

# V.D.15 Development of Alternative and Durable High Performance Cathode Supports for PEM Fuel Cells

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## Fiscal Year (FY) 2011 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 conductive metal oxides (CMO) for improved activity and durability over standard Pt/Vulcan XC-72.
- Demonstrate durability and performance advantages of alternative cathode supports such as carbon nanotubes (CNTs), ordered graphitic mesoporous carbon (OGMC), graphene and graphitized carbon nanotubes (GCNT).
- Demonstrate durability and performance of non-carbon CMO supports such as tin-doped indium oxide (ITO).

## Technical Barriers

This project addresses the following technical barriers from Fuel Cells section (3.4) of the Fuel Cell 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 DOE lifetime criteria.

Membrane electrode assembly (MEA) tests are in progress for lead supports using CMO modification of novel carbon supports, and have shown 3-4X improvement in stability over baseline Vulcan XC-72 carbon supports (Table 1). Rotating disc electrode (RDE) tests have also shown significant improvement in durability over baseline. Optimization of GCNT diameter and CMO content are further expected to improve performance and durability.

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

Parameter	Units	2010 Stack Target	PNNL 2011 Status
Accelerated test loss, 200 h @ 1.2 V at 80°C	mV at rated power	< 30	3-4X improvement over baseline for MEA
	% electrochemical surface area (ESA) loss	< 40	3-4X improvement for RDE and MEA tests
Durability with cycling at 80°C	Hours	5,000	To be determined

## FY 2011 Accomplishments

- Determined optimum GCNT diameter for best performance and durability.
- Used lessons learned from ITO-graphene systems to develop highly stable ITO-modified GCNT with 4X stability of baseline Vulcan carbon support.
- Demonstrated electronic percolation through CMO-modified carbon support<sup>3</sup> and identified need for improving conductivity of non-carbon support by conductivity measurement.
- Improved non-carbon support performance without compromising durability by adding CNT after Pt-CMO synthesis.
- Improved ESA for non-carbon support by tailoring mesoporosity and particle size using hard template synthesis.

<sup>1</sup>Through end of FY 2010

<sup>2</sup>Work will continue through March 2012

<sup>3</sup>Also referred to as hybrid support

- Synthesized non-carbon support using solvothermal annealing method with favorable particle size and crystallinity.



## 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 ESA 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 DOE technical targets for durability and performance, we have developed new classes of alternative and durable cathode supports, based on modifying the carbon surface by conductive metal oxides [4] such as tin-doped ITO, TiO<sub>2</sub> and SnO<sub>2</sub>. Alternate supports such as CNT, graphene sheets, OGMC and GCNT were also investigated to take advantage of their superior properties [5-7]. In addition, conductive metal oxides were also used as an alternative to carbon-based supports. The durability and performance have been enhanced due to the following advantages for our cathode supports [8]:

- Thermodynamic stability of Pt-CMO-carbon triple junction, as shown by periodic density functional theory (DFT) calculations, prevents Pt agglomeration.
- Preference of metal oxide nanoparticles to stay at the carbon defect sites lowers carbon corrosion.
- More uniform dispersion of Pt, allowing better performance at equivalent loading.
- Direct contact of Pt with carbon allows use of low cost conductive and non-conductive stable oxides.
- Higher durability of CNT, OGMC and GCNT over Vulcan XC-72 carbon baseline provides potential for an order of magnitude improvement over baseline in durability with metal oxide modification.
- Carbon free metal oxides (ITO) with tailored conductivity and mesoporosity show positive trend in terms of activity and performance.

## Approach

New classes of carbon supports modified by CMOs have been developed to improve durability and performance of

the cathode catalysts. In order to prevent alloy formation, electrocatalysts were synthesized by the chemical reduction method using ethylene glycol [9]. Durability of various carbon supports such as Vulcan XC-72 carbon, multiwalled CNT (referred to as CNT in this report), GCNT, OGMC and graphene were compared. DFT calculations performed in FY 2010 on Pt-ITO-graphene were leveraged to study benefits of CMO-modified GCNT support. Conductivity studies were performed on hybrid support Nafion<sup>®</sup> layers to verify electronic percolating through the catalyst layer. Measurements were also done with ITO/Nafion<sup>®</sup> layers to explore pathways for improvement of performance.

Non-carbon support synthesis was modified to reflect the need for higher conductivity and higher triple phase boundary length. In FY 2010, for CMO supports, a doubling in performance with no loss in stability was obtained using cetyl trimethyl ammonium bromide (CTAB) surfactant assisted CMO synthesis. In FY 2011, in order to improve electronic conductivity and tailor particle crystallinity and mesoporosity, both hard template and solvothermal annealing methods were used to synthesize ITO support.

As described in earlier reports, the durability was investigated ex situ using an internally developed accelerated test protocol, with voltage stepped from 1.4-0.85 V vs. normal hydrogen electrode (NHE). An investigation of the effect of CMO modification of GCNT 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, and measurement of ESA, oxygen reduction reaction activity at 0.9 V and polarization curves performed every 20 hours.

## Results

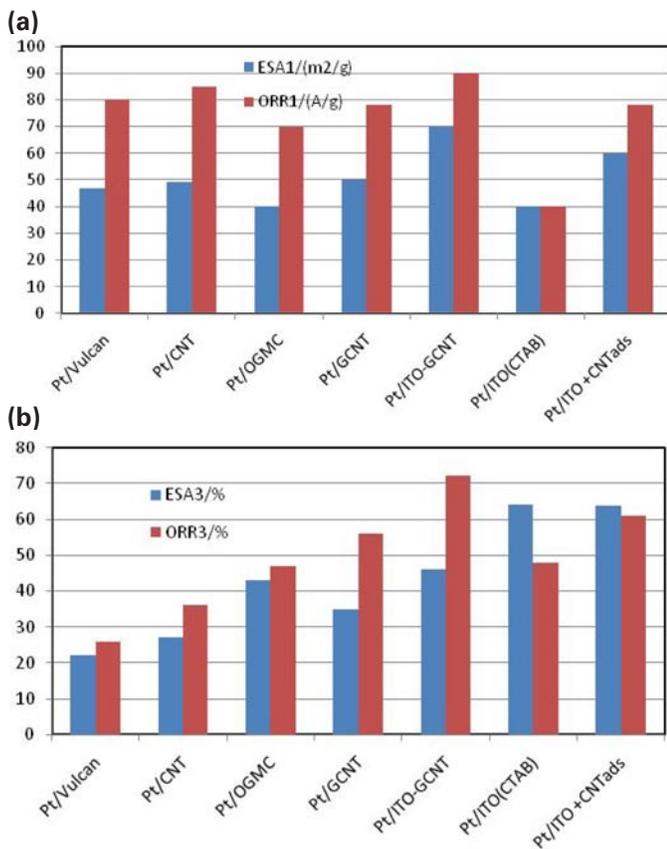
DFT calculations in FY 2010 predicted a stable Pt/CMO/graphene interface, with Pt nanoparticles in contact with both CMO and graphene, followed by verification from transmission electron microscope (TEM) images. Durability for CNT supported catalysts was found to be >2X of baseline in FY 2010. In FY 2011, ITO-modified GCNT was found to have 3-4X higher durability than baseline. Optimization of GCNT diameter has also been carried out. With the current ITO synthesis method, 10-20 and 20-30 nm GCNT provided high ESA, with a significant drop for GCNT supported catalyst of >50 nm. The durability was also adversely affected with increasing GCNT diameter, possibly due to poor coverage of GCNT with ITO. ITO synthesis procedure is currently being modified to provide better coverage on GCNT to further improve both the performance and durability.

In FY 2010, significant improvement in ESA for CMO-supported catalysts was obtained using CTAB assisted synthesis that dispersed ITO precursor more uniformly, with a doubling of ESA to 40 m<sup>2</sup>/g. Addition of conductive CNT to the synthesized Pt/CNT improved performance without compromising durability, with ESA increasing

to 60 m<sup>2</sup>/g. Using hard template synthesis, the ESA was increased further by another 10% from 40 to 45 m<sup>2</sup>/g. Tests are ongoing to determine ex situ durability, followed by in situ assessment of performance and durability. Synthesis of mesoporous ITO using solvothermal annealing is currently ongoing to further optimize ITO mesoporosity and conductivity.

The lead cathode catalysts are shown in Figure 1, with Pt/Vulcan XC-72 as the baseline. CTAB assisted synthesis of Pt/ITO showed doubling of ESA to 85% of baseline value, while its durability was 2-3X that of baseline. Addition of electronically percolative CNT after Pt/ITO synthesis improved the ESA to 20% higher than baseline, while durability was still 2-2.5X higher. Modification of GCNT surface with ITO resulted in better distribution of Pt nanoparticles, resulting in 40% increase in ESA and 35% improved durability over non-ITO modified GCNT support. Based on these results, these compositions were selected for in situ MEA testing.

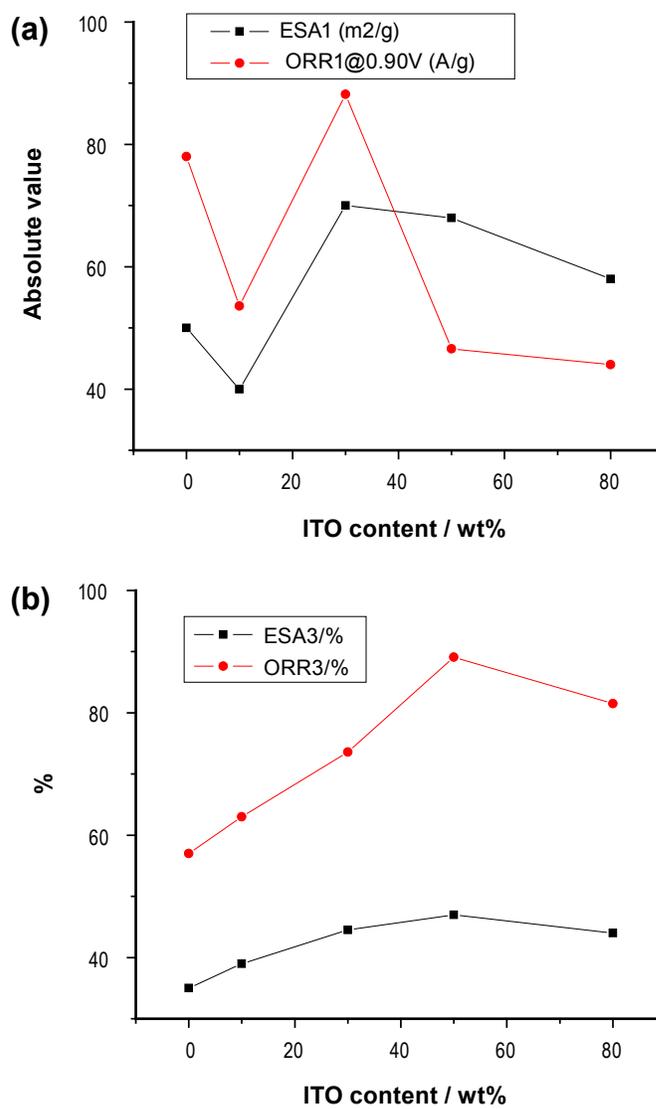
In FY 2011, ITO modification of GCNT was carried out to improve durability and performance. The optimum ITO content was determined to be 30 wt% as shown in Figure 2. This was complemented by conductivity studies on ITO-carbon composite layers in Nafion<sup>®</sup> that showed that just 30 wt% carbon is sufficient for electronic



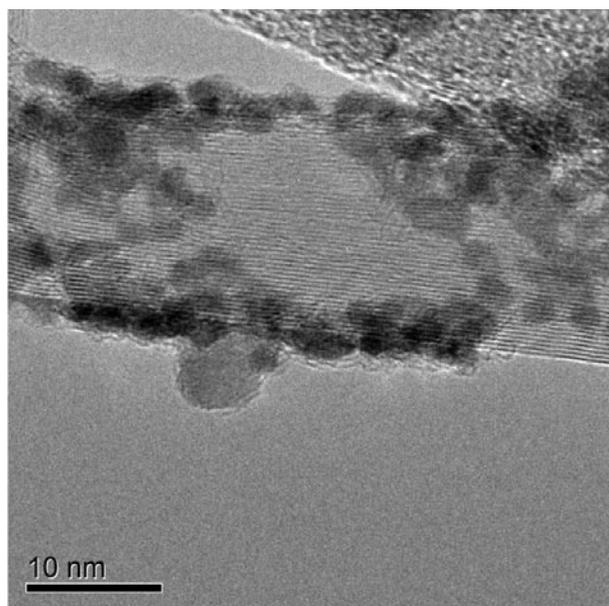
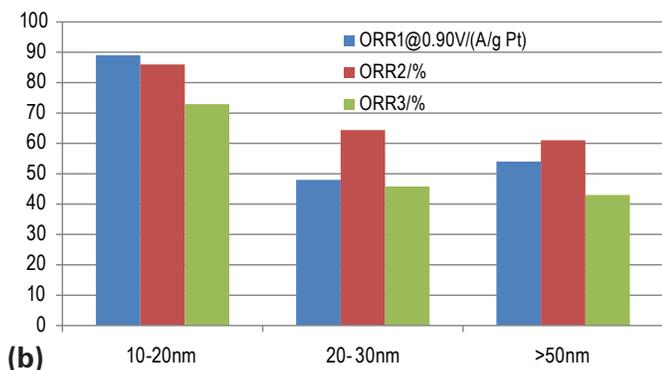
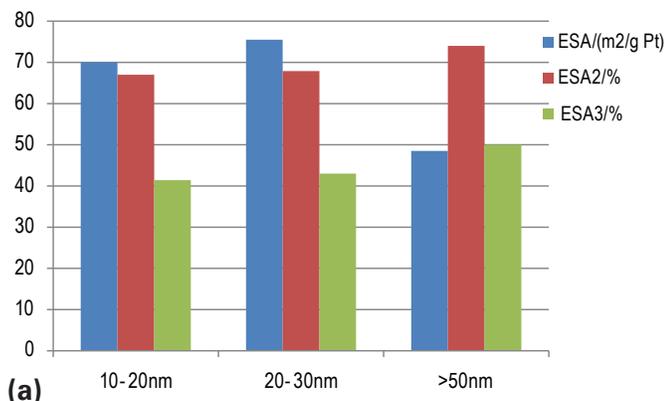
**FIGURE 1.** ESA (a) and Durability (b) for Lead Cathode Catalysts - RDE Potential Step between 0.85 V (30 sec) to 1.4 V (150 sec) vs. NHE

percolation. Use of this ITO content on GCNT with different diameter showed that activity decreased for >20 nm GCNT, while activity and ESA decreased for >50 nm GCNT (Figure 3). While retention of ESA was the same for all three diameters, the durability in terms of activity retention dropped for GCNT diameter >20 nm. These results show that GCNT support of 10-20 nm was optimum for in situ testing. Efforts are underway to functionalize GCNT to facilitate more uniform ITO deposition and more uniform dispersion of ITO precursor during synthesis. This involved functionalizing with sulfuric and nitric acid to take advantage of the positively charged ITO precursors, and use of polyelectrolytes to enhance ITO precursor dispersion.

MEA tests were conducted on select catalysts, with degradation done by potential hold at 1.2 V at 80°C/7.4 psig/100 % relative humidity, followed by

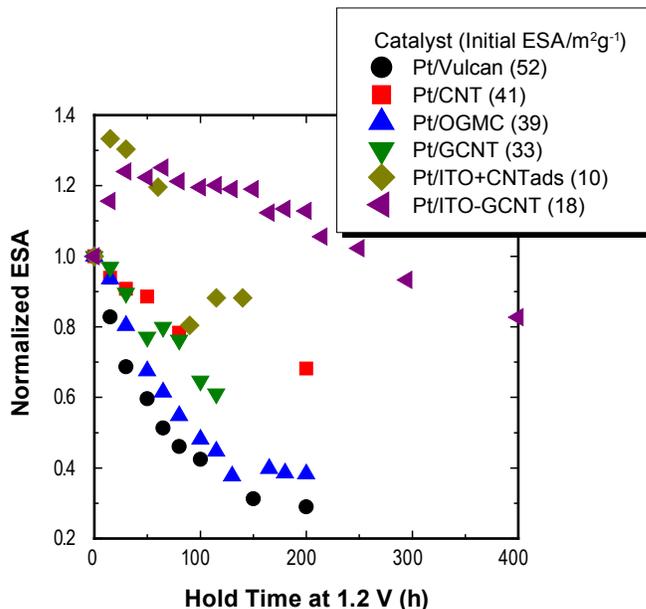


**FIGURE 2.** Optimization of ITO Content in ITO-GCNT (a) ESA/Activity, (b) Durability



**FIGURE 3.** Optimization of GCNT Diameter for ITO Modification of GCNT (a) ESA and ESA Retention after 20 and 40 hours (b) Activity and Activity Retention (c) TEM for Optimized Pt/ITO-GCNT for Optimized 10-20 nm dia GCNT

measurement of ESA, activity and polarization curves. In FY 2010, significantly higher durability was achieved for Pt/CNT and slightly higher durability for Pt/OGMC compared to baseline both in terms of ESA degradation.

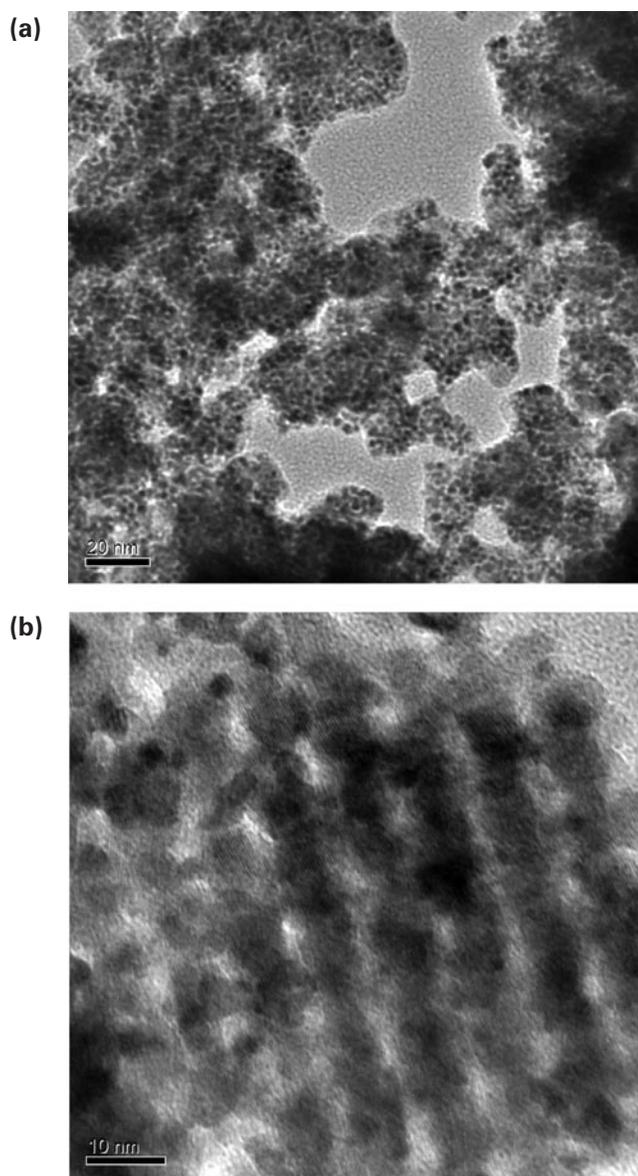


**FIGURE 4.** MEA Durability Results for Lead Supports (Initial ESA in brackets.)

Figure 4 shows the in situ durability for Pt-supported ITO-modified GCNT, compared with GCNT and baseline supports, with initial ESA provided. While the baseline supported catalyst lost 70% of its ESA in 50 hours and the GCNT supported catalysts lost 40% in 120 hours, Pt/ITO-GCNT lost only 20% of its ESA after 400 hours, thus making it >3-4X more stable than the baseline.

For non-carbon supports, while Pt/ITO was quite stable, its in situ ESA and performance was quite poor (2 m<sup>2</sup>/g). Conductivity tests on ITO/Nafion<sup>®</sup> layer showed an insulating characteristic for this layer. Hence about 20 wt% CNT was added to Pt/ITO in order to increase electron percolation. This resulted in an increase of ESA to 10 m<sup>2</sup>/g, with 3X durability of baseline (Figure 4). As seen in Figure 1, the ex situ durability was also 3X that of baseline, while ESA had tripled to 60 m<sup>2</sup>/g over Pt/ITO (data for Pt/ITO not shown).

While in situ tests showed better durability than baseline for non-carbon supports, efforts are ongoing to improve activity and ESA. In order to improve the electronic conductivity of ITO while also increasing the triple phase boundary length, solvothermal annealing and hard template synthesis of ITO was carried out to tailor mesoporosity and conductivity. The ESA had increased to 45 m<sup>2</sup>/g for ITO synthesized by the hard template method. X-ray diffraction and Brunauer-Emmett-Teller measurements showed that the particle size was around 20 nm, with pore size in the 8-10 nm range. Figure 5 shows TEM images of Pt/ITO synthesized by the above methods. Conductivity measurements on this sample will be carried out prior to in situ testing.



**FIGURE 5.** Pt/ITO (a) CTAB-Assisted (b) Hard Template Method – Evidence of Mesoporosity for the Hard Template Method

## Conclusions and Future Directions

Significant progress has been made in improving supported cathode performance and durability:

- Optimum ITO content in the ITO-GCNT was found to maximize activity and durability.
- Optimum GCNT diameter was determined to maximize performance and durability of ITO-graphene supports.
- Demonstrated >3-4X stability of Pt/ITO-GCNT over baseline Pt/Vulcan carbon.
- Demonstrated 3X durability of Pt/ITO over baseline with improved performance by CNT addition.
- Synthesized non-carbon ITO support with desired mesoporosity and conductivity.

Future work will involve improving the performance of non-carbon CMO supports by incorporating mesoporosity within the supports using hard template and solvothermal annealing approach and improving MEA formulation for these novel supports. ITO deposition on GCNT will be optimized to increase uniformity of coverage by modification of GCNT surface properties and increasing the dispersion of ITO precursors. Electrode architecture optimization will be performed by controlling the Nafion® content, catalyst layer thickness, Pt content, layer porosity and pore size distribution. Accelerated test protocol that increases throughput by 3-6X will also be developed.

## FY 2011 Publications/Presentations

1. S. Park, Y. Shao, H. Wan, P.C. Rieke, V.V. Viswanathan, S.A. Towne, L.V. Saraf, J. Liu, Y. Lin, Y. Wang, “Design of graphene sheets-supported Pt catalyst layer in PEM fuel cells”, *Electrochem. Commun.* 13 (2011) 258-261.
2. S. Park, Y. Shao, R. Kou, V.V. Viswanathan, S.A. Towne, P.C. Rieke, J. Liu, Y. Lin, Y. Wang, “Polarization Losses under Accelerated Stress Test using Pt Catalyst Supported on Multiwalled Carbon Nanotubes in PEM Fuel Cells”, *J. Electrochem. Soc.* 158 (3) (2011) B297-B302.
3. Kou R, Y Shao, D Mei, Z Nie, D Wang, CM Wang, VV Viswanathan, SK Park, IA Aksay, Y Lin, Y Wang, and J Liu. 2011. “Stabilization of Electrocatalytic Metal Nanoparticles at Metal-Metal Oxide-Graphene Triple Junction Points.” *Journal of the American Chemical Society* 133(8):2541-2547. doi:10.1021/ja107719u.
4. Shao Y, R Kou, D Mei, VV Viswanathan, IA Aksay, Y Lin, Y Wang, and J Liu. 2011. “An experimental and theoretical study of Pt-ITO-graphene electrocatalysts: improved durability and activity at triple junction points.” Presented by Yuyan Shao, Yong Wang and Jun Liu at 241<sup>st</sup> ACS National Meeting & Exposition, Anaheim, CA on March 28, 2011. PNNL-SA-76989.
5. Shao Y, R Kou, D Mei, VV Viswanathan, IA Aksay, J Liu, and Y Wang. 2011. “Pt-ITO-Graphene Electrocatalysts: Stabilization of Pt Nanoparticles at Triple Junction Points” Presented by Yuyan Shao, Yong Wang at 22<sup>nd</sup> North American Catalysis Society Meeting, Detroit, MI on June 6, 2011. PNNL-SA-77000.

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6. 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).
7. S. Park, Y. Shao, H. Wan, P. C. Rieke, V.V. Viswanathan, S.A. Towne, L.V. Saraf, J. Liu, Y. Lin, Y. Wang, "Design of graphene sheets-supported Pt catalyst layer in PEM fuel cells", *Electrochem. Commun.* **13** (2011) 258-261.
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