

V.C.2 Development of Alternative and Durable High Performance Cathode Supports for PEM Fuel Cells

Yong Wang (Primary Contact), Jun Liu, Yuehe Lin, Vilayanur Viswanathan, Jahun Kwak, Rong Kou, Yuyan Shao
 Pacific Northwest National Laboratory (PNNL)
 902 Battelle Boulevard, PO Box 999
 MS K2-12
 Richland, WA 99352
 Phone: (509) 371-6273; Fax: (509) 371-6242
 E-mail: Yong.wang@pnl.gov

DOE Technology Development Manager:
 Kathi Epping Martin
 Phone: (202) 586-7425; Fax: (202) 586-9811
 E-mail: Kathi.Epping@ee.doe.gov

Subcontractors:

- Automotive Fuel Cell Corporation (AFFC), Burnaby, BC
- Oak Ridge National Laboratory, Oak Ridge, TN
- University of Delaware, Newark, DE

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Objectives

Develop new classes of alternative support materials that meet the 2010 DOE performance targets by achieving the following specific objectives:

- Understand structural and compositional requirements of tungsten carbide (WC) and conductive metal oxides (CMOs) for improved activity and durability over standard Pt/C.
- Develop commercially viable processes to synthesize carbon-supported WC and CMOs.
- Demonstrate durability and performance advantages of alternative cathode supports.

Technical Barriers

This project addresses the following technical barriers from Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research for Fuel Cells, Development and Demonstration Plan:

- (A) Durability
- (C) Performance

Technical Targets

This project is directed at conducting durability and activity studies of Pt on various supports, with the objective of meeting the following 2010 DOE targets for electrocatalysts for transportation:

- <30 mV electrochemically active surface area (ECSA) loss after 100 hours at 1.2 V
- >5,000 hours at 80°C
- >0.44 A/mg Pt at 900 mV internal resistance (ir)-free

While comparison with DOE targets cannot yet be quantitative due to 3-electrode tests being conducted, as seen in Table 1, our electrodes show 15% improvement in activity and 23% improvement in performance over commercial Etek samples.

TABLE 1. Progress Towards Meeting Technical Targets for Electrocatalysts for Transportation Applications

Parameter	Units	2010 Stack Target	PNNL 2008 Status
ECSA	mV after 100 h at 1.2 V	<30	3-electrode RDE tests show 23% improvement over Etek
Durability with cycling at 80°C	Hours	5,000	
Mass activity	A/mg Pt at 900 mV ir-free	0.44	3-electrode RDE tests show 15% improvement over Etek

RDE - rotating disk electrode

Accomplishments

- Demonstrated X-ray photoelectron spectroscopy (XPS) measurements with in situ electrochemical cycling.
- Demonstrated scanning tunneling microscope (STM)/scanning electron microscope (SEM) images with ex situ electrochemical cycling.
- Developed commercially viable process for synthesis of ordered mesoporous carbon.
- Demonstrated more uniform dispersion of Pt in ordered mesoporous carbon (OMC) compared to XC72.
- Demonstrated synergistic effect of WC modification on catalytic activity for oxygen reduction with OMC support.
- Demonstrated higher thermal and electrochemical stability for WC modified OMC.

- Demonstrated 23% higher electrochemical durability for TiO₂ modified XC72 compared to Etek.
- Demonstrated 15% higher activity for TiO₂ modified XC72 compared to Etek.
- Conducted preliminary CO₂ evolution tests in membrane electrode assemblies (MEAs).
- Conducted preliminary scanning electrochemical microscope (SECM) tests.



Introduction

Cathode support and catalyst durability is a major technical barrier with respect to commercialization of fuel cells for transportation [1]. Carbon catalyst supports are susceptible to oxidative degradation at high potential, high temperature and start-stop conditions [2]. Oxidation of support leads to detachment of Pt from support, while repeated oxidation and reduction of catalyst leads to dissolution and reprecipitation [3]. The dissolution of platinum is accompanied by penetration of Pt into the membrane or gas diffusion layer, while reprecipitation leads to agglomeration of Pt in the catalyst layer. This leads to an overall decrease in ECSA along with non-uniform current density distribution, leading to sintering of Pt catalysts caused by localized heating.

In order to overcome these barriers and meet the 2010 DOE technical targets for durability and performance, we are developing new classes of alternative and durable cathode supports, based on modifying the carbon surface with WCs [4] and CMOs [5] such as TiO₂ and SnO₂. The durability and performance are expected to be enhanced due to the following advantages for our cathode supports, thus enabling the hydrogen economy:

- A protective barrier between carbon and Pt to mitigate carbon corrosion.
- Enhanced stability of Pt particles due to bonding between Pt and WC, oxycarbides or metal oxide substrates.
- More uniform dispersion of Pt, allowing better performance at equivalent loading.
- Potential synergistic effect due to Pt-like catalytic activity of WC.

Approach

New classes of carbon supports modified by WC and CMOs are being developed to improve durability and performance of the cathode catalysts. Various synthesis approaches such as wet impregnation of platinum precursor onto carbon support and ex situ Pt

nanoparticles formation were investigated. Durability of various carbon supports such as XC72, carbon multi-walled nanotubes, mesoporous carbon with various degrees of graphitization and graphene were compared. A technique to combine STM experiments with ex situ electrochemical measurements for nanoscale resolution of the degradation of Pt/C electrocatalyst was developed. These experiments form a benchmark for examination of alternative supports and electrocatalyst formulations. Carbon supports were modified with WC and various conductive metal oxides such as TiO₂, SnO₂, indium tin oxide (ITO). The durability was investigated using an internally developed accelerated test protocol, with voltage stepped from 1.4-0.85 V. Work in progress involves investigation of effect of lead modifications on various supports such as multi-walled nanotube (MWNT), graphene and OMC.

Results

In Fiscal Year 2008, over 75 combinations of supported catalysts were synthesized, characterized, and tested for performance and durability. We developed a technique to combine STM with ex situ electrochemical measurements for nanoscale resolution of Pt/C electrocatalyst degradation. This technique in conjunction with XPS measurements, is expected to solidify our understanding of catalyst support interactions for various formulations. A cost-effective process was developed for synthesis of high surface area ordered mesoporous carbon with various degrees of graphitization to provide enhanced durability and power density. A modified accelerated test protocol was developed to investigate durability of supported catalysts.

In situ electrochemical cycling, in conjunction with XPS measurements indicated that WC was more stable in the presence of Pt, possible due to preferential bonding of Pt to defect sites present on the polycrystalline WC surface. The cyclic voltammetry (CV) curves (not shown) showed an onset of oxidation at 0.8 V vs. normal hydrogen electrode (NHE) for WC, while presence of 0.8 monolayer (ML) of Pt enhances the region of stability, showing an increase in onset of oxidation to 1 V. XPS measurements performed after 50 cycles of CV measurements showed oxidized W features at 35.5 and 37.7 eV in the absence of Pt, while these features were absent with 0.8 ML Pt (Figure 1). In order to better understand the interactions between catalyst and support, a technique was developed to study a model Pt/highly ordered pyrolytic graphite system by STM and ex situ cyclic voltammetry. Experiments were carried out to investigate Pt/C samples before and after electrochemical stressing to identify changes that occur at the atomic scale. STM images of as-deposited samples (not shown) show the particle size to be 2-3 nm, with Pt particles preferentially decorating step edges. During

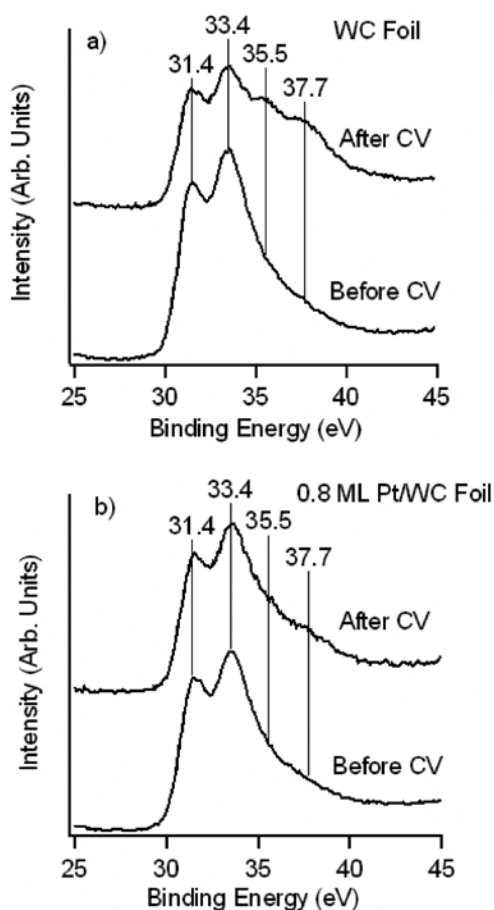


FIGURE 1. XPS Spectra of the W 4f Region before and after 50 CV Cycles between 0 and 1.0 V for WC and 0.8 ML Pt/WC Surfaces

electrochemical cycling, the CV curves show a gradual reduction in the Pt related peak area (Figure 2a). This is accompanied by an increase in Pt particle size to 10 nm as seen in Figure 2b. The STM image shows that there is no change in the carbon substrate under these conditions. Time resolved studies (not shown) of the Pt/C interface at the nanoscale show clear, reproducible evidence of degradation in terms of Pt agglomeration caused by weak Pt-C bonding. SEM images (not shown) show that some of the Pt particles detached from the carbon surface and agglomerated into larger particles, with an increase in uncovered carbon area. These experiments provide a benchmark for evaluation of alternative supports.

A commercially viable approach to synthesize tungsten carbide supported on mesoporous carbon was developed. $H_3PW_{12}O_{40}$ precursor was wet impregnated on mesoporous carbon and calcined at different temperatures under hydrogen to yield various compositions of tungsten carbide. With increasing calcination temperature from 600°C to 1200°C, pure tungsten forms initially, followed by formation of W₂C and WC, with WC content being >90% at 1,200°C.

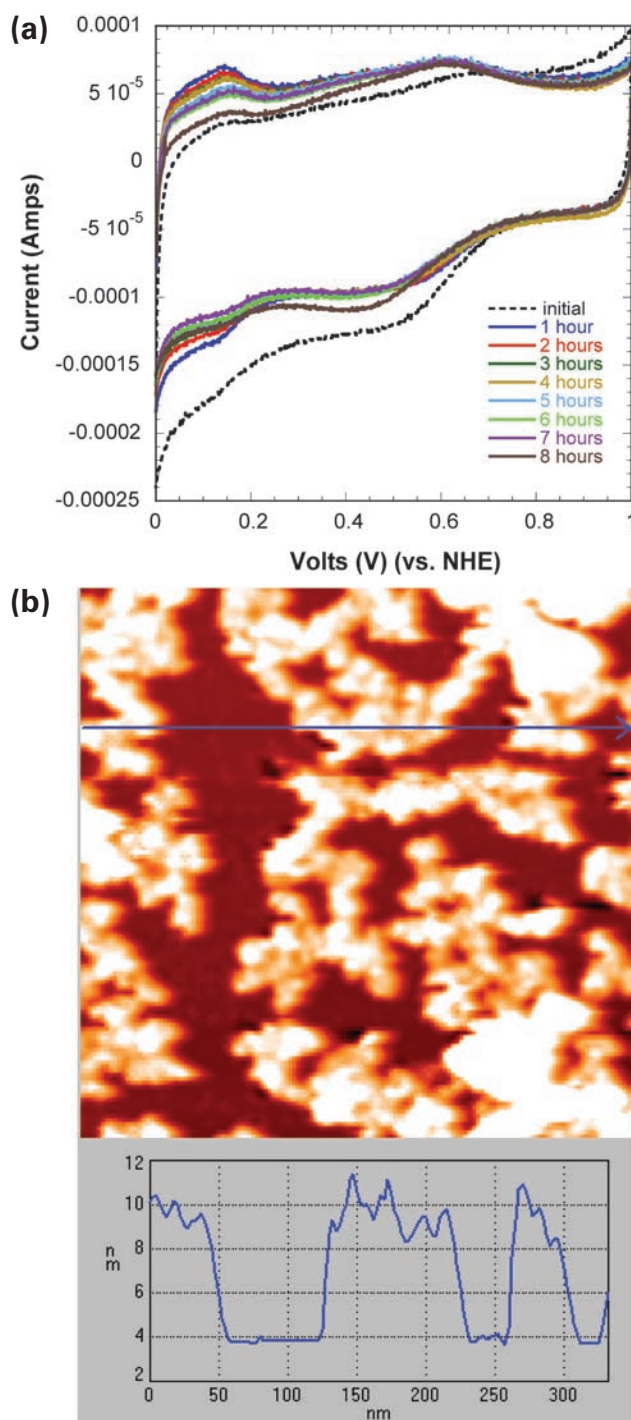


FIGURE 2. (a) Cyclic Voltammetry for Pt/C between 0-1.0 V vs. NHE in 0.5 M H_2SO_4 , (b) STM Image after Eight Hours Cycling

A transmission electron microscopy image (Figure 3) showed that compared with commercial carbon support, a more uniform dispersion of Pt with small particle size (1-3 nm) was obtained on mesoporous carbon and WC modified (not shown) mesoporous carbon surfaces.

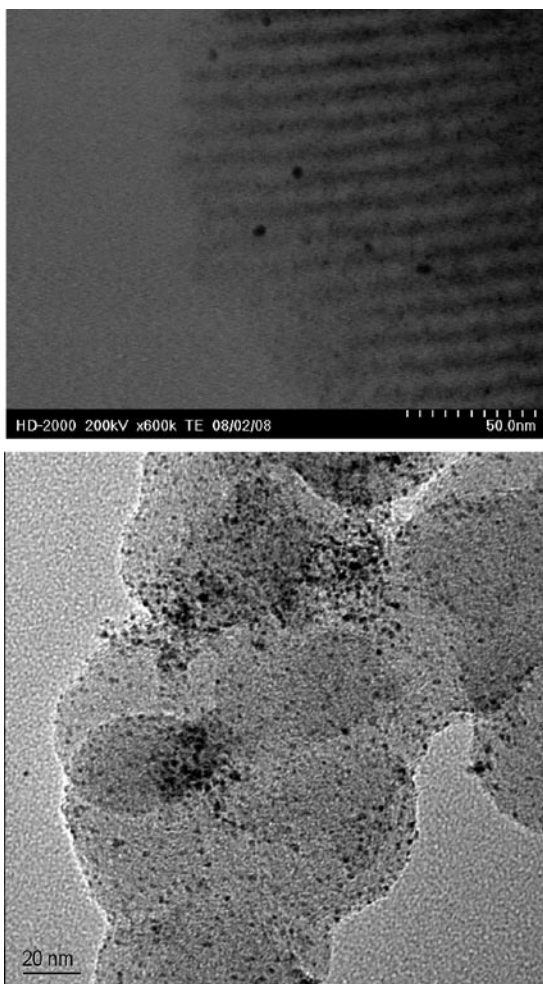


FIGURE 3. Pt on Ordered Mesoporous Carbon (Top), and TiO₂ Modified XC72 (Bottom)

The oxygen reduction activity for Pt/OMC was enhanced by modification of OMC with WC (not shown). 1,000 CV cycles were performed between 0-1 V (vs. NHE) on Pt/XC72R and Pt/WC/OMC. Oxygen reduction activity was determined by performing linear sweeps before and after the CV cycles. Figure 4 shows the smaller degradation for Pt/WC/OMC compared to Pt/XC72R after 1,000 cycles. Thermal stability of the electrocatalysts was investigated by thermal gravimetric analysis (TGA). The stability for Pt/OMC and Pt/XC72R was identical, with a weight loss of 90% in the 500-800°C range, while Pt dispersed on WC modified OMC had a 60% weight loss in the 500-800°C range (figure not shown).

A systematic study was conducted to determine the effect of TiO₂ modification of XC72 on the stability of the electrocatalyst, using a Pt loading of 15 μg/cm². Activity was determined by linear sweep voltammetry in 0.5 M H₂SO₄ saturated with oxygen at 10 mV/s from 1-0.2 V vs. NHE, along with determination of ECSA from H desorption during cyclic voltammetry using a scan rate of 50 mV/s from 0-1 V vs. NHE. The accelerated test protocol consisted of stepping the voltage from 1.4 V (10 sec) to 0.85 V (5 sec), accompanied by determination of activity at periodic intervals. It was determined that maintaining the potential above 0.85 V accelerated degradation compared to a constant potential hold, without contribution from continuous generation of fresh Pt due to reduction of PtO_x to Pt. Hence this protocol allowed determination of carbon support degradation without interference from Pt that catalyzes carbon support degradation. After the initial screening, additional tests would involve stepping down to 0.6 V to determine the catalytic effect of Pt on carbon support degradation.

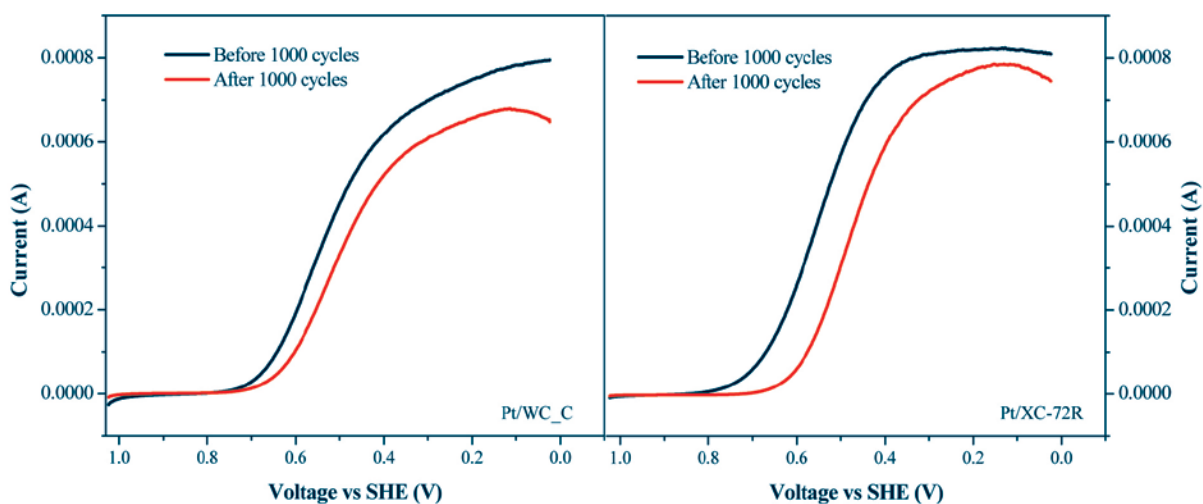


FIGURE 4. Oxygen reduction curves (1,600 rpm, 10 mV/s) for Pt/WC/OMC and Pt/XC-72R after 1,000 CV cycles between 0 to 1.0 V versus NHE in 0.05 M H₂SO₄ at 5 mV/s.

Nb-doped TiO₂ nanoparticles were loaded onto XC72, followed by heat treatment in helium. Heat treatment in the 100-500°C range did not alter the crystal structure of Nb doped TiO₂. Pt precursor was loaded by wet impregnation, followed by reduction in hydrogen in the 100-500°C range to obtain Pt nano clusters. The Pt size distribution was independent of the calcination temperature, possibly due to stability of Nb doped TiO₂ across this temperature range. The loading of TiO₂ was varied from 0.5-20 wt%, and was determined by TGA analysis. The platinum particle size varied from 2-5 nm, with particle size decreasing with increasing TiO₂ content, accompanied by more uniform distribution of platinum nanoparticles (Figure 3). Activity increased with TiO₂ loading, while stability was high at both low and high TiO₂ loadings. From this study, 20 wt% TiO₂ was found to be optimum in terms of both performance and durability. Preliminary studies were also conducted to determine performance and stability of SnO₂-modified XC72. The SnO₂ composition was varied from 2-20%. The activity decreased with increasing SnO₂ content, while stability increased, leveling off at 10% SnO₂.

Figure 5a compares the activity for various electrode compositions at various intervals during accelerated testing, while Figure 5b shows the percent drop in activity. The initial activity for both 20% TiO₂ and 2% SnO₂ modified samples was higher than Etek. After 22 h of degradation, the activity for the oxide modified samples was 33% higher than Etek sample, while after 44 h, it was 66% higher. The activity of the oxide modified samples was equivalent to that for baseline XC72 supported catalysts prepared in-house after 22 hours degradation, but was 20% higher after 44 hours. The initial activity of MWNT supported catalysts was lower than baseline Etek, but was 20% higher than Etek after 44 hours degradation. As seen in Figure 5b, durability of MWNT and oxide modified samples was significantly higher than Etek and in-house prepared XC72 supported samples. By tailoring the platinum particle size distribution, we plan to improve initial activity, thus taking advantage of the high durability of the alternate support materials investigated.

SECM provides an effective means to rapidly test various supported catalyst compositions. Microspots of catalyst support on ITO-coated glass were deposited and tested using SECM. Preliminary results were obtained for oxygen reduction current at each microspot. Additional work needs to be done on optimization of imaging parameters such as tip potential, substrate potential, distance between tip and substrate, and electrolyte concentration.

In order to determine durability of supported catalyst in a fuel cell, MEAs were prepared with and without platinum in the cathode. Humidified hydrogen was fed to the anode, while humidified nitrogen was fed to the cathode. The fuel cell was potentiostatted at 1.4 V and CO₂ evolution from the cathode detected using

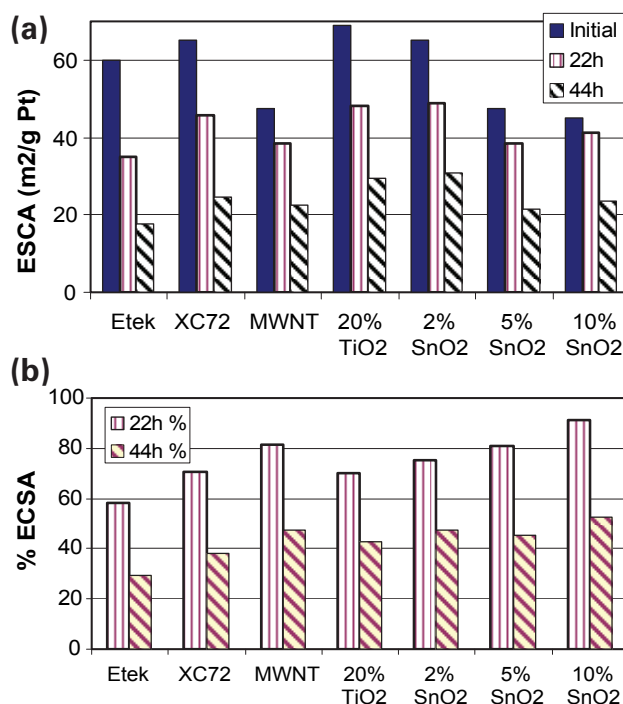


FIGURE 5. (a) ECSA for 20 wt% Pt on Various Supports after 1.4 (10 sec)-0.85 V (5 sec) Step Cycling for 22 and 44 hours (b) % ECSA remaining after Potential Step Cycling

SRS RGA 200 mass spectrometer. As expected, CO₂ evolution was 3X times higher for platinum catalyzed support. In order to provide more reliability, an Agilent 3000A Micro gas chromatograph was connected downstream of the SRS RGA 200, and calibration of instruments carried out in the 10-1,000 ppm CO₂ range. Multiple MEAs have been fabricated with and without Pt in order to determine CO₂ evolution at 1.4 V. Periodic polarization curves will be obtained to correlate decrease in performance with cumulative CO₂ evolution. These tests will be repeated with the lead support candidates identified through accelerated testing.

Conclusions and Future Directions

Significant progress has been made in development of analytical techniques to study catalyst support interactions and in synthesis of supported catalysts with higher durability than commercial supported catalysts:

- Capabilities developed in terms of XPS/ in situ electrochemical tests and STM/ex situ electrochemical tests can be used to study lead supported catalyst candidates.
- Synergistic effect of WC modification on catalytic activity and higher thermal/electrochemical stability can be leveraged to develop high performance, durable catalysts.

- Higher electrochemical durability was demonstrated for TiO₂ and SnO₂ modified XC72 over commercial supported catalysts.
- Potential synergistic effect of TiO₂/SnO₂ modification of carbon support in terms of activity and durability will be examined.
- Oxide and carbide modification of alternate carbon supports such as MWNT, OMC and graphene will be studied.
- High throughput SECM will be used to study multiple compositions.
- Lead compositions will be tested in single fuel cell for performance and durability (including CO₂ evolution) using test stand which has been built and tested.

FY 2008 Publications/Presentations

1. Erich C. Weigert¹, Michael B. Zellner¹ and Jinguang G. Chen, “Electrochemical and XPS Studies of Stability and Activity of Transition Metal Carbide Surfaces (Mo₂C and WC) with and without Pt-Modification”, *J. Phys. Chem. C.* to be submitted.
2. Paul V. Larsen, Chengdu Liang, Mahesh Waje, Sheng Dai, and Yushan Yan, “Graphitic Mesoporous Carbon as a Durable Fuel Cell Catalyst Support”, Prepared for submission to JACS.
3. Y. Shao, J. Wang, R. Kou, V.V. Viswanathan, J.H. Kwak, J. Liu, Y. Wong, Y. Lin, “Effect of Electrochemical Stress Conditions on Degradation of PEM Fuel Cell Catalyst Support”, Prepared for submission.
4. Y. Wang, J. Liu, Y. Lin, V.V. Viswanathan, J.H. Kwak, R. Kou, Y. Shao, J. Wang, S. Dai, Q. Zhu, S. Campbell, J. Chen, B. Willis, “Development of Alternative and Durable High Performance Cathode Supports for PEM Fuel Cells” FreedomCAR & Fuel Partnership - Fuel Cell Tech Team Meeting, April 13, 2008, USCAR, Southfield, MI.

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1. R. Borup *et al.*, “Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation”, *Chem. Rev.* 107 3904-3951 (2007).
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3. Y. Shao, G. Yin, and Y. Gao, “Understanding and Approaches for the Durability Issues of Pt-based Catalysts for PEM Fuel Cell”, *J. Power Sources* 171 558-566 (2007).
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5. G. Chen, S.R. Bare, and T.E. Mallouk, “Development of Supported Bifunctional Electrocatalysts for Unitized Regenerative Fuel Cells”, *J. Electrochem. Soc.*, 149 (8) A1092-A1099 (2002).