

V.E.3 Development of Alternative and Durable High Performance Cathode Supports for PEM Fuel Cells

Yong Wang (Primary Contact),
 Vilayanur V. Viswanathan, Jun Liu, Yuehe Lin,
 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: yongwang@pnl.gov

DOE Technology Development Manager:
 Nancy Garland
 Phone: (202) 586-5673; Fax: (202) 586-9811
 E-mail: Nancy.Garland@ee.doe.gov

Subcontractors:

- Stephen Campbell, Automotive Fuel Cell Cooperation (AFCC), Burnaby, BC
- Sheng Dai and Qing Zhu, Oak Ridge National Laboratory, Oak Ridge, TN
- Jingguang Chen, University of Delaware, Newark, DE
- Brian Willis, University of Connecticut, Storrs, CT

Project Start Date: January, 2007
 Project End Date: December, 2010

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 CMO.
- Demonstrate durability and performance advantages of alternative cathode supports such as ordered mesoporous carbon (OMC) and grapheme.

Technical Barriers

This project addresses the following technical barriers from Fuel Cells section (3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research for Fuel Cells, Development and Demonstration Plan:

- (A) Durability (of Cathode Catalyst Supports)
- (C) Performance (of Supported Cathode Catalyst)

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 electrocatalyst support for transportation:

- <30 mV loss and <40% electrochemically active surface area (ECSA) loss after 200 hours at 1.2 V/95°C at rated power.
- >5,000 hours at 80°C

Membrane electrode assembly (MEA) tests are in progress for lead supports, and have shown 2X improvement in stability over baseline XC72 supports (Table 1). Alternate supports such as carbon nanotubes (CNTs) have shown no degradation after 100 hours, thus providing a synergistic opportunity for metal oxide modification of CNTs. Rotating disk electrode (RDE) tests have also shown significant improvement in durability over baseline.

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

Parameter	Units	2010 Stack Target	PNNL 2009 Status
Accelerated test loss, 200 h @ 1.2 V at 95°C	mV at rated power	<30	MEA tests show 2X improvement over baseline
	% ECSA loss	<40	3-electrode RDE tests show improvement over baseline. TBD for MEA
Durability with cycling at 80°C	Hours	5,000	TBD

TBD – to be determined

Accomplishments

- Model system studies demonstrated Pt agglomeration with stable carbon surface at 1.0 V thus separating Pt agglomeration effects from carbon corrosion.
- Density functional theory (DFT) calculations guided selection of materials with better durability and activity.
- Modification of OMC with WC increased activity.
- CNTs showed higher stability and activity than XC72.
- Modification of carbon supports with metal oxides TiO₂ showed improved (2X) stability.

- Graphene-supported catalysts showed improved activity and stability over XC72 supported catalysts in RDE tests.



Introduction

Conventional cathode catalyst supports are susceptible to corrosion during high potential excursions, high temperature and under start-stop conditions [1]. Hence lack of cathode support durability is a major technical barrier with respect to commercialization of fuel cells for transportation [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. These lead 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 have developed new classes of alternative and durable cathode supports, based on modifying the carbon surface with WCs [4] and CMOs [5] such as indium tin oxide (ITO), TiO_2 and SnO_2 . Alternate supports such as CNT, graphene sheets were also investigated to take advantage of their superior properties [6,7]. The durability and performance have been enhanced due to the following advantages for our cathode supports:

- Formation of a protective barrier between carbon and Pt mitigates carbon corrosion.
- Bonding between Pt and WC or metal oxide substrates enhances the stability of Pt particles.
- More uniform dispersion of Pt, allowing better performance at equivalent loading.
- Potential synergistic effect due to Pt-like catalytic activity of WC.
- Higher activity and durability of CNT and graphene over XC72 provides potential for an order of magnitude improvement with metal oxide modification.
- Carbon-free metal oxides (ITO) successfully identified as candidates for catalyst support.

Approach

New classes of carbon supports modified by WC and CMO have been 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. In order to prevent alloy formation, ethylene glycol method was selected for all future sample preparation mid-way through the year [8]. Durability of various carbon supports such as XC72, carbon multi-walled nanotubes, mesoporous carbon with various degrees of graphitization and graphene were compared. DFT modeling was performed to identify potential supports with better oxygen reduction reaction (ORR) activity and stability than Pt-XC72. Scanning tunneling microscopy (STM) was done on a Pt-HOPG model system before and after ex situ electrochemical measurements in order to determine degradation mechanism of the supported catalyst. 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 TiO_2 , SnO_2 , ITO. The durability was investigated using an internally developed accelerated test protocol, with voltage stepped from 1.4-0.85 V vs. normal hydrogen electrode. An investigation of the effect of metal oxide modification of various supports such as multi-wall carbon nanotube, graphene and OMC was conducted. MEA tests were performed on various supports with and without metal oxide modification, with the fuel cell held at 1.2 V at 80°C for 100+ hours, and activity at 0.9 V and polarization curves measured every 20 hours.

Results

In Fiscal Year 2009, MEA tests were conducted on metal oxide modified XC72, along with unmodified alternate carbon supports. 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 X-ray photoelectron spectroscopy (XPS) measurements, has solidified our understanding of catalyst-support interactions, which can be applied to 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.

DFT modeling showed that Pt-WC (0001) and Pt-VC (111) have better ORR activity and stability than Pt-C. Figure 1 shows the DFT structures of Pt supported on WC(0001) and CWC(0001). Characterization of model Pt-HOPG systems by scanning electron microscopy (SEM), STM and XPS before and after 9-hour cyclic voltammetry (CV) cycling (0-1 V) indicated Pt agglomeration occurred, while the carbon support remained unchanged (Figures 2a,b). In situ Pt 4f XPS data showed that Pt-support binding energy decreased

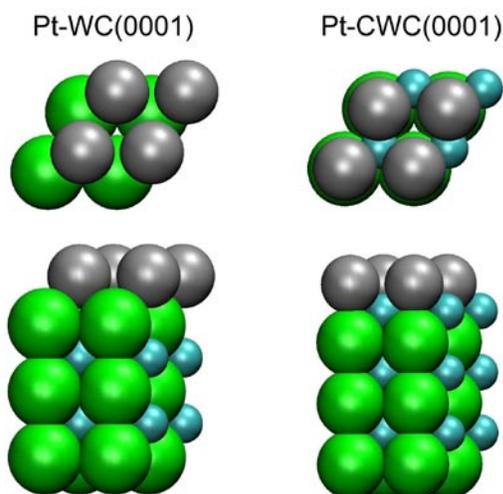


FIGURE 1. DFT Structures of WC-Supported Pt

after cycling (Figure 2c), evidence of Pt sintering. These experiments allowed separation of Pt agglomeration from carbon support corrosion, and provide a benchmark for evaluation of alternative supports. Future experiments will look at results for excursion to 1.2-1.4 V and Pt supported on WC.

A commercially viable approach developed in FY 2008 was used to synthesize WC supported on OMC. A wet impregnation method was used to disperse $H_3PW_{12}O_{40}$ precursor on mesoporous carbon which was calcined at different temperatures under hydrogen to form carbide and conductive graphite phases. The oxygen reduction activity for Pt/OMC was enhanced by modification of OMC with WC as shown in Figure 3a.

The mesoporosity was retained after forming WC, with the pore size distribution essentially remaining unchanged (Figure 3b).

MEA tests were conducted on metal oxide modified carbon supports. As shown in Figure 4a, SnO_2 , ITO and TiO_2 modified XC72 provided higher durability after 100-h hold at 1.2 V/80°C. While Pt-XC72 retained 60% of performance at 0.8 A/cm², the corresponding numbers for Pt on SnO_2 , ITO and TiO_2 modified XC72 were 65, 80 and 100%, respectively. Comparison of Pt-XC72 with Pt-CNT showed no degradation for the latter after 110 hours at 1.2 V/80°C, while the XC72 supported catalyst lost 20% in performance at 0.8 A/cm² (Figure 4b). Accelerated testing at 1.4 V hold showed that after 2.3 hours, TiO_2 and SnO_2 modified support had degraded the least (30%), and even outperformed CNT supported catalysts (40% degradation), with Pt-XC72 having degraded by 80% (Figure 5). These results show the immense promise for TiO_2 and SnO_2 -modified CNT as durable supported catalysts.

Performance of carbon-free metal oxide support was investigated using ITO (data not shown). The polarization curves showed a maximum current density of 0.15 A/cm², with no degradation after 20 hours. While the poor performance was due to low ITO surface area, these results show that controlling ITO/carbon ratio can potentially lead to high performance and durability.

Carbon loss was determined by measuring carbon dioxide evolution using mass spectrometry, with the amount of degradation linearly related to carbon loss (data not shown).

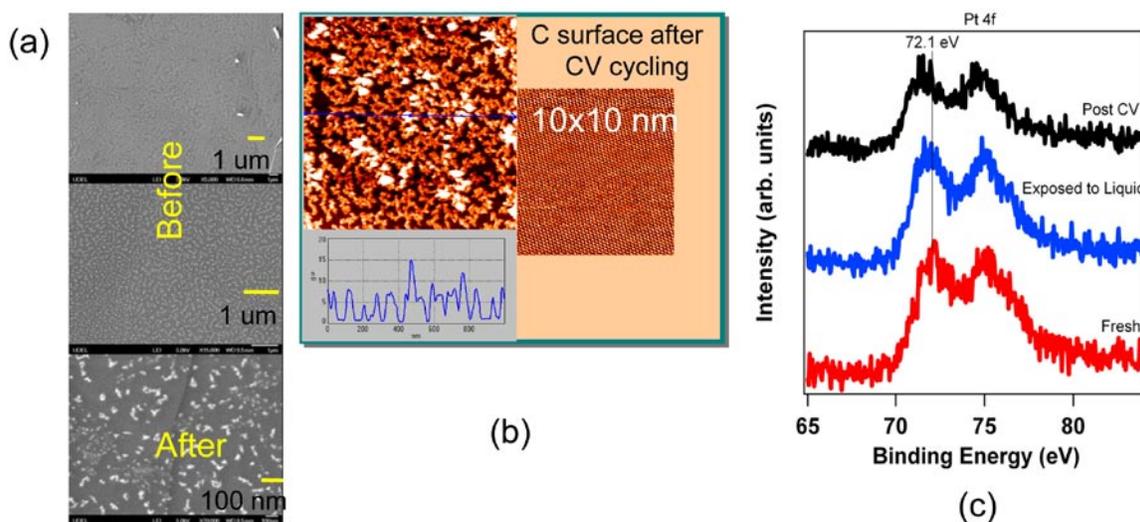


FIGURE 2. (a) SEM micrographs of Pt-C before and after 9 hrs CV 0-1 V (b) STM after CV cycling (c) In situ Pt 4f XPS data for fresh Pt/HOPG, exposed to H_2SO_4 , after 180 CV cycles 0-1 V.

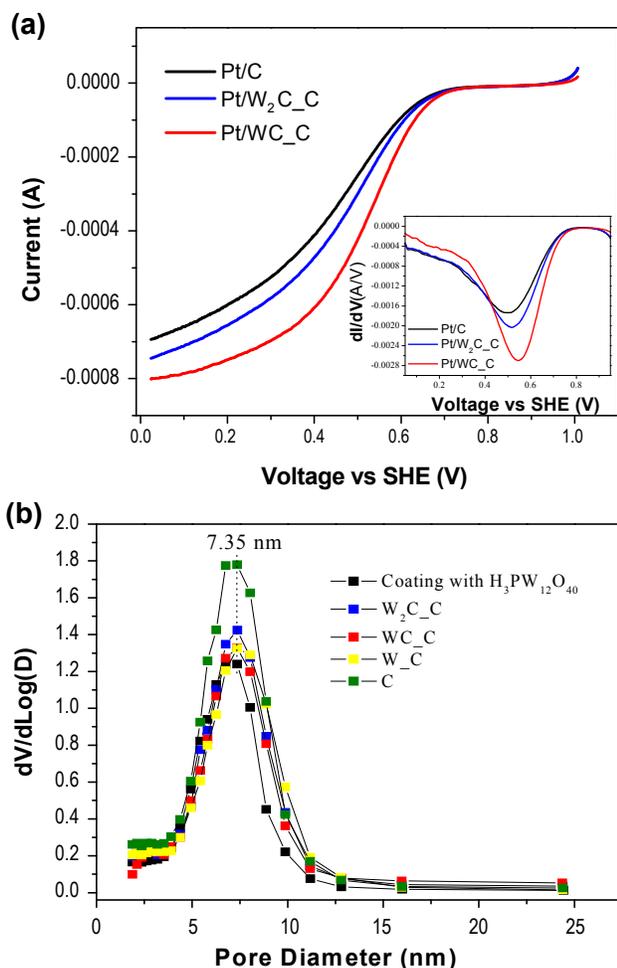


FIGURE 3. (a) Activity of Pt on OMC with and without WC 0.05 M oxygen-saturated H_2SO_4 -1,600 rpm, 10 mV/s (b) Pore size distribution for OMC and WC supported on OMC.

While MEA tests are ongoing for graphene supported catalysts, RDE tests showed a 25% increase in activity and a 50% improvement in stability after 5,000 CV from 0.6-1.1 V (Figure 6). Pt had agglomerated after cycling for XC72 supported catalyst, while it remained unchanged for graphene supported catalyst.

Conclusions and Future Directions

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

- Capabilities developed in terms of XPS/ in situ electrochemical tests and STM/ ex situ electrochemical tests have been used to study model Pt-HOPG and Pt-WC systems to understand Pt-support interactions and degradation mechanisms.

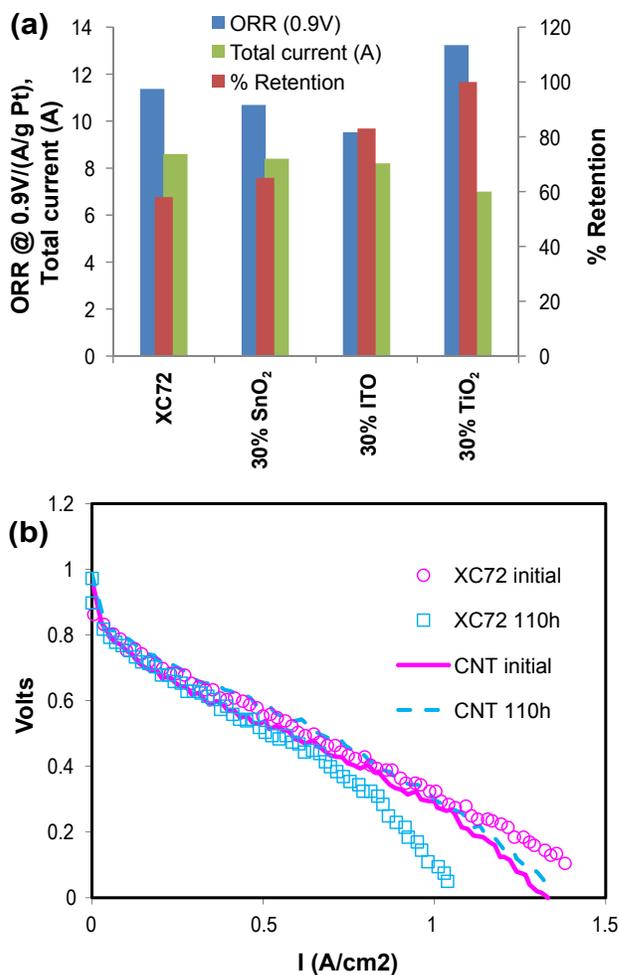


FIGURE 4. (a) MEA activity and stability of 20% Pt on metal oxide modified XC72 after 60 h hold at 1.2 V/80°C (b) MEA stability after 1.2 V/80°C hold for XC72 and CNT.

- Carbide supports (WC and VC) identified by DFT calculations hold promise for MEAs with high durability and activity.
- Synergistic effect of WC on Pt has been leveraged to develop Pt on WC-modified OMC support with higher activity.
- A 2X better electrochemical durability was demonstrated for TiO_2 and SnO_2 modified XC72 over commercial supported catalysts.
- There was no degradation for CNT-supported catalysts during 1.2 V hold. This provides potential for TiO_2 and SnO_2 modified CNT to have an order of magnitude higher durability than commercial supported catalysts.
- Oxide modification of alternate carbon supports such as OMC and graphene showed better activity and durability in RDE tests.
- Carbon-free metal oxide catalysts (ITO) have been shown to be active towards ORR.

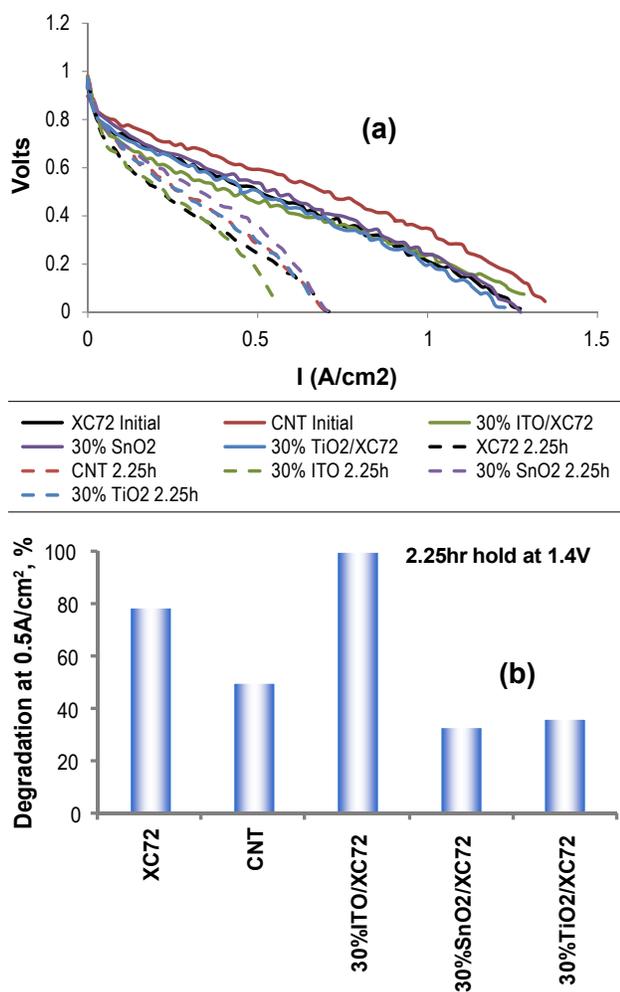


FIGURE 5. Durability of MEAs with CNT, XC72 and metal oxide modified XC72 after 1.4 V/80°C hold for 2.25 h (a) polarization curves, (b) % degradation at 0.5 A/cm².

- The future work will involve investigation of VC-modified carbon supports, metal oxide modified alternate carbon supports such as CNT, OMC and graphene, and continued study of model systems at more aggressive potentials (1.2-1.4 V).

FY 2009 Publications/Presentations

- Y. Shao, R. Kou, J. Wang, V. Viswanathan, J. Kwak, J. Liu, Y. Wang, and Y. Lin, "The influence of the electrochemical stressing (potential step and potential-static holding) on the degradation of polymer electrolyte membrane fuel cell electrocatalysts", *Journal of Power Sources* 185 280 (2008).
- Y.Y. Shao, J. Liu, Y. Wang, and Y.H. Lin, "Novel catalyst support materials for PEM fuel cells: current status and future prospects", *Journal of Materials Chemistry* 19 46 (2009).
- Y. Shao, R. Kou, J. Wang, V. Viswanathan, J. Liu, Y. Wang, and Y. Lin, *Journal of Nanoscience and Nanotechnology*, in press (2009).

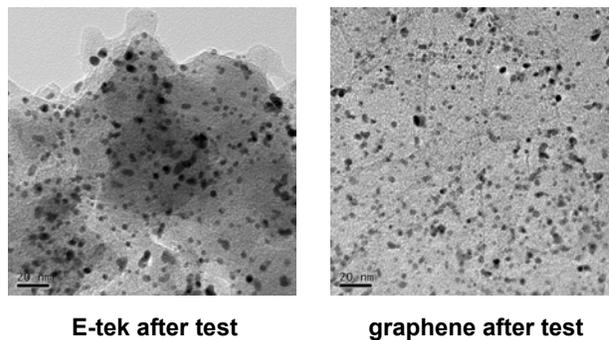
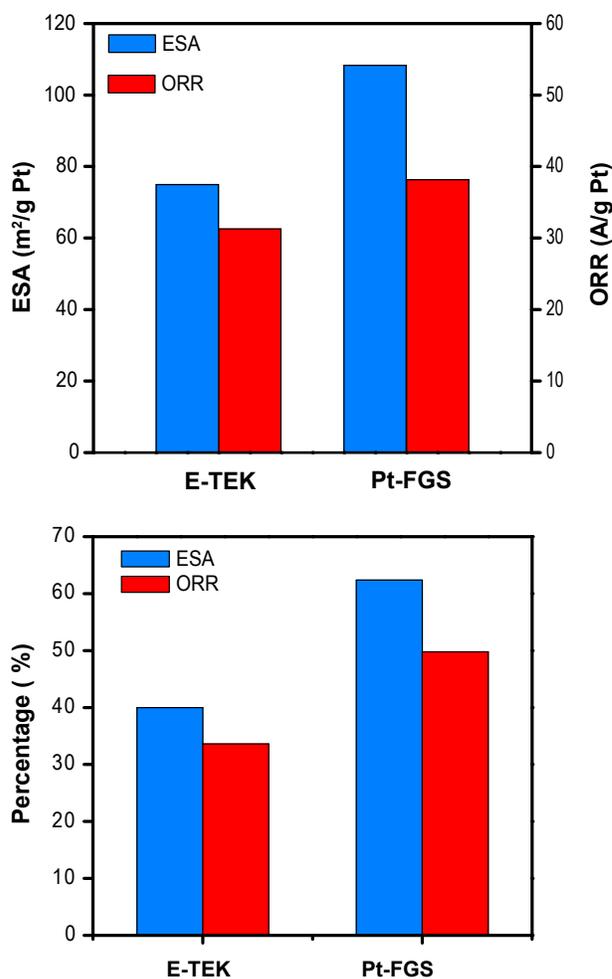


FIGURE 6. RDE (5,000 CV 0.6-1V) test results for Pt-graphene (a) ESA and activity (b) durability % retained (c) transmission electron microscope (TEM) Pt-Etek (d) TEM Pt-graphene.

- R. Kou, Y. Shao, D. Wang, M. Engelhard, J. Kwak, J. Wang, V. Viswanathan, C. Wang, Y. Lin, Y. Wang, I. Aksay and J. Liu, "Enhanced activity and stability of Pt catalysts on functionalized graphene sheets for electrocatalytic oxygen reduction", *Electrochemistry Communications*, 11 954-957 (2009).

5. Y. Shao, J. Wang, R. Kou, M. Engelhard, J. Liu, Y. Wang, Y. Lin, "The corrosion of PEM fuel cell catalyst supports and its implications for developing durable catalysts", *Electrochimica Acta*, **54** 3109-3114 (2009).
 6. P.V. Shanahan, L.B. Xu, C.D. Liang, M. Waje, S. Dai, Y.S. Yan, "Graphitic mesoporous carbon as a durable fuel cell catalyst support," *J. Power Sources* **185** 423-427 (2008).
 7. C. D.Liang, Z. J. Li, S. Dai, "Mesoporous Carbon Materials: Synthesis and Modification," *Angew. Chem. Inter. Ed.* **47** 3696-3717 (2008).
 8. E.C. Weigert, D.V. Esposito and J.G. Chen, "Cyclic Voltammetry and XPS Studies of Electrochemical Stability of Clean and Pt-Modified Tungsten and Molybdenum Carbide (WC and Mo₂C) Films", *Journal of Power Sources*, in press (2009).
 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).
 4. H.H. Hwu and J.G. Chen, "Surface Chemistry of Transition Metal Carbides", *Chem. Rev.*, **105** 185-212 (2005).
 5. G. Chen, S.R. Bare, and T.E. Mallouk, "Development of Supported Bifunctional Electrocatalysts for Unitized Regenerative Fuel Cells", *J. Electrochem. Soc.*, **149** A1092-A1099 (2002).
 6. Y. Shao, J. Liu, Y. Wang and Y. Lin, "Novel catalyst support materials for PEM fuel cells: current status and future prospects" *J. Mat. Chem.*, **19** 46-59 (2009).
 7. R. Kou, Y. Shao et al., Enhanced activity and stability of Pt catalysts on functionalized graphene sheets for electrocatalytic oxygen reduction", **11** 954-957 (2009).
 8. W.Z. Li, C.H. Liang, W.J. Zhou et al., Preparation and characterization of multiwalled carbon nanotube-supported platinum for cathode catalysts of direct methanol fuel cells", *J. Phys. Chem. B*, **107** 6292-6299 (2003).
- ## References
1. K.H. Kangasniemi, D.A. Condit, and T.D. Jarvi, "Characterization of Vulcan Electrochemically Oxidized under Simulated PEM Fuel Cell Conditions", *J. Electrochem. Soc.*, **151** E125-E132 (2004).
 2. R. Borup *et al.*, "Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation", *Chem. Rev.* **107** 3904-3951 (2007).