# Development of Alternative and Durable High Performance Cathode Supports for PEM Fuel Cells

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# Overview

## Timeline

- Project start date Jan 2007
- Project end date  Dec 2010
- Percent complete 25%

## Budget

- Total project funding
  - DOE share $4,234K
  - Contractor share $255K
- Funding received in FY07
  - $1,241K (federal, requested)
  - $820K (federal, approved)
  - $72K (cost share)
- Funding received in FY08
  - $1,300K (federal, requested)
  - $1,400K (federal, approved)
  - $72K (cost share)

## Barriers

- A. Durability of cathode catalyst supports
- C. Performance of cathode supported catalyst

## Partners

- AFCC– guidance on fuel cell testing
- Oak Ridge National Laboratory – mesoporous carbon supports
- University of Delaware – Model materials
- Pacific Northwest National Laboratory
  - Synthesis and test of cathode/fuel cell
  - project management

# Objectives

| | |
|---|---|
| Overall | ➢ Develop and evaluate new classes of alternative and durable high-performance cathode supports |
| 2007 | ➢ Provide fundamental understanding of Pt/support model systems<br>➢ Synthesize high surface area cathode supports<br>➢ Select the potential support with better stability than commercial carbon black support |
| 2008 | ➢ Identify lead cathode compositions with better durability than carbon black supported Pt cathode |
| 2009 | ➢ Identify compositions with 2X better stability than carbon black supported catalyst for cell demonstration. |
| 2010 | ➢ Demonstrate durability under accelerated test protocols that meet DOE lifetime criteria |

# Milestones, Schedule and Go/no-go Decisions

| Task Number | Project Milestones | Task Completion Date | | | | Progress Notes |
|---|---|---|---|---|---|---|
| | | Original Planned | Revised Planned | Actual | Percent Complete | |
| 1 | Better stability of model Pt/WC | 09/30/07 | 09/30/07 | 9/30/07 | 100% | completed |
| 2 | High surface area WC and CMO | 09/30/07 | 12/31/07 | 12/31/07 | 100% | completed |
| 2 | Select carbon support | 09/30/07 | 12/31/07 | 9/31/08 | 50% | Delayed[1] |
| 2&3 | Identify lead compositions | 09/30/08 | 12/31/08 | | 30% | On track |
| 2&3 | Identify compositions for cell test | 09/30/09 | 12/31/09 | | 0% | Not started |
| 3 | Demonstrate target durability | 09/30/10 | 12/31/10 | | 0% | Not Started |

[1] delayed due to both the reduced budget in FY07 and a longer time to develop an appropriate test protocol

Go/no-go decisions:
Year 1: Decided to use mesoporous carbon as both scaffold and as template for CMO synthesis
Year 2: Continue effort if stable compositions can be identified
Year 3: Move forward with cell test if durable supported catalyst can be identified

# FY08 Revised Milestones

- Complete electrochemical evaluation of Pt/WC cathode stability

- Down-select carbon support from CNT, mesoporous carbon and carbon black
  - % drop in ECSA and Iorr < 80% of drop for carbon black.

- Identify lead cathode compositions and microstructure
  - % drop in ECSA and Iorr < 60% of drop for carbon black standard

# Approach - Overall

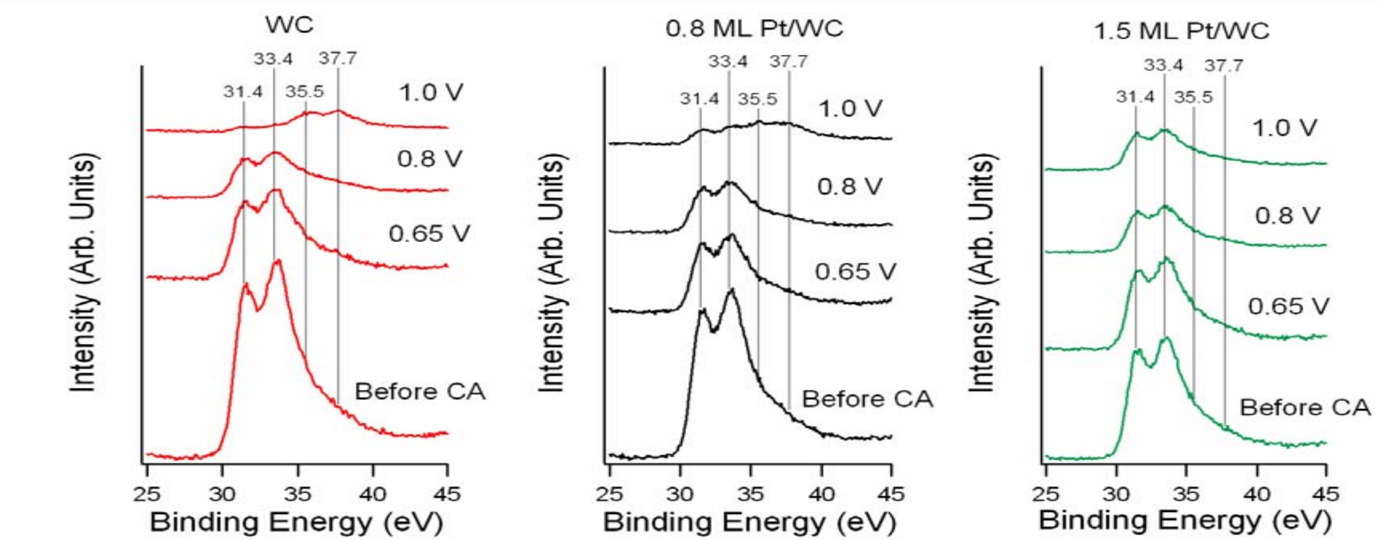
- Develop and evaluate new classes of alternative and durable cathode supports using graphitized carbons as scaffolds and protect the carbon surface with
  - Tungsten carbide (WC)
  - Oxycarbides
  - Conductive metal oxides (ITO)
  - $SnO_2$
  - $TiO_2$
- Enhance Pt dispersion and stability on these new classes of cathode supports

# Approach – Specific Tasks

- Fundamental understanding of model systems with well defined structures and compositions.
- Synthesis of high surface area cathode supports based on carbon scaffolds.
- Characterization and electrochemical evaluation of cathode supports

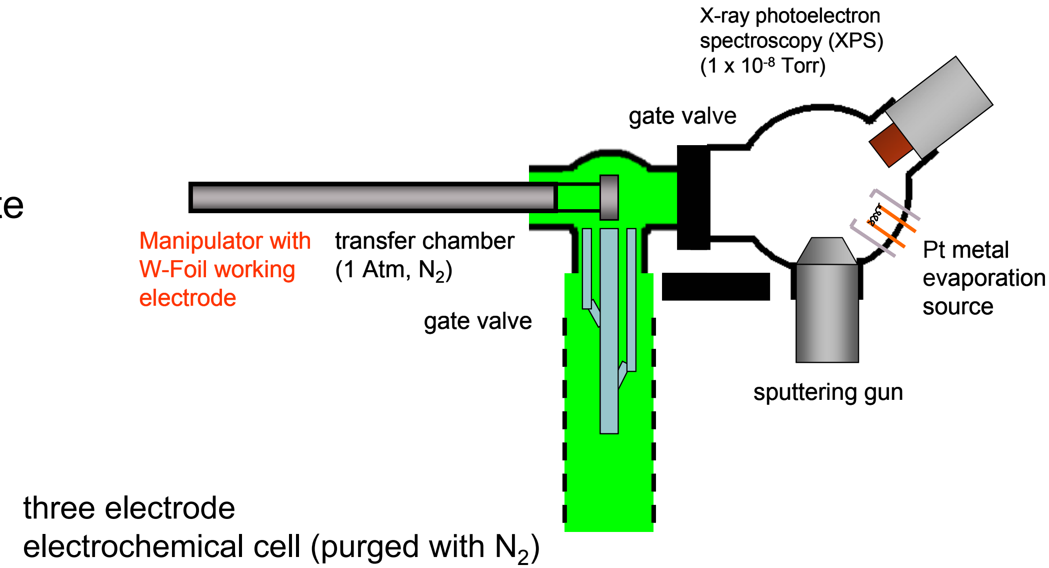
# Technical Accomplishments/Progress/Results

# Model Cathode Material Studies
## *In-Situ* XPS and Electrochemistry



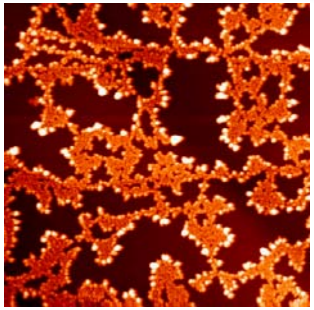

**Deposition of Pt on WC improves stability at high potential limits**

- Deaerated room temperature electrolyte
- 0.05 M $H_2SO_4$ (supporting)
- 0.2 M $CH_3OH$ (fuel molecule)

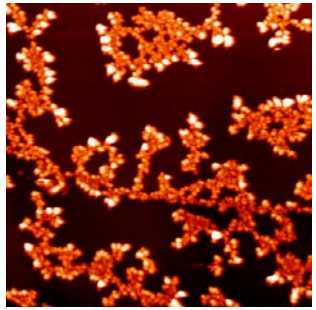


# STM investigations of Electrocatalyst-Support Interaction (Pt/HOPG)

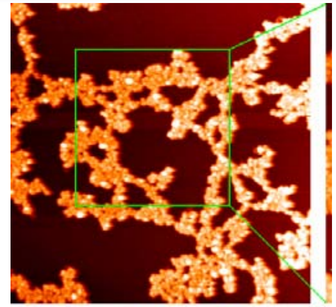
Low Pt Coverage



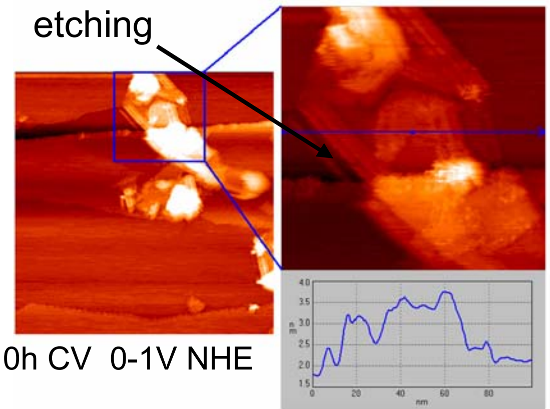
Pre-anneal



Post-anneal 300C, 3h



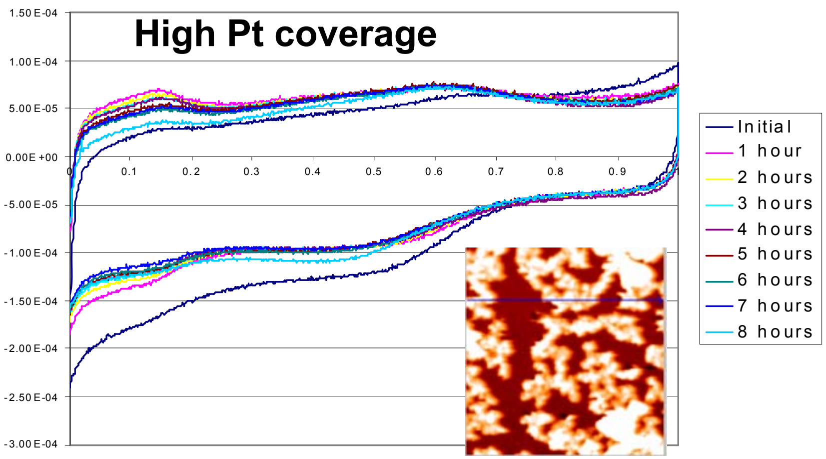
100 CV cycles 0-0.8V NHE
No changes




10h CV 0-1V NHE

Pt particles absent, carbon surface smooth, but shows signs of etching.

CV 0 to 1.0 V (NHE) 9 hours, 0.5M H2SO4
Steady decrease in Pt features with time associated with Pt aggregation




- For low Pt coverage, thermal stress alone does not induce changes in the Pt/C interaction. CV for 10 hours 0-1V V leads to total loss of Pt and signs of carbon etching.
- For high Pt coverage, very little Pt loss during CV 0-1V for 9h.

# Synthesis of High Surface Area Cathode Materials

- **Development of novel ordered mesoporous carbon (OMC)**
- **Dispersion of Pt**
  - **Substrates: XC-72, carbon nanotubes (CNT) and OMC**
  - **Loading method : incipient wetness approach**
  - **Activation temperature effects**
  - **New method: Pt-nanoparticle to maintain constant Pt particle size**
- **Metal oxide modification of XC-72**
  - **$SnO_2$,$In_2O_3$,$TiO_2$ etc.**
- **Synthesis of high surface area ITO and WC substrates**

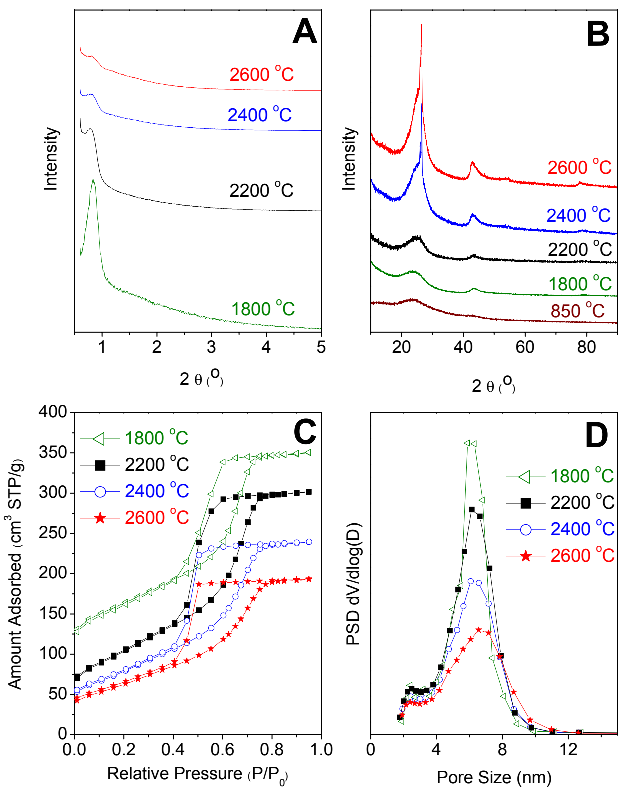
# Synthesis of Highly Stable Mesoporous Carbons

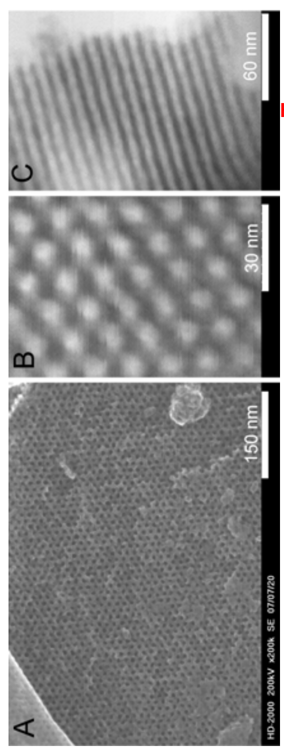
**Accomplishments:**

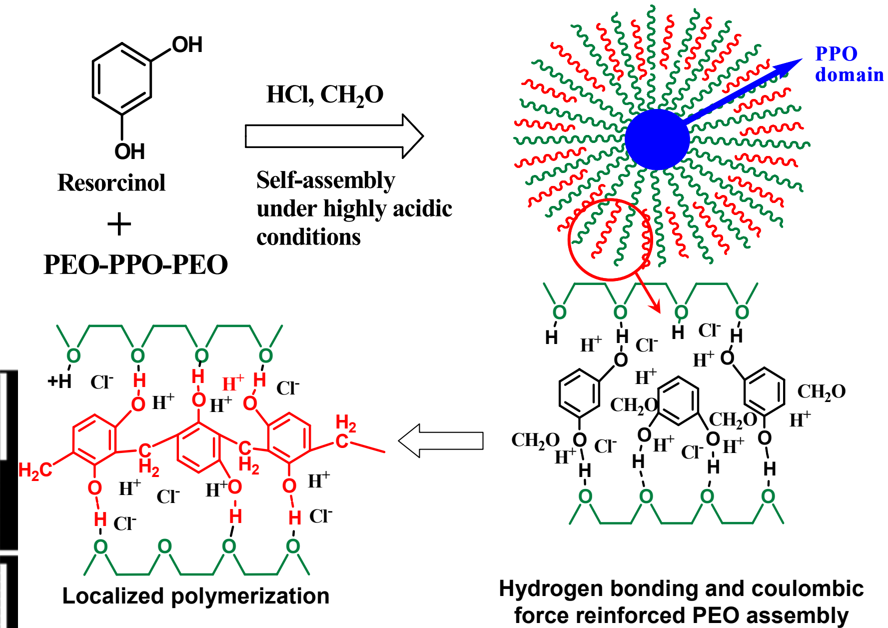
***Synthesis*** **– Established the protocol for synthesis of highly stable mesoporous carbons retaining porosity under graphitization conditions.**

**less expensive precursors**

***Processing*** **–Mesoporous carbons were used to disperse conducting oxide materials.**




Mesoporous Carbon Can Be Fully Graphitized while Retaining Mesoporous Structure

Conductivity of mesoporous sheets:

4 Ω·cm (850°C) → 3 mΩ·cm (2400°C)

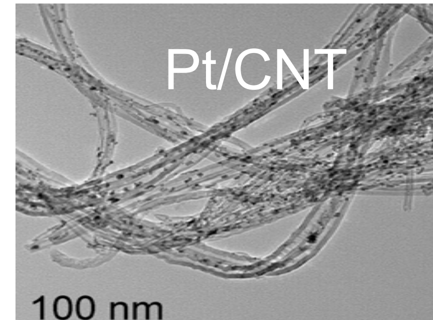
# Synthesis of High Surface Area Cathode Materials

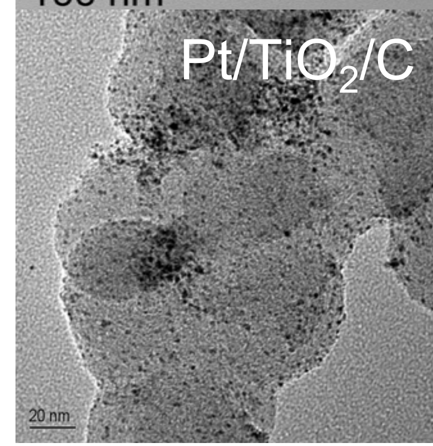
## Matrix of supports and modifications

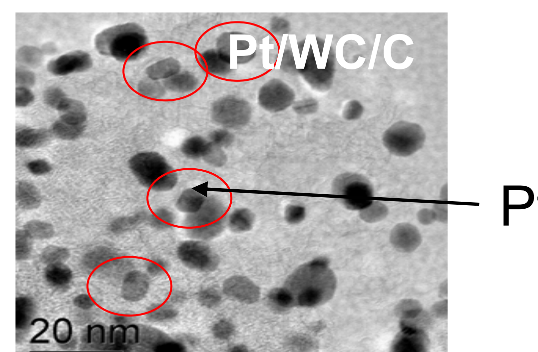
| Modification \ Support | Vulcan X72 | MWCNT | Meso-porous carbon | Graphene |
|---|---|---|---|---|
| none | Testing complete | Testing complete | Test in progress | Test in progress |
| $TiO_2$ | Testing complete | | | |
| $SnO_2$ | Test in progress | | | |
| ITO | | | | |
| WC | | | Test in progress | |
| $SiO_2$ | Test in progress | | | Test in progress |

● Testing complete (red) ● Test in progress (teal)

- Pt nanoparticles can be uniformly dispersed on carbon supports using an incipient wetness method
- Metal oxide modified Vulcan XC-72 were synthesized
  - The presence of metal oxide ($TiO_2$) stabilizes the dispersion of Pt
- High surface area ITO and WC were synthesized
  - Pt preferably bonds to WC

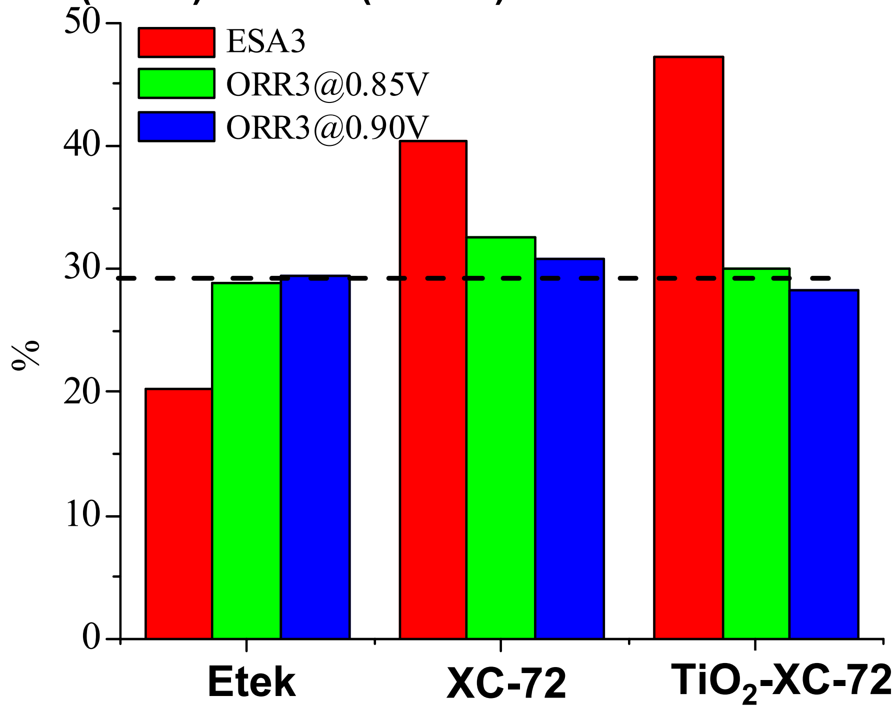


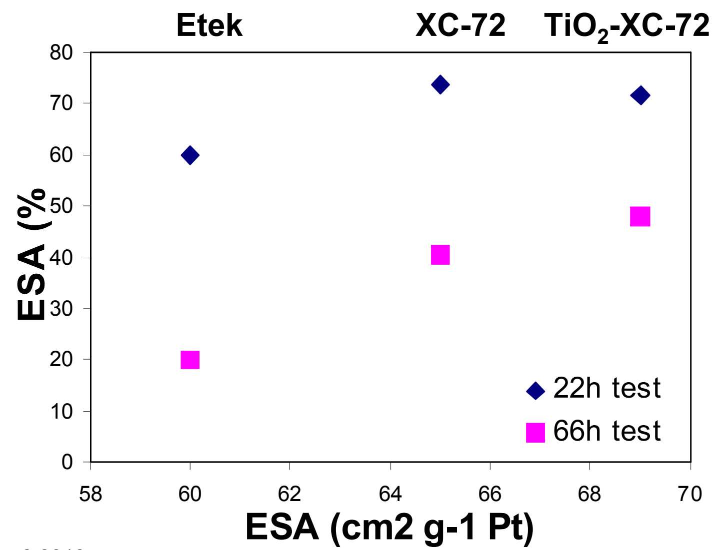



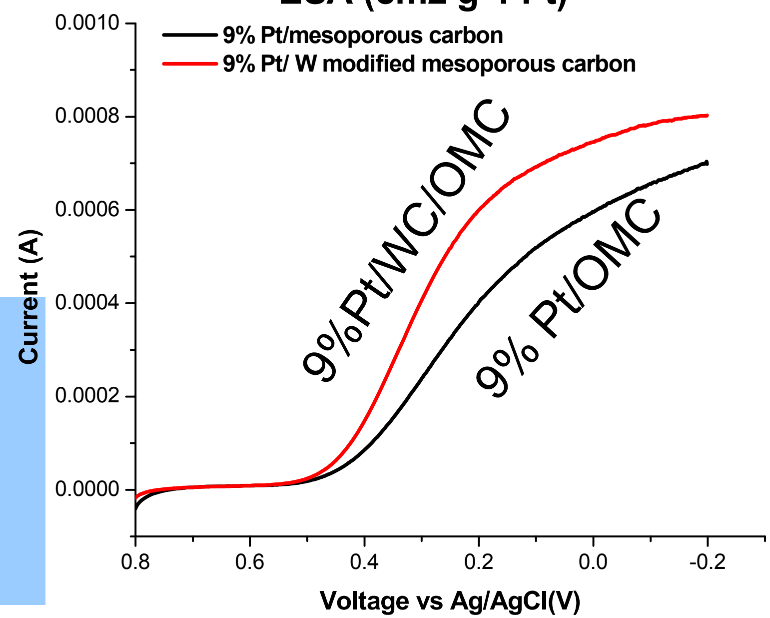



# Electrochemical Testing of Cathode Materials

**Potential step between 0.85V (5 sec) to 1.4V (10 sec) vs. NHE**




- $TiO_2$-XC-72 improved stability & activity over Etek
- WC modification improves activity for Pt/OMC

Future:

- Increase stability while maintaining high activity
- Investigate other conductive metal oxides

# Future Work

**FY08**

- Develop fundamental understanding of interfacial interaction on Pt/C and Pt/WC
- Continue investigation of other conductive metal oxide modified XC-72
  - Replace XC-72 with CNT and OMC

**FY09**

- Evaluate lead compositions under more severe conditions
  - Potential step between 1.4-0.6V to determine the effect of PtOx/Pt oxidation/reduction on support.
- Identify compositions with 2X better stability than carbon black supported catalyst for cell demonstration.

**FY10**

- Demonstrate durability under accelerated test protocols that meet DOE lifetime criteria

# Summary of Technical Accomplishments

- **Demonstrated improved stability of WC in the presence of Pt and identified degradation of Pt/HOPG model system**

- **Developed conductive ordered mesoporous carbon (OMC)**

- **Demonstrated improved stability (% drop in ESA <70% of that of Etek) and activity (15% over Etek) with $TiO_2$-modified XC-72**