

## V.D.14 Engineered Nano-Scale Ceramic Supports for PEM Fuel Cells

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Start Date: September 2009

Project End Date: 2013

### Fiscal Year (FY) 2011 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<sup>2</sup>)
- Cost (<\$3/kW)
- Activity (0.44 A/mg<sub>Pt</sub> @ 0.9 V<sub>iR-free</sub>)
- Electrocatalysis support loss (<30 mV after 100 hrs @ 1.2 V)
- Electrochemical surface area loss (<40%) tested per GM protocol (Mathias, M.F., et al., Interface [Electrochemical Society], Fall 2005, p. 24)

### FY 2011 Accomplishments

#### Synthesis of Non-Carbon Support Materials

- “Go” decision made for Mo<sub>2</sub>N supports synthesized via polymer assisted deposition (PAD) approach: ahead of schedule.
  - Quarter (Q)8 target moved up to Q5-Q6.
- Evaluation of titania supports prepared by PAD approach ahead of schedule.
  - Q6 targets moved up to Q3-Q4.
- Go/No-Go decision on hexaboride supports: ahead of schedule.
  - No-Go: Q6 decision moved up to Q4.
    - Unable to synthesis using aerosol through plasma (A-T-P) process (Q4).
    - PAD process produced only small amounts of LaB6 (Q6).
- Performance evaluation of Pt/NbRu<sub>y</sub>O<sub>z</sub> catalysts: ahead of schedule.
  - No-Go: poor activity due to formation of NbOx passivation layer on Pt (Q6).

#### Testing, Characterization and Evaluation

- Full electrochemical characterization of Mo<sub>2</sub>N support and its precursors with and without platinum in organic and aqueous solutions.
- Initial electrochemical characterization of TiO and TiO<sub>2</sub> supports.

## Theory and Computation

- Calculations were performed using plane wave periodic density functional theory to create a structural model of gamma  $\text{Mo}_2\text{N}$ : NaCl structure with half of the nitrogen sites vacant creating MoN and Mo-rich surfaces for Pt adhesion.
- The most favorable sites for single Pt atoms and a monolayer was constructed based on these results.
- Nitrogen depleted surface layer on the  $\text{Mo}_2\text{N}$  promotes stronger binding of platinum compared to other defect models and other  $\text{Mo}_x\text{N}_y$  phases.



## Introduction

Catalyst support durability is currently a technical barrier for commercialization of proton exchange membrane fuel cells (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 ( $0.20 \text{ mg/cm}^2$ ).

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 capable of supporting high Pt dispersions. Several strong candidates for use as PEMFC catalyst supports include: transition metal nitrides and sub-stoichiometric titanium oxides, which hitherto now have been prepared by other research groups with relatively low surface areas (ca.  $1\text{--}50 \text{ m}^2/\text{g}$  typical [16–19]).

This report describes our FY 2011 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. Following a down-select process, we are employing a materials synthesis process called PAD that was largely developed at LANL for a variety of applications. 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. This project is presently driving studies into the application of the PAD technique for bulk powder synthesis. The UNM component of the collaborative research project focuses on developing aerosol synthesis methods for high surface area, conductive ceramic supports. Following a No-Go decision made this year (FY 2011) for conductive Nb-RuO<sub>x</sub> oxide supports, their goal will be to develop a new approach for nitride and sub-stoichiometric titania as a potential route to the PAD-prepared nitride supports already identified as encouraging non-carbon supports for PEMFCs in this project to date.

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.

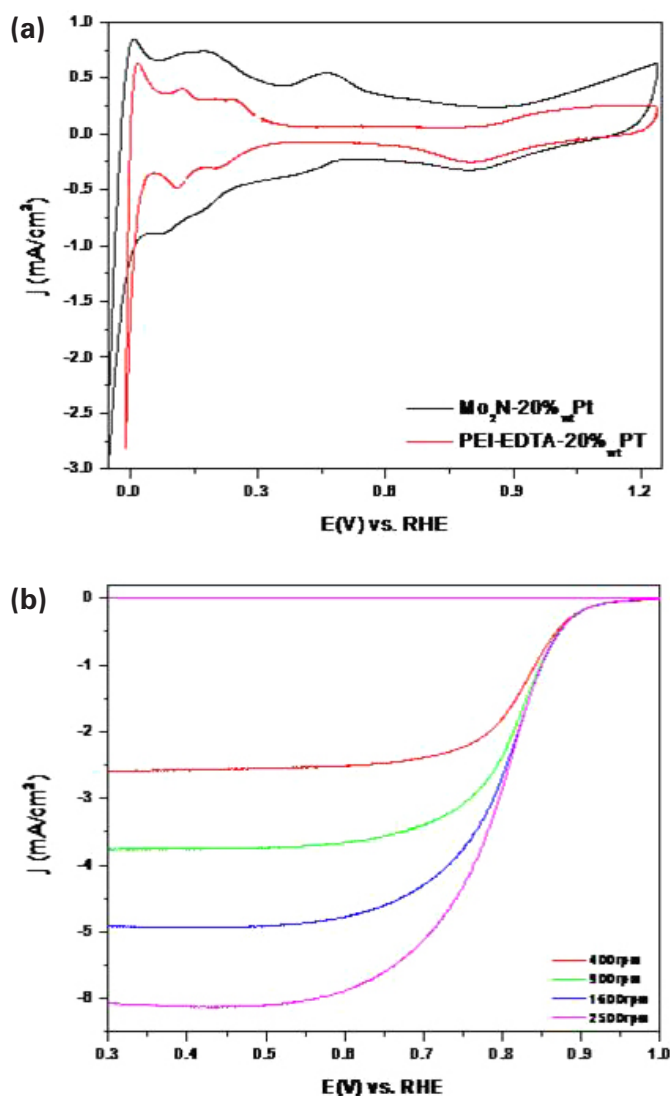
## Results

### Molybdenum Nitride

The use of the PAD process has 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  $\text{Mo}_2\text{N}$ . The materials are prepared by first creating a water-based solution of the desired metal bound to a polyethyleneimine (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 and the EDTA decomposes to give gaseous products, which aid in foam formation.

During FY 2011, a full electrochemical characterization of the newly synthesized supports was conducted with and without platinum in organic and aqueous solutions in order to study the possible redox reactions of the supports, their possible degradation reactions and electrocatalytic activity for oxygen reduction reaction (ORR).  $\text{Mo}_2\text{N}$ , TiO and  $\text{TiO}_2$  show good stability for the length of the experiments conducted in a half cell, and their long-term durability study will be conducted in FY 2012 in a fuel cell.

The electrocatalytic activity of Pt deposited on  $\text{Mo}_2\text{N}$  was studied using electroanalytical techniques such as rotating ring-disk electrode (RRDE) and cyclic voltammetry (CV). Platinum was added (20% wt) to  $\text{Mo}_2\text{N}$  support using an incipient wetness method and deposited on glassy carbon electrode for electrochemical characterization. Figure 1(a) shows the CVs of Pt on  $\text{Mo}_2\text{N}$  and PEI-EDTA supports in deaerated 0.5 M  $\text{H}_2\text{SO}_4$  solutions. Characteristic Pt redox reactions in acidic medium were observed with both samples including hydrogen adsorption/desorption. The Pt/ $\text{Mo}_2\text{N}$  catalyst has a redox couple at  $E=0.44\text{V}$  vs. reference hydrogen electrode (RHE) that was not observed with the Pt/PEI-EDTA catalyst and thus is attributed to the  $\text{Mo}_2\text{N}$  support and not the carbon precursor used during its synthesis, this is also supported by the results obtain with the support devoid of platinum. The average electrochemically active surface area calculated from the hydrogen adsorption and desorption peaks of the Pt/ $\text{Mo}_2\text{N}$  catalyst is  $120\text{ m}^2/\text{g}$ , more than 60% higher than that obtained with a commercial ETEK Pt/C catalysts ( $74\text{ m}^2/\text{g}$ ). Figure 1(b) shows the RRDE measurements conducted with the Pt/ $\text{Mo}_2\text{N}$  catalyst. These results show the high ORR activity (expected from Pt-based catalysts), the kinetics and mechanism of the reaction



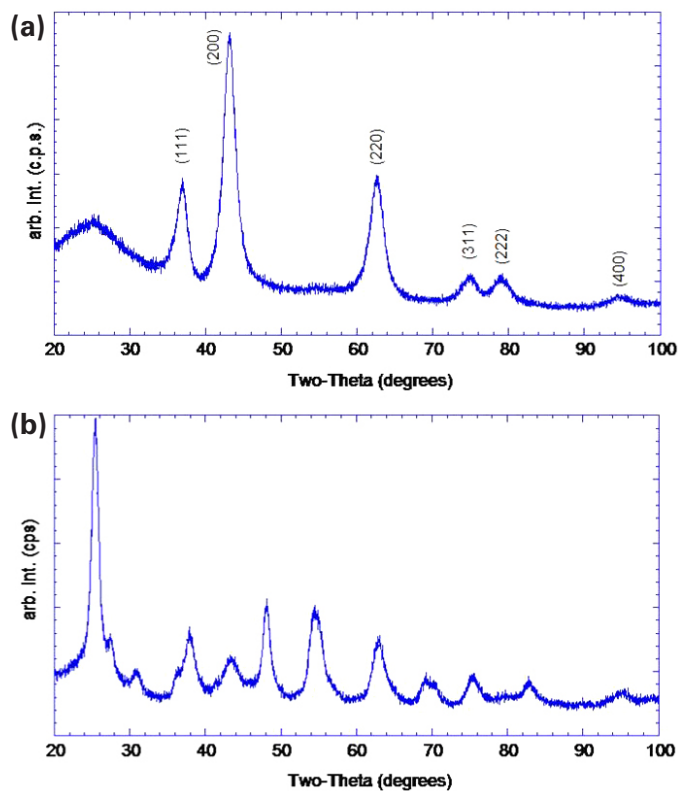
**FIGURE 1.** (a) CV characterization of 20%<sub>wt</sub> platinum deposited on  $\text{Mo}_2\text{N}$  sample prepared at 950°C using the PAD process and 20%<sub>wt</sub> platinum deposited on PEI-EDTA (in deaerated 0.5 M  $\text{H}_2\text{SO}_4$  at 100 mV/s). (b) RRDE characterization of 20%<sub>wt</sub> Pt/ $\text{Mo}_2\text{N}$  sample prepared at 950°C using the PAD process (in  $\text{O}_2$  saturated 0.5 M  $\text{H}_2\text{SO}_4$  at 100 mV/s).

do not seem to be affected from the  $\text{Mo}_2\text{N}$  support or any interaction it might have with Pt.

### Sub-Stoichiometric Titanium Oxides

High surface area, conductive foams were successfully synthesized for titanium as both  $\text{TiO}$  and  $\text{TiO}_{2-n}$  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 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. In FY 2011, effort on the titania supports was reduced in order to provide extra resources to study the moly-nitride materials. However, initial electrochemical characterization was carried out on the two samples produced to date. Figure 2 shows the X-ray diffraction (XRD) traces of a PAD-prepared stoichiometric TiO sample (Figure 2(a)) and sample whose XRD trace shows a primary anatase phase ( $\text{TiO}_{2-x}$ ) along with rutile (Figure 2(b)). Both samples are black in appearance and are conductive. The initial Brunauer-Emmett-Teller (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  $\text{m}^2/\text{g}$ ). These surface areas are significantly higher than commercial, conductive Magnéli phase  $\text{Ti}_4\text{O}_7$  synthesized through bulk synthesis and reduction (ca. 1-2  $\text{m}^2/\text{g}$ ) or even through hydrogen reduction of nano-crystalline anatase or rutile  $\text{TiO}_2$  powders (ca. 25-50  $\text{m}^2/\text{g}$ ) [16,17]. We have started structural characterization of these recently prepared titania supports. Electrochemical characterization was conducted with Pt deposited on TiO and  $\text{TiO}_2$  supports. As with the  $\text{Mo}_2\text{N}$  support, the platinum's ORR activity was not affected by the support in comparison to carbon supported Pt.



**FIGURE 2.** (a) XRD trace from 20 to 100° degrees two-theta of a PAD-prepared stoichiometric TiO sample and (b) a sample whose XRD trace shows a primary anatase phase ( $\text{TiO}_{2-x}$ ) along with rutile.

## Quantum Chemical Calculations on Catalyst Surface Structure and Activity

In FY 2011, the theory and modeling work was directed to the study of the structure of the interface between the ceramic support and platinum, and the correlation between this and the resulting catalytic activity. The aim of this work is to understand how the support modifies the electronic structure of the platinum to influence the thermodynamics and kinetics of the fundamental steps in the catalytic process. An important target is the computed binding energy of platinum to the surface and relating this to measured catalytic lifetime.

The modeling focused on the dominant  $\gamma$ - $\text{Mo}_2\text{N}$  phase identified from the characterization of the synthesized samples. The computational strategy was as follows:

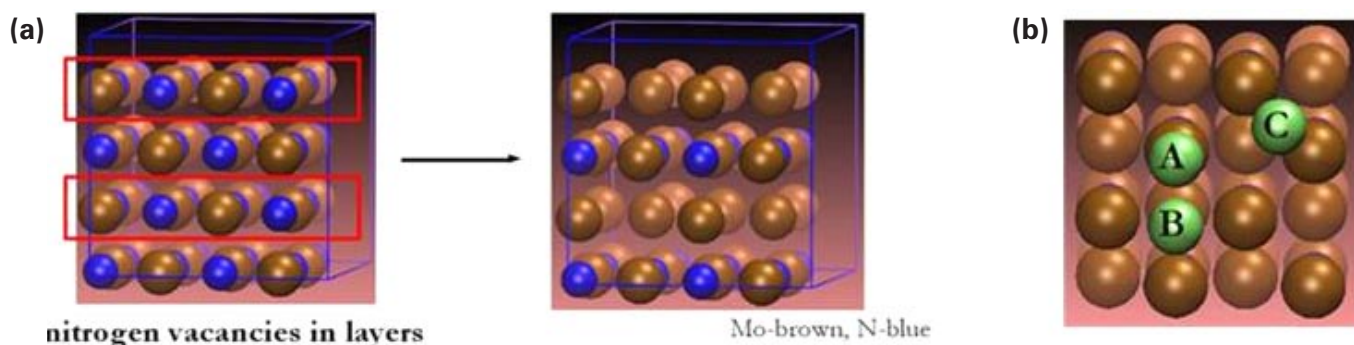
1. Construct structural models for  $\text{Mo}_2\text{N}$  phase considering the effect of non-stoichiometry and defect structures.
2. Calculate binding energies for platinum monolayers on surface models.
3. Calculate trends in predicted over-potential for models.

The quantum chemical calculations are based on the plane wave density functional method as implemented in the VASP software. In Q4, we will transition this approach to the study of titanium oxide phases.

The structure of  $\gamma$ - $\text{Mo}_2\text{N}$  phase is based on the rock salt crystal structure with half the nitrogen sites vacant. There are several models that can be constructed based on this stoichiometry. For example, the highest symmetry model has planes of nitrogen atoms empty as shown in Figure 3(a). This results in the creation of nitrogen-rich and nitrogen-poor surfaces. The binding energies of single platinum atoms on several surface models were calculated. The results for the three sites on a nitrogen-poor  $\gamma$ - $\text{Mo}_2\text{N}$  surface are shown in Figure 3(b). The results indicate the four-fold coordination site is dominant. Using this result models for a single monolayer of platinum on the ceramic surface were constructed. It is found that the monolayer is bound more strongly to the nitrogen-poor (defective) surface than to the nitrogen-rich (non-defective) surface. This causes a shift in the calculated d-band center for platinum and perturbs the binding energies of intermediates in the oxygen reduction reaction.

## UNM Development Work on Conductive Oxide Supports

Mesoporous  $\text{Nb}_2\text{O}_5$  and  $\text{NbRu}_y\text{O}_z$  (12 wt%) powders were synthesized by aerosol pyrolysis of alcohol solutions of  $\text{NbCl}_5$ ,  $\text{RuCl}_3$  with the addition of pluronic block copolymer P123 as a templating agent. A post acid etch step opened up the internal surface of the as-prepared material yielding a BET surface area as large as 180  $\text{m}^2/\text{g}$ . Electrical resistance of the compacted powders was assessed and  $\text{NbRu}_y\text{O}_z$  reduced under a 10%  $\text{H}_2/\text{N}_2$



**FIGURE 3.** (a) Construction of the high symmetry defect model for  $\gamma$ - $\text{Mo}_2\text{N}$  (b) Calculated binding sites for a single platinum atom on the nitrogen-poor  $\gamma$ - $\text{Mo}_2\text{N}$  surface (A=on-top, B=bridge, C=four-fold sites)

mixture displayed low resistivity. An optimized synthesis and post-processing scheme was identified producing a black catalyst support. Platinized catalysts were prepared both in situ to the aerosol process and using an incipient wetness approach with the former, direct incorporation of Pt producing better dispersion of Pt nano-particles in the meso-porous support as revealed by transmission electron microscopy (TEM). CV (10 mV/s in 0.1M  $\text{HClO}_4$ ) was performed on  $\text{NbRu}_y\text{O}_z$  supported Pt catalysts 30 wt% Pt) and compared to 30 wt% Pt/XC-72 carbon. These results showed low electrochemical activity and after considerable investigation, it was found that the low activity may be attributed to the formation of  $\text{NbO}_x$  passivation layer over the Pt nano-particles. It was found that controlled thermal treatment (crystallization) reduced the mobility of Nb and improved the electrochemical performance but still resulted in performance well below commercial Pt/C benchmarks. As a result of these findings, a NoGo decision was made and a Go/No-Go milestone was advanced in the project. Given the favorable results to date for the nitride and titania supports, future work for UNM will focus on aerosol synthesis of high surface area powders without the residual carbon contamination resulting from the PAD process.

## Conclusions

- Thermal gravimetric analysis-mass spectrometer (TGA/MS) experiments performed on  $\text{Mo}_2\text{N}/\text{C}$  and  $\text{Pt}/\text{Mo}_2\text{N}/\text{C}$  materials showed carbon residue cannot be removed from ceramic supports by methanization (reducing conditions, 6%  $\text{H}_2$ ) or oxidation (air).
- Carbon is present from PAD process and, unless it can be removed during initial pyrolysis step, will be present if the PAD process is used to form high surface area support powders.
  - Measurements indicate variable amount of residue but typical amounts ca. 40-50 wt% C remaining in titania supports determined by energy dispersive X-ray.
  - Precision TGA (oxidizing conditions) will be used to better estimate quantify of carbon residue in

moly-nitride system (assuming stoichiometric gamma phase).

- The effect of carbon residue on durability and fuel cell performance is not yet known.
- $\text{Mo}_2\text{N}-\text{C}$  possesses required surface area and electronic conductivity for fuel cell use.
  - Required stability in acid conditions and under potential cycling.
- 20 wt%  $\text{Pt}/\text{Mo}_2\text{N}-\text{C}$  (incipient wetness) has comparable activity for ORR as ETEK.
- Pt appears to be associated with  $\text{Mo}_2\text{N}$  and not the residual carbon and this conclusion is supported by:
  - TGA/MS experiments
  - ORNL TEM characterization
  - CV experiments
- Experimental evidence collected to date indicates a stronger Pt-support interaction than with Pt-C catalysts.
- Computational work identified most favorable binding sites for adhesion of Pt atoms, and a monolayer of Pt was constructed based on these results.
  - The structure of the ceramic surface and, in particular, the defect structure appears to be vital to the binding properties of platinum.
  - The modeling results indicated a nitrogen depleted surface layer promotes strong binding of platinum to the support surface.
- $\text{Mo}_2\text{N}-\text{C}$  although not completely understood, is acceptable to move forward to MEA prep and fuel cell testing.

## Future Directions

- Scale up amount of PAD-produced  $\text{Mo}_2\text{N}$ , formulate inks, and prepare MEAs for single cell testing.
- Begin fuel cell testing and lifetime-durability observations with  $\text{Pt}/\text{Mo}_2\text{N}-\text{C}$  system. Optimize inks and MEA fabrication based on  $\text{Pt}/\text{Mo}_2\text{N}$  catalysts and prepare single-cell fuel cell for performance and

- durability testing. Obtain fuel cell performance data for Pt/Mo<sub>2</sub>N catalyst prepared using the PAD approach.
- Resume sub-oxide titania support work with focus on half-cell durability, oxidation resistance (sub-oxides), and stability of carbonaceous PAD residue (TiO<sub>2</sub>).
  - Develop aerosol precursors and aerosol synthesis method to prepare high surface area (>200 m<sup>2</sup>/g) Mo<sub>2</sub>N catalyst supports with reduction in residual carbon compared the PAD approach (UNM).
  - Calculate the over-potential for the oxygen reduction reaction on a model for platinum supported on molybdenum nitride and compare this value with that for Pt (111).
  - Characterization and testing of support materials (ongoing through entire project).

### FY 2011 Publications/Presentations

1. E. Brosha, K. Blackmore, A. Burrell, and J. Phillips, "Engineered Nano-scale Ceramic Supports for PEM Fuel Cells," 2010 Fuel Cell Seminar and Exposition, October 18–22, 2010, San Antonio, TX.
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