2010 U.S. DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting

Engineered Nano-scale Ceramic Supports for PEM Fuel Cells

Project ID # FC044

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Los Alamos National Laboratory

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This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

- **Timeline**
  - Project start : September 2009
  - Project end : September 2013
  - Percent complete (as of June 2010) : 18%

- **Budget**
  - Total project funding : $500K/yr
    - DOE $425K
    - UNM (sub) $75K
  - Funding Received 2009: $345K
  - Funding Received 2010: $405K

- **Technical Barriers Addressed**[2]

A. Durability (Pt sintering, dissolution, corrosion loss, effects from load-cycling & high potential)

B. Cost (Better Pt utilization balanced by cost difference of new support)

C. Electrode Performance (Pt sintering, corrosion loss, and loss of ESA)

- **Partners**
  - LANL (Project Lead)
  - University of New Mexico
  - ORNL (no-cost partner)

2. (Multi-Year Research, Development and Demonstration Plan, Section 3.4.4 "Technical Challenges")
*From http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

Relevance - Objectives

- Project Objective : Develop a ceramic alternative to carbon material supports for a polymer electrolyte fuel cell cathode.

- Ceramic support 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 MEA architecture & preparation methods.

- Materials properties goals include:
  - high surface area
  - high Pt utilization
  - enhanced Pt–support interaction
  - adequate electronic conductivity
  - resistance to corrosion
  - synthesis method / procedure amendable to scale-up
  - reasonable synthesis costs

Relevance - Technical Targets

DOE Technical Targets[1,*]

- Precious metal loading: ~0.2 mg/cm^2 (2015 target)
- Cost: < 3$/kW (2015 target)
- Activity (precious-metal based catalyst): 0.44 A/mg$_{Pt}$ @ 0.90 V$_{iR\text{-}free}$

  720 μA/cm^2 @ 0.90 V$_{iR\text{-}free}$
- Electrocatalysis support loss: <30 mV after 100 hrs @1.2V
- Electrochemical surface area (ESA) loss: <40%

- Technical performance and lifetime targets now in place for Pt/C PEMFC catalysts naturally extend to Pt/ceramic catalysts.

1. (Multi-Year Research, Development and Demonstration Plan, Table 3.4.12)

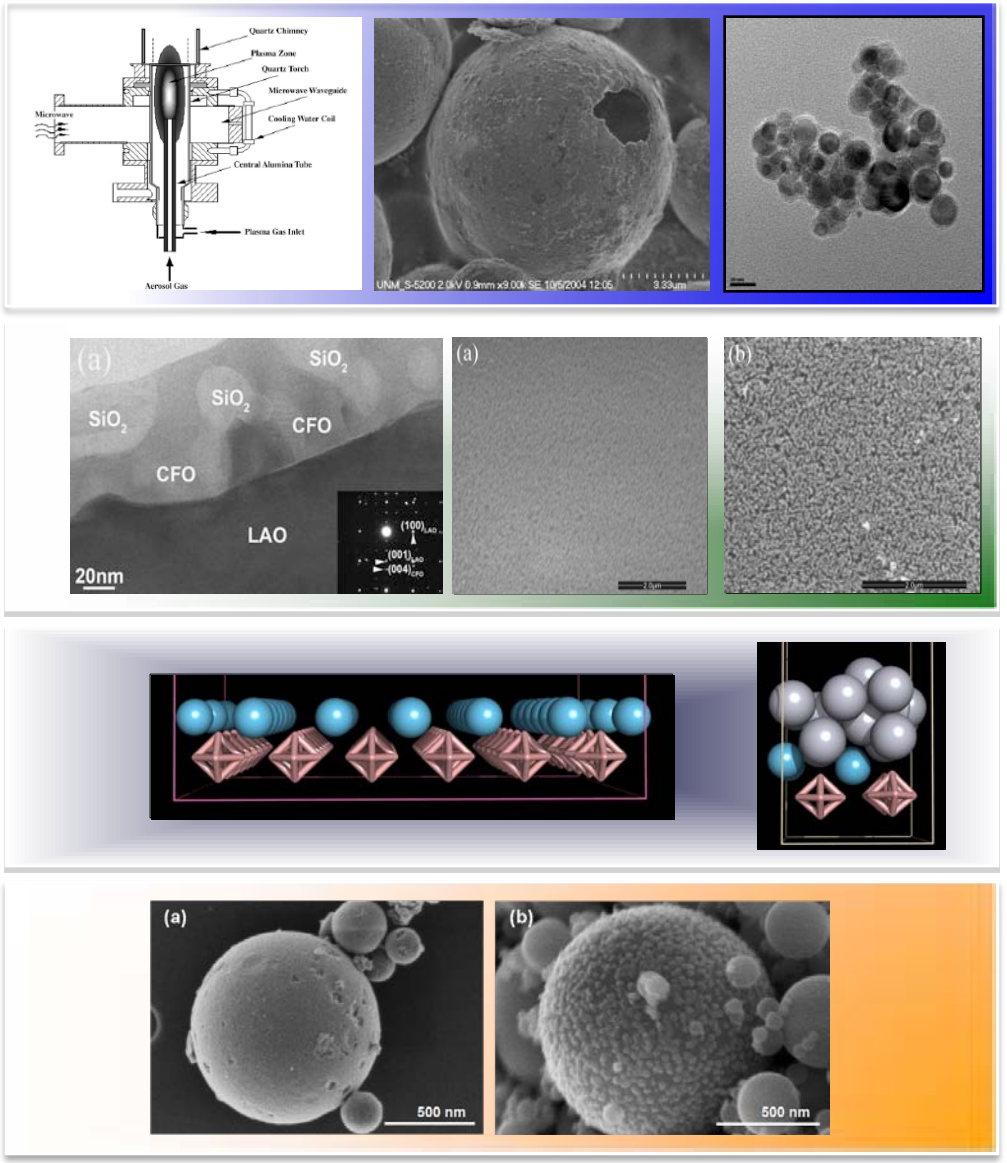
*From http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

Approach: focus on select support candidate materials

- Rare-earth hexaborides
  - High electronic conductivity, refractory, stable in acid media
  - Unique property first discovered by LANL : spontaneous noble metal deposition
- Transition metal nitrides
  - Corrosion resistance, high electronic conductivity, catalytic properties
- Sub-stoichiometric titania (TiO_{2-x}) : Ti_4O_7 (Magnéli phase)
  - High electronic conductivity, refractory, stable in acid media
  - Reports of strong metal-support interactions with noble metals
  - Resistance to oxidation
  - Demonstrated electro-catalytic activity for both hydrogen and oxygen / Pt
- Conductive metal oxides : NbO_2 and RuO_2 (UNM)
  - Demonstrated corrosion stability (UNM)
  - Highly dispersed Pt on conductive mesoporous spheres can be synthesized in a single step process (UNM)

Approach: Experimental Synthesis Methods

- Microwave aerosol-through-plasma (ATP) torch synthesis of $(RE)B_6$ and TiO_{2-x}
  - Utilize flow of plasma gas through plasma to create high temperature/short contact times
  - T > 3500K, t < 0.1 sec
  - Plasma gas mixtures: Air, Ar, O_2, N_2 and H_2
- Polymer assisted deposition (PAD) for $(RE)B_6$ and nitrides.
  - PAD precursor routes to produce ceramic materials with high surface area.
  - Films (CVs), powders (bulk catalysts, MEA prep)
- Theory/Modeling support to aid experimental effort to provide data on stability in absence of Pt particles
  - Surface/cluster models useful to predict effects of particle size reduction, conductivity.
  - Study nature of Pt binding sites, interaction energy, etc.
- Conductive NbO_2 and RuO_2 supports (UNM)
  - Spray pyrolysis methods to prepared conductive metal oxide supports.



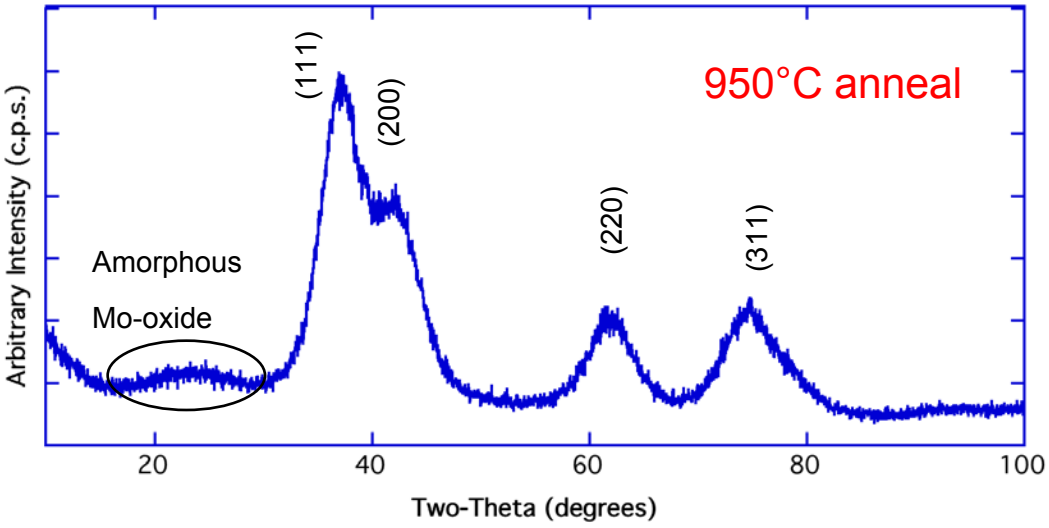
Technical Accomplishments and Progress: PAD Synthesis Results – Alternative Ceramic Supports Work *Ahead of Schedule*

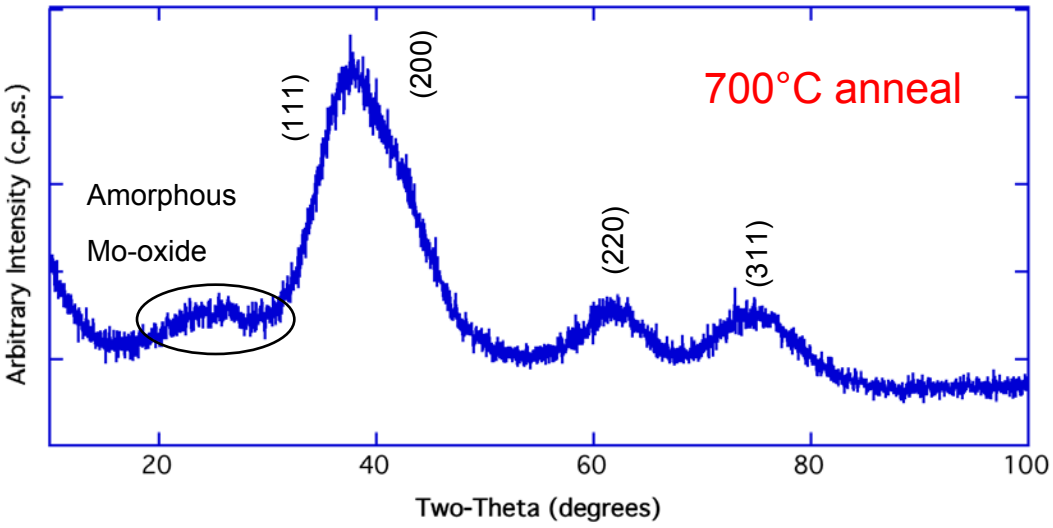
- On schedule and presently developing PAD approach to prepare lanthanide-boron materials using this method.
  - Precursors and synthetic route identified, and initial experiments are providing feedback to control reaction route.
- Synthesis of alternative ceramic supports pushed ahead of schedule.
  - Mo-N materials have been prepared and look very promising.
- Transition metal nitrides are being studied as corrosion barriers (nitriding stainless steel surfaces and coating of foils for PEMFCs – e.g. ORNL & NREL work)
  - Need powders with high surface area
- High electronic conductivity and stable in acidic conditions
  - Materials being studied for passivation coatings for PEMFC components
- Similar properties to transition metal carbides
- ORR on carbon-supported Molybdenum Nitride (Mo_2N) has been studied:

  H. Zhong *et al.*, *Electrochem, Comm.* **8** (2006) 707-712
  - showed activity without Pt present but no reports since then.

Technical Accomplishments and Progress: Nano-sized Mo-Nitride Ceramics Produced

- Molybdenum Nitride Synthesis :
  - Mo_2N cubic phase
- Ammonium molybdate/polyethylene imine (with EDTA) to produce a gel (100°C) followed by 700°C & 950°C anneals in forming gas ($6\%H_2/Ar$).
- Full profile fitting of XRD data indicate approximate crystallite size of 1.6nm, less (ca. 1nm) for 700°C prepared sample.





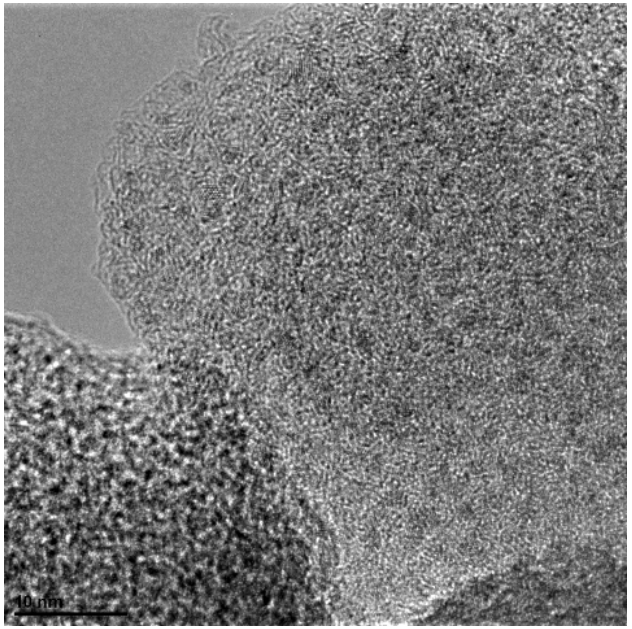
Technical Accomplishments and Progress: Mo_2N supports via PAD Characterization Pass Prerequisite Materials Requirements

- BET analysis indicates exceptional surface area : ca. 500m^2/g
- Electronic conductivity.
- ICP/MS analysis indicates that the ceramic is stable in aqueous / 0.5M H_2SO_4.

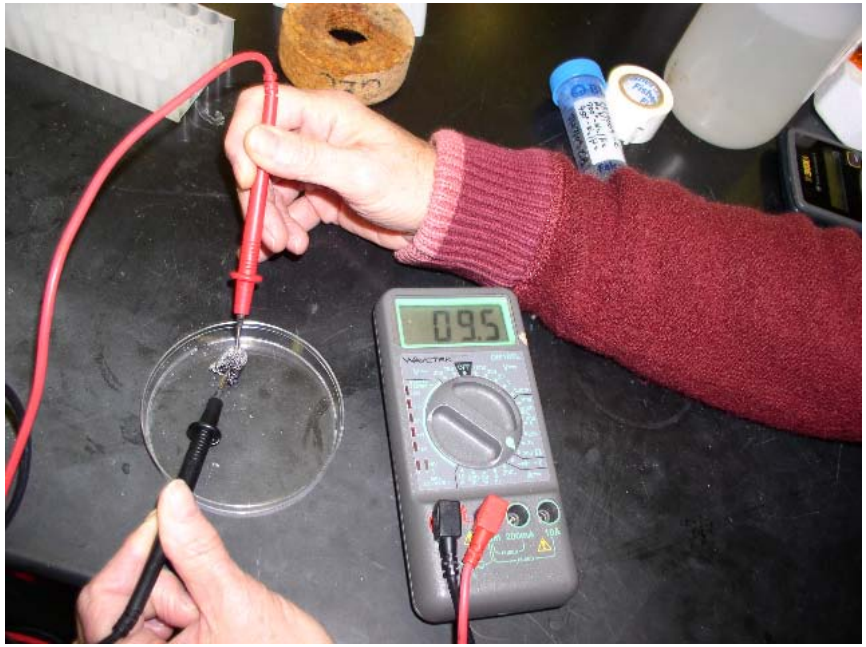
ICP results

Tap	D.I. System	Millipore	Acid Blank	Mo2N/H2O	Mo2N/Acid
960 ng/L	1000 ng/L	12 ng/L	0.12 µg/L	123 µg/L	200 µg/L
	1200 ng/L	< 2 ng/L			
	990 ng/L	6.8 ng/L			
		9.9 ng/L			

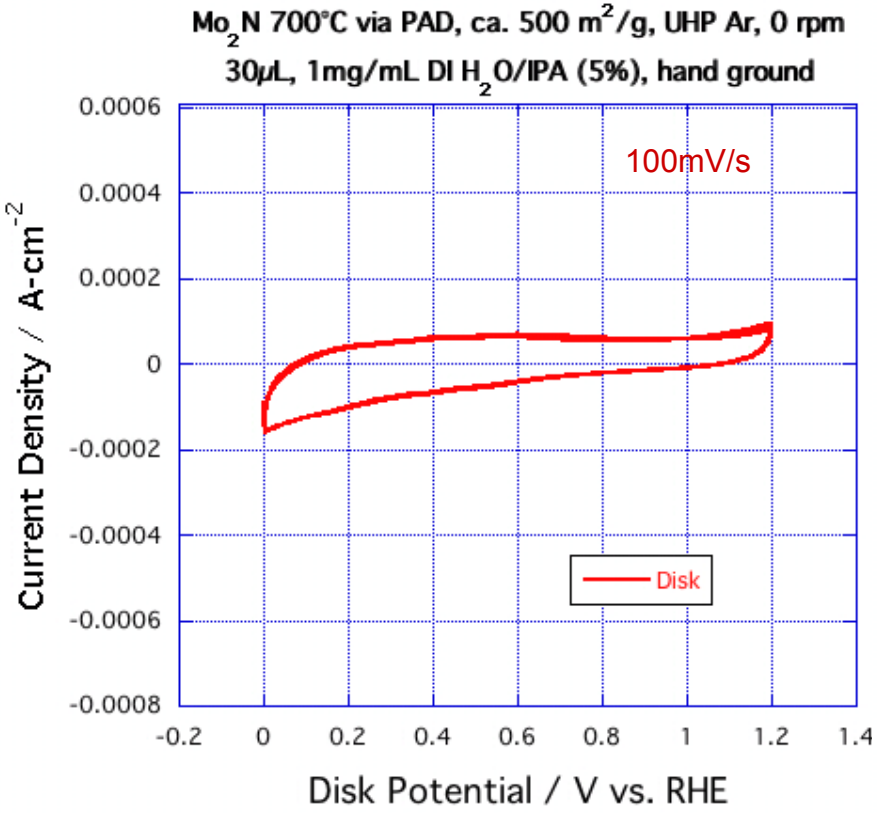
Initial TEM Results from K. More

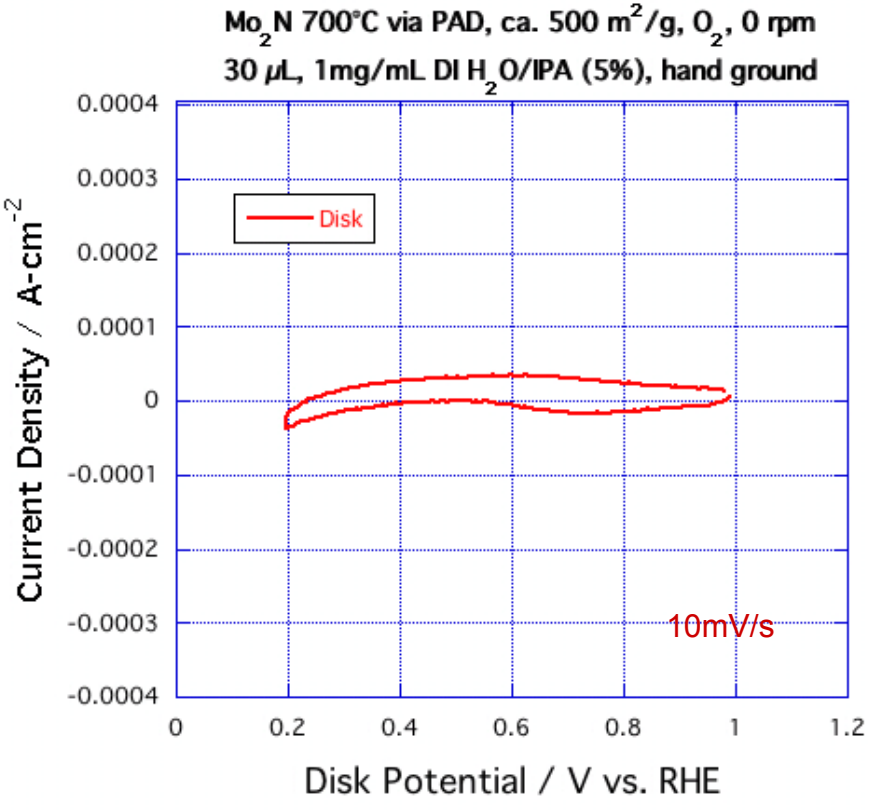


e^- Conductivity of Mo_2N Foam



Technical Accomplishments and Progress: Mo_2N – Electrochemical Characterization Indicates Stable Support



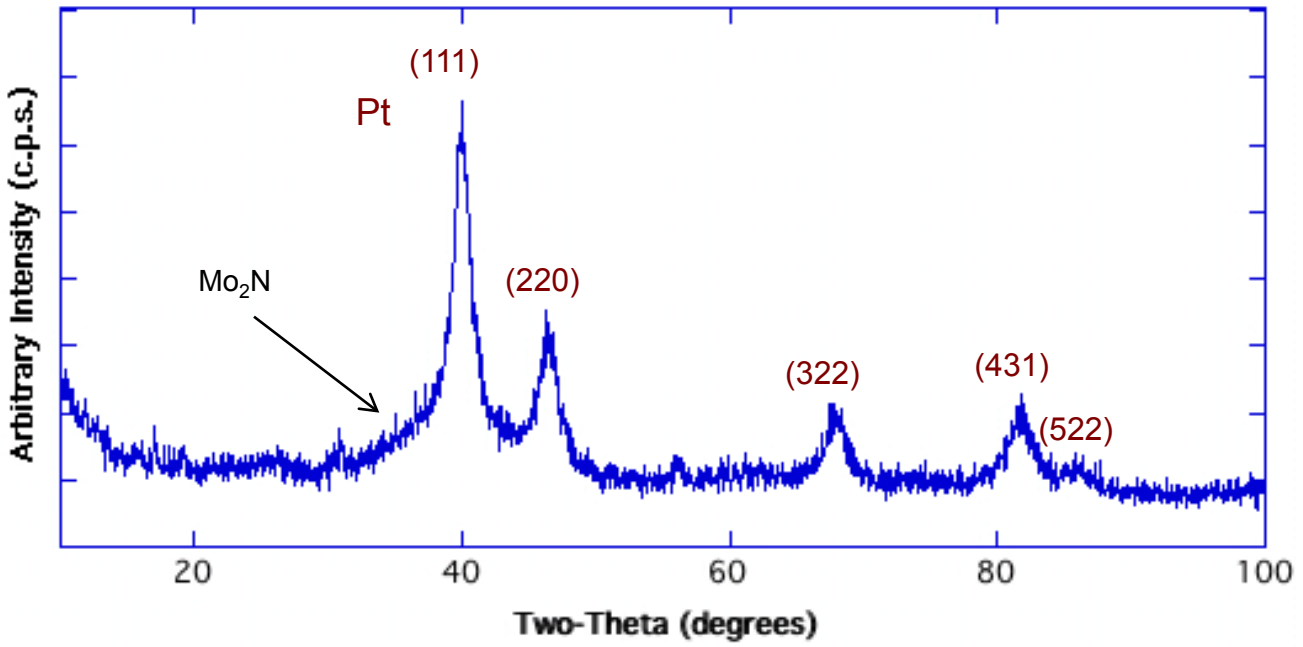


- Standard preparation of glassy carbon disk electrode for CV characterization.
- Suspension prepared in same manner as carbon supports.
- CV characterization shows no Faradaic activity and no ORR.

Technical Accomplishments and Progress: Pt disposition onto Mo_2N

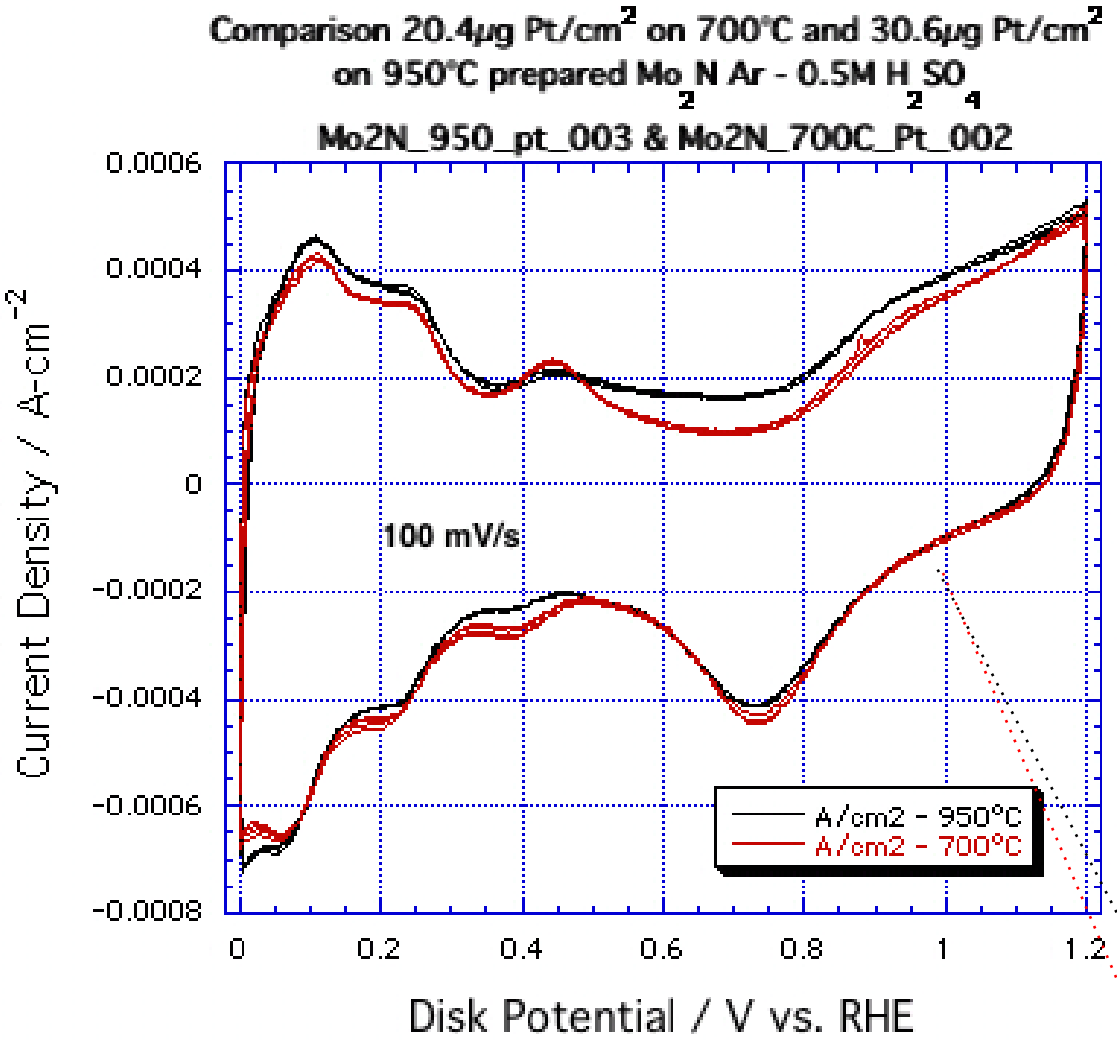
- Mo_2N lightly ground to break up foam post synthesis.
- 0.2M H_2PtCl_6 solution added in an incipient wetness "like" approach to prepare Mo_2N-supported Pt at 20 wt%.
- 6% H_2/Ar reduction initially at 70-80°C.
- Isothermal TGA used, lower T, longer reduction decreases Pt crystallite sizes.
- Pt disposition process has not been optimized.

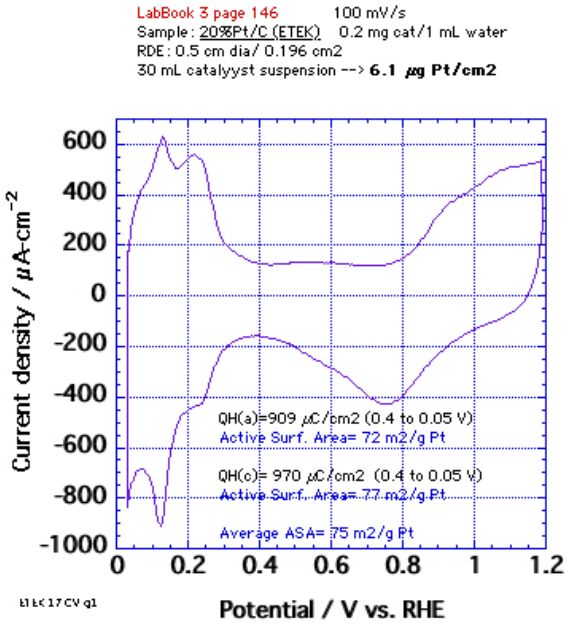
700°C – prepared support, 20 wt% Pt, 70°C, 12 hr reduction



Average Pt crystallite size determined using MDI Shadow® ~ 36Å

Technical Accomplishments and Progress: Pt/Mo_2N CV Characterization with 0.5M H_2SO_4 Shows Pt/Carbon-like Activity



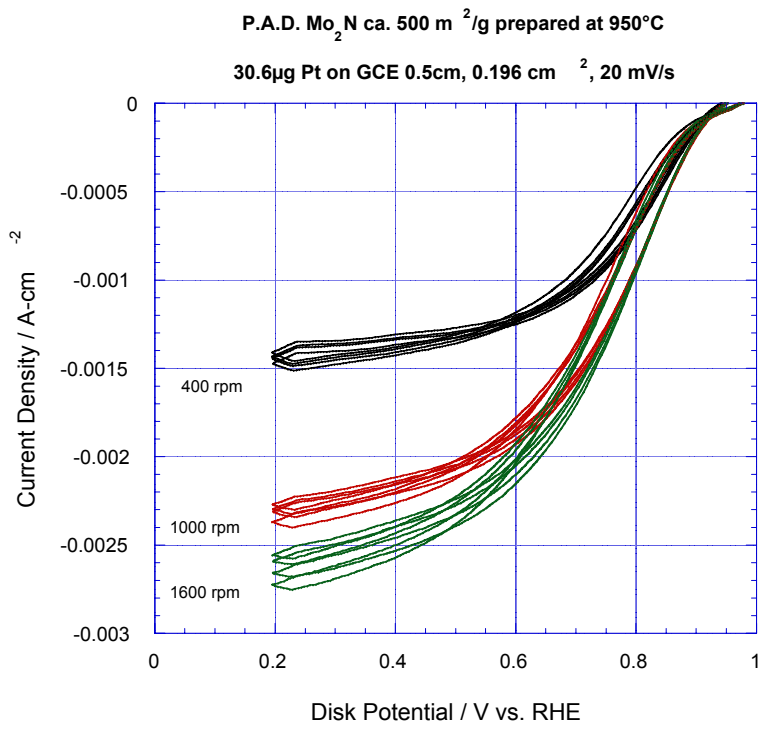


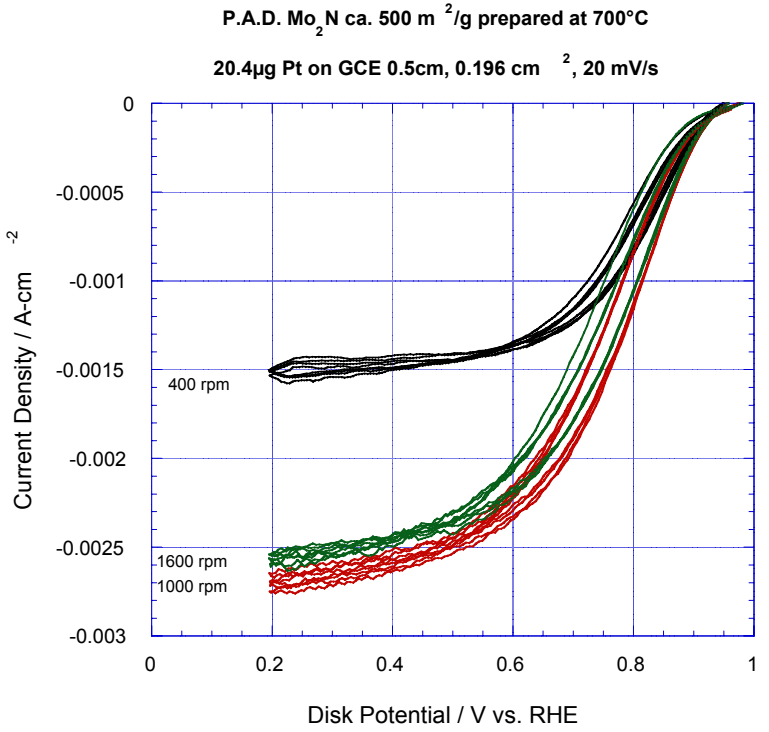
Compare with ETEK catalyst

	EASA
$Q_{H(a)}$ = 630 µC/cm²	9.8 m²/g
$Q_{H(a)}$ = 890 µC/cm²	20.8 m²/g

- Pt/Mo_2N catalyst shows activity but is not optimized.

Technical Accomplishments and Progress: ORR Activity Shown



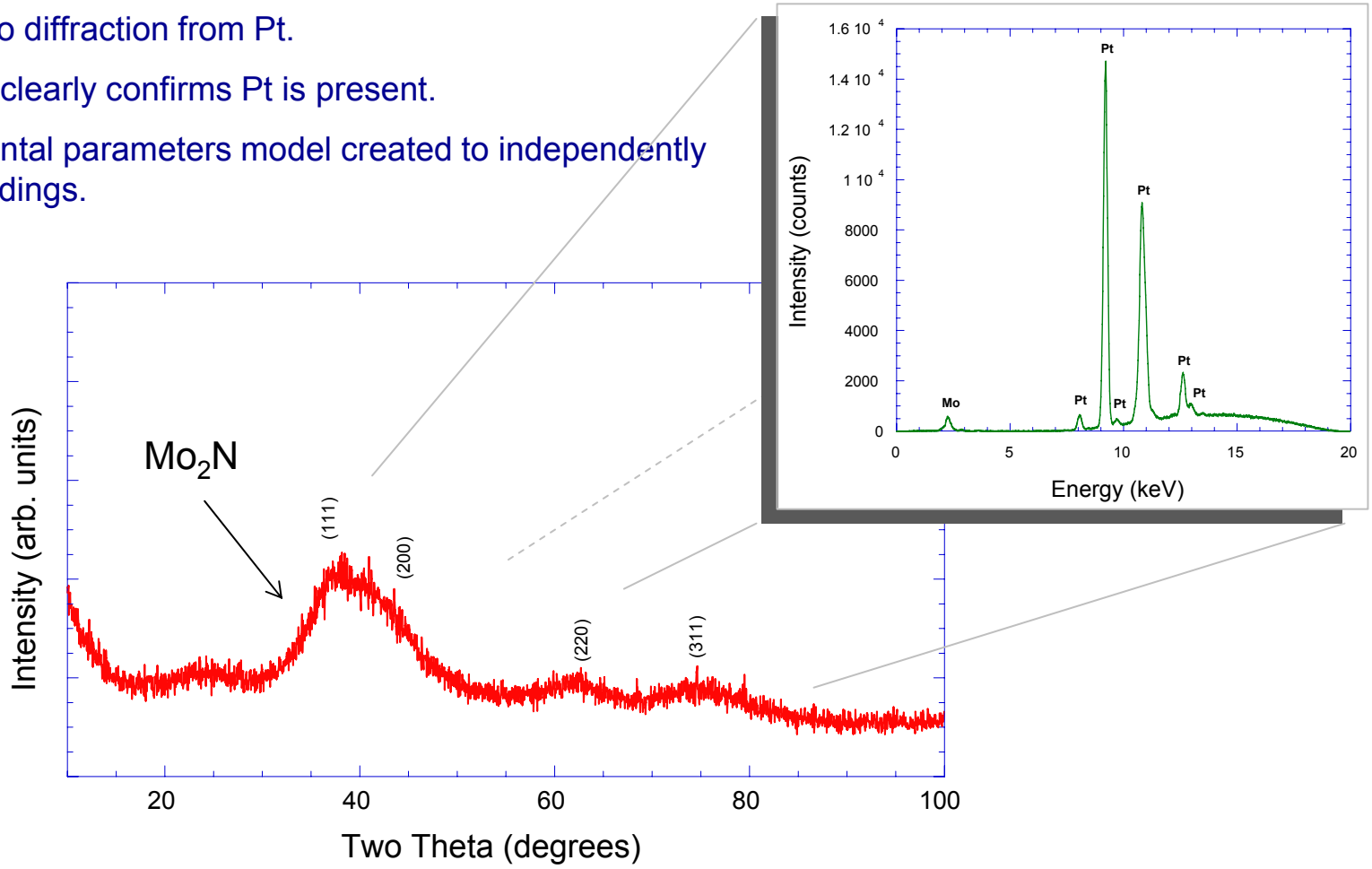


- Rotating disk electrode (disk only): glassy carbon, 0.196cm^2
- Despite lower Active Surface Area determined using hydrogen desorption, ORR is comparable to 20wt% Pt/XC-72 ETEK catalyst.
- Sample with lower loading (20.4µg) out performs higher loading (30.6µg) w.r.t. EASA and ORR.
- Particle adhesion to glassy carbon electrode may be a problem (data on right)*.

*T.J. Schmidt *et al.*, *J. Electrochem. Soc.* **145** (7) 1998.

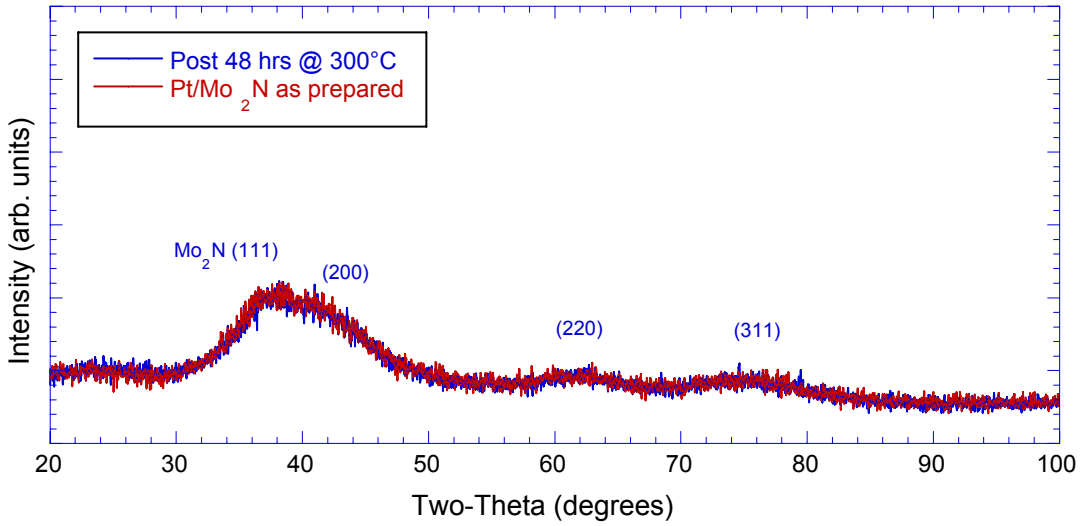
Technical Accomplishments and Progress: *In-situ* Pt/Mo_2N Formation Using PAD Process Leads to Ultra-high Dispersions

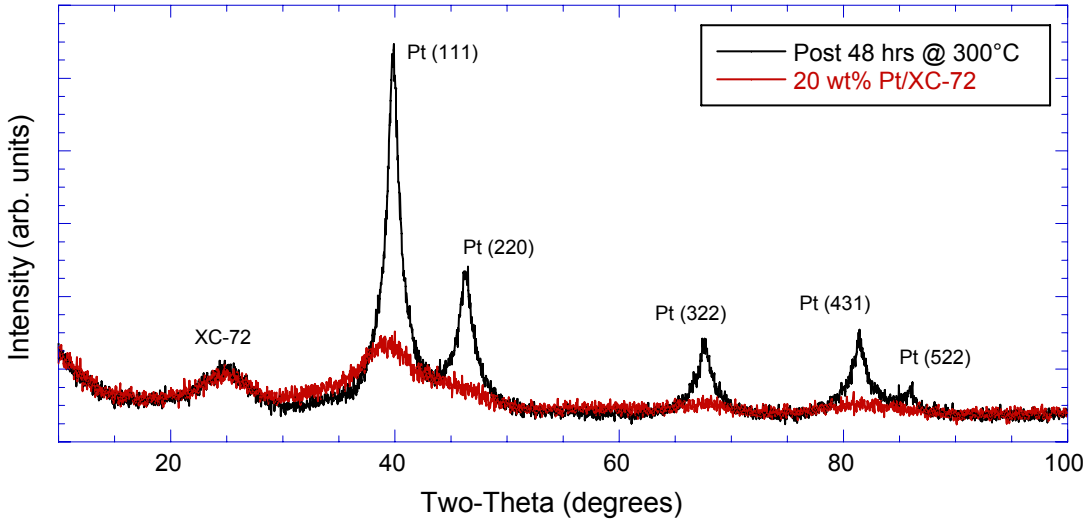
- PAD precursor modified to contain Pt.
  - Prepared under reducing conditions at 700°C, 1hr.
- 20 wt% Pt on Mo_2N directly prepared from polymer precursor.
- XRD shows no diffraction from Pt.
- XRF analysis clearly confirms Pt is present.
- XRF fundamental parameters model created to independently confirm Pt loadings.



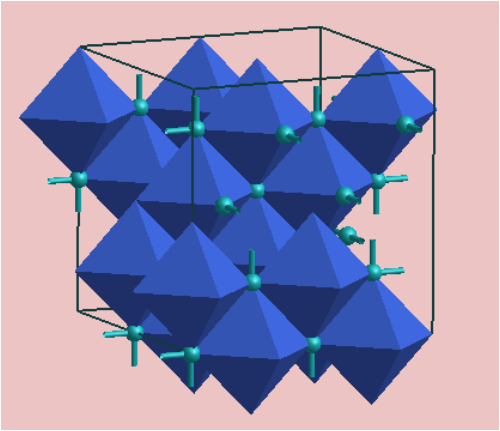
Technical Accomplishments and Progress: Evidence for Enhanced Pt Interaction with Support

- Pt/Mo_2N and Pt/XC-72 samples were subjected to a 48 hr anneal at elevated T.
  - 300°C, 48 hr
  - UHP N_2 atmosphere
- No grain growth/coalescence observed in Pt/Mo_2N sample.
- Expected change seen in the Pt/Carbon sample.
- Profile fitting of XRD data show average Pt crystallite size increased from 12Å to 40Å on the carbon support.
- **Electrochemical experiments must be performed to determine stability under potential cycling.**



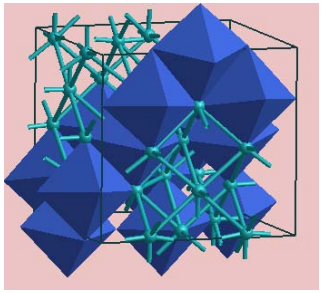


Technical Accomplishments and Progress: Calculated Mo-N bulk phase structures & structural properties

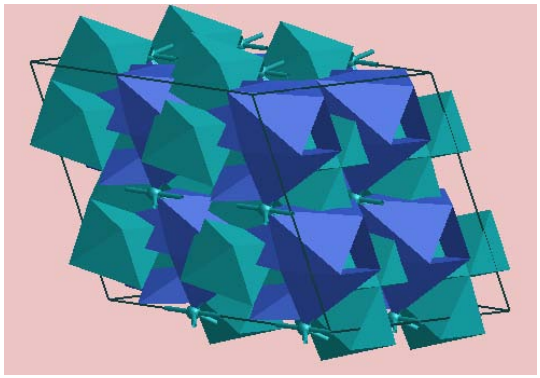


gamma-Mo_2N

	a (Å)	c (Å)	V (Å^3)
beta - experiment	4.20	8.01	282.6
beta - calculated	4.26	7.90	286.2
delta - experiment	5.75	5.62	160.7
delta - calculated	5.80	5.66	164.9
gamma - experimental	4.16		72.1
gamma - calculated	4.11	4.29	75.6



beta-$Mo_{16}N_7$



delta-MoN

Good reproduction of bulk structures.

Modeling of surfaces started.

- Key: N-blue, Mo-cyan

Summary

- As of AMR meeting date: Project is On Schedule to meet first year milestones.
- Ceramic materials with critical physical/chemical requirements for PEMFC support applications (e.g. surface area, conductivity, stability, etc.) have been prepared. Optimization now required:
  - Materials synthesized and initial characterization survey nearly complete.
  - Mo_2N ceramic support is a strong candidate with high surface area, electronic conductivity, and stability.
  - Evidence for enhanced Pt-support interaction with Pt/Mo_2N, electrochemical active surface area (ECSA), and demonstrated oxygen reduction activities (ORR).
- Preparation of TiO_{2-x} and Zr-Nitride ceramic support materials is in progress.
  - "Black", reduced TiO_{2-x} ceramics have been prepared using PAD approach and characterization has begun.
  - "Blue" reduced TiO_{2-x} ceramics have been prepared using A-T-P plasma torch method.
  - Solution precursors for Zr-N and samples have been prepared and will serve to compare this ceramic to Mo_2N.
- As expected, high surface area RE-hexaboride materials are proving to be a challenge.

Two FY11 Go/No-go decision milestones and one FY12 Go/No-go decision milestone will be moved forward in project timeline.

Collaborations / Distribution of Technical Personnel

(Prime – Fed. Lab. within DOE H_2 prg.)

- Materials characterization & electrochemistry : Eric Brosha (PI)
- Rare earth hexa-boride supports; Jonathan Phillips
- Sub-stoichiometric TiO_{2-x} supports; Jonathan Phillips
- PAD synthesis, high surface area powder supports; Anthony Burrell and Karen Blackmore
- MEA prep/FC testing; Tommy Rockward
- Support Modeling; Neil Henson

(Sub - University within DOE H_2 prg.)

- Conductive RuO_2 and NbO_2 Supports; Timothy Ward

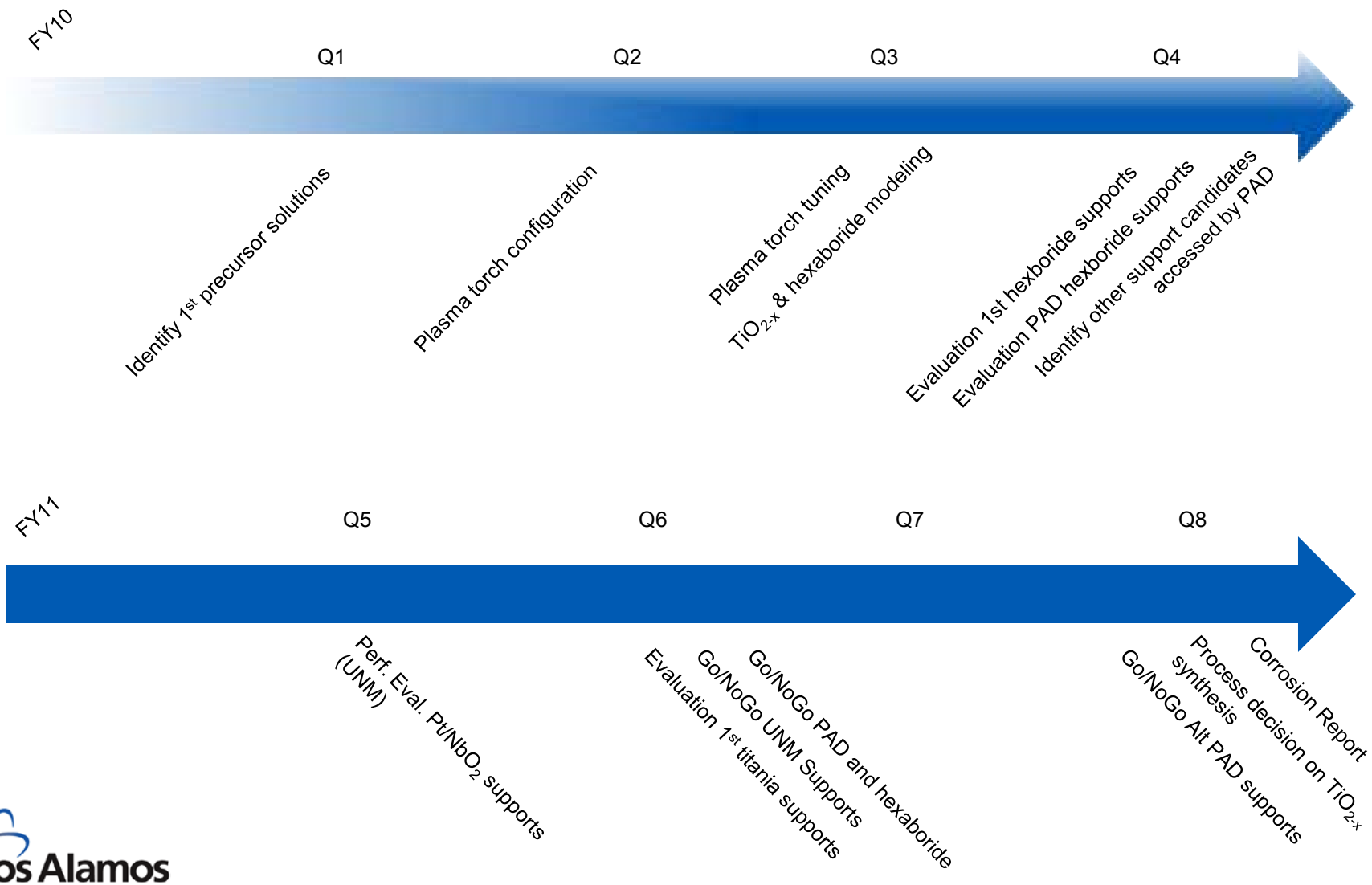
(Sub – Fed. Lab. within DOE H_2 prg.)

- Characterization; Karren More (PI – special materials)

Proposed Future Work – FY10 Q4 and into FY11

- Finish A-T-P tuning & focus on direct hexaboride synthesis : accelerate Go/No-Go decision (milestone) for this material via plasma torch.
- Continue A-T-P synthesis work started in Q2 on the titania materials using oxide (rutile) and hydroxide containing aerosols (FY11 milestone).
- PAD synthesis work (all milestones):
  - Optimize precursors and synthesis conditions to prepare desired TiO_{2-X} materials.
  - Synthesize and study Zr nitrides/compare properties to Mo materials.
  - Make identified synthetic PAD chemical route to hexaboride synthesis work.
- Characterize/evaluate hexaboride supports and fast-track to Go/No-Go (milestone).
- Accelerate portions of project using best support material(s) : e.g. start looking at how to make ink formulations for nitride materials (MEA studies).
- Complete UNM sub-contract procurement process and ramp up University led component of project.

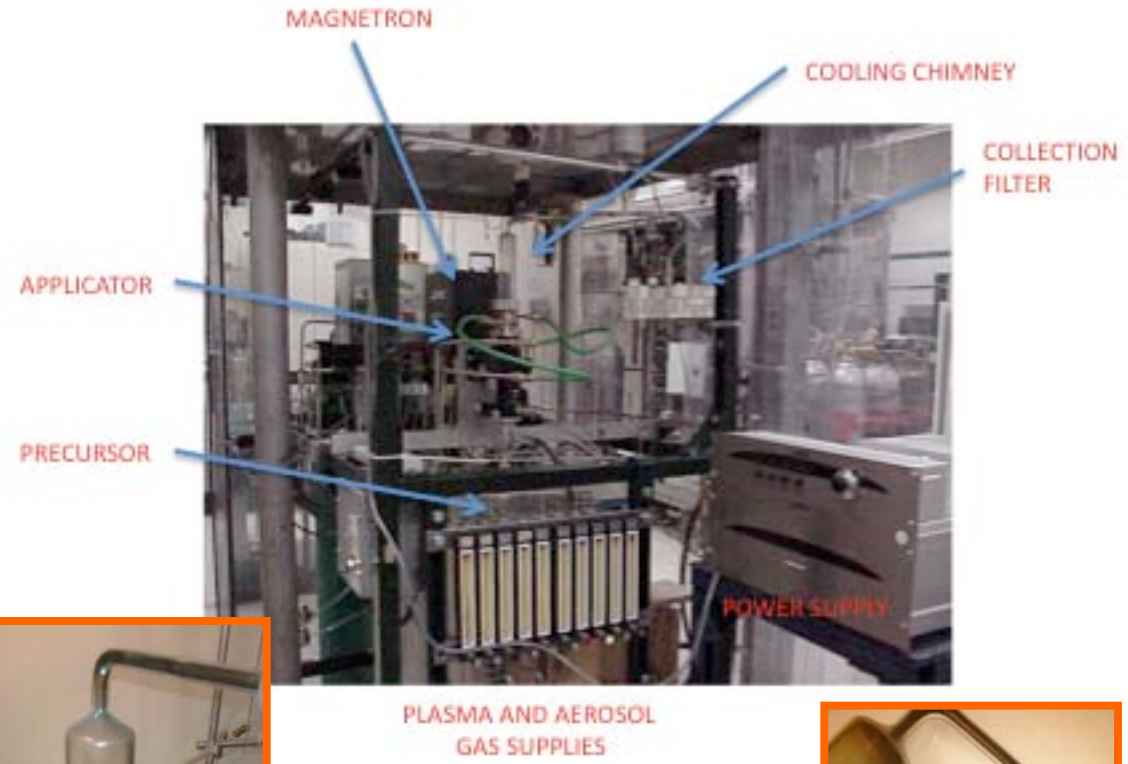
Proposed Future Work – FY10 Q4 and into FY11 (Project Timeline)



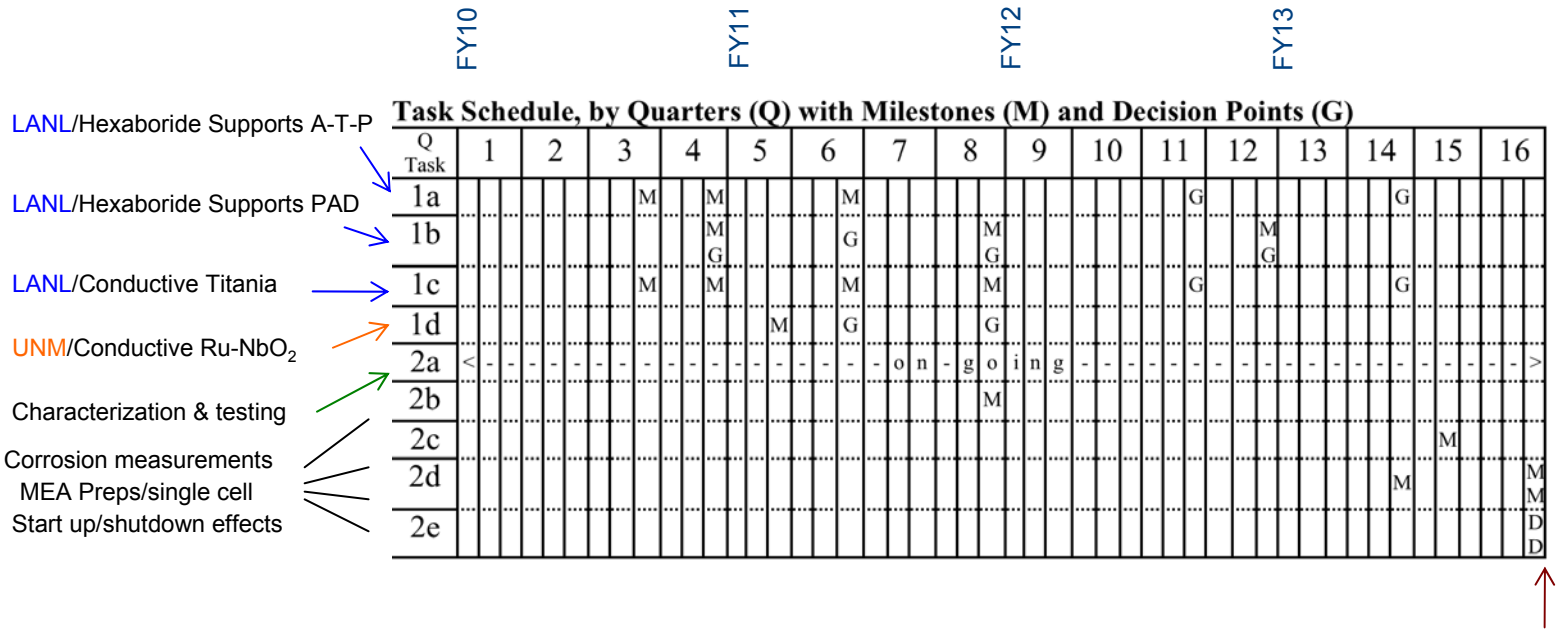
Supplemental Slides

Technical Accomplishments and Progress: A-T-P Synthesis Work *On Schedule*

- On schedule to meet milestones for FY10.
- Plasma torch assembled a walk-in hood facility.
- Awaiting safety approval/certification to become fully operational.
- Precursors identified and test runs have been made:
  - lanthanide and barium cation and boron sources for hexaborides.
  - Nano-sized rutile/anatase for TiO_{2-x} synthesis
- Initial testing/tuning runs have produced material for analysis.



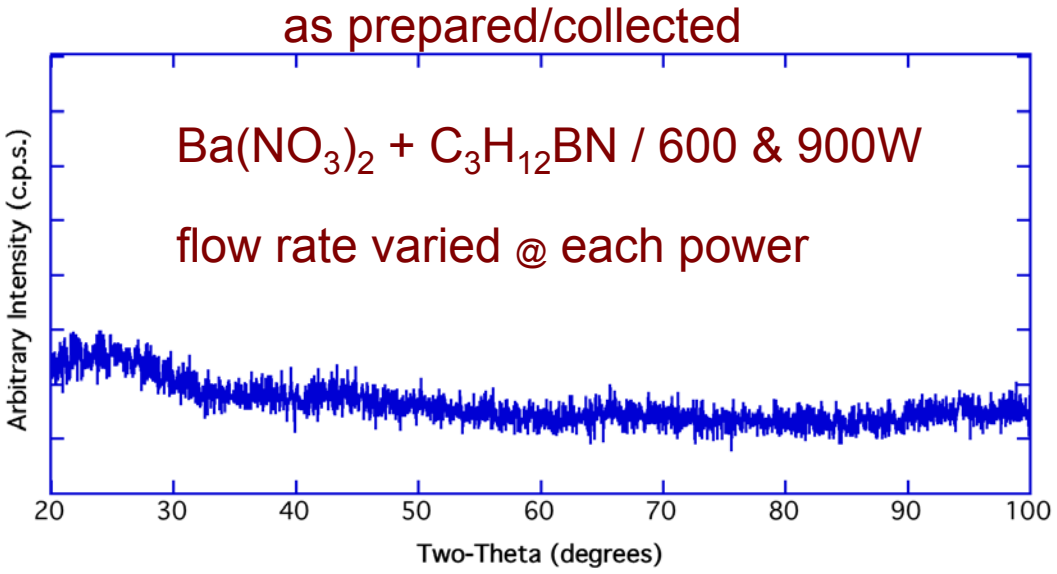
Milestones & Go / No-Go Decisions / Criteria from Proposal

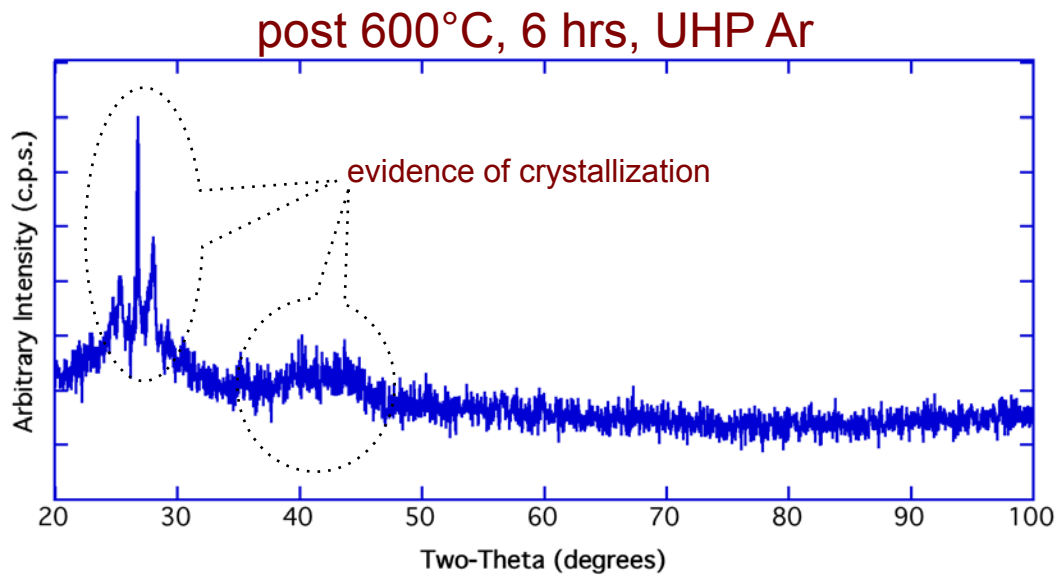


- Criteria used to judge G/NG decision points
  - Particle size, surface area, conductivity
  - Pt - support interaction, activity
  - Corrosion studies
  - Modeling input
  - MEA fabrication

Technical Accomplishments and Progress: A-T-P Synthesis - Initial Tuning Work

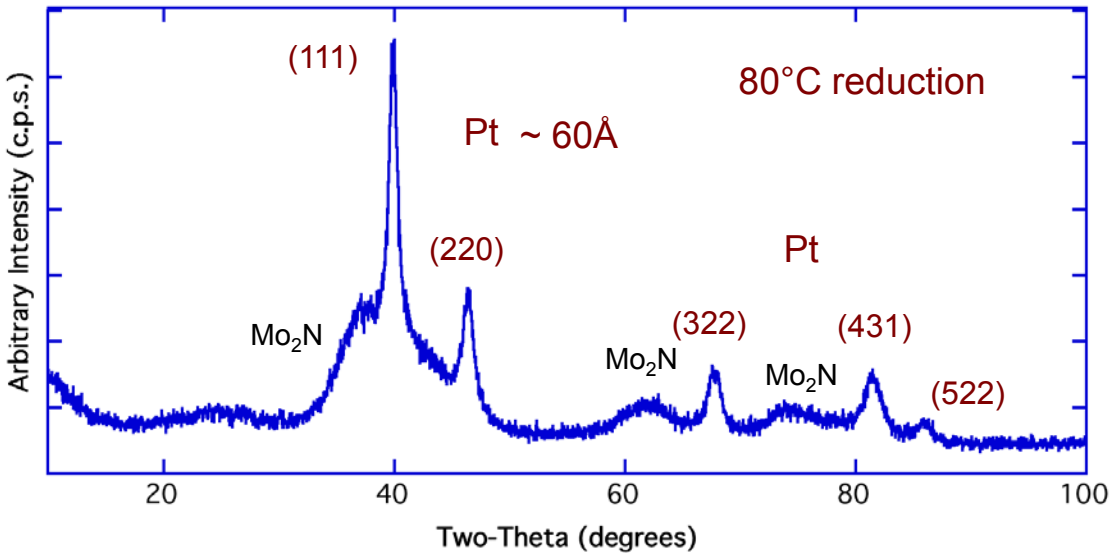
- As prepared/collected material from plasma torch shows no diffraction. (Both Eu & Ba trials)
- XRF confirms presence of barium (in the case of that sample).
- Samples post annealed show crystallization.
  - 600°C, UHP Ar begin to show crystalinity
  - Samples heated to 800°C show formation $Ba_2B_2O_4$ and possibly $Ba_2B_4O_7$
  - Confirms both Ba and B are present in the collected, amorphous powder
- Presently using DSC to precisely measure onset of crystallization and to find source of oxygen.
- Torch tuning/optimization.

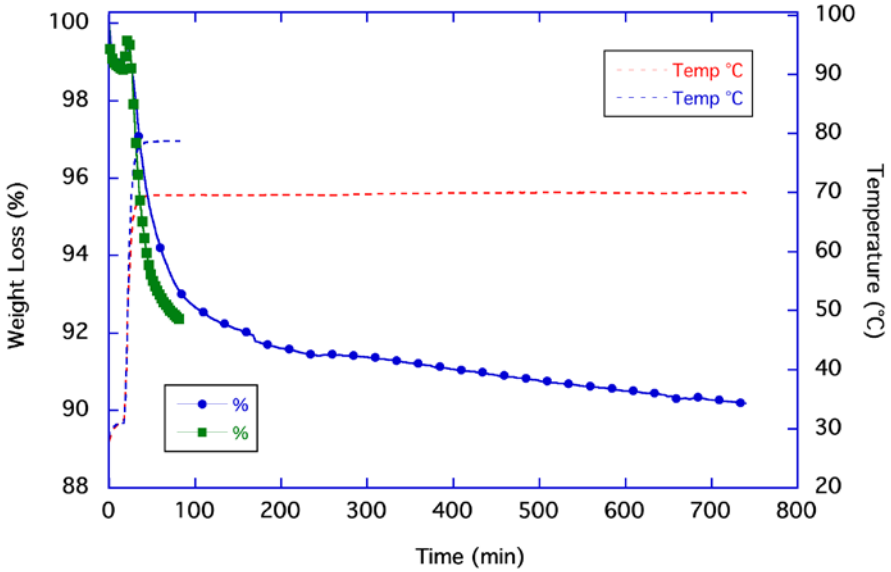




Technical Accomplishments and Progress: Mo_2N via PAD Synthesis/Pt disposition

- Mo_2N lightly ground to break up foam.
- 0.2M H_2PtCl_6 solution added in an incipient wetness "like" approach to prepare Mo_2N-supported Pt at 20 wt%.
- 6% H_2/Ar reduction initially at 80°C, 1 hr.
- Via TGA experiments, lower T, longer reduction decreased Pt particle sizes.

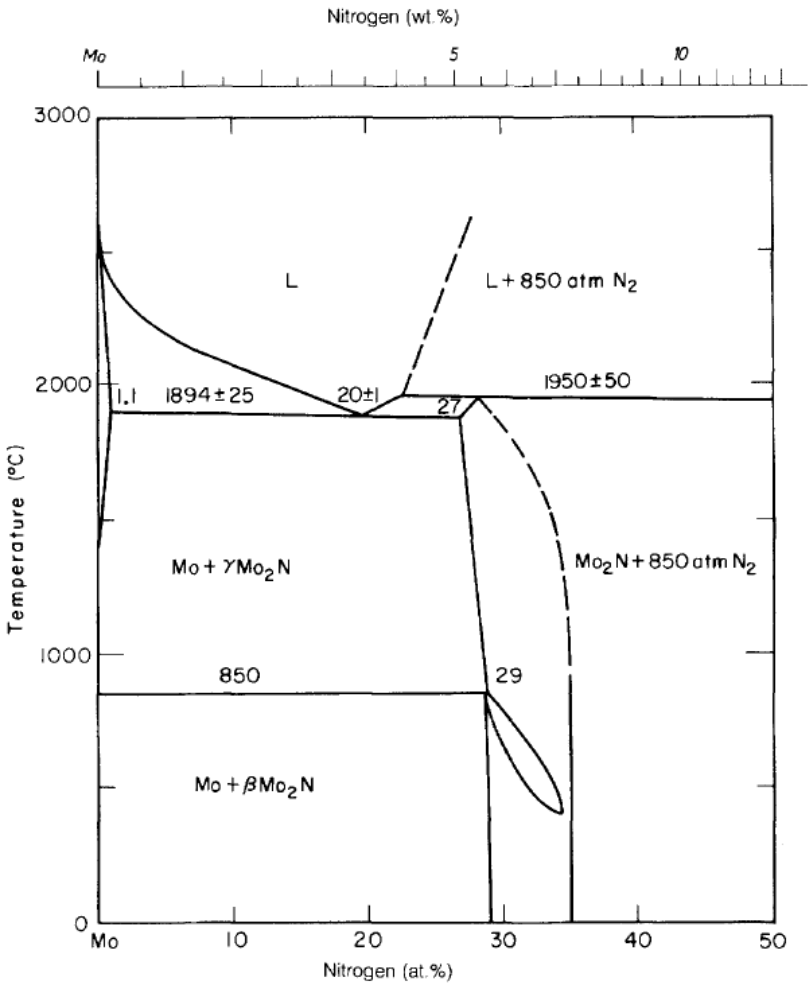




Technical Accomplishments and Progress: Computational Studies of Molybdenum Nitride Supports for Platinum Electrodes

- **Aim** :
  - calculations to predict the thermodynamics and activation barriers for fundamental electrode processes occurring at platinum surfaces when supported on thin films of molybdenum nitride to optimize materials properties
- **Approach** :
  - calculations to be performed using plane wave periodic density functional theory calculations (VASP software)
  - build models for known Mo-N bulk phases and optimize
  - based on these, build models for Mo-N dominant surfaces using guidance from experimental characterization and literature
  - determine most favorable binding sites for single and multiple platinum atoms on surfaces

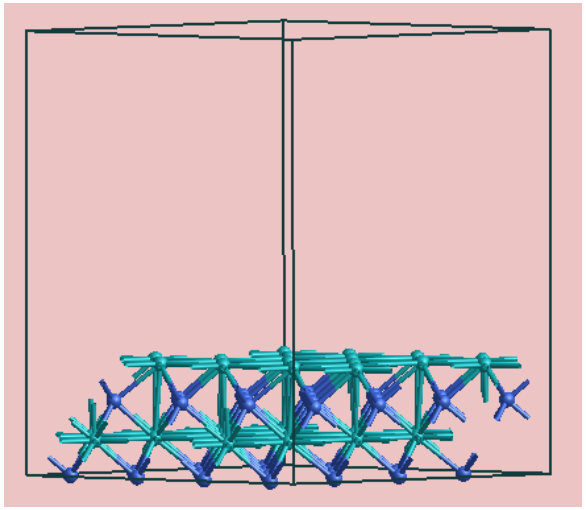
Technical Accomplishments and Progress: Computational Studies of Molybdenum Nitride Supports for Platinum Electrodes

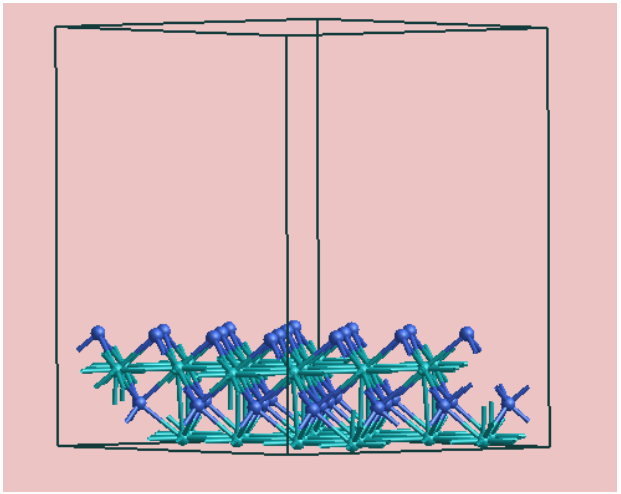


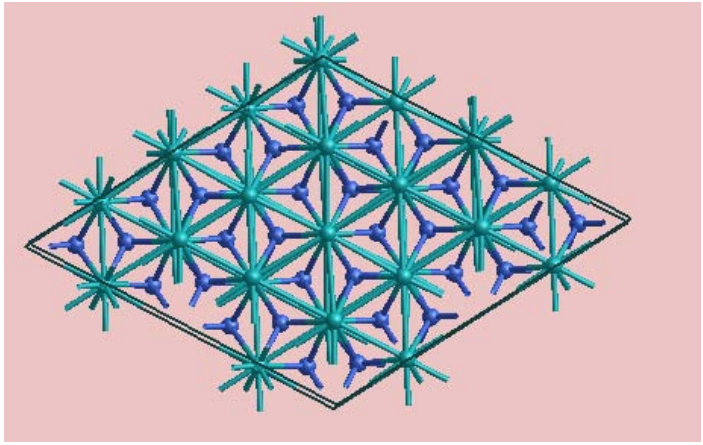
- Several Mo-N phases present under varying conditions
  - delta-MoN is stoichiometric with hexagonal crystal structure, unstable at all temperatures, formed at high N_2 pressures
  - gamma-Mo_2N is cubic with half the nitrogen sites vacant
  - beta-$Mo_{16}N_7$ is tetragonal with a quarter of the nitrogen sites vacant
  - some evidence to suggest that unique structures are stabilised as thin films not observed in bulk

Technical Accomplishments and Progress: Models for surfaces - Mo-N materials modeling

- Starting point – most ordered structure : delta-MoN







- (001) surface : Mo and N rich
- 1, 2 and 3 coordinate binding sites for Pt on both

A-T-P Potential for Advanced Catalysts Synthesis in the News

Introducing Aerosol-through-Plasma to the Market:

A Promising Technology

- IN THE NEWS: CAN IT CONQUER A $12 BILLION/YEAR MARKET?

From a Nov. 5,'09 announcement-
Volvo Technology Transfer (VTT) has become one of four major investors in Arizona-based SDCmaterials. VTT has identified a unique opportunity to promote a state-of-the-art technology which looks set to revolutionise the catalyst industry.
SDCmaterials develops advanced nano-material formulations, which will significantly cut the cost of developing and manufacturing catalysts for the automotive industry. SDC's patented* technology, which has significantly reduced the use of precious metals, is currently being tested by a leading German automotive manufacturer, with early indications suggesting that it could enter series production in 2010.
The technology has been developed for use in standard diesel engines and can be applied to all engine-powered vehicles. VTT's CEO Anders Brännström hopes that this technology might become a ground-breaking feature of the Volvo Group's future product range.
"We're extremely excited about the SDC opportunity," he says. "Thanks to this technology, we have the potential to reduce the cost of expensive catalytic materials by up to 60 per cent."

*Phillips, J., 'Plasma Generation of Supported Metal Catalysts', U.S. Patent *5,989,648*

Acknowledgments

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