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

PNNL:

Yong Wang
Conrad Zhang
Vilayanur Viswanath
Yuehe Lin
Jun Liu

Ballard Power Systems:

Stephen Campbell

University of Delaware:

Jingguang Chen

ORNL:

Sheng Dai

Project kick-off meeting
Feb 13-14, 2007

Battelle

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Technical Issues and Objective

- Current technical issues
  - Carbon support
    - Susceptible to oxidation under fuel cell operating conditions.
    - Oxidation further catalyzed by Pt
    - Corrosion leads to Pt migration and agglomeration
  - Low Pt utilization (Current ~ 30% for Pt/Carbon Black)
- Objective
  - Develop and evaluate new classes of alternative and durable high-performance cathode supports

Specific DOE Barriers/Targets to be Addressed

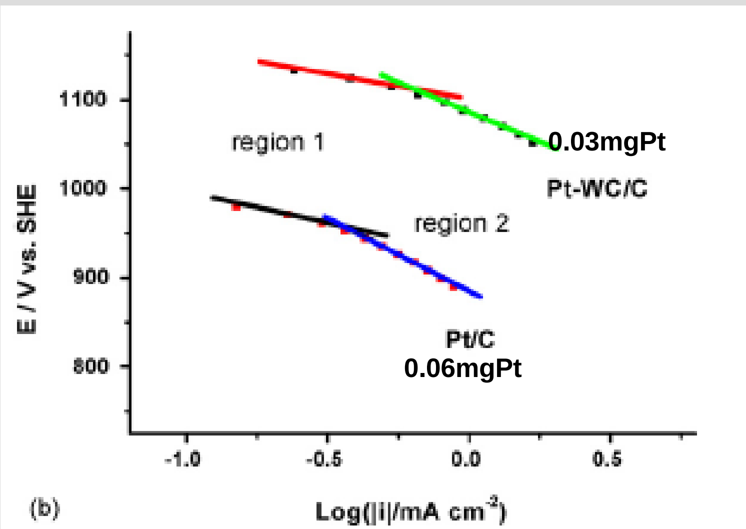
- Barriers - Performance
  - Loss of electrochemical surface area – catalyst migration and agglomeration
  - High cost – high precious metal loading
- Targets:
  - Pt group metal content: 0.3 g/kW for stack
  - Pt group metal total loading: 0.3 mg/cm^2 for stack
  - Mass activity: 0.44 A/mg Pt @ 900 mV$_{IR\ free}$
  - Specific activity: 720 μA/cm^2
  - Non-Pt catalyst activity per unit volume of supported catalyst: 130 A/cm^3 @ 800 mV$_{IR\text{-}free}$
  - Durability for typical driving cycling
    - 5000 hours @ $\leq$ 80ºC
    - 2000 hours @ $\geq$ 80ºC

Approach and Expected Outcomes

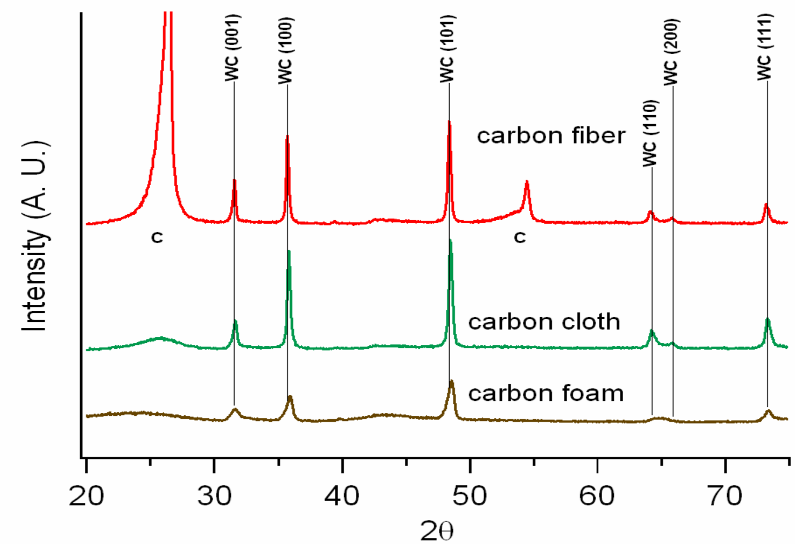
- Approach
  - Develop and evaluate new classes of alternative and durable cathode supports using graphitized carbons as the scaffolds and protect the carbon surface with
    - Tungsten carbide (WC)
    - Oxycarbides
    - Conductive metal oxides (ITO)
- Expected outcomes
  - A protective barrier between carbon and Pt to mitigate the carbon corrosion
  - An enhanced stability of Pt particles because of the bonding between Pt and the WC, oxycarbide or metal oxide substrate
  - A better dispersion of Pt to reduce the loading of Pt in the electrocatalysts
  - A possible synergistic effect because WC is catalytically active with Pt-like properties.

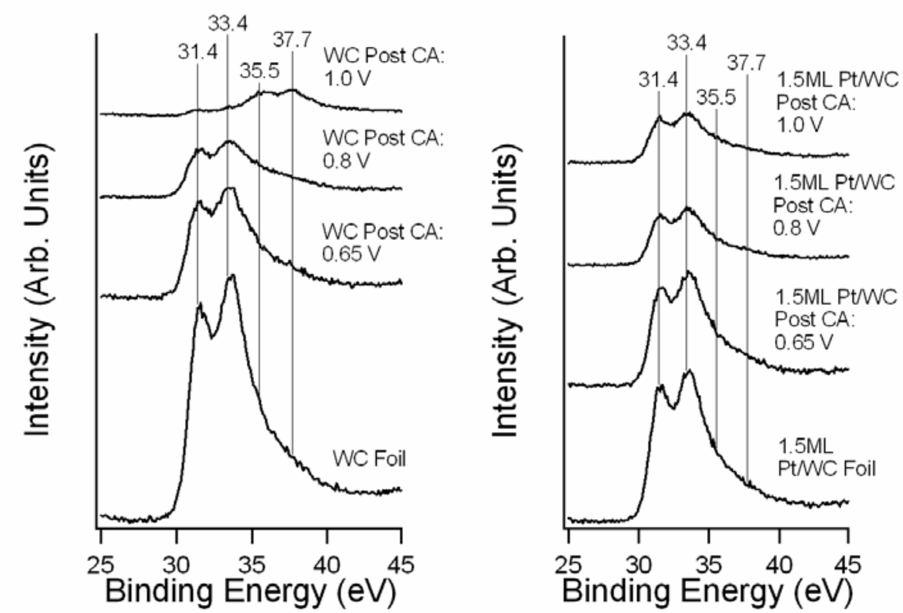
Previous Results: Stability of WC and Pt/WC
XPS of W Region after Chronoamperometry (CA) Measurements

- WC is stable up to 0.8V (NHE) in dilute sulfuric acid, with the onset of oxidation at 1.0V (NHE)
- Presence of Pt on WC enhances the electrochemical stability of WC
- Tungsten carbides and oxycarbides retain Pt-like properties, Higher activity of Pt-WC at half the Pt loading



Nie et al, J.Power Sources, **162** (2006) 173.

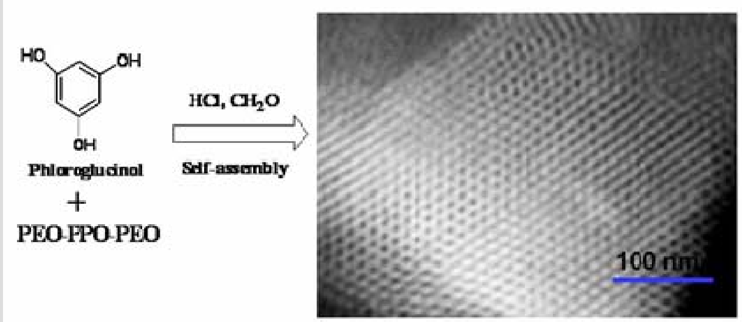




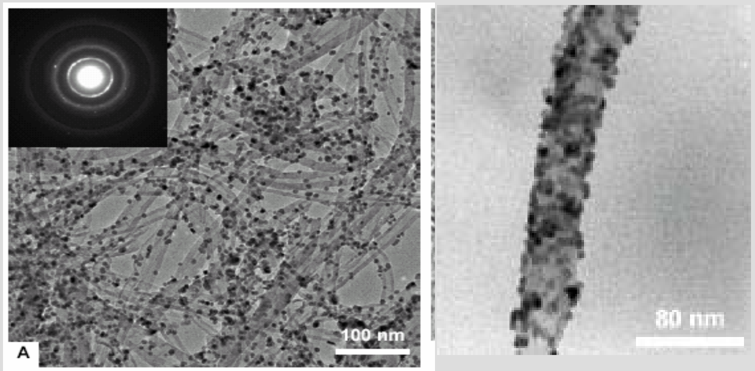
Battelle

Previous Results with Multiwalled Carbon Nnotubes (MWCNTs) and Mesoporous Carbon

- High surface area, large porosity
- MWCNTs
  - Catalysts (Pt, Pt-Ru) deposited on outside wall of CNTs are full accessible for fuel cell reactions (100% vs 30%)
  - CNTs, with highly ordered graphite structure, are very stable under fuel cell operation conditions
  - The exchange current density (from Tafel plot) for O_2 reduction reaction on Pt-CNT electrode is about one order larger than that of commercial Pt/C even though the loading of catalysts is much less in our system.



The dark-field TEM image of ordered mesoporous carbon synthesized at ORNL.



TEM image of MWCNTs decorated by platinum nanoparticles synthesized in supercritical carbon dioxide - PNNL

Electrodes	*Exchange current /A/cm²*	*Refs*
Pt/CNTs (25% Pt/CNTs, 0.07mg/cm²)	8.9e-7	Lin[1]
Pt/C/Nafion (commercial, 20% Pt/C, 0.4 mg/cm²)	1.09e-7	Britto et al[2]

1 Lin, Cui, Yen, Wai. JPC B, 2005, 109, 14410-14415
2 Britto et. al *Adv. Mater.* **1999**, *11*, 54.

Tasks and Organizational Responsibilities

- Task 1: Understand the structural and compositional requirements of WC and CMO for improved electrochemical activity and durability over standard Pt/C cathode materials.
- Task 2: Develop commercially viable approaches to synthesize carbon-supported WC and CMO.
- Task 3: Demonstrate the durability and performance advantages of the alternative cathode supports.

Project Manager

PNNL- Wang

Task 1
Understanding of Model Systems

UD – Chen, Willis
PNNL – Rieke

Task 2d & 3a, b, c, d
Evaluation of Supports and Electrocatalysts

BPS – Campbell
PNNL – Lin, Viswanathan, Rieke, Wang
ORNL – Dai

Task 2a, b, c
Synthesis of High Surface Area Supports

PNNL – Liu, Zhang, Wang
ORNL – Dai

Task 3e
Fuel Cell Test

BPS – Campbell
PNNL – Lin, Viswanathan, Rieke

Project Timeline

Tasks	Year 1	Year 2	Year 3	Year 4
1a, 1b, &1c Fundamental understanding of model systems (UD and PNNL)				
2a, 2b, 2c, &2d Synthesis of high surface area cathode supports (PNNL, ORNL, and BPS)				
3a &3b Support durability studies (PNNL and BPS)		○		
3c &3d Durability and activity of supported electrocatalysts (PNNL and BPS)			○	
3e Fuel cell performance test (PNNL and BPS)				

● Go-no go decision

Go/no-go decisions:

- **Year 2: Development effort will continue if support compositions with better stability than carbon black can be identified.**
- **Year 3: Start fuel cell testing if supported catalyst meets the milestone set up for Yr 3.**

Milestones

- **Year 1**
  - Demonstrate that the stability of model Pt/WC under cathode operating conditions is better than model WC
  - Develop methodology for synthesis of high surface area WC and CMO, with surface area of at least 30 m2/g .
  - Downselect carbon support which has the potential to exhibit better stability than carbon black support.
- **Year 2**
  - Identify lead cathode compositions which have great potential of achieving better durability than carbon black supported Pt cathode.
- **Year 3**
  - Identify compositions with mass activity > 0.44 A/mg Pt and 5x better stability than carbon black supported catalyst for cell demonstration. Stability will be conducted under load cycling, idle, start/stop conditions.
- **Year 4**
  - Demonstrate durability under accelerated test protocols that meet the lifetime criteria under development at DOE (e.g., 30,000 load cycles between 0.7-0.9V IR-free with <30mV loss at $1.5A/cm^2$ and <30mV loss at $1.5A/cm^2$ under 30,000 simulated start/stop cycles (hold at 1.2v for 200hrs))"

Budget by fiscal year

- FY2007
  - $1,213K (federal, requested)
  - $800K (federal, approved)
  - $72K (cost share)
- FY2008
  - $1,241K (federal, requested)
  - $72K (cost share)
- FY2009
  - $1,261K (federal, requested)
  - $72K (cost share)
- FY2010
  - $932K (federal, requested)
  - $39K (cost share)