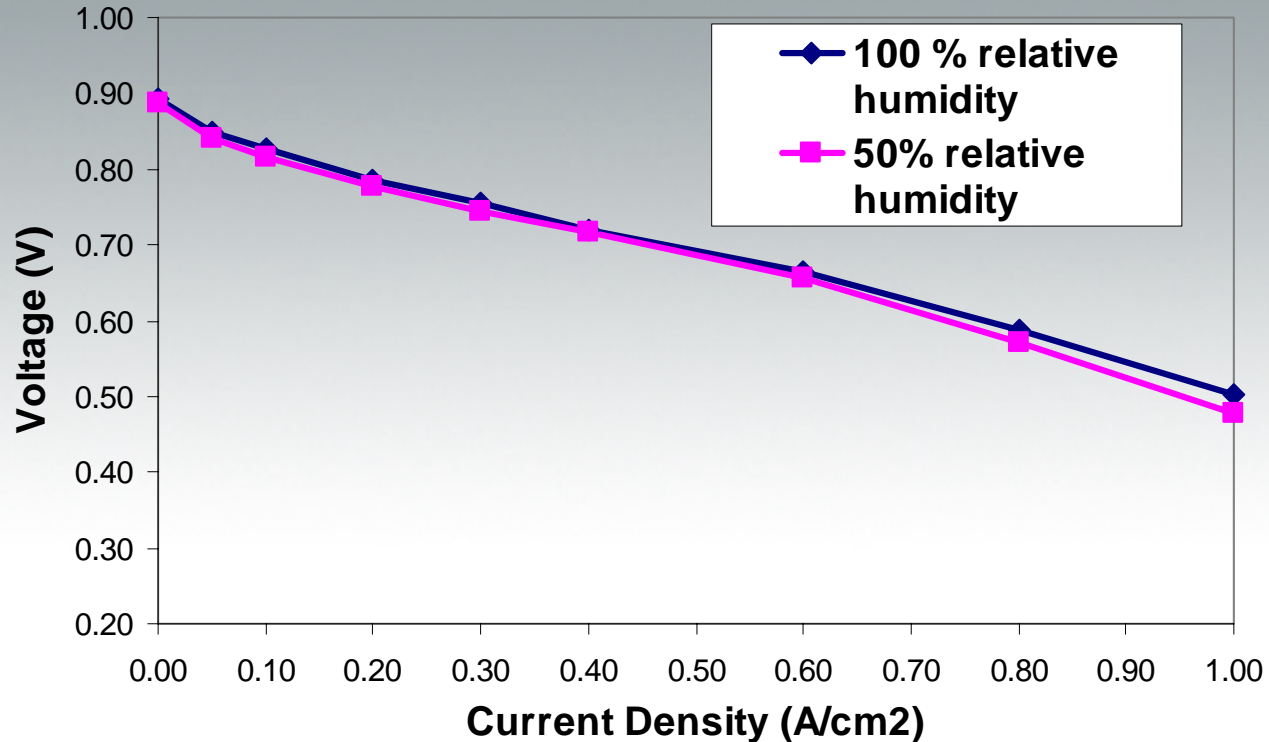
80°C, stoich flows
A/C = 3/3, 50% RH,
7 psig

- >100mV Loss at 1A/cm² after 50hrs
- Improvement is related to the coverage of functional groups on carbon surface
- Functional groups stabilize the carbon surface



Surface Modification Enables Operation at Low Relative Humidity Conditions

CABOT



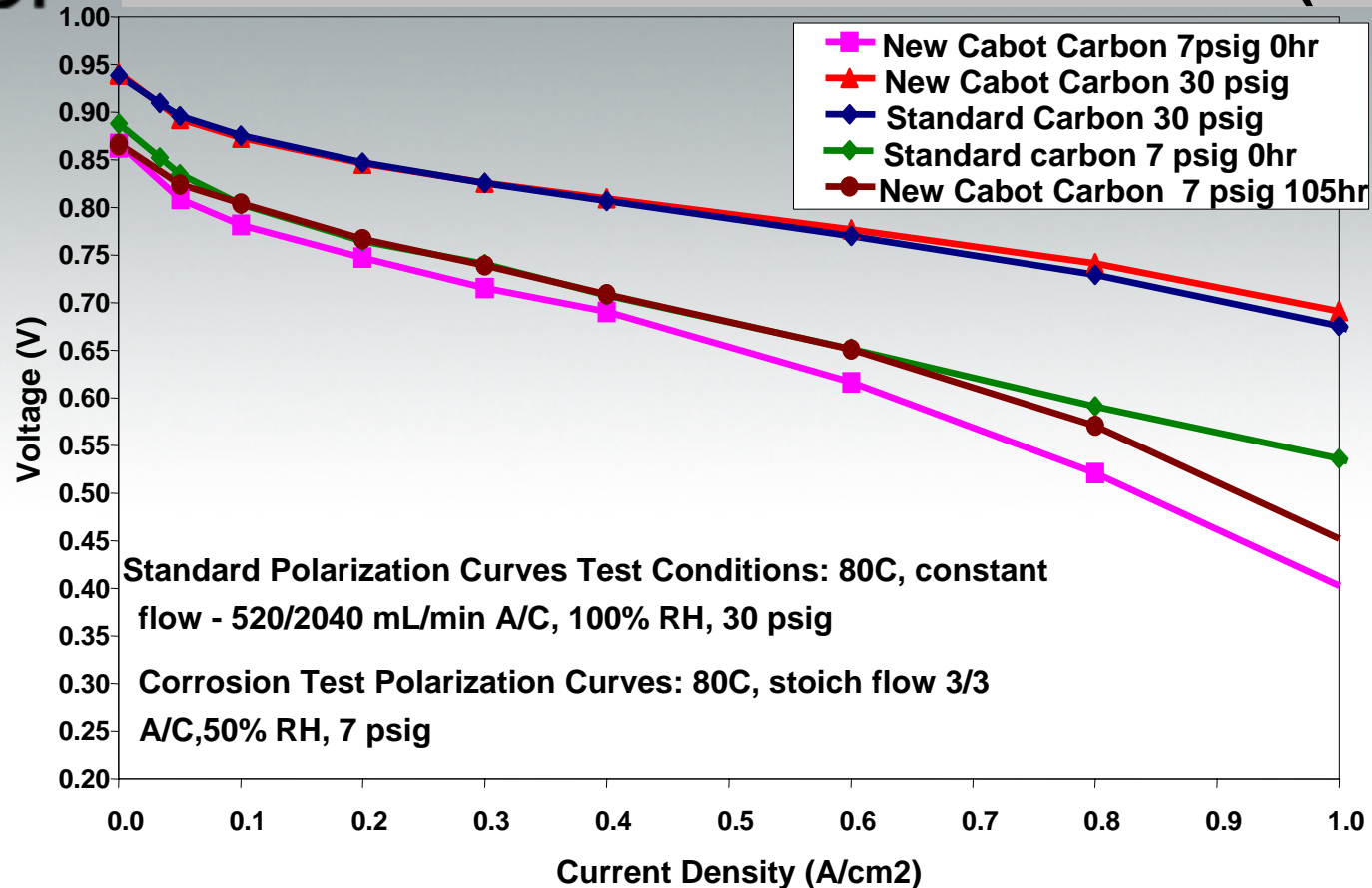
- **100 % relative humidity test: flow stoich = 2.0 (A/C), cell temperature 80°C back pressure =10 psig (A/C), RH=100% (A/C)**
- **50 % relative humidity test: flow stoich = 2.0 (A/C), cell temperature 80°C back pressure =10 psig (A/C), RH=50%/50% (A/C)**



Superior Corrosion Resistance with New Cabot Carbon Support

CABOT

60% Pt / Corrosion Resistant Carbon (CRC)



- Identical initial absolute performance after layer optimization
- No loss of performance after 105 hrs corrosion test



Summary

- **Alloy Electrocatalysts:**
 - Two fold mass activity improvement by Pt-alloy catalysts
 - High absolute performance combined with low precious metal loadings in a single cell and short stack
 - Significant durability improvement under cycling protocols
- **New Carbon Supports:**
 - Surface modification of carbon supports effectively enhances carbon corrosion resistance and enables operation at low relative humidity operating conditions
 - No performance loss after 105 hours of standard corrosion protocol without sacrificing initial performance
- **Combination of durable Pt alloy catalysts with corrosion-resistant carbon supports is a viable way for next generation automotive fuel cell materials**



Future Work

- Cabot's press release on November 13th, 2006 announced plans to introduce new products in Q1, 2007:
 - **Superior Durability Electrocatalysts** based on Corrosion Resistant Carbon (CRC) supports
 - **Superior Performance Electrocatalysts** for Operation at Low Relative Humidity based on Modified Carbon Blacks (MCB)
- For additional information:
 - Visit us at Cabot's boot #102
 - info@cabotfuelcells.com
 - Presentations at ECS meeting, Cancun



Acknowledgements

CABOT

- Cabot Corporation
- DOE Hydrogen Program, Award DE-FC0402AL67620
- NIST ATP Program 70NANB4H3019
- The whole Cabot team and especially: Greg Romney, Fred Von Gotteberg, Yakov Kutsovsky, Martin Green, Geoffrey Moeser, Yvette Herrera, Leonard Perez, Jason Zack
- Madhusudhana Dowlapalli, Plamen Atanassov, Ceramic and Composite Materials Center, University of New Mexico



Cabot's Facility in Albuquerque