DOE Hydrogen Program

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%

Barriers

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

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)

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** ➢ **Synthesize high surface area cathode supports** ➢ **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**

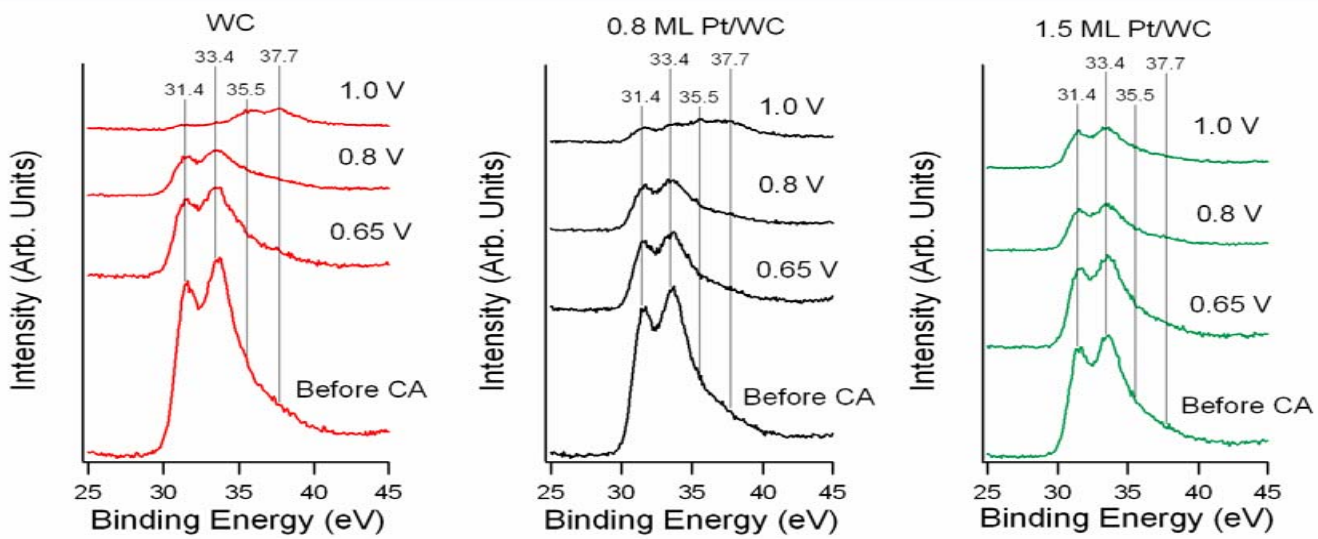
Approach – Specific Tasks

- **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

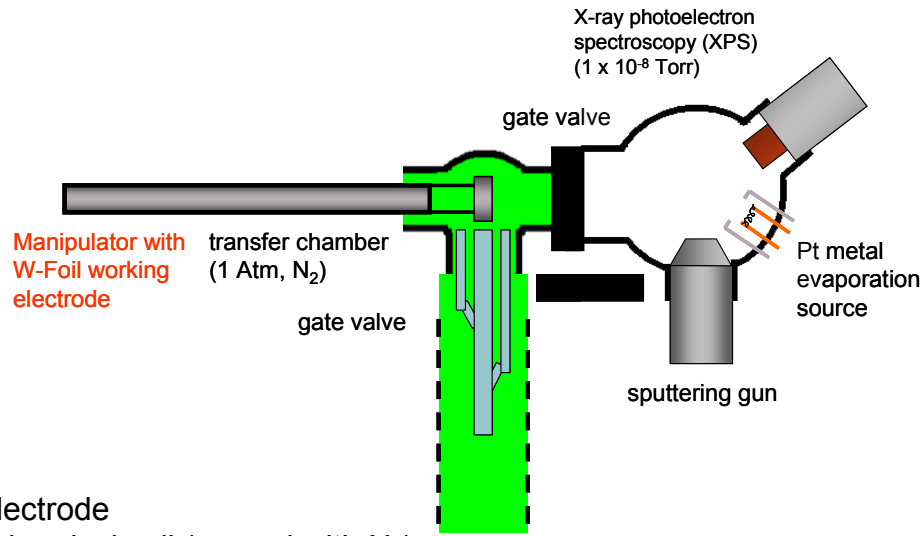
Model Cathode Material Studies

In-Situ XPS and Electrochemistry



Deposition of Pt on WC improves stability at high potential limits

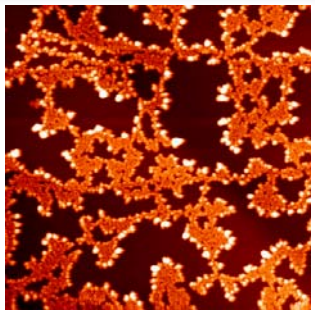
- Deaerated room temperature electrolyte
- 0.05 M H_2SO_4 (supporting)
- 0.2 M CH_3OH (fuel molecule)



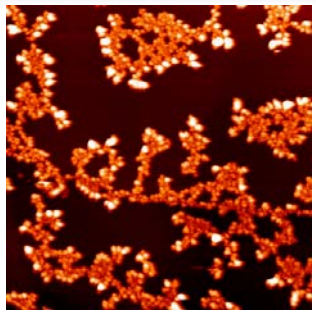
three electrode electrochemical cell (purged with N_2)

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

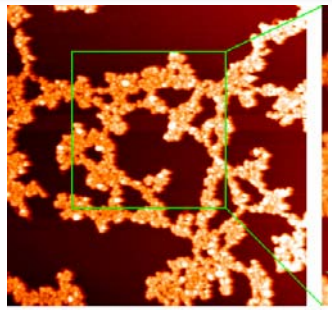
Low Pt Coverage



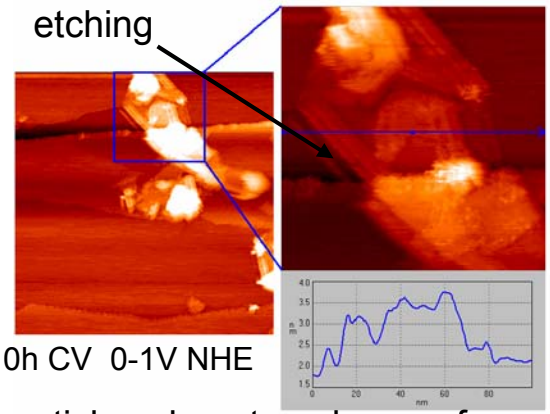
Pre-anneal



Post-anneal 300C, 3h



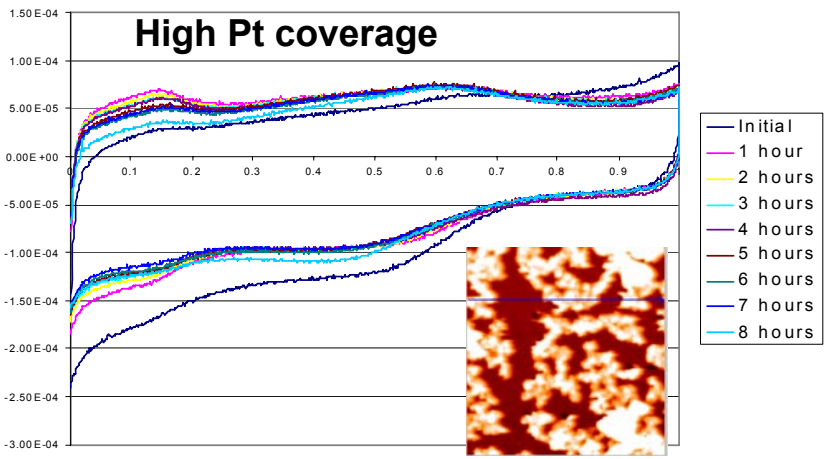
100 CV cycles 0-0.8V NHE
No changes



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**

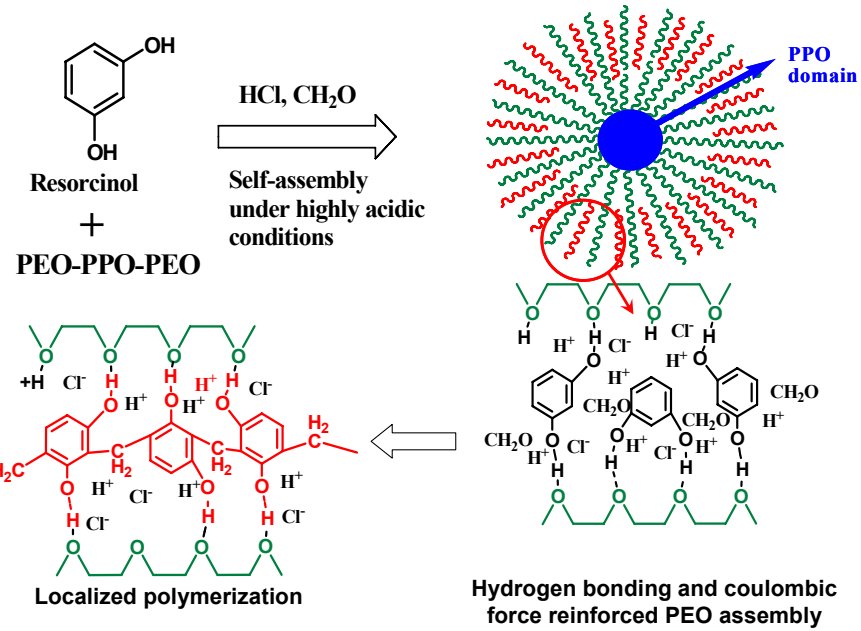
Synthesis of Highly Stable Mesoporous Carbons

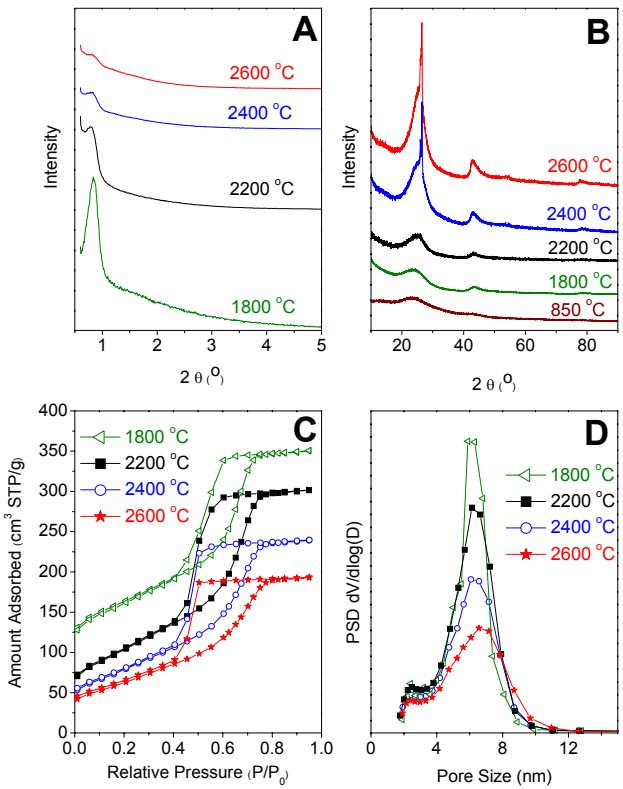
Accomplishments:

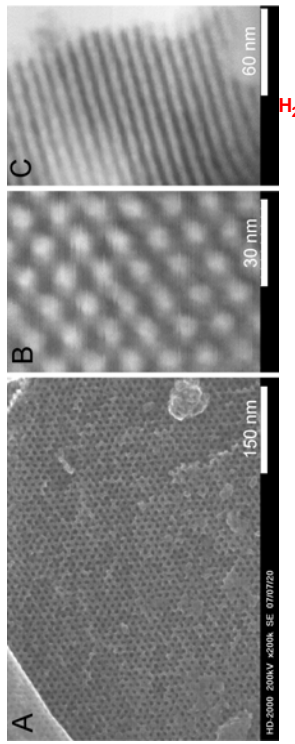
Synthesis **– Established the protocol for synthesis of highly stable mesoporous carbons retaining porosity under graphitization conditions.**

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:

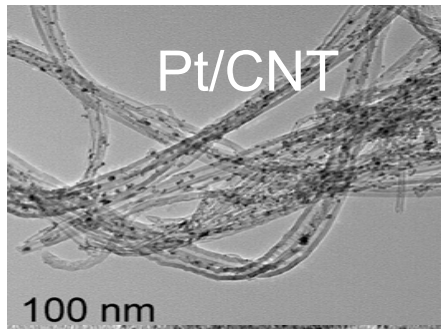
4 Ω·cm (850°C) → 3 mΩ·cm (2400°C)

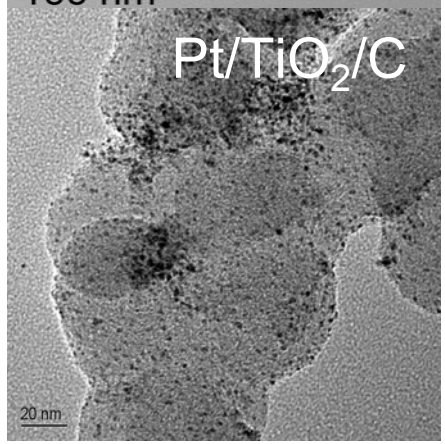
Synthesis of High Surface Area Cathode Materials

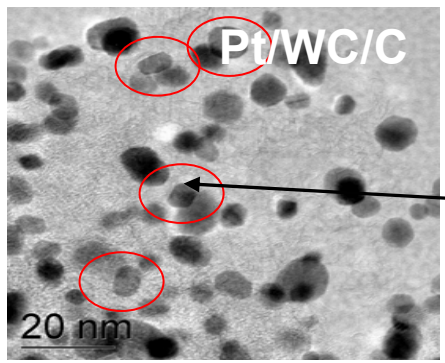
Matrix of supports and modifications

Modification \ Support	Vulcan X72	MWCNT	Meso-porous carbon	Graphene
none	●	●	●	●
TiO_2	●			
SnO_2	●			
ITO				
WC			●	
SiO_2	●			●

● Testing complete ● Test in progress

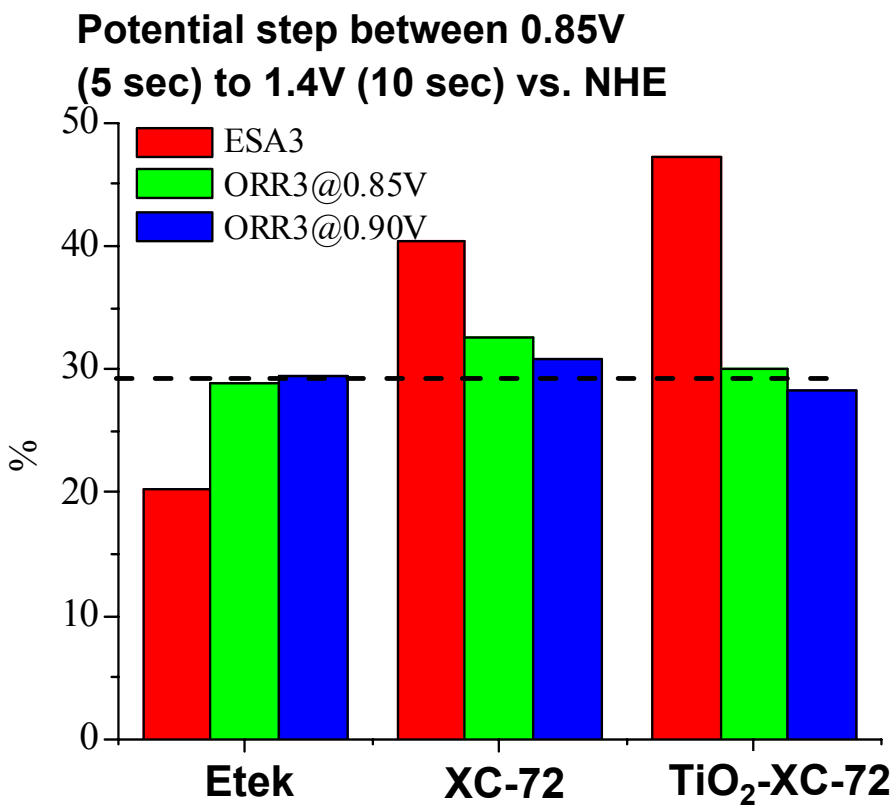


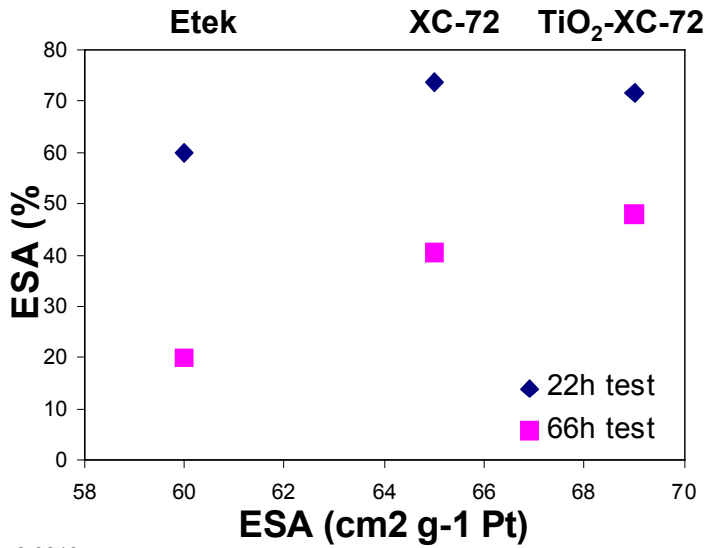


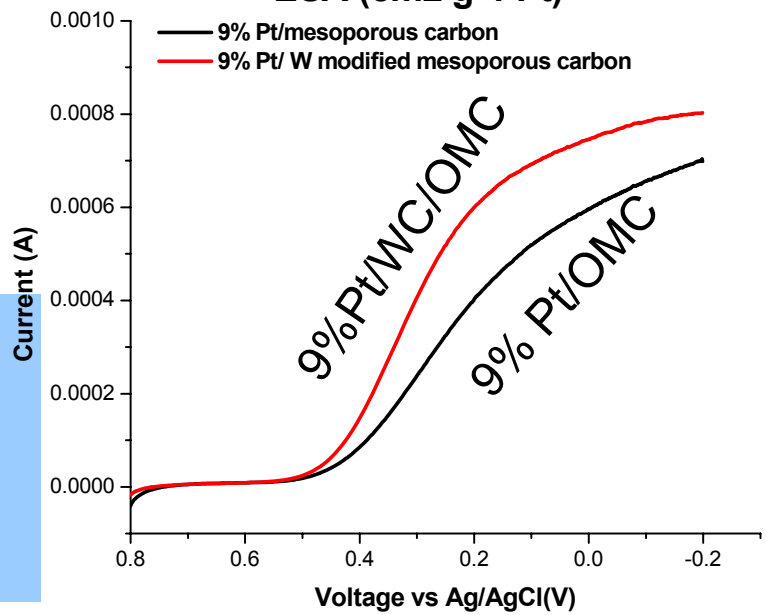


- **Pt nanoparticles can be uniformly dispersed on carbon supports using an incipient wetness method**
- **Metal oxide modified Vulcan XC-72 were synthesized**
  - **The presence of metal oxide (TiO_2) stabilizes the dispersion of Pt**
- **High surface area ITO and WC were synthesized**
  - **Pt preferably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

Electrochemical Testing of Cathode Materials







- 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**