# V.N.3 Engineered Nano-Scale Ceramic Supports for PEM Fuel Cells

Eric L. Brosha[1] (Primary Contact),
Karen J. Blackmore[1], Anthony K. Burrell[1],
Neil J. Henson[1], Jonathan Phillips[1],
Tommy Rockward[1], Karren More[2],
Timothy Ward[3]
[1]Los Alamos National Laboratory (LANL)
MS D429, P.O. Box 1663
Los Alamos, NM 87545
Phone: (505) 665-4008
E-mail: brosha@lanl.gov

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

Subcontractors:
[2] Oak Ridge National Laboratory (ORNL),
Oak Ridge, TN
[3] University of New Mexico (UNM), Albuquerque, NM

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## Objectives

- Develop a ceramic alternative to carbon material supports for a polymer electrolyte fuel cell cathode.
- Ceramic support replacement for carbon must:
  - Have enhanced resistance to corrosion and Pt coalescence.
  - Preserve positive attributes of carbon such as cost, surface area, and conductivity.
  - Be compatible with present membrane electrode assembly (MEA) architecture and preparation methods.
- Ceramic properties goals:
  - High surface area
  - High Pt utilization
  - Enhanced Pt-support interaction
  - Adequate electronic conductivity
  - Corrosion resistance
  - Synthetic methods amenable to scale-up
  - Reasonable synthesis costs

## Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability: Pt sintering, corrosion loss, effects from load-cycling and high potential.
(B) Cost: Better Pt utilization balanced by cost difference of new support vs. carbon.
(C) Performance: Pt sintering, corrosion loss, and loss of electroactive surface area.

## Technical Targets

- Precious metal loading (0.2 mg/cm$^2$)
- Cost (<$3/kW)
- Activity (0.44 A/mg$_{Pt}$ @ 0.9 V$_{iR\text{-}free}$)
- Electrocatalysis support loss (<30 mV after 100 hrs @ 1.2 V)
- Electrochemical surface area loss (<40%)

## Accomplishments

### Synthesis of Non-Carbon Support Materials

- Ceramic materials with critical physical/chemical requirements for polymer electrolyte membrane fuel cell (PEMFC) catalyst support applications have been prepared.
- Utilized polymer-assisted deposition process to prepare conductive, cubic phase $Mo_2N$ with surface area ca. 500 m$^2$/g.
- Transmission electron microscope (TEM) analysis confirms highly crystalline structures less than 2 nm with carbonaceous material forming agglomerates.
- Prepared Pt/$Mo_2N$ catalysts with Pt dispersed with an average Pt crystallite size as small as 36 Å.
- Synthesized black, conductive sub-stoichiometric titanium oxides ($TiO_{2-x}$, TiO) with surface areas up to 250 m$^2$/g.
  - Oxygen deficient titanium oxide phases (TiO) exhibit average crystallite sizes as small as 40 Å.
- Accelerate Go/No-Go decision point for rare earth hexaboride materials.

### Testing, Characterization and Evaluation

- Mo-N ceramics are electronically conductive and are stable in acid media (0.5M $H_2SO_4$).
- Performed initial cyclic voltammatry (CV) characterization using glassy carbon disk electrode showing Pt/C-like activity for both hydrogen redox and oxygen reduction reaction (ORR).
- ORNL TEM analysis of first samples of $Mo_2N$ confirming small particle sizes.

Theory and Computation

- Completed density functional theory (DFT) calculations to optimize the structures of bulk molybdenum nitride polymorphs (∂-MoN, β-$Mo_{16}N_7$ and γ-$Mo_2N$). Experimental crystal structures are reproduced to within 3% confirming validity of approach.
- Started studies of platinum adhesion on selected molybdenum oxides surfaces. Platinum shown to be most stable in three-fold site of (001) surface of ∂-MoN.

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## Introduction

Catalyst support durability is currently a technical barrier for commercialization of PEMFCs, especially for transportation applications. Degradation and corrosion of the conventional carbon supports leads to losses in active catalyst surface area and, consequently, reduced performance. As a result, the major aim of this work is to develop support materials that interact strongly with Pt, yet sustain bulk-like catalytic activities with very highly dispersed particles. This latter aspect is key to attaining the 2015 DOE technical targets for platinum group metal (PGM) loadings (0.20 $mg/cm^2$).

The benefits of the use of carbon-supported catalysts to drastically reduce Pt loadings from the early, conventional Pt-black technology [1–4] are well known. The supported platinum catalyzed membrane approach widely used today for fabrication of MEAs was developed shortly thereafter these early reports [5–7]. Of direct relevance to this present work, are the investigations into Pt particle growth in PEMFCs [8], and subsequent follow-on work showing evidence of Pt particles suspended free of the support within the catalyst layer [9]. Further, durability work has demonstrated the detrimental effects of potential cycling on carbon corrosion [10-14] and the link between electrochemical surface area and particle growth [15].

To avoid the issues with carbon degradation altogether, it has been proposed by numerous fuel cell research groups to replace carbon supports with conductive materials that are ceramic in nature [16, 17, and references therein]. Intrinsically, these many conductive oxides, carbides, and nitrides possess the prerequisite electronic conductivity required, and offer corrosion resistance in PEMFC environments; however, most reports indicate that obtaining sufficient surface area remains a significant barrier to obtaining desirable fuel cell performance. Ceramic materials that exhibit high electrical conductivity and necessary stability under fuel cell conditions must also exhibit high surface area as a necessary adjunct to obtaining high Pt dispersions and Pt utilization targets. Our goal in this work is to identify new synthesis approaches together with materials that will lead to ceramic supports with high surface areas and high Pt dispersions. Several strong candidates for use as PEMFC catalyst supports include: transition metal nitrides and sub-stoichiometric titanium oxides, which hither to now have been prepared by other researcher groups with relatively low surface areas (ca. 1–50 $m^2/g$ typical [16-19]).

To achieve our goals of engineering high surface area, conductive ceramic support for utilization in PEMFCs, a multi-institutional and multi-disciplinary team with experience synthesizing and investigating these materials has been assembled. This team is headed by LANL and includes ORNL and the UNM. This report describes our Fiscal Year (FY) 2010 technical progress related to applying advanced synthetic methods towards the development of new ceramic supports for Pt catalysts for PEMFCs.

## Approach

Our approach to preparing ceramic powders with prerequisite properties for use as a PEMFC Pt catalyst support is centered on the application of several novel materials synthesis methods. Initially, in this first year of work, the methods were conducted in parallel to insure the best possible results that ceramic support materials would be available with desirable physical characteristics for platinum disposition and subsequent electrochemical characterization for oxygen reduction activity. The first synthesis method used in this work is the aerosol through plasma (A-T-P) process. In this method, largely developed at LANL, a gas or liquid aerosol containing precursor species is passed through the hot zone ($T > 3{,}500$ K) of plasma (virtually any gas including Ar, oxygen, nitrogen, air) with a residence time on the order of 0.1 second. The particles, modified by the plasma, then enter a zone of rapid cooling ($10^5$ K/s or more) where nucleation and growth of new structures generally takes place. A particularly relevant example of the capability of the process was the production of supported metal particles. We are also employing a new materials synthesis process called polymer assisted deposition (PAD) that was developed at LANL. This is a solution method for the formation of materials ranging from oxides to nitrides and oxynitrides. In general we have employed this methodology to prepare conformal epitaxial films of metal oxides and nitrides. However, high surface area powder materials can also be obtained using an accelerated heating rate to generate low density, foam-like structures. The UNM component of the collaborative research project will focus on developing synthesis methods for high surface area, oxygen-reduction catalysts supported on conductive metal oxides. Their goal will be develop a new approach for $Pt/NbO_2$ electrocatalysts synthesis based on sol-gel synthesis of mesoporous niobia.

Computational methods will be used to complement the experimental effort. Although these techniques provide insight into fundamental processes occurring at the atomic level, our work will focus primarily in two areas, that of aiding the characterization and understanding of experimental data and providing additional direction to the experimental team in the preparation of new support materials with optimized properties. The theory and modeling work will focus on several areas of importance to the development and optimization of new electrode support materials. Initially, computational studies have been carried out to understand the structure and stability of the support materials in the absence of platinum particles. Following this, the parameters may then be used to study the nature of the platinum binding sites on the support and the platinum adhesion energy, the mobility of platinum on the support and the interplay between the electronic structure of the support and the platinum particle, which is reflected in the calculated density of states. Comparison of these values with bulk platinum can be used as a predictive tool for the optimization of the material.

## Results

### Alternative Support Materials

The use of the PAD process has immediately been successful at producing conductive ceramic materials with high surface areas. A milestone for this task has been accelerated such that the Go/No-Go decision in Q8 may be brought forward to early FY 2011. High surface area, conductive foams were successfully synthesized for molybdenum as $Mo_2N$. The materials are prepared by first creating a water-based solution of the desired metal bound to a polyethylene imine (PEI) polymer and ethylenediamine tetraacetic acid (EDTA). The solution is concentrated to a thick gel before being heated in a tube furnace to 700 and 950˚C under forming gas. During the heating process, the polymer depolymerizes and EDTA decomposes to give gaseous products, which aid in foam formation. The two-point resistance of a typical piece of foam structure (ca. 1 cc in approximate volume) was on the order of 9-10 ohms. A special insulated fixture of fixed volume has been fabricated and will be used in the near future to quantify the two-point resistance of ceramic supports in powder form under uniform compaction.

Figure 1 shows the X-ray diffraction (XRD) pattern obtained for $Mo_2N$ sample final anneal temperature of 950°C in 6%$H_2$/Ar. The data have been fit to a cubic crystal structure (indices indicated) with a lattice parameter calculated to be 4.268 Å. Full profile fitting of the diffraction data indicates an average crystallite size of 1.6 nm. The Brunauer-Emmett-Teller (BET) surface area for this sample was approximately 500 $m^2/g$. This is an exceptionally high surface area for a transition metal nitride powder. TEM analysis performed by ORNL also indicate highly crystalline structures on the order of 2 nm with 0.2 to 2 µm agglomerates comprised of carbonaceous material holding together the smaller crystallites. Samples prepared using the PAD process typically show broad, amorphous diffraction characteristics ca. 26° two-theta and this would be explained by the presence of carbon. The exact weight percentage of carbon in these samples is presently being determined. Also to be determined is whether the residual carbon is only present in between $Mo_2N$ particles or whether it is in solution with the moly-nitride. $Mo_2N$ samples have also been prepared at 700°C with slightly higher surface area and a smaller average crystallite size on the order of 1 nm. A glassy carbon electrode (0.5 cm dia.) was prepared using a 1 mg/ml suspension of the as-synthesized $Mo_2N$ (both 700 and 950°C preparation temperatures) after grinding the sample in an alumina mortar with isopropyl alcohol. Initial CV characterization (in 0.5 M $H_2SO_4$) showed no Faradic activity when the voltage was swept at a sweep rate of 100 mV/s from 0 to 1.2 V using a hydrogen electrode with 6% $H_2$ forming gas. The rotating disk electrode experiment (0.5 M $H_2SO_4$ saturated with $O_2$) did not show any oxygen reduction activity.

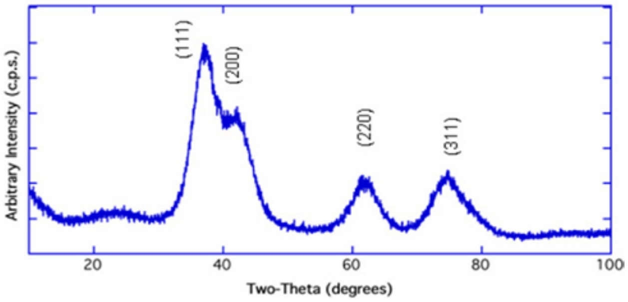

**FIGURE 1.** XRD trace from 10 to 100° degrees two-theta of a $Mo_2N$ sample prepared at 950°C using the LANL PAD process. Unit cell indices are indicated. Full profile fitting to a primitive cubic cell, a=4.268Å. Average crystallite size from profile fitting data is 16Å.

Figure 2 is the XRD pattern obtained after Pt disposition (20 wt%) onto the 700°C-prepared $Mo_2N$ using incipient wetness approach and hexachloroplatinic acid post reduction. The $Mo_2N$ sample prepared at 950°C was treated to a similar Pt disposition with the same loading with similar XRD but with slightly larger average Pt crystallite sizes. The dried samples were placed into a tube furnace and annealed at 70°C for 12 hours to reduce the platinum salt. Full profile analysis of these data indicates an average Pt crystallite size of 36 Å. Two new suspensions were prepared using the $Pt/Mo_2N$ catalysts. The catalyst samples were applied to two glassy carbon electrodes (0.5 cm dia.) at

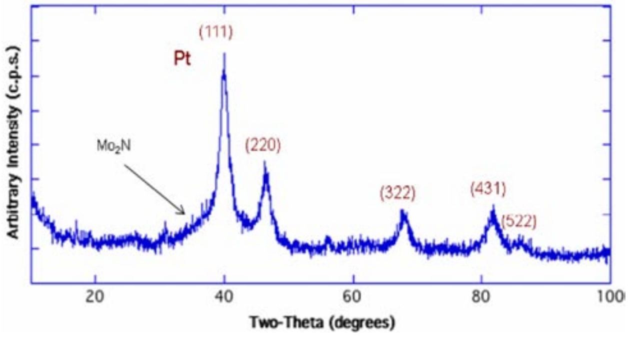

**FIGURE 2.** XRD trace from 10 to 100° degrees two-theta of a $Mo_2N$ sample prepared at 700°C after Pt disposition (20 wt%) and subsequent anneal for 12 hrs at 70°C in 6%$H_2$. Unit cell indices for Pt are indicated. Full profile fitting of the support and Pt yield an average Pt crystallite size of 36Å.

two different Pt loadings: 30.6 µg Pt/cm$^2$ for the sample prepared with the 950°C annealed $Mo_2N$ and 20.4 µg Pt/cm$^2$ for the sample prepared with the 700°C annealed $Mo_2N$ sample.

Figure 3 (a-top) shows the CVs of these catalyst samples. In both experiments, the conditions were identical: 0.5 M $H_2SO_4$ saturated with Ar with voltage scanned at a rate of 100 mV/S for 8 cycles each. The CVs shows hydrogen activity similar to Pt/XC-72 carbon with an apparent reversible oxidation peak at 0.45 V and reduction peak at 0.4 V. It is interesting that both CVs show similar activity despite different Pt loadings. This would tend to suggest that more work must be done to better optimize and utilize the Pt. Although the nature of the redox couple at potentials beyond the features well known to hydrogen redox reactions have not been explained, integration of the area under the anodic peak (up to 0.6 V) yields an electrochemical active surface area (EASA) values of 9.8 m$^2$/g$_{Pt}$ and 20.8 m$^2$/g$_{Pt}$ for the platinized $Mo_2N$ prepared at 950 and 700°C, respectively. These particular values for EASA serve as a reference mark and an upper bound only. In our near-term future work, we will probe these features and calculate a more accurate EASA for these materials. The Ar was removed from the electrolyte and it was replaced with $O_2$. The disk electrode was rotated between 400 and 1600 rpm and the CV characterization was performed at a scan rate of 20 mV/s. Figure 3 (b-bottom) shows the results for oxygen reduction activity for the $Mo_2N$ sample prepared at 950°C and at a loading of 30.6 µg Pt/cm$^2$. As with the hydrogen CVs, the $Mo_2N$ sample prepared at the lower temperature, 700°C, and at a lower Pt loading, 20.4 µg Pt/cm$^2$, again shows comparable ORR current densities.

## Sub-Stoichiometric Titanium Oxides

High surface area, conductive foams were successfully synthesized for titanium as both TiO and $TiO_{2-n}$ using a modified PAD process. As with the molybdenum nitride materials, the titanium oxide ceramics are prepared by first creating a water-based solution of the desired metal bound to a PEI polymer and EDTA. The solution is concentrated to a thick gel before being heated in a tube furnace to 950˚C under forming gas. During the heating process, the polymer depolymerizes and EDTA decomposes to give gaseous products, which aid in foam formation. In the case of titanium oxide materials, the variation of the flow rate and purge time determine the extent of oxygen reduction. This important control parameter is presently being studied in greater detail and will be greatly expanded upon in future reports. As of preparation of this report, high surface area, black titanium oxide foams have

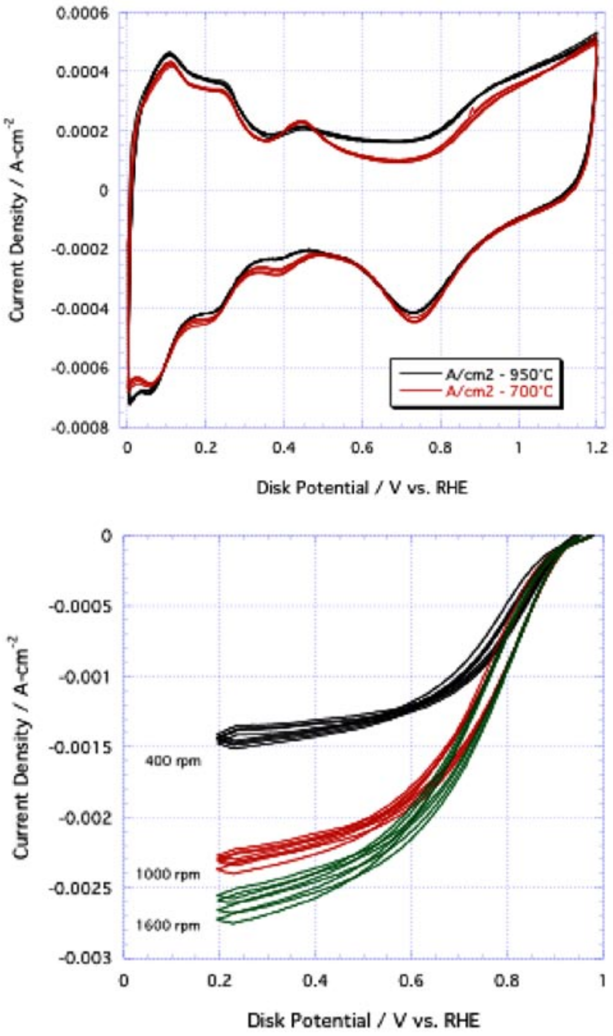

**FIGURE 3.** (a-top) CV characterization of platinized $Mo_2N$ samples prepared at 700 and 950°C using the PAD process. Pt loadings are 20.4 µg Pt/cm$^2$ and 30.6 µg Pt/cm$^2$ respectively (0.5 M $H_2SO_4$, 100 mV/s). (b-bottom) RDE characterization of platinized $Mo_2N$ samples prepared at 950°C using the PAD process. Pt loading is 30.6 µg Pt/cm$^2$ (0.5 M $H_2SO_4$, 100 mV/s).

been prepared using the PAD approach. The black color is highly indicative $TiO_{2-x}$ with $0<x\leq1$. The two-point resistance of a typical piece of foam (ca. 1 cc in approximate volume) was similar to that of the $Mo_2N$ foams; e.g. on the order of 10 ohms. The initial BET surface area measurements performed on the first samples of black titania powders confirm gas accessible surface areas similar to Vulcan XC-72 (e.g. 200–250 $m^2/g$). These surface areas are significantly higher than commercial, conductive Magnéli phase $Ti_4O_7$ synthesized through bulk synthesis and reduction (ca. 1-2 $m^2/g$) or even through hydrogen reduction of nano-crystalline anatase or rutile $TiO_2$ powders (ca. 25-50 $m_2/g$) [16,17]. We have started structural characterization of these recently prepared titania supports.

### Rare-Earth Hexaborides

Lanthanum hexaboride solution was prepared using the PEI polymer and EDTA as a water solution. Preliminary experiments were conducted to create a crystalline mixed phase materials; however, further investigation is required to obtain a pure sample. Initial attempts to use A-T-P process or rare earth hexaborides including cations such as europium, barium, and lanthanum have proven to be unsuccessful at this point. Elemental analysis using XRF indicate the presence of rare earth component in the amorphous powders collected from the plasma torch exhaust however XRD data show the materials are devoid of any apparent long range structure. Subsequent annealing at high temperature (given very slow kinetics at moderate temperatures) initiates crystallization and grain growth but only at temperatures sufficiently high to cause enough grain growth to the extent that original purpose for applying the A-T-P process becomes moot. The remainder of FY 2010 will be used to further adjust and optimize synthesis conditions for this process.

### Computational Studies of Molybdenum Nitride Supports

Computational studies of ceramic support candidates commenced in FY 2010 to provide theoretical input to experimental work. Periodic density functional calculations were carried out using the VASP software on three bulk molybdenum nitride polymorphs (rhombohedral ∂-MoN, tetragonal $\beta$-$Mo_{16}N_7$, and cubic $\gamma$-MoN). These calculations provide a calibration for the quantum chemical method used via a comparison of the experimental and calculated structural parameters. The calculations reproduce the structure data to within 4%, confirming the validity of the computational approach. The simplest surface structure was then selected as a model for the catalyst substrate ({(001) surface of ∂-MoN}) and a geometry optimization calculation was performed to examine the effects of surface relaxation compared to the bulk structure. Using this structure, the effects of surface adhesion of platinum were investigated. Three platinum binding sites on the MoN surface were considered: the on-top site, a bridging site and a three-fold binding site as shown in Figure 4. The calculated binding energies for each of the sites was found to decrease in the order: three-fold ~ bridging >> on-top. The binding energy for the three-fold site is calculated to be comparable to that of a single platinum atom on a Pt(111) surface (approximately 550 $kJmol^{-1}$). The bulk structures of three Mo-N phases (tetragonal $\beta$, rhombohedral ∂, and cubic $\gamma$) were calculated with excellent agreement to literature data. The simplest surface structure (∂-MoN) was then selected, a model created, and the relative binding energies for the three possible Pt sites were calculated. The results were obtained using plane wave DFT with VASP software from calculations of the same class used to obtain the parent molybdenum nitride structures.

## Conclusions

- Synthesis of high surface area ceramic nitride and oxide materials.
  - $Mo_2N$ synthesized at 700 and 950°C using polymer-assisted deposition with BET surface area of 500 $m^2/g$.
  - $Mo_2N$ samples are electronically conductive.
  - PAD procedure modified to prepare sub-stoichiometric $TiO_{2-x}$ and TiO with BET surface areas exceeding 200 $m^2/g$.
- Pt disposition onto $Mo_2N$ support samples produced an active catalyst.
  - Initial CV and rotating disk electrode characterization performed.
  - Pt utilization and optimization required.

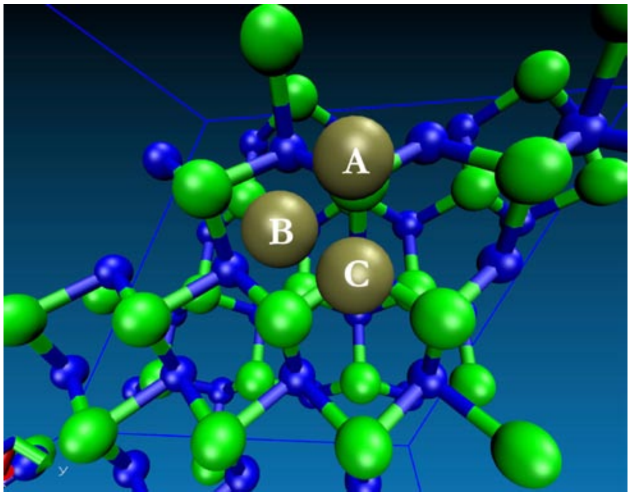

**FIGURE 4.** Calculated binding sites for Pt on ∂-MoN (001) surface showing onto p (A), bridging (B) and three-fold (C) sites.

- TEM analysis confirms average crystallite sizes calculated from full profile fitting of the XRD data (e.g. <2 nm crystallites) and has found evidence of residual carbon remaining from the synthesis process.
- Plane wave DFT and VASP calculations reproduce the crystal structure data to within 4%, confirming the validity of the computational approach and the calculated binding energies for Pt nucleation on the surface of ∂-phase MoN.

## Future Directions

- Finish rare earth hexaboride work – proceed to Go/No-Go decision early in FY 2011.
- Understand the nature and extent of carbon residual in materials prepared via PAD approach. Understand effect on durability and performance of PEMFC catalysts prepared using this approach.
- Better optimize the incipient wetness disposition/utilization of Pt onto high surface area $Mo_2N$ materials.
- Continue electrochemical characterization of the $Pt/Mo_2N$ catalysts – increase number of potential cycles, study and determine the nature of the redox couple at 0.45 V.
- Continue computational studies of platinum thin films on molybdenum nitride surface and use the developed method to investigate titanium oxide phase as supports.
- Begin Pt disposition onto high surface area, sub-stoichiometric titania and perform electrochemical characterization.
- TEM characterize next round of $Mo_2N$ and $Pt/Mo_2N$ supports as well as perform initial characterization of sub-stoichiometric titania materials.

## FY 2010 Publications/Presentations

**1.** E. Brosha, K. Blackmore, A.Burrell, N. Henson, J. Phillips, and T. Rockward, "Engineered Nano-scale Ceramic Supports for PEM Fuel Cells", DOE EERE Fuel Cell Technologies Kick off meeting, September 30 – October 1, 2009, Washington, D.C.

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