

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,
 Sehkyu Park, Yuyan Shao, Haiyin Wan
 Pacific Northwest National Laboratory (PNNL)
 902 Battelle Boulevard, PO Box 999
 MS K2-12
 Richland, WA 99352
 Phone: (509) 371-6273
 E-mail: yongwang@pnl.gov

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

Subcontractors:

- Stephen Campbell, AFCC Automotive Fuel Cell Cooperation Corp., Burnaby, BC
- Sheng Dai, Qing Zhu, Jeseung Lee, Oak Ridge National Laboratory, Oakridge, TN
- Jinguang Chen, Irene Hsu, University of Delaware, Newark, DE
- Brian Willis, University of Connecticut, Storrs, CT

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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 (CMO) for improved activity and durability over standard Pt/C.
- Demonstrate durability and performance advantages of alternative cathode supports such as carbon nanotubes (CNTs) ordered graphitic mesoporous carbon (OGMC) and grapheme.
- Demonstrate durability and performance of non-carbon CMO supports such as indium tin 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 life time criteria.

Membrane electrode assembly (MEA) tests are in progress for lead supports, and have shown 2X improvement in stability over baseline vulcan carbon/XC72 supports (Table 1). Alternative supports such as CNTs have shown no degradation after 100 hours, thus providing a synergistic opportunity for metal oxide modification of CNTs. Rotating disc 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 2010 Status
Accelerated test loss, 200 h @ 1.2 V at 80°C	mV at rated power	<30	>2X improvement over baseline for MEA
	% ESA loss	<40	>2X improvement for RDE and MEA tests
Durability with Cycling at 80°C	hours	5,000	TBD

ESA – electrochemically active surface area; TBD – to be determined

Accomplishments

- Optimum ITO content in graphene found to maximize activity and durability:
 - Activity and durability are 1.5X and 1.7X of baseline.
 - Pt distributed uniformly at ITO/graphene interface as predicted by density functional theory (DFT) model.
- Demonstrated Pt/CNT stability of >2X over Pt/XC72.
- Demonstrated 2X durability of Pt/OGMC over Pt/XC72.
- Demonstrated 3X durability of Pt/ITO non-carbon support over baseline.

- Obtained consistency between RDE and MEA test results.
- Validated DFT prediction for higher Pt/WC activity and higher Pt/VC stability.



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 with conductive metal oxides [4] such as ITO, TiO₂ and SnO₂. Alternate supports such as CNT, graphene sheets were also investigated to take advantage of their superior properties [5,6]. 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:

- Formation of a protective barrier between carbon and Pt mitigates carbon corrosion.
- Bonding between Pt and metal oxide substrates enhances the stability of Pt particles.
- More uniform dispersion of Pt, allowing better performance at equivalent loading.
- Higher activity and durability of CNT, OGMC and graphene over XC72 provides potential for an order of magnitude improvement with metal oxide modification.
- DFT modeling indicates stable Pt/ITO/graphene interface.
- Carbon-free metal oxides (ITO) successfully identified as candidates for catalyst support.

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 ethylene glycol method [7]. Durability of various carbon supports such as XC72, carbon multi-walled nanotubes (CMWNT, also referred to as CNT in this report), ordered graphitized mesoporous carbon and graphene were compared. DFT modeling was performed to identify potential supports with better oxygen reduction reaction (ORR) activity and stability than Pt-XC72. DFT predictions were validated by experiments.

Carbon supports were modified with WC and various conductive metal oxides such as TiO₂, SnO₂, and 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 (NHE). An investigation of the effect of CMO modification of various supports such as CNT, graphene and OGMC 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, ORR activity at 0.9 V and polarization curves performed every 20 hours.

Results

DFT predictions for high activity of Pt/WC was validated with experiments, while DFT prediction for high Pt/VC stability was also validated with Auger electron spectroscopy (AES). Optimum CMO composition for graphene supported catalyst was found, leading to 50-70% improvement in activity and durability over baseline. DFT modeling predicted a stable Pt/CMO/graphene interface, with Pt nanoparticles in contact with both CMO and graphene, with verification from transmission electron microscopy (TEM) images. Durability for OGMC and CNT-supported catalysts was found to be >2X of baseline. CMO supported catalysts, which were previously shown to be highly durable, have shown rapid improvement in ESA and activity using RDE tests. MEA formulation methods for non-carbon and conductive metal oxide modified supports are currently being optimized. MEA tests were conducted on alternative carbon supports such as CNTs, OGMC and graphene, with tests ongoing on CMO modified graphene and non-carbon supports.

DFT analysis had predicted the superior activity and stability of Pt on WC (0001) and superior stability of Pt on vanadium carbide (VC). In order to verify the activity enhancement of Pt/WC (0001) over Pt, the performance of Pt-WC synthesized by atomic layer deposition (ALD) was determined by cyclic voltammetry (CV), with results corresponding to 30 ALD cycles surpassing Pt foil performance significantly. In order to verify superior stability of Pt on VC in the presence of oxygen, Auger electron spectroscopy was carried out on Pt/V(110) and on Pt/VC before and after exposure

to 3,000 L oxygen at 300 K. For the former, Pt signal decreased, accompanied by an increase in the V signal, while for Pt/VC, the Pt signal did not decrease upon exposure to oxygen. These results were also confirmed by high resolution electron energy loss spectroscopy (HREELS).

The lead cathode catalysts developed are shown in Figure1, with Pt/VC as the baseline. CNT and OGMC were found to be very stable supports. TiO₂ modification of Vulcan carbon improved both ESA and stability. The dispersion of Pt on graphene was not uniform, with agglomeration of Pt particles present. Modification of graphene surface with ITO resulted in better distribution of Pt nanoparticles, resulting in improved activity and durability. The results for Pt/ITO was very encouraging, with excellent durability. Based on these results, Pt/OGMC, Pt/CNT, Pt/graphene, Pt/ITO/graphene and Pt/ITO were selected for MEA testing.

The consistency between RDE and MEA results are shown in Figure 2 from some commercial ETEK catalyst,

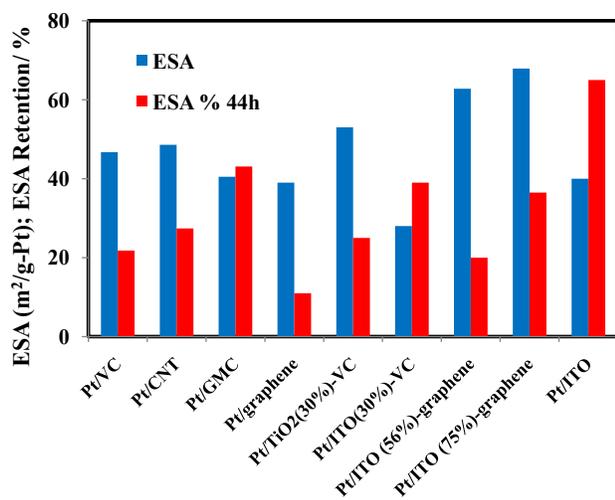


FIGURE 1. ESA and Durability for Lead Cathode Catalysts - RDE Potential Step between 0.85 V (30 sec) to 1.4 V (150 sec) vs. NHE

Pt/VC baseline, and Pt/CNT. The trends for ESA and durability are the same for both types of measurements.

Metal oxides protect carbon substrate from oxidation. Figure 3 shows the polarization curves and CVs of carbon with/without metal oxide coating. The oxidation current densities (A/g carbon) were reduced for metal oxides coated graphene and carbon black, indicating that metal oxides protect carbon from oxidation. The CVs of metal oxide coated carbon are similar to that of pure carbon in the potential range of 0-1.4 V (proton exchange membrane fuel cell electrode

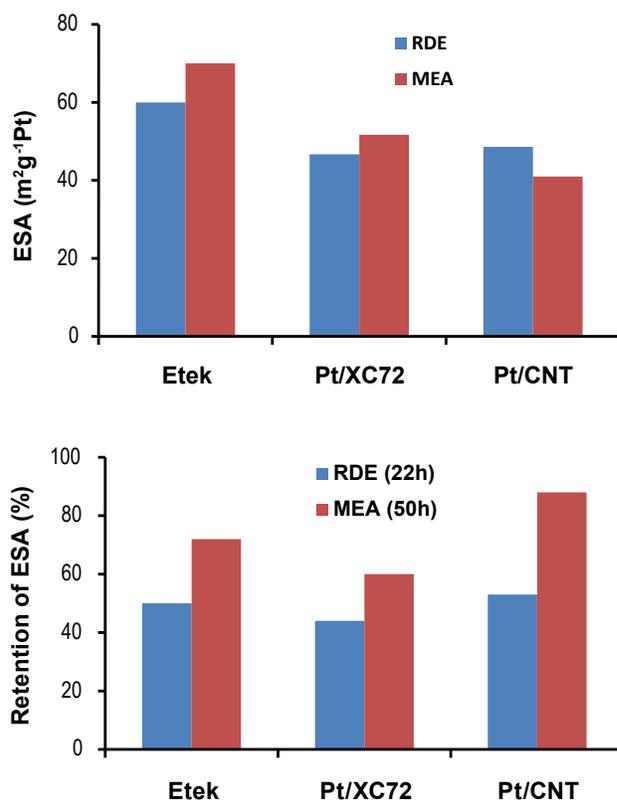


FIGURE 2. Consistency between RDE and MEA Results

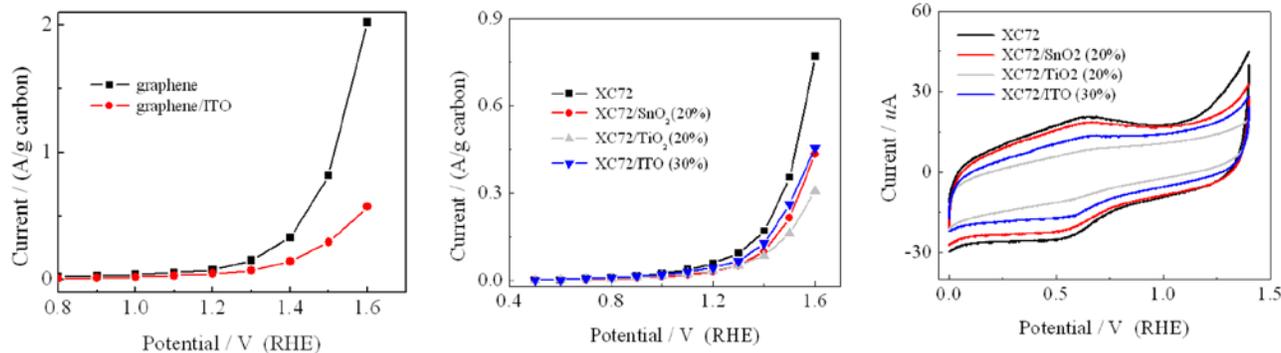


FIGURE 3. Polarization Curves and CVs of Carbon With/Without Metal Oxide Coating in Nitrogen-Saturated 0.5 M H₂SO₄

potentials), which reveals that metal oxides (ITO, SnO_2 , TiO_2) are stable.

ITO/graphene nanocomposites were synthesized in organic solvent by the hydrothermal method. Graphene, indium precursors and tin precursors were mixed in the organic solvent. Under the proper temperature and reaction time, ITO nanoparticles nucleate and grow on the surface of the graphene. Through this one-pot synthesis, uniform ITO nanoparticles were evenly dispersed on the graphene sheets. High activity was obtained for ITO/graphene substrates. Optimization of ITO content showed that at 75% ITO, the activity and durability were maximized as shown in Figures 4a and 4b. TEM images show the uniform dispersion of Pt using ITO mediated graphene (Figure 4d), while Pt agglomeration on graphene is seen without ITO (Figure 4c). Tests are ongoing to determine its effectiveness in an MEA.

Periodic DFT calculations were done to study the thermodynamic stability of Pt/ITO-graphene in both vacuum and oxygen atmosphere. The Pt/ITO/graphene system was found to be the most stable compared to Pt/ITO and ITO/graphene, with the highest interaction energy. The DFT model structure shows Pt at the interface of ITO/graphene (Figure 5a). Figure 5b shows the cross-section TEM for Pt/ITO/graphene, with Pt present at the interface of ITO/graphene, as predicted by the DFT calculations. A schematic showing Pt location in the Pt/ITO/graphene system is also shown (Figure 5c).

MEA tests were conducted on select catalysts, with degradation done by potential hold at 1.2 V at $80^\circ\text{C}/7.4$ psig/100% relative humidity, followed by measurement of ESA, activity and polarization curves. As seen in Figure 6, significantly higher durability was achieved for Pt/CNT and Pt/OGMC compared to baseline both in terms of ESA degradation and decrease in current at 0.6 V. During MEA formulation for graphene-based support, some vulcan carbon was added to the Pt/graphene catalyst (Pt/graphene + XC72) in order to increase the space between graphene sheets, and thus allow access of Nafion[®] to the inter-sheet space.

Conclusions and Future Directions

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

- DFT modeling predictions for higher Pt/WC ORR activity was verified by ALD deposition of Pt on WC and measurement of activity.
- DFT modeling prediction for higher Pt/VC stability in the presence of oxygen was verified by AES and HREELS.
- Optimum ITO content was found to maximize activity and durability.

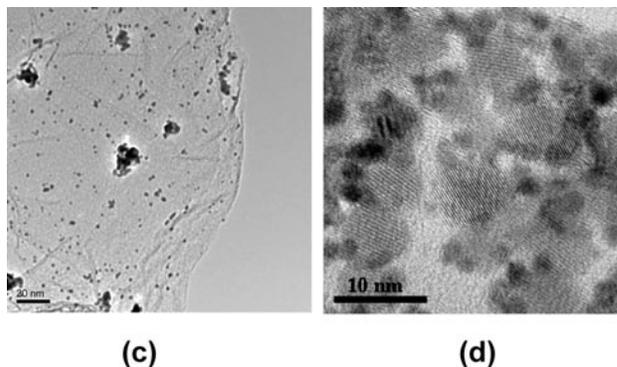
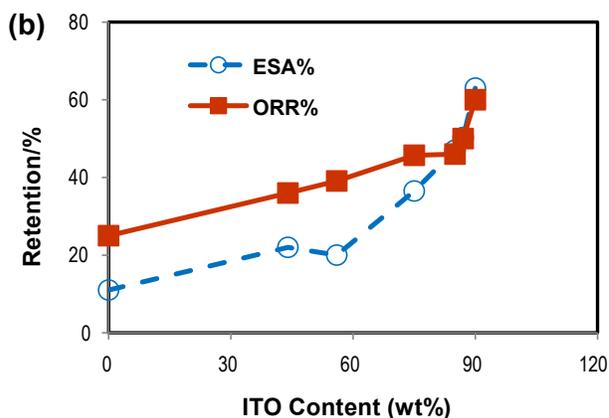
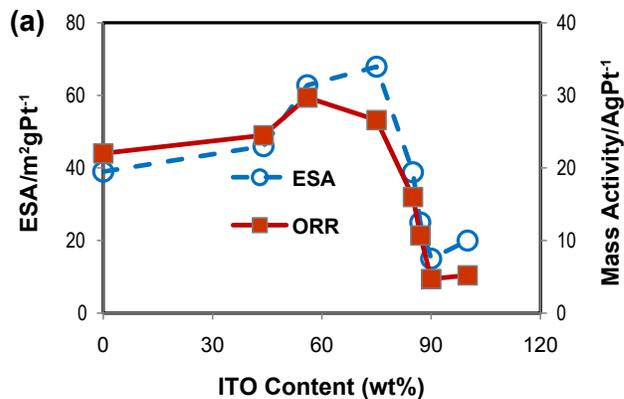


FIGURE 4. Optimum ITO content for activity and durability of Pt/ITO-graphene system (potential step between 0.85 V [30 sec] to 1.4 V [150 sec] vs. NHE). Optimum ITO content for activity (a) and durability (b) of Pt/ITO-graphene system (potential step between 0.85 V [30 sec] to 1.4 V [150 sec] vs. NHE). TEM images for Pt/graphene (c) and Pt/ITO/graphene (d)

- ITO mediation enabled uniform Pt distribution in the Pt/ITO/graphene system. DFT prediction of stable Pt/ITO/graphene configuration with Pt at the edge of ITO/graphene was verified by TEM.
- Demonstrated > 2X stability of Pt/CNT over Pt/XC72.
- Demonstrated 2X durability of Pt/OGMC over Pt/XC72.

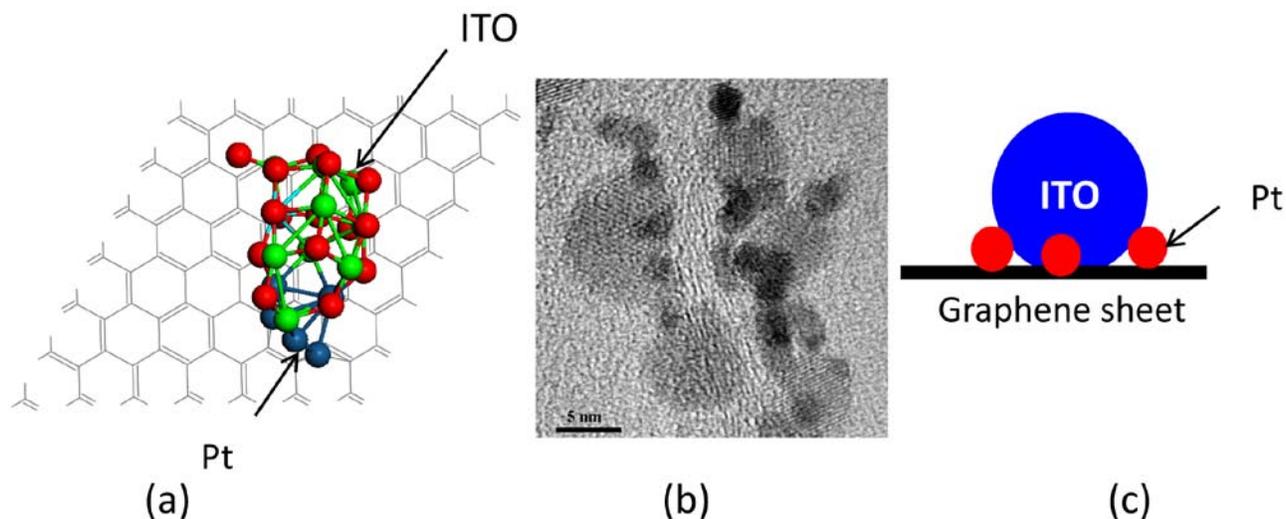


FIGURE 5. Pt/ITO/Graphene DFT Model Structure (a), TEM (b), Schematic (c)

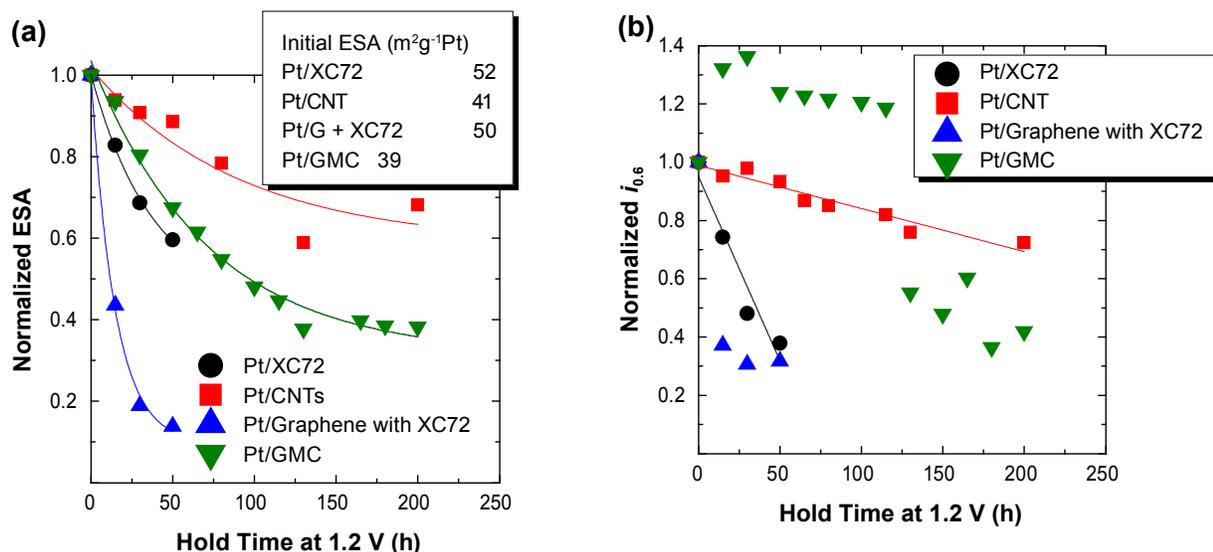


FIGURE 6. MEA Durability results for novel carbon supports (a) ESA degradation, (b) degradation of current at 0.6 V. Pt/G + XC72 – vulcan carbon XC72 added to Pt/grapheme.

- Demonstrated 3X durability of Pt/ITO over baseline.
- Obtained consistency between RDE and MEA results.

Future work will involve improving the performance of non-carbon CMO supports by incorporating mesoporosity within the supports and improving MEA formulation for these novel supports. CMO modification of alternative carbon supports such as CNT and OGMC, which show 2X higher durability than baseline vulcan carbon, will also be conducted.

FY 2010 Publications/Presentations

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