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

Yong Wang (Primary Contact),
Vilayanur Viswanathan, Jun Liu, Yuehe Lin,
Sehkyu Park, Yuyan Shao

Pacific Northwest National Laboratory
902 Battelle Boulevard, PO Box 999
MS K2-12
Richland, WA 99352
Phone: (509) 371-6273
Email: yongwang@pnl.gov

DOE Manager
HQ: Nancy Garland
Phone: (202) 586-5673
Email: Nancy.Garland@ee.doe.gov

Subcontractors:
AFCC Automotive Fuel Cell Cooperation Corp.,
Burnaby, BC: Stephen Campbell

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Fiscal Year (FY) 2012 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 (cathode catalyst supports)

(C) Performance (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 have been performed 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. Promising results have been obtained for carbon-free supports, with ex situ results showing similar electrochemical surface area (ESA) values and excellent durability. Electrode architecture optimization is ongoing to improve in situ performance of these supported catalysts.

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

Parameter	Units	2015 Stack Target	PNNL 2011 Status
Accelerated test loss, 200 h @ 1.2 V at 80ºC	mV at rated power	<30	10% retention for baseline after 100 hours
	% ESA loss	<40	42% retention of ESA for baseline after 100 hours
Durability with cycling at 80ºC	Hours	5,000	To be determined

FY 2012 Accomplishments

Throughout the course of the project, we achieved the following:

- Thermodynamic stability of Pt-CMO-carbon triple junction using periodic density functional theory (DFT) calculations.
- Verification of formation of Pt-CMO-carbon triple junction by microscopy and its high stability by ex situ and in situ electrochemical tests.
- Identification of contribution of catalyst layer ohmic and ionic resistances to MEA performance and degradation, providing insights into electrode architecture optimization.
- High durability of carbon-free CMO support of various aspect ratios, mesoporosity and Pt loading.

For FY 2012 specifically, we achieved the following:

- Synthesized TiO_2 nanorod supported catalyst with continuous Pt nanowire networks.

- Determined effect of ITO mesopore size on ex situ performance, with ESA equal to vulcan carbon baseline.
- Developed accelerated stress test (AST) protocol to increase throughput by 4X.
- Obtained promising in situ trends for Pt-ITO by optimizing electrode architecture and platinum loading.
- Methodology developed to estimate ionic resistance and concentration polarization in the supported catalyst layer for various carbon supports, and their degradation during AST, which can guide electrode architecture optimization for various supports.

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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_2 and SnO_2. 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 ex situ and in situ electrochemical tests and periodic 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 >4X 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.
- Metal oxides with optimized aspect ratio and Pt wt% in the support provide pathway for enhanced durability and performance.
- Identification of catalyst layer ohmic and mass transfer resistance contribution to MEA performance and degradation provides opportunity to tailor electrode architecture for electrodes with various supports.

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 in FY 2011 on hybrid support-Nafion® layers to verify electronic percolation through the catalyst layer. Measurements were also done with ITO/Nafion® layers to explore pathways for improvement of performance. Various diameters of CNTs were modified with ITO to get a more uniform coating. The effect of functionalization of the nanotubes on activity and stability was also studied.

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. In FY 2012, further optimization was conducted for ITO synthesis, with increase in mesopore size by 50% to 12 nm to facilitate Nafion® electrolyte and gas access to the catalyst site. TiO_2 supports of various shapes were synthesized, and a continuous Pt nanowire network was successfully deposited on TiO_2 nanorod supports, with ESA equivalent to baseline.

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. 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 80ºC, and measurement of ESA, oxygen reduction reaction activity at 0.9 V and polarization curves performed every 20 hours.

Results

In FY 2011, ITO-modified GCNT was found to have 3-4X higher durability than baseline. In FY 2012, various functional groups on CNTs and GCNTs were investigated. No major effect of functional groups on ex situ performance was found. In order to allow use of more cost-effective supports, CNTs of various diameters were modified with ITO to get a more uniform coating. A uniform coating was obtained on 30-50 nm CNTs. Ex situ tests however, did not show significant improvement in activity over prior ITO modified GCNT and CNT. Hence in situ tests were not done for these supported catalysts.

In FY 2011, using hard template synthesis of ITO, the ESA was increased by 12% from 40 to 45 m^2/g. However, the activity was low, hence further optimization was done related to ITO synthesis in FY 2012. Using hard-template synthesis, the mesopore size was increased by 50% to 12 nm in order

to facilitate Nafion® and reactant access to the catalyst site. Figure 1 a-f show transmission electron microscope (TEM) and scanning transmission electron microscope (STEM) images of 20 wt% Pt loaded onto mesoporous ITO. An ordered ITO structure is obtained, with mesopores in the 10-12 nm range. Ex situ tests showed significant improvement over previous results obtained on ITO supports, with an ESA of 55 m^2/g and mass activity of 55 A/g (Figure 1 g, h). Durability tests (ex situ) also showed extremely stable results.

In FY 2012, we also investigated the effect of metal oxide support aspect ratio on performance and durability. TiO$_2$ nanorods were synthesized by hydrolysis/hydrothermal method. The effect of Pt loading on the TiO$_2$ support was studied. As seen in Figure 2a, for 20 wt% Pt, Pt nanoparticles were mostly isolated from each other, thus relying on the conductivity of the TiO$_2$ nanorod support, associated with low ESA. 50% Pt corresponded to a continuous Pt nanowire network around the nanorod (Figure 2b), and led to higher ESA of 55 m^2/g. (Figure 2c). However, the mass activity of both samples was low. TiO$_2$ nanoparticles were subsequently synthesized by surfactant assisted method using CTAB surfactant, with Pt loading at 50 wt%. Figure 3a shows TEM images for these supported catalysts, while Figure 3b
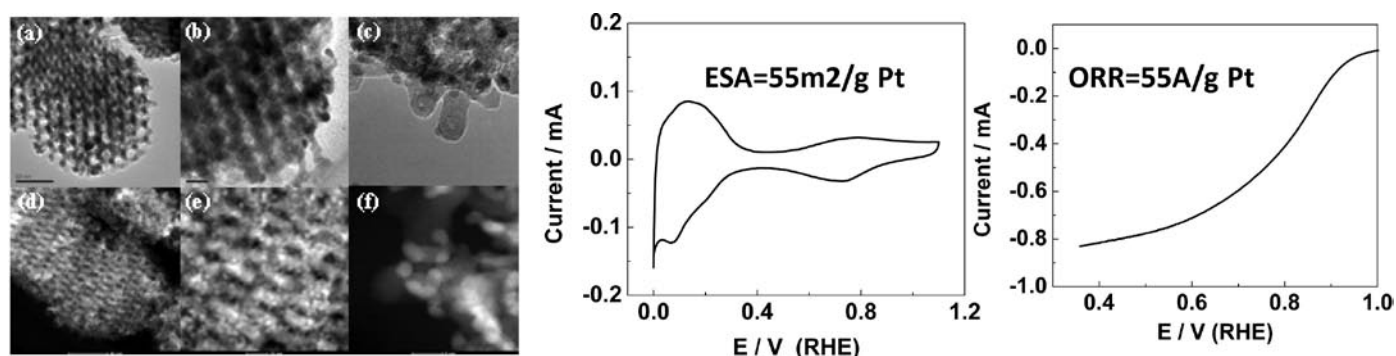

FIGURE 1. TEM and STEM data for Pt/mesoporous ITO: a, b and c) low and high magnification of TEM images; d, e and f) low and high magnification of STEM images; g) ESA, h) oxygen reduction reaction
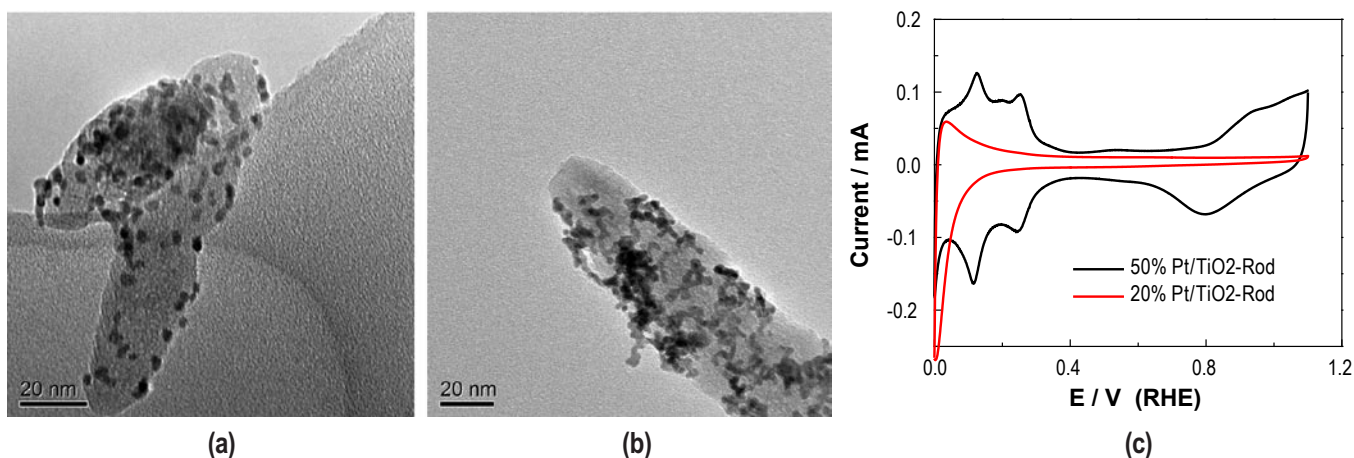

FIGURE 2. Effect of % Pt on TiO$_2$ nanorod support. (a) 20 wt% Pt, (b) 50 wt% Pt, (c) ESA for 20 wt% and 50 wt% Pt
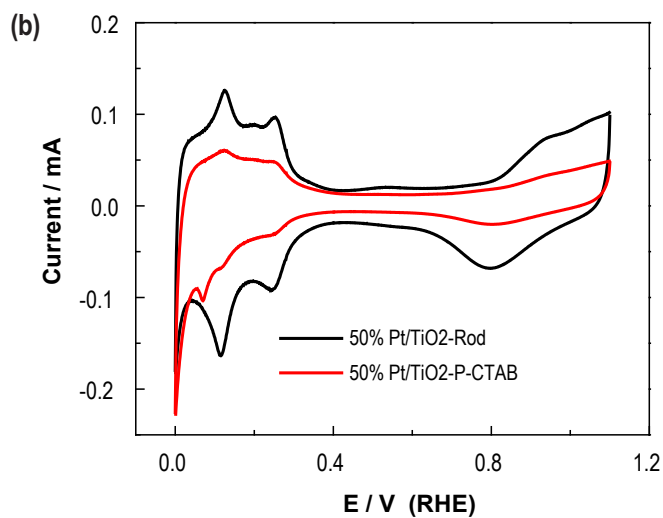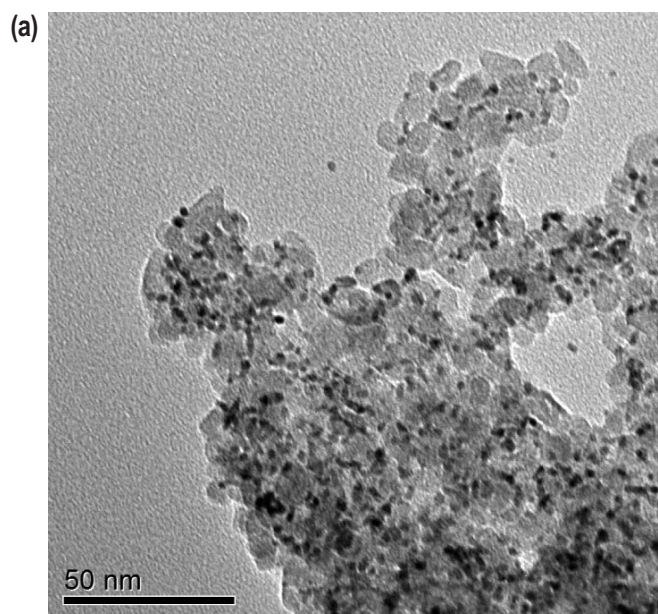
(a)

(b)

FIGURE 3. Pt supported on CTAB assisted TiO_2 nanoparticles. (a) TEM Pt/TiO_2 (CTAB), (b) ESA comparison of Pt/TiO_2 (CTAB) with Pt/TiO_2 nanorods

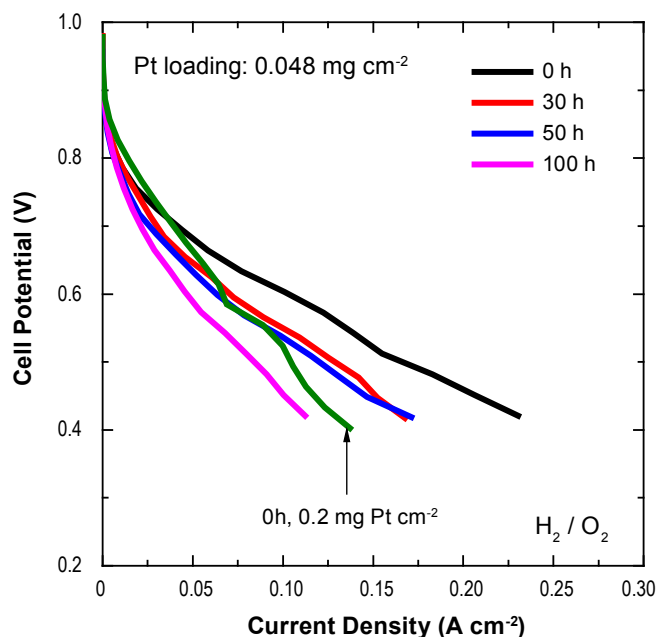FIGURE 4. Polarization curves at various AST durations for 50 wt% Pt/mesoporous ITO at 0.048 mg Pt/cm^2, compared with initial polarization curve for 0.2 mg Pt/cm^2

shows the performance comparison with 50 wt% Pt on TiO_2 nanorods. The ESA for Pt supported on CTAB assisted TiO_2 was much lower, indicating the influence of synthesis method and morphology on performance.

In FY 2011, Pt/ITO-GCNT was found to be the most durable low carbon support during in situ tests, with >3-4X more stability than the vulcan carbon baseline. In FY 2012, a protocol was successfully developed to increase testing throughput by 5X by increasing the hold potential to 1.4 V.

In situ tests were done on 20 wt% Pt/mesoporous ITO, which yielded 55 m^2/g ESA and 55 mA/g mass activity in ex situ tests as mentioned earlier. For a loading of 0.2 mg Pt/cm^2 the performance was quite poor, with a high ohmic resistance adversely affecting performance. This was hypothesized as

being due to the catalyst layer being too thick, leading to high electronic resistance of ITO, with the hydrophilicity of the electrode potentially adversely impacting ionic conductivity in the catalyst layer. Adding Teflon® to counter ITO hydrophilicity did not help, possibly due to decrease in electronic conductivity. Decreasing Nafion® content also lowered performance, thus showing ionic conductivity in the catalyst layer also plays an important role. The Pt loading was decreased by 4X, with significantly improved results as shown in Figure 4. Increasing the Pt wt% in the Pt/ITO is expected to enable thinner catalyst layers and higher electronic conductivity, while increasing ITO conductivity would lower electronic resistance. These options are being investigated to provide an anticipated 4X improvement in performance over the current Pt/ITO results.

Since electrode architecture is clearly important, in FY 2012, fundamental studies on MEA catalyst layer degradation were carried out on Pt/OGMC and Pt/baseline vulcan carbon support. Using a transmission layer model, the catalyst layer ohmic resistance was determined from alternating current (AC) impedance data, flowing N_2 at the cathode [10]. The high frequency resistance was quite stable, indicating absence of membrane degradation from attack by hydroxyl radicals formed by decomposition of hydrogen peroxide in the presence of trace metal contaminants. This was confirmed by the stability of the hydrogen crossover current data over the AST duration. The catalyst layer ionic resistance, while increasing slowly initially, increased at a much higher rate after 100 hours of the AST, accompanied
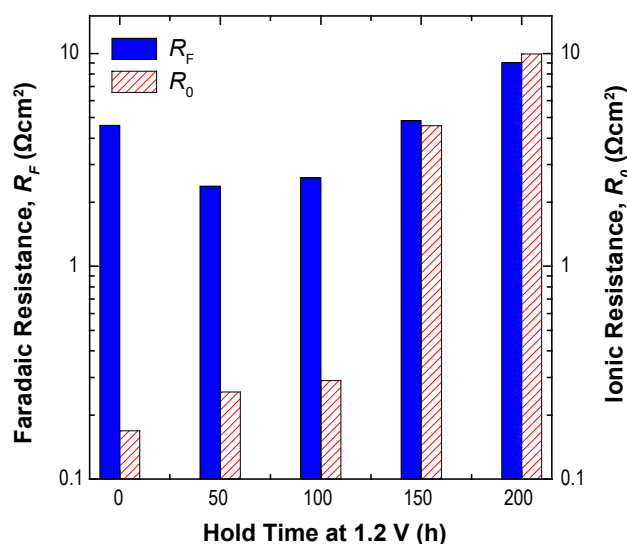
FIGURE 5. Comparison of Faradaic resistance R_F and ionic resistance in the Pt/OGMC cathode catalyst layer R_0 as a function of hold time at 1.2 V.

by an increase in faradaic resistance from AC impedance using air at the cathode at 0.9 V (Figure 5). This indicates that the increase in catalyst layer ohmic resistance plays a major role in the increase of Faradic resistance. The increase in catalyst layer resistance was probably caused by support corrosion and associated increase in contact resistance at the membrane/supported catalyst and supported catalyst/gaseous diffusion layer (GDL) interfaces.

Experiments repeated with vulcan carbon showed a similar increase in catalyst layer resistance with AST duration [11]. With increasing potential hold time, the internal resistance-corrected polarization curves showed a single Tafel slope of 51 mV/decade initially in the 0.001-0.1 A/cm^2 region, with a second slope of 110-118 mV/decade in the 0.01-0.1 A/cm^2 region, at higher hold times, with this slope increasing with AST duration. This appears to indicate a mixed kinetic and mass transfer controlled process at high hold times, attributed to increasing presence of oxygen containing functional groups in the support leading to higher hydrophilicity and greater support corrosion. The kinetic overpotential, concentration overpotential in the catalyst layer and concentration overpotential in the GDL microporous layer were extracted from the polarization curves. As seen in Figure 6a, the kinetic overpotential increased very slowly with AST duration, while the concentration overpotential in the catalyst layer and non-catalyst layers jumped at 50 hours and 100 hours respectively. The charge transfer resistance obtained for fresh electrodes from AC impedance at various potentials showed charge transfer resistance (Rct) decreasing with decrease in potential, thus showing no limitations from mass transfer. At 100 hours hold, Rct showed a minimum at 0.75 V and started increasing, due to mass transfer limitations both in the
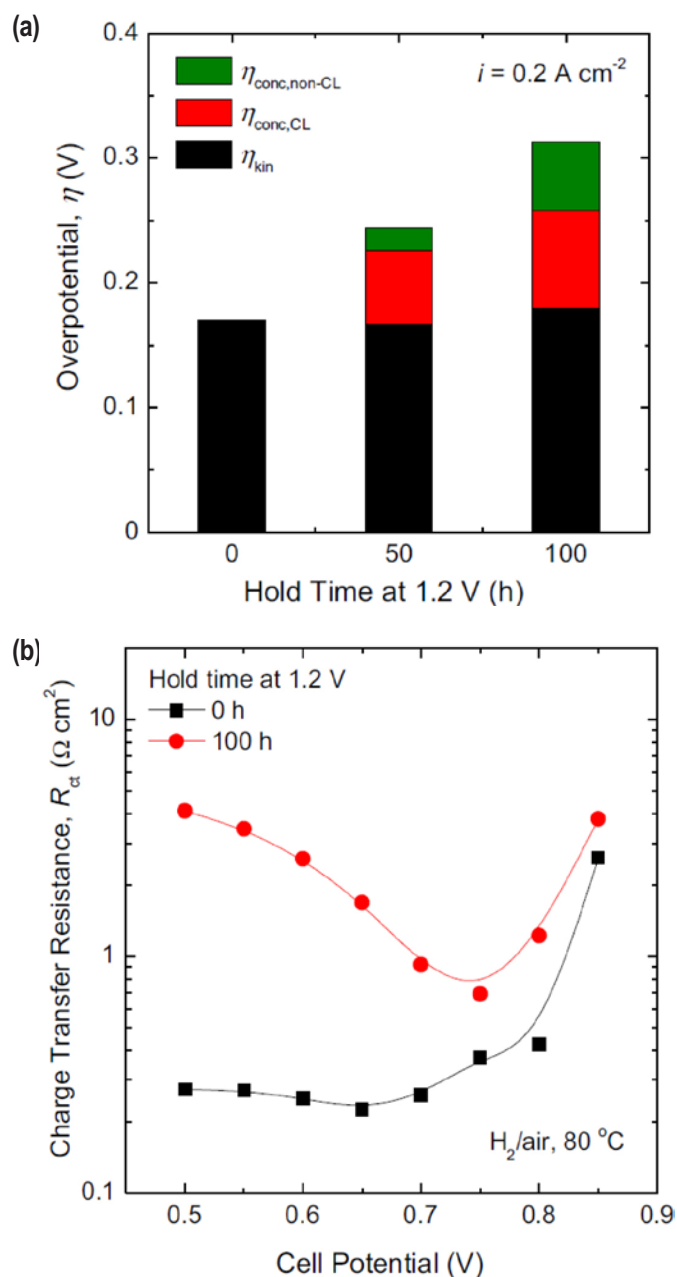

FIGURE 6. Pt/Vulcan carbon AST results (a) kinetic and concentration overpotentials at 0.2 A/cm^2, (b) Rct from AC impedance using H$_2$/air at various potentials before and after AST

catalyst layer and in the non-catalyst layer (Figure 6b). Since at 100 hours, mass transport in the non-catalyst layer also is significant, this work shows the importance of tailoring the architecture of the microporous layer to avoid flooding at the catalyst GDL interface. The catalyst layer contribution to increased charge transfer resistance arises from both the increase in catalyst layer ionic resistance and catalyst layer mass transport resistance, thus providing a pathway for MEA architecture optimization for various catalyst supports.

Conclusions and Future Directions

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

- A stable Pt-CMO-carbon triple junction was predicted using periodic DFT calculations and verified experimentally.

- Optimum CMO content was determined for both ex situ and in situ tests to adequately cover the carbon support defect sites and for maximum activity and performance.

- High durability of carbon free CMO support of various aspect ratios, mesoporosity and Pt wt% in support was obtained with ESA similar to vulcan carbon baseline in ex situ tests.

- Pathway was established for improving in situ performance of carbon free support by increasing Pt wt% in the supported catalyst, decreasing catalyst layer thickness and increasing support conductivity.

- Identification of significant contribution of catalyst layer ohmic and ionic resistances to MEA performance and degradation, thus providing insights into electrode architecture optimization.

Ongoing work will involve improving the performance of non-carbon CMO supports by increasing support electronic conductivity, further optimization of mesoporosity within the supports, controlling Pt wt% in the support, and improving MEA formulation for these novel supports by decreasing catalyst layer thickness and adjusting Nafion® content. Electrode architecture optimization will also be performed of low carbon CMO modified supports. The completion of these tasks would position this project well for continuation of this work, focusing on:

- CMO modification of inter-connected carbon network with subsequent deposition of a thin continuous Pt film either between CMO particles or on the CMO particles.

- Pt deposition on oriented TiO_2 nanorods with varying Pt/TiO_2 ratio.

- Investigation of other oxides such as SiO_2 nanoparticles and nanowires, CeO_2 and sulfonated ZrO_2.

- Optimization of electrode architecture focusing on thin catalyst layers, catalyst layer porosity and pore size distribution, low Pt loading and Nafion® content.

FY 2012 Publications/Presentations

1. S. Park, Y. Shao, H. Wan, V.V. Viswanathan, S. Towne, P.C. Rieke, J. Liu, Y. Wang, "Degradation of the Ionic Pathway in a PEM Fuel Cell Cathode", *J. Phys. Chem. C* 115 (45) (2011) 22633-22639.

2. S. Park, Y. Shao, V.V. Viswanathan, J. Liu, and Y. Wang, "Non-Kinetic Losses Caused by Electrochemical Carbon Corrosion in PEM Fuel Cells", *Int. J. Hydrogen. Energy* 37 (2012) 8451-8458.

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. S. Park, Y. Shao, V.V. Viswanathan, J. Liu, and Y. Wang, "Irreversible Losses in a PEM Fuel Cell during Accelerated Stress Test of Catalyst Support", 221st Meeting of The Electrochemical Society, 6–10 May, Seattle, WA, USA.

5. S. Park, Y. Shao, H. Wan, V.V. Viswanathan, J. Liu, and Y. Wang, "Development of novel electrocatalyst support in proton exchange membrane fuel cells for automotive applications", 2011 AIChE annual meeting, 16–21 October 2011, Minneapolis, MN, USA.

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8. 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 .

9. 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 (26) 6292-6299 (2003).

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11. S. Park, Y. Shao, V.V. Viswanathan, J. Liu, and Y. Wang, "Non-Kinetic Losses Caused by Electrochemical Carbon Corrosion in PEM Fuel Cells", *Int. J. Hydrogen. Energy* 37 (2012) 8451-8458.