2011 U.S. DOE Hydrogen and Fuel Cells 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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Neil Henson,

Los Alamos National Laboratory

May 9-13, 2011

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 May 2011) : 41%

- **Budget**
  - Total project funding : $500K/yr
    - DOE $425K
    - UNM (sub) $75K
  - Received FY10: $405K
  - Funding Received (anticipated) FY11: $250K

- **Technical Barriers Addressed**[2]

A. Durability (Pt sintering, 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)
  - UNM
  - ORNL (no-cost partner)
  - SDC Materials Inc. (industrial input & manufacturing sounding board, materials exchange)

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 amenable 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 $\mu A/cm^2$ @ 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

- Transition metal nitrides: Mo-N, Zr-N
  - 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 and demonstrated electro-catalytic activity for both hydrogen and oxygen / Pt
  - TiO: conductive but not as high as Magnéli phase
- 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

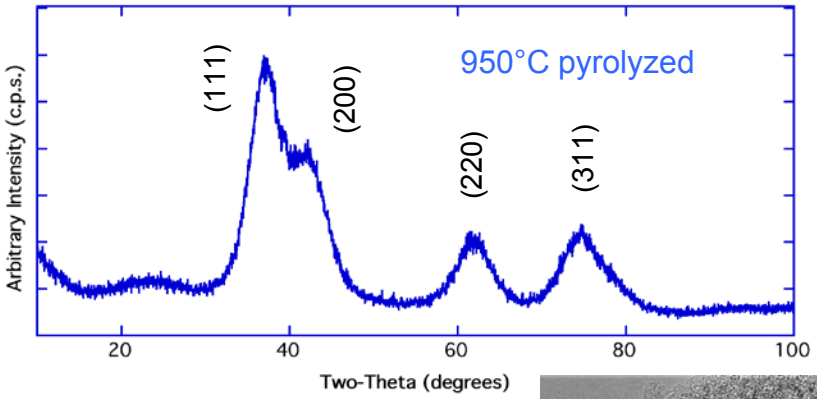
- Polymer assisted deposition (PAD) nitrides and sub-oxides of titania.
  - PAD precursor routes to produce ceramic materials with high surface area.
  - Powders, bulk catalysts prepared by forming metal organic get followed by pyrolysis under controlled atmospheres
  - Molybdenum nitrides: Ammonium molybdate/polyethylene imine (with EDTA) to produce a gel (100°C) followed by 950°C anneal in 4-6%H_2 and N_2
- Theory/Modeling support to aid experimental effort to provide data on stability of the support in absence of Pt particles and nature of Pt-support interactions
  - 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 $NbRu_yO_z$ supports / specific target materials (UNM)
  - Aerosol spray pyrolysis of alcohol solutions with addition of pluronic block co-polymers as templating agent followed by post-synthesis acid etch
  - Apply methods for nitrides and sub-oxides of titania

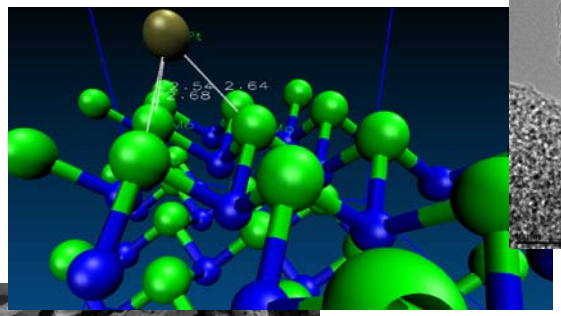
Approach: FY10 & FY11 Milestones / Go-NoGo Decisions

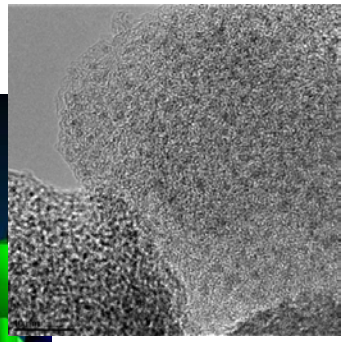
- As of AMR meeting date: Project is *On Schedule* to meet 2nd year milestones and candidate materials have been identified. Original goals of project are being met.
- **Go** Decision made for Mo_2N supports synthesized via PAD approach: *ahead of schedule.*
  - Q8 target moved up to Q5-Q6.
- Evaluation of titania supports prepared by PAD approach: *ahead of schedule.*
  - Q6 targets moved up to Q3-Q4
- Go/NoGo decision on hexaboride supports: *ahead of schedule.*
  - **No-Go**: Q6 decision moved up to Q4
    - Unable to synthesis using A-T-P process (Q4)
    - PAD process produced only small amounts of LaB_6 (Q6)
- Performance evaluation of $Pt/NbRu_yO_z$ catalysts: *ahead of schedule.*
  - **No-Go** : poor activity due to formation of NbO_x passivation layer on Pt (Q6)
- Report on corrosion/durability (FY11, Q8): *On schedule.*
- Process decision on TiO_{2-x} supports (FY11, Q8): *On schedule.*

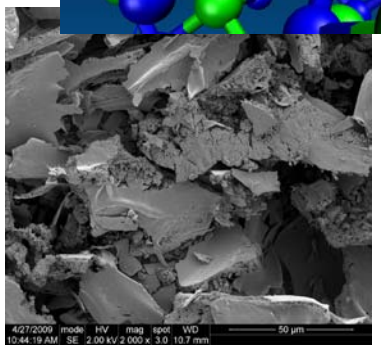
Technical Accomplishments and Progress: Nano-sized Mo-Nitride Ceramics Produced (Previously Reported 2010 AMR)

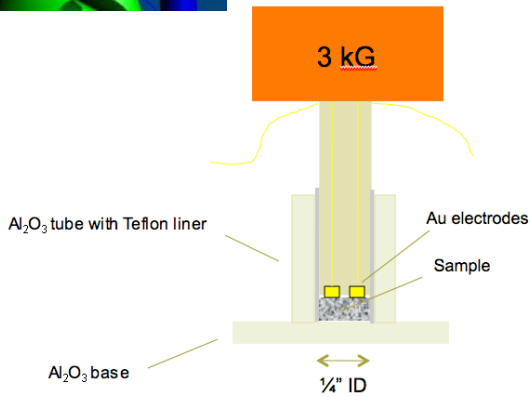
- Molybdenum Nitride Synthesis :
  - Mo_2N cubic phase.
  - XRD: average crystallite sizes ca. 1 – 2nm.
    - 700 – 950°C pyrolysis T with 950°C optimum
- BET: 250 – 300m^2/g typical with SA as high as 500m^2/g recorded.
- Electronic conductivity (resistance)
  - 2-pt measurement, powder measured by compacted powder in ¼" dia. fixture with uni-axial applied force.
  - Mo_2N (950°C): **3.3Ω**
  - Vulcan XC-72R measured in same fixture: **1.8Ω**
- ORNL TEM Analysis
  - < 2nm particle sizes with agglomerates of nano-particles, ~0.2μm to over 2μm
  - Highly crystalline structure consistent with cubic Mo_2N and nicely faceted





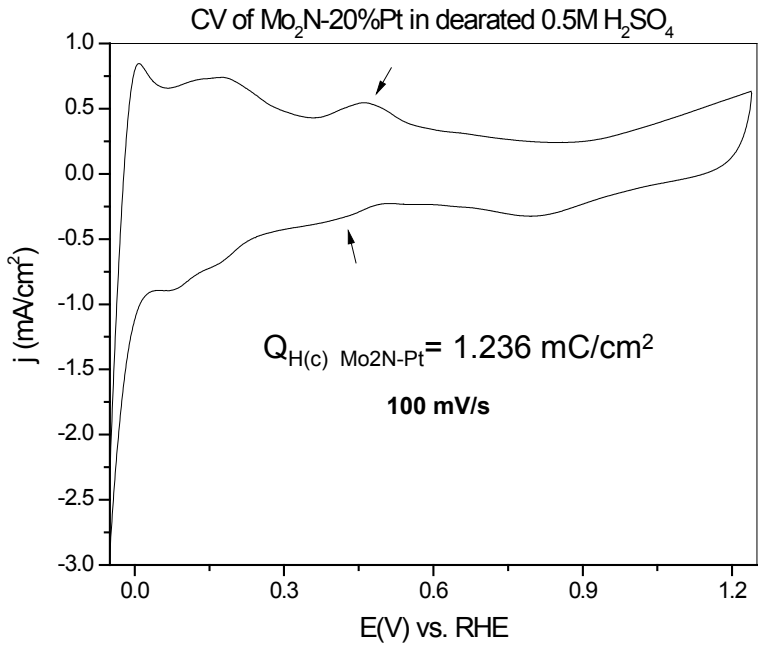


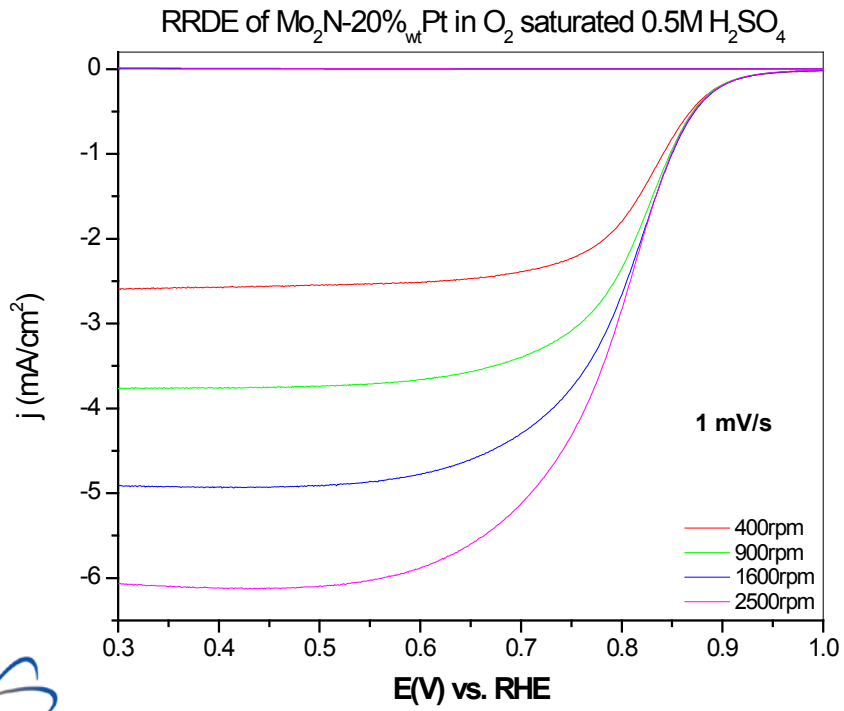




Technical Accomplishments and Progress: Pt/Mo_2N : ORR Activity Shown/Improved from FY10

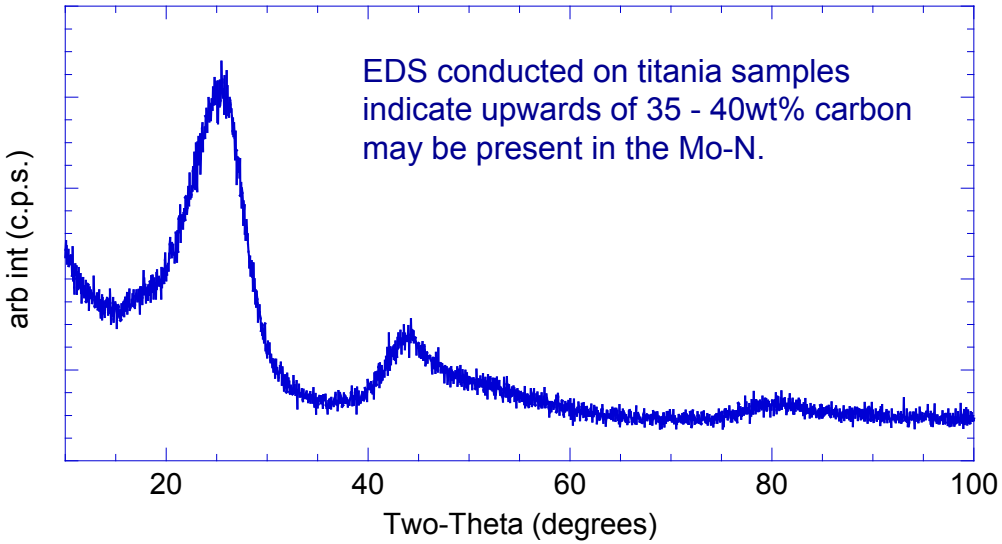
- Platinum on Mo_2N shows the expected electrochemical features.
- The support does not seem to interfere with the activity of the Pt towards the ORR.
- ORR catalysis mechanism is not affected by the support.

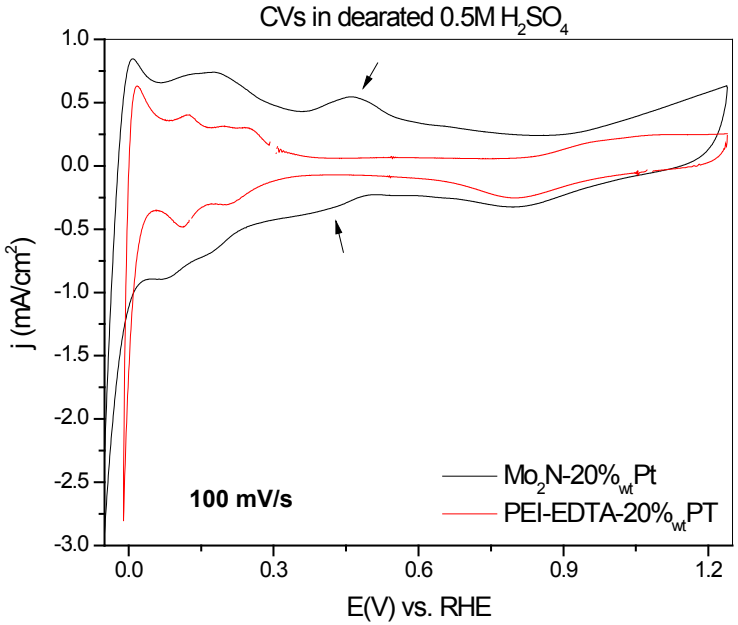




- The reversible ($2e^-$ process) redox couple observed at E=0.44V is attributed to the Mo_2N and not to the carbon precursor (The process is TBD).
- Higher capacitance currents observed with the Mo_2N due to higher surface area.
- Higher EASA was obtained with the Mo_2N-Pt sample.

Technical Accomplishments and Progress : Source, Properties, and Influence of Carbon Remnants



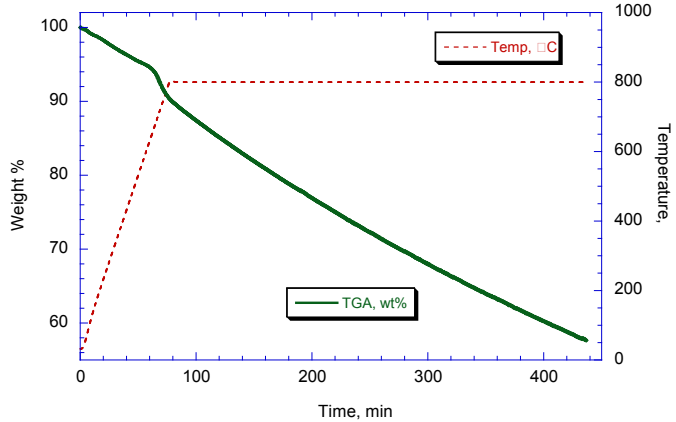


- Early EDAX measurements of Mo_2N suggested Carbon – confirmed with PAD TiO.
- Sample prepared without Mo source: PEI/EDTA pyrolyzed at 950°C; same procedure used for Mo_2N synthesis.
- BET surface area is low (over 100x lower) compared to Mo_2N; 1.7 m^2/g
- Confirms broad peak at 25° in all XRD data is from the carbon remnants.
- Platinized carbon residue not a significant contributor to activity.

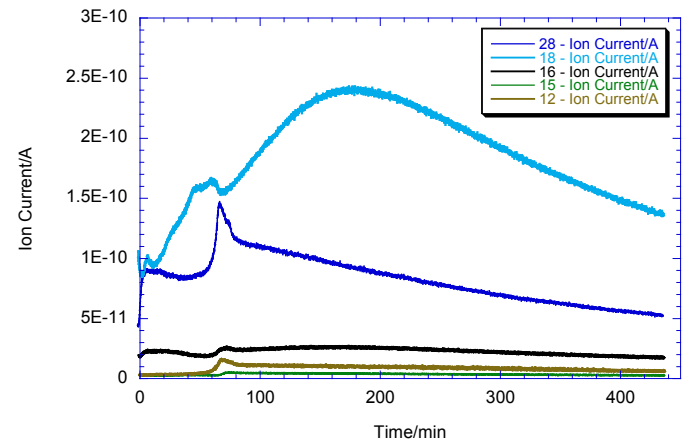
Technical Accomplishments and Progress : Anneal Mo_2N Longer in H_2 to remove carbon? - XRD post TGA/MS experiment

10 K/min in 6%H_2 and isotherm 800°C for 6 hrs with MID scan

Water formation evident - reacting with carbon to form CO with indications of trace ammonia.

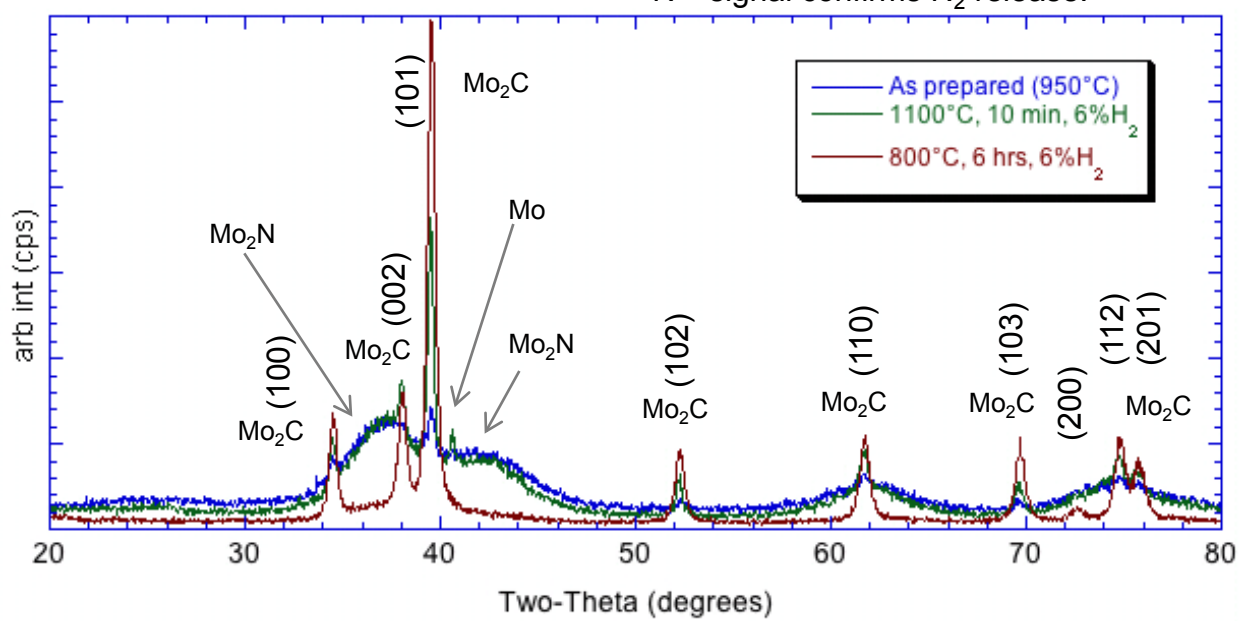


28 ion current comprised of both CO and N_2.

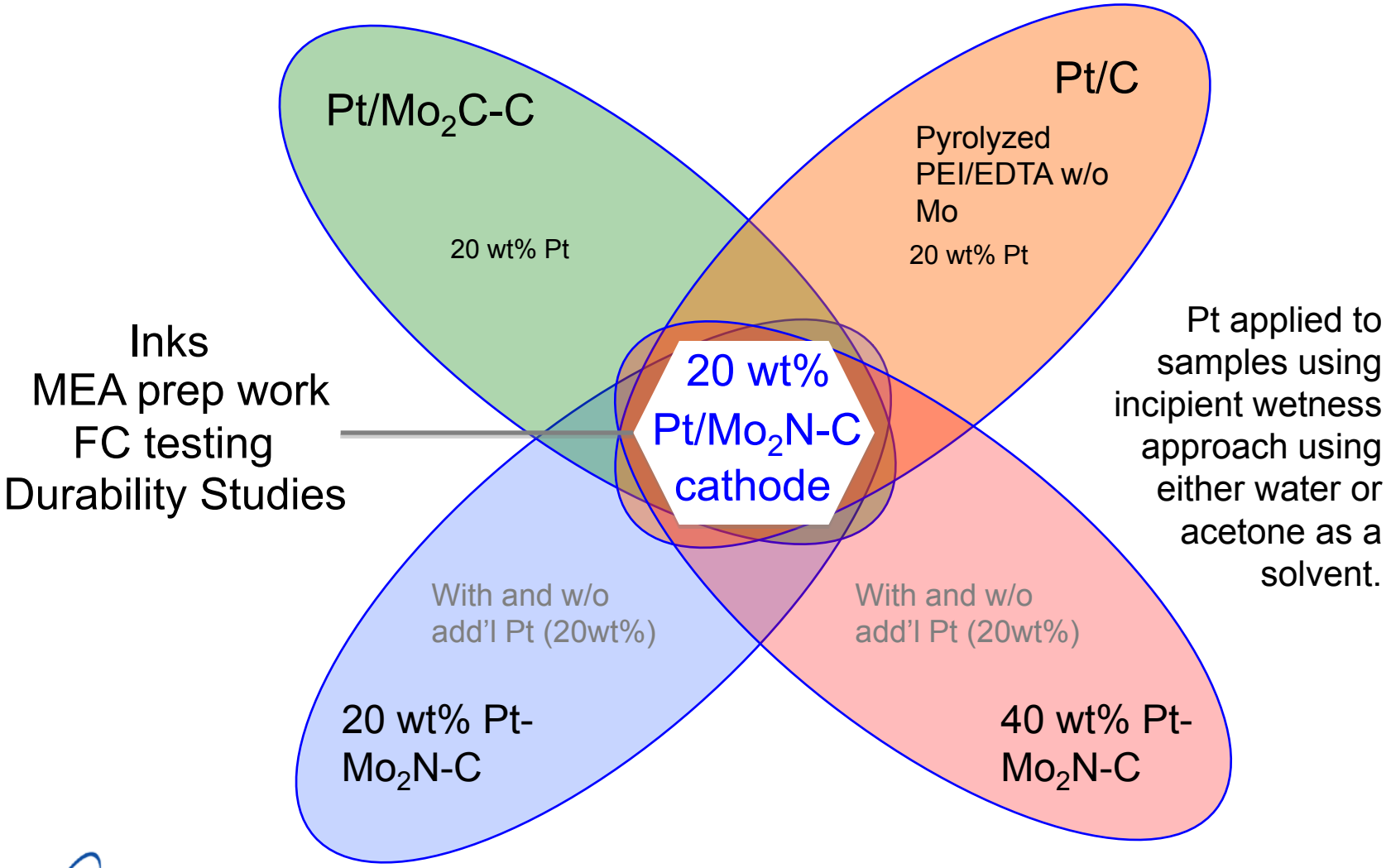


N^{++} signal confirms N_2 release.

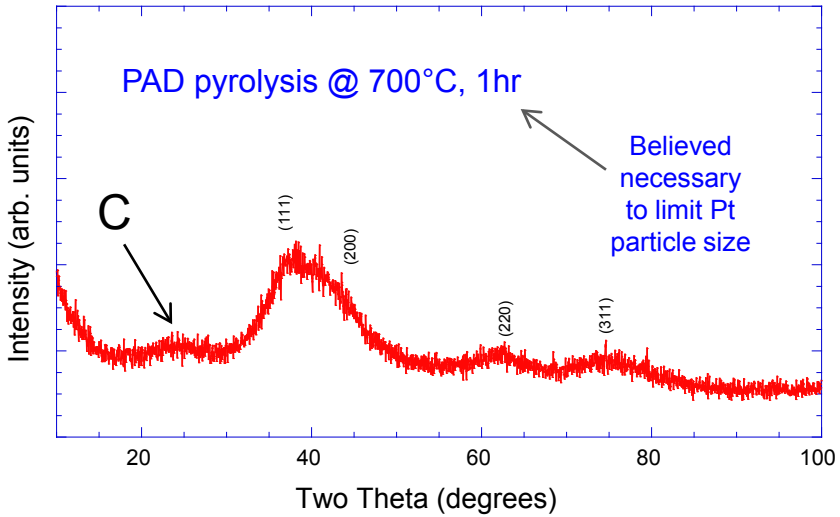
- Release of N_2 commensurate with decomposition of Mo_2N.
- Prolonged anneal ca. synthesis temperature fosters Mo_2C formation at the expense of Mo_2N.
- Residual carbon <u>remains</u>.

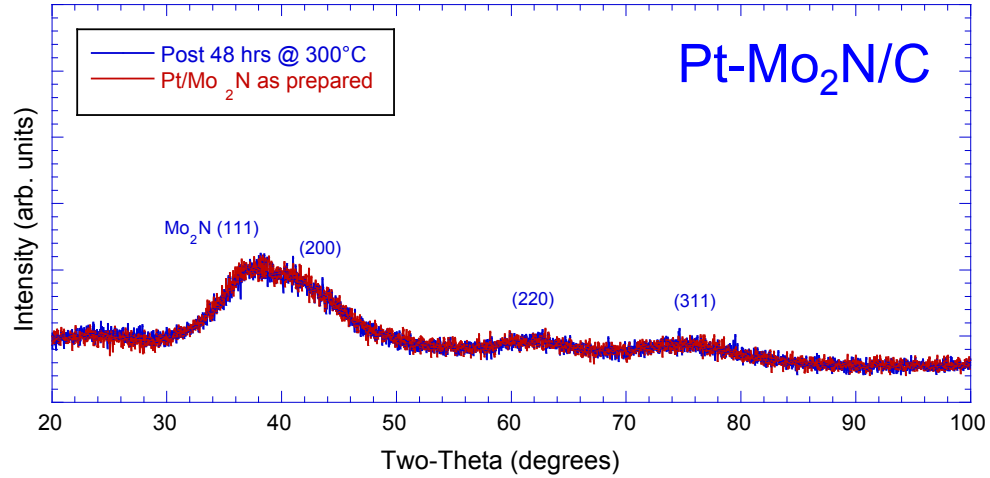


Technical Accomplishments and Progress : Electrochemical Studies Methodology

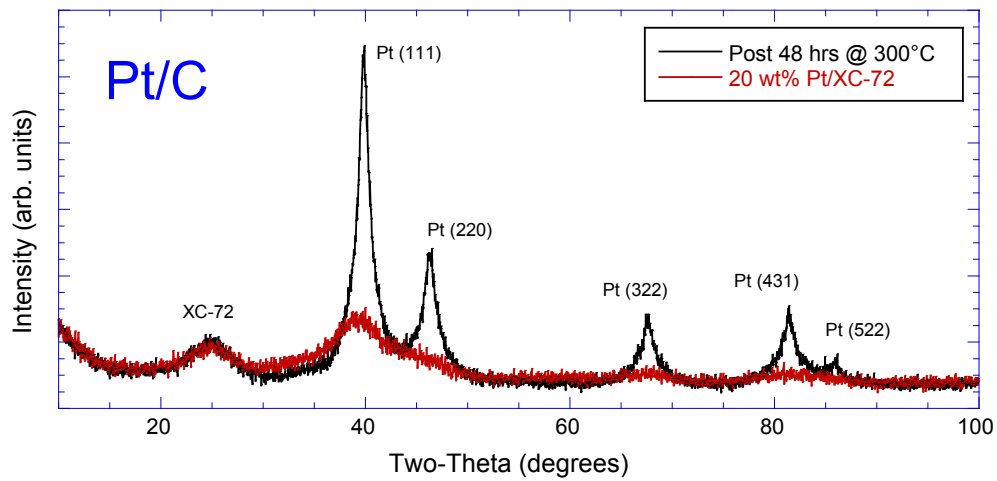


Technical Accomplishments and Progress: *In-situ* Pt-Mo_2N Formation Using PAD Process Leads to Stable, Ultra-high Pt Dispersions





- XRF confirms Pt is present in sample.
- ORNL TEM analysis:
  - 10 at% Pt homogeneously distributed across/within Mo_2N but *not as individual nano-particles*.

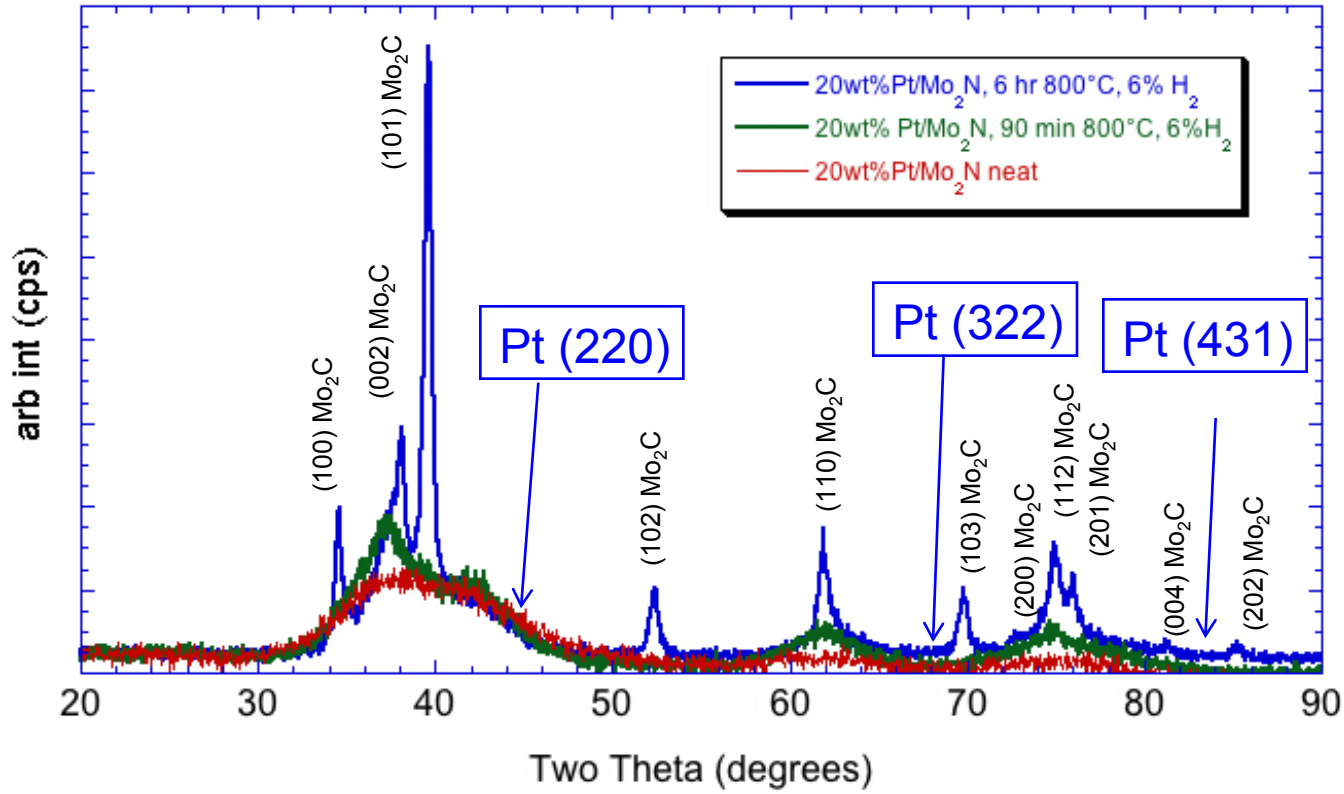


Pt ave. crystallite size increases to 40Å from 12Å

Technical Accomplishments and Progress : More Aggressive Thermal Treatment and Evidence of Enhanced Pt-Support Interaction

Isothermal TGA
800°C, 6%H_2, 6 hrs

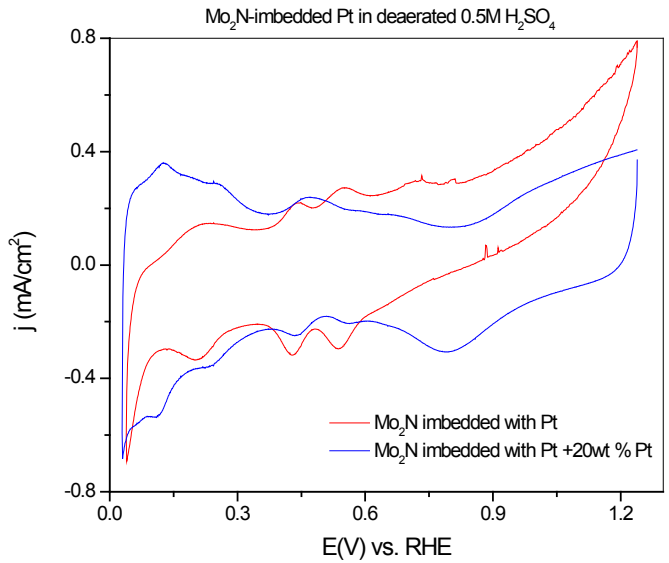
No evidence in XRD of Pt agglomeration

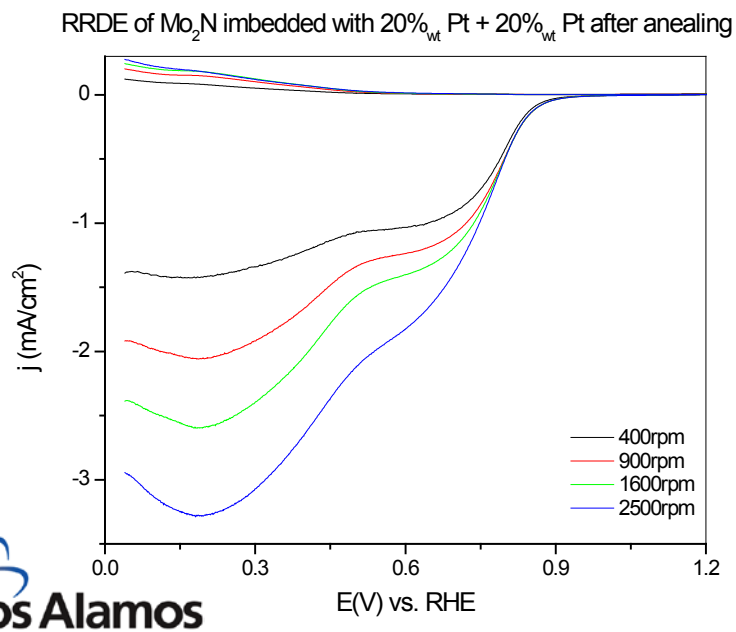


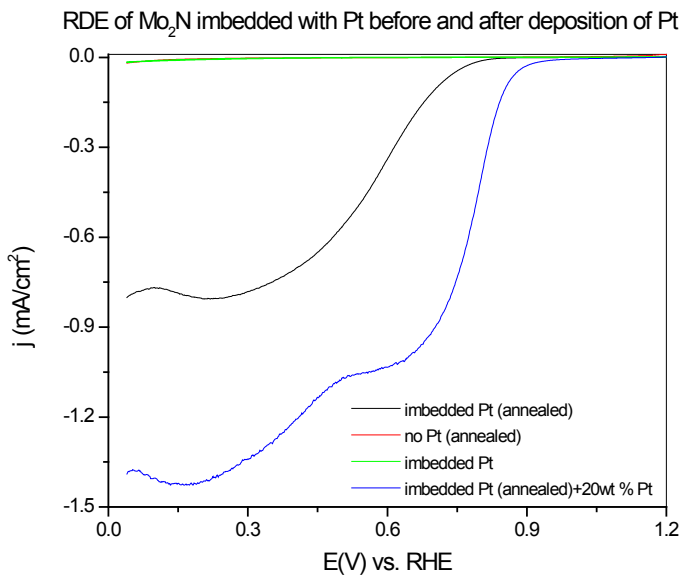
- Repeat of TGA/MS experiments to remove excess C in presence of H_2 produce similar results: Most C reacts with Mo to form Mo_2C. No methane formation!
- After TGA experiments in 6%H_2, XRD data shows formation of Mo_2C as expected and Mo_2N sintering.

Technical Accomplishments and Progress : *In-situ* Pt/Mo_2N – Electrochemical Activity from Multiple Catalytic Sites Post Anneal

- Although not seen in XRD, Pt was observed using electrochemistry.
- New redox couple was observed when Pt was imbedded in the Mo_2N (TBD).
- The imbedded Pt shows catalytic activity lower than deposited Pt.
- Annealing of the sample is necessary in order to obtain ORR activity.

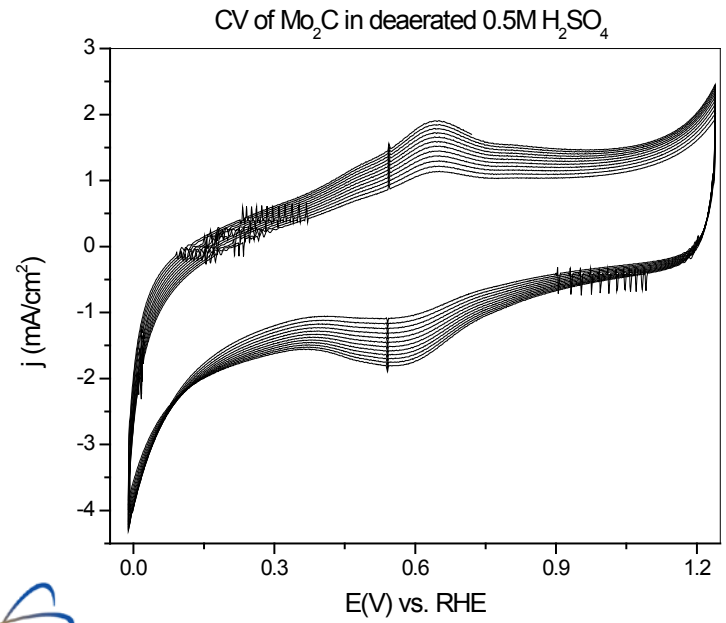


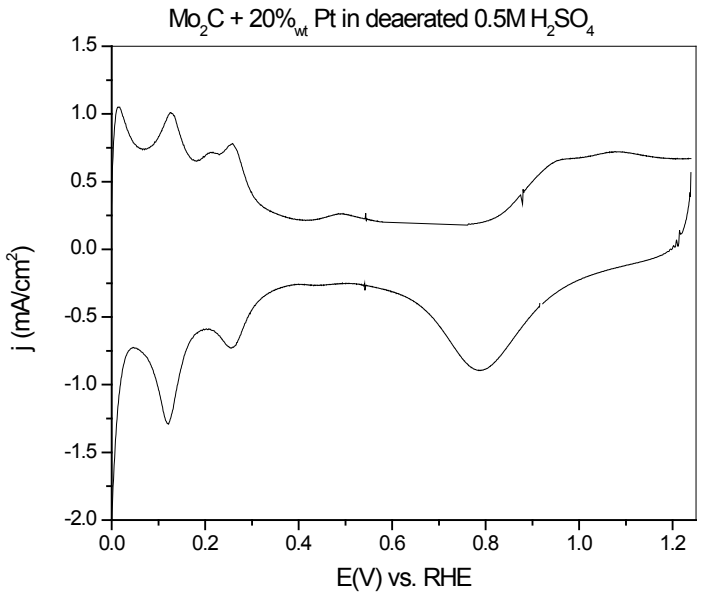


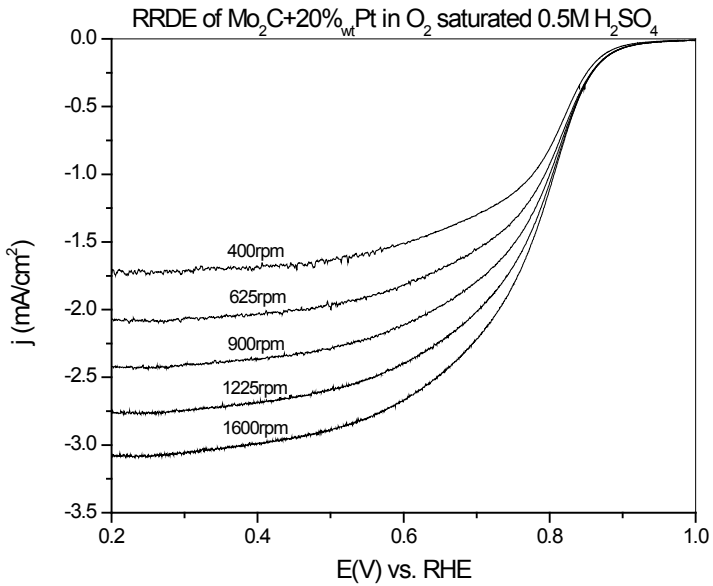


Technical Accomplishments and Progress : Electrochemistry of Mo_2C with / without Pt

- Mo_2C devoid of Pt shows instability. The growth of the redox peaks continues with cycling.
- After adding Pt the support is stable, the Pt activity is as expected both in CV of dearated solutions and RRDE measurements.

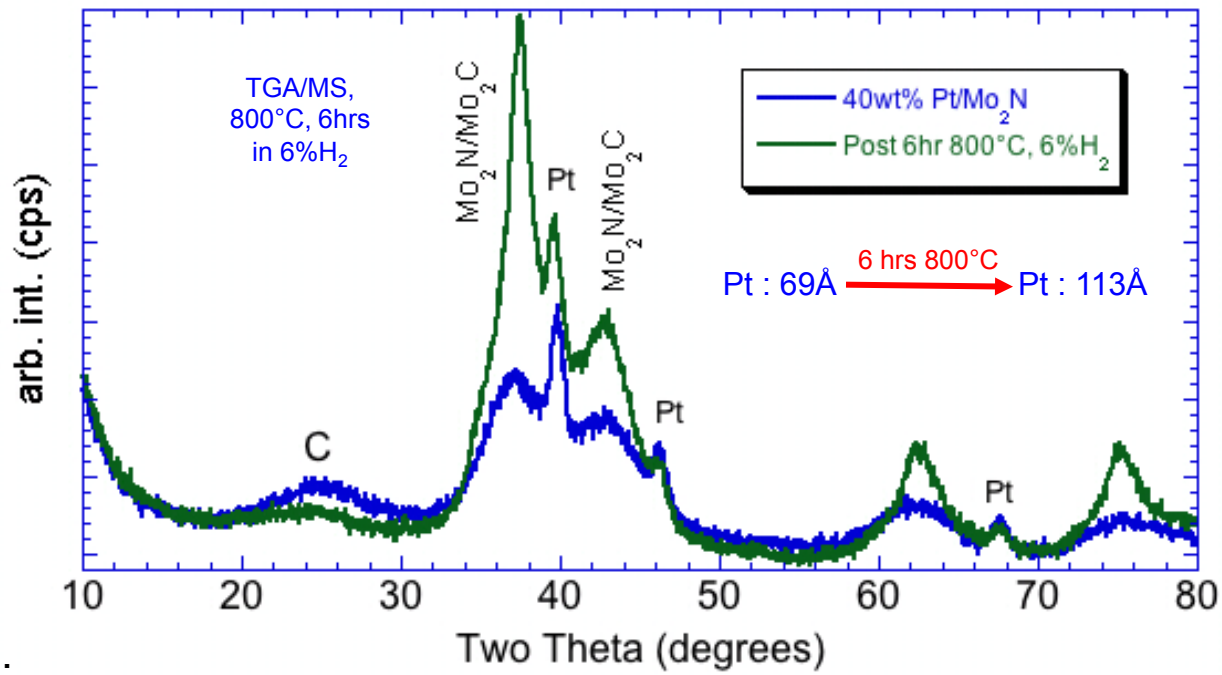






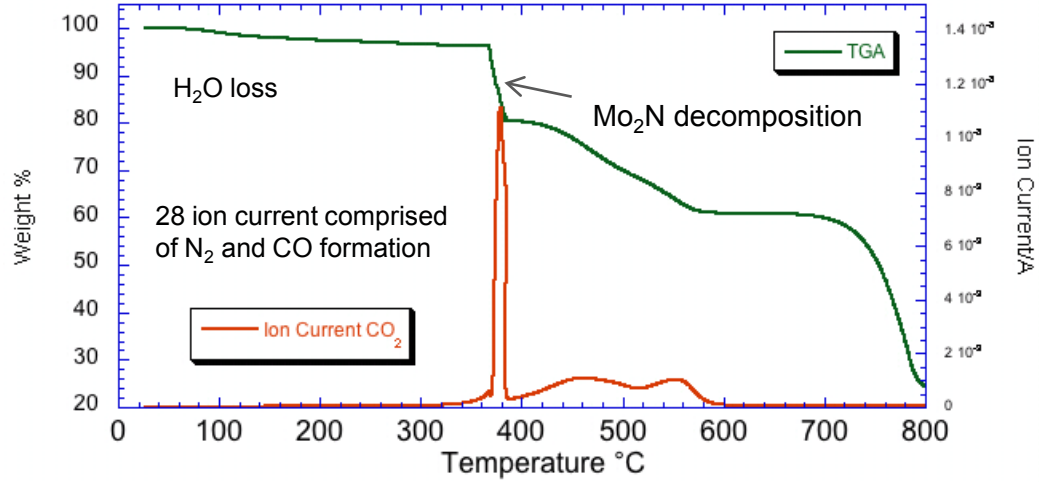
Technical Accomplishments and Progress : More Aggressive Thermal Treatment and Evidence of Enhanced Pt-Support Interaction, 40wt%Pt

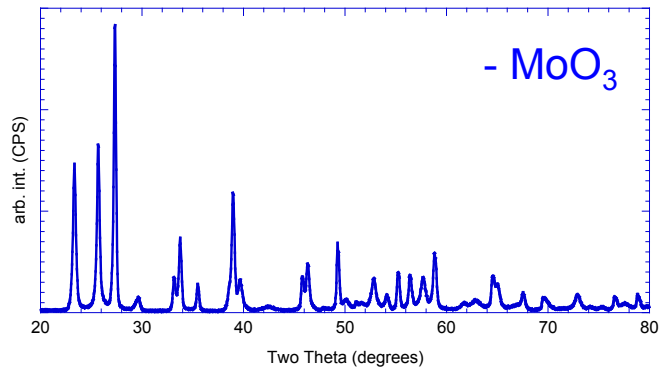
- Mo_2N-C prepared with 40 wt % Pt incorporated into support
  - Pyrolyzed at 950°C
  - 290m^2/g as delivered
- At 40 wt%, now see Pt in XRD
  - Small relative Pt (111) intensity
  - 2 types of Pt?
- Repeat TGA/MS exp's: no methane formation observed.
- Full profile fitting of the XRD data indicate Mo_2N grain growth, Mo_2C formation and an increase in Pt average crystallite size.

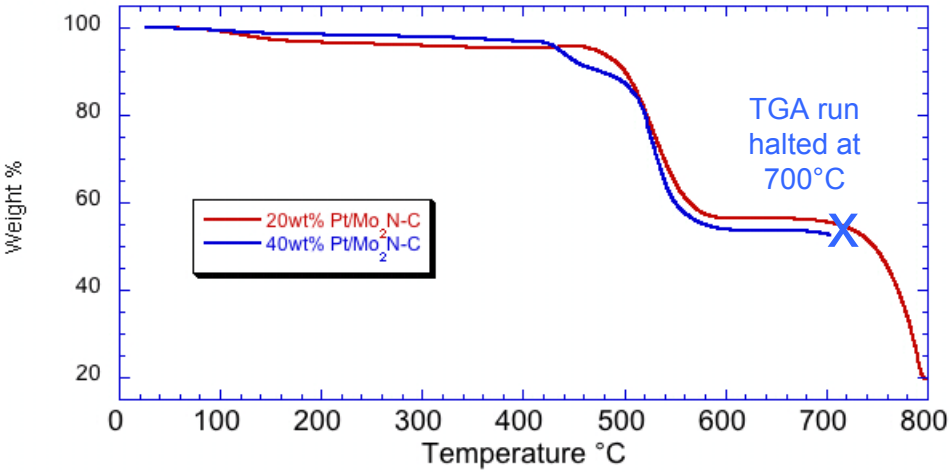


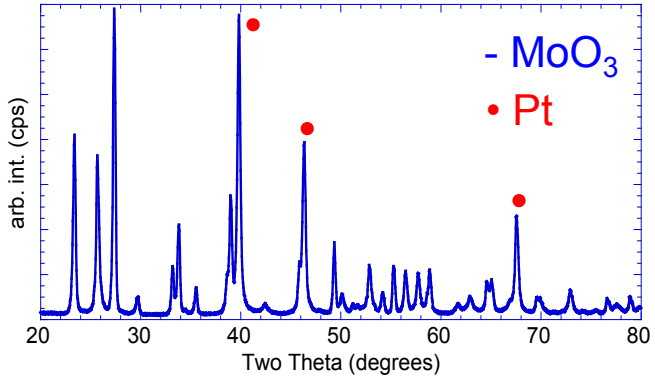
Presently trying to: a) achieve required activity in the as-prepared Pt-Mo_2N-C by studying the properties of a range of Pt doping: 5 – 40 wt% and b) use Pt nucleated during PAD pyrolysis and Mo_2N-C formation as anchors for subsequent Pt disposition.

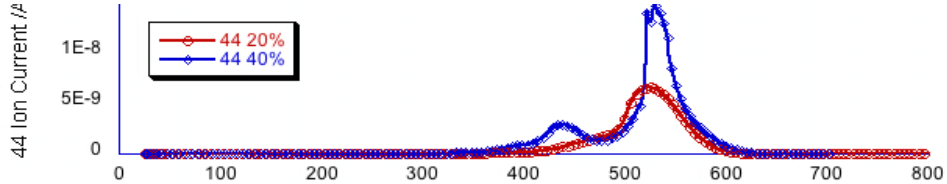
Technical Accomplishments and Progress : Thermal Stability / Studies indicate Pt -Mo_2N interaction stronger than Pt -MoO_3











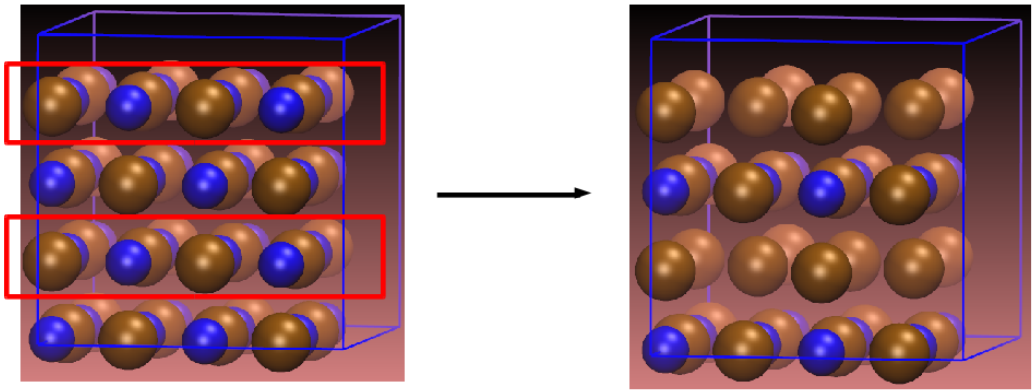
- 40wt% Pt/Mo_2N-C: Pt size increased from 69Å to 360Å commensurate with loss of nitride structure.
- Dramatic *increase* in Pt mobility once Mo_2N converts to MoO_x.

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

- **Aims for FY11 :**
  - Focus on dominant γ-Mo_2N identified from characterization of samples
  - Construct structural models for phase – effect of non-stoichiometry and defect structures
  - Calculate binding energies for platinum mono-layers on surface models
  - Calculate trends in predicted over-potential for models
- **Approach :**
  - Calculations to be performed using plane wave periodic density functional theory calculations (VASP software)

A structural model of γ-Mo_2N

NaCl structure with half of the nitrogen sites vacant

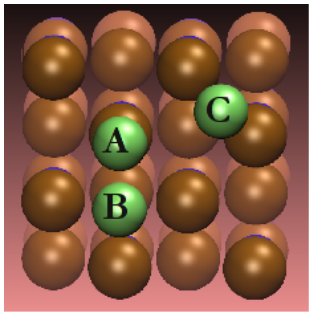


nitrogen vacancies in layers

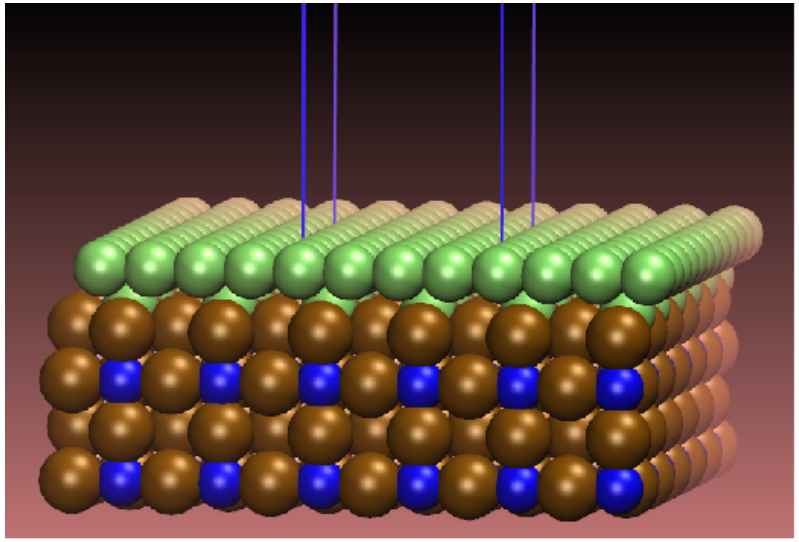
Mo-brown, N-blue

creates MoN and Mo-rich surfaces for Pt adhesion

Technical Accomplishments and Progress: Platinum strongly bound to defective surface



- identify most favourable sites for single Pt atoms
  B (4-fold) > C (bridge) > A (on-top)
- and construct a monolayer based on these results



Mo-brown, N-blue, Pt-green

- nitrogen depleted surface layer promotes stronger binding of platinum compared to other defect models, and other Mo_xN_y phases.
- reduces calculated overpotential for oxygen reduction reaction.

Collaborations / Distribution of Technical Personnel

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

- Materials characterization: XRD, XRF and thermal analysis; Eric Brosha (PI)
- Electrochemical characterization, ink and MEA prep; Lior Elbaz
- PAD synthesis, high surface area powder supports; Anthony Burrell and Karen Blackmore
- Support Modeling; Neil Henson

(Sub - University within DOE H_2 prg.)

- Conductive aerosol derived supports; Timothy Ward and Rosalba Rincon
- XPS characterization; Kateryna Artushkova

(Sub – Fed. Lab. within DOE H_2 prg.)

- TEM Characterization; Karren More (PI – special materials)

- Discussions about manufacturing ceramic supports, materials exchanges, characterization of commercial materials and exchange of data; Rich Zvosec

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Proposed Future Work – FY10 Q4 and into FY11

- Characterization and testing of support materials (on-going throughout the entire project).
- Q8 (M): report on durability of the Pt/Mo_2N catalyst; electrochemical observations with extended CV cycling.
- Scale-up amount of PAD-produced Mo_2N and prepare inks and prepare MEAs .
- Begin fuel cell testing and lifetime-durability observations with Pt/Mo_2N-C.
- Resume sub-oxide titania support work: CV characterization.
- New UNM focus: High surface area Mo_2N and TiO_{2-x} through aerosol synthesis route (primary)/characterization.
- Tech Team meeting participation (Nov ‘11).
- Publications.

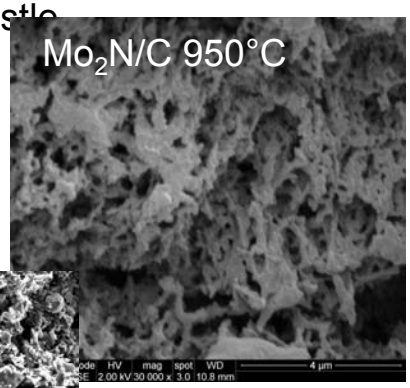
Summary of Technical Progress

- Carbon is present from PAD process and, unless it can removed during initial pyrolysis step, will be present if the PAD process is used to form high SA powders
  - Measurements: ca. *40-50 wt% residual Carbon*
  - It is not clear yet what role the carbon is/will play as a catalyst support
- Mo_2N-C possesses required SA and electronic conductivity for fuel cell use
- Required stability in acid conditions and under potential cycling
- 20 wt% Pt/Mo_2N-C (incipient wetness) has comparable activity for ORR as ETEK
- Pt appears to be associated with Mo_2N and not the residual carbon
  - TGA/MS experiments
  - ORNL TEM characterization
  - CV experiments
- Experimental evidence collected to date indicates a stronger Pt-support interaction than with Pt-C catalysts - backed by modeling results
- Mo_2N-C although not completely understood, is acceptable to move forward to MEA prep and FC testing : "**GO**"

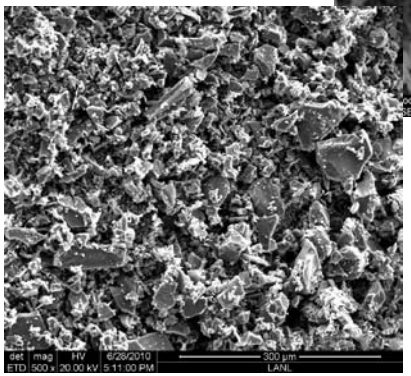
Technical Back Up Slides

Mo_2N & TiO_{2-x} supports via PAD

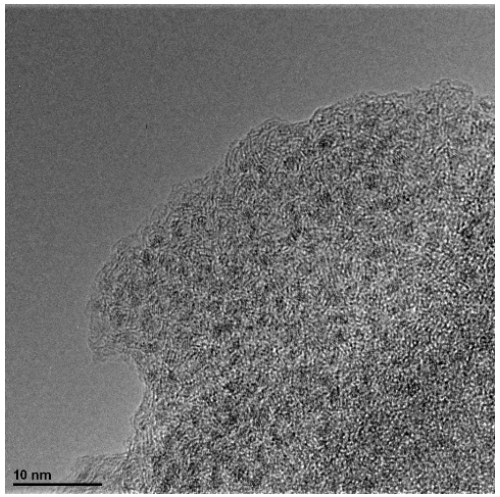
- Surface area as high as 500 m^2/g; 250-300 m^2/g typical
- SEM analysis of Mo-N prepared via PAD.
- Piece of ceramic foam, crushed & prior to grinding using mortar/pestle

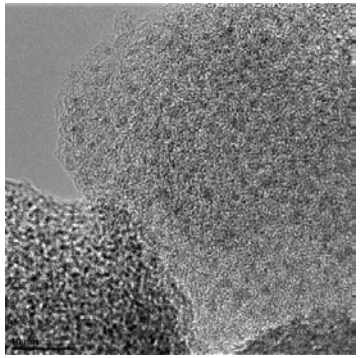


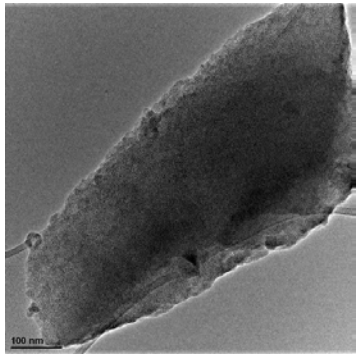
TiO_{2-x}/C 950°C



- TEM from ORNL: Very small particle sizes (< 2nm).
- Highly crystalline structure consistent with cubic Mo_2N and nicely faceted.
- Presence of agglomerates of nano-particles and these can be quite large, ~0.2μm to over 2μm.
- "Unclear what is holding particles together." - carbonaceous materials resulting from the PAD precursor?

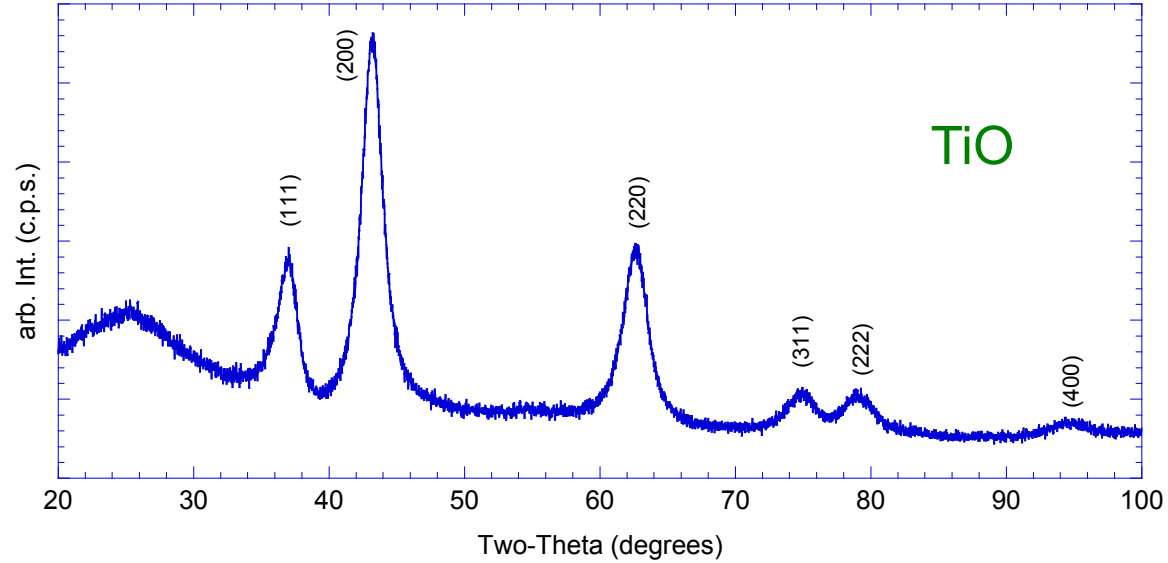


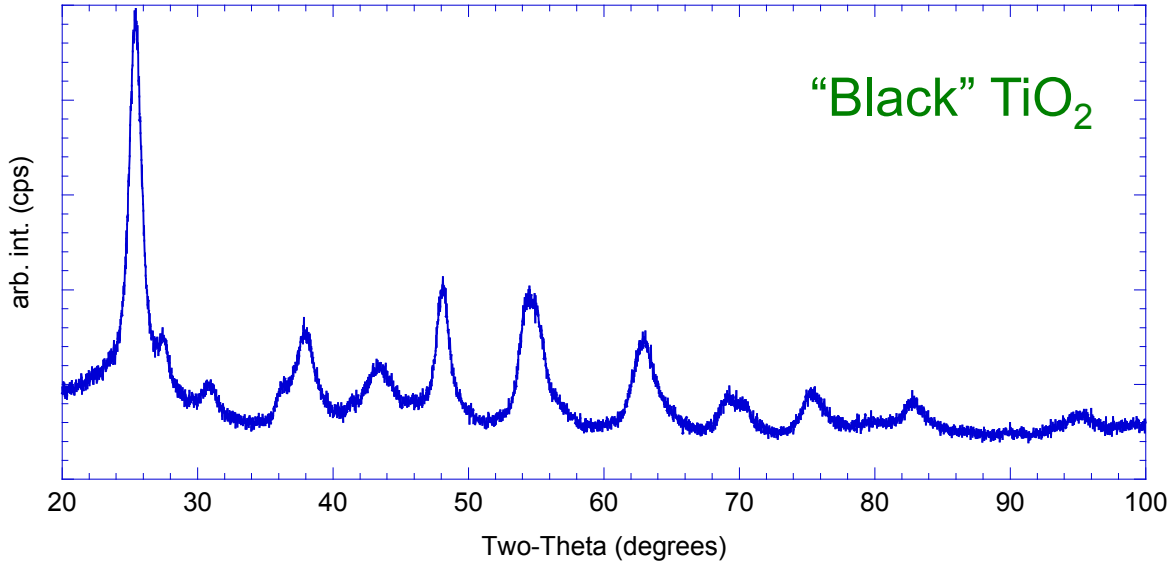




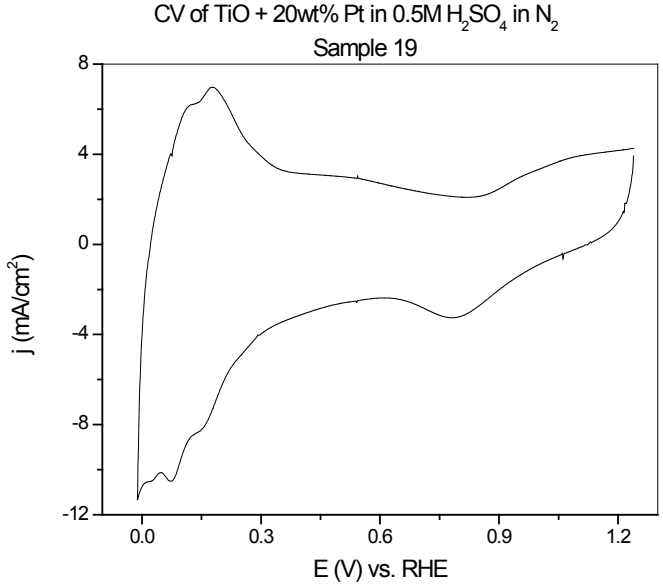
XRD: TiO_{2-x} supports via PAD

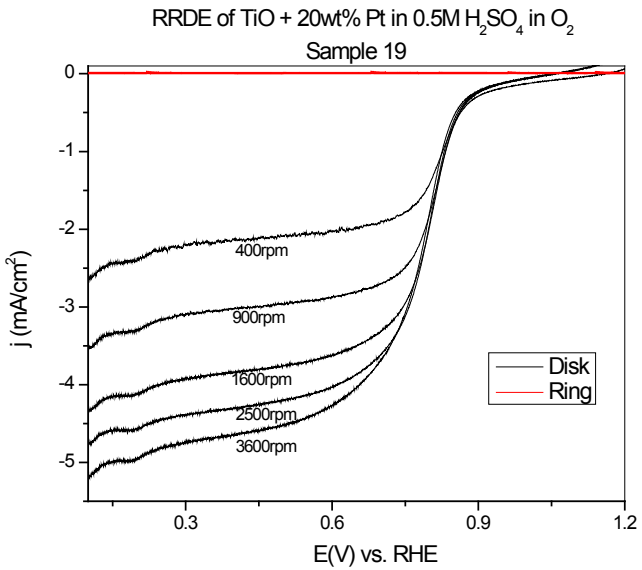
- PAD approach modified for titania work.
- Black, conductive oxides produced without need for post reaction, high temperature H_2 reduction.
- Flow rate and purge time affects resulting phase.
  - Ti_4O_7 yet produced
- Full profile analysis indicates average crystallite sizes ~ 40-42Å for TiO and est. 70Å for Black TiO_2 phase.
- $\mathbf{a}_{TiO}$ = 4.191(2) Å
  - Lit: = 4.177 Å
  - PDF#008-0117

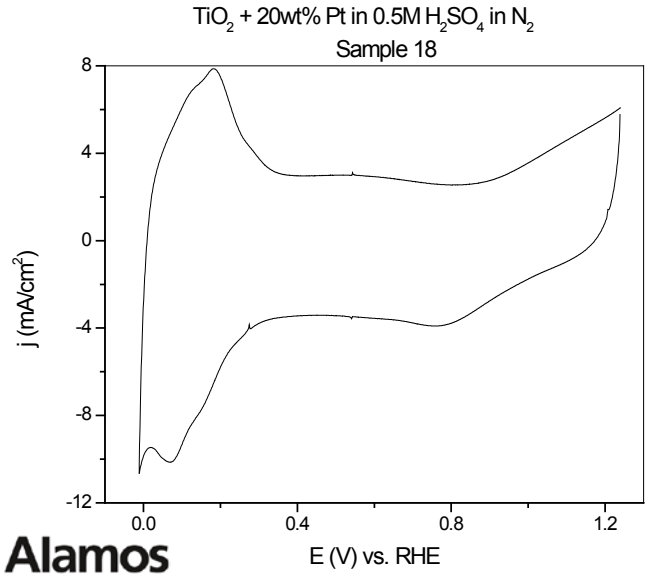


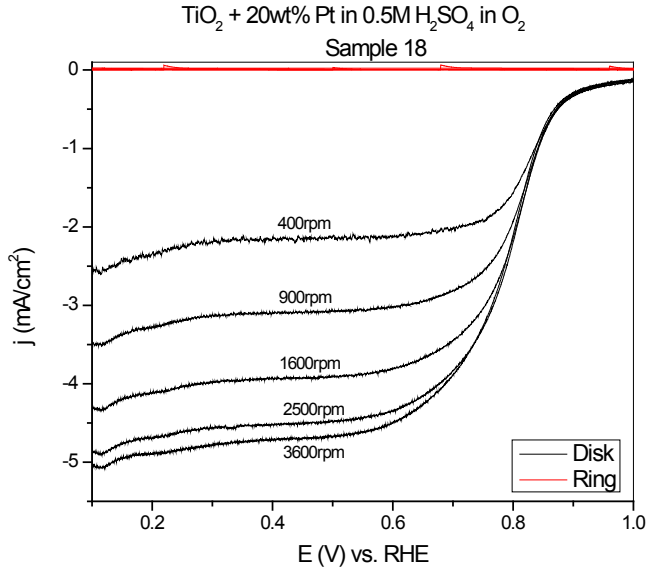


CV and RRDE Characterization : Pt/TiO_2 and Pt/TiO

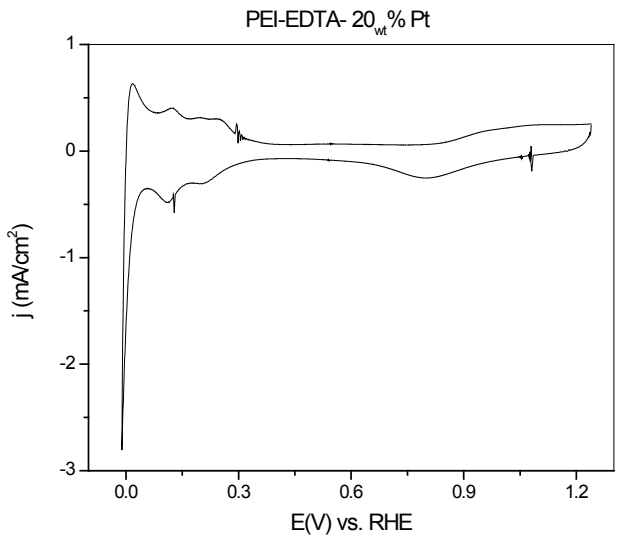


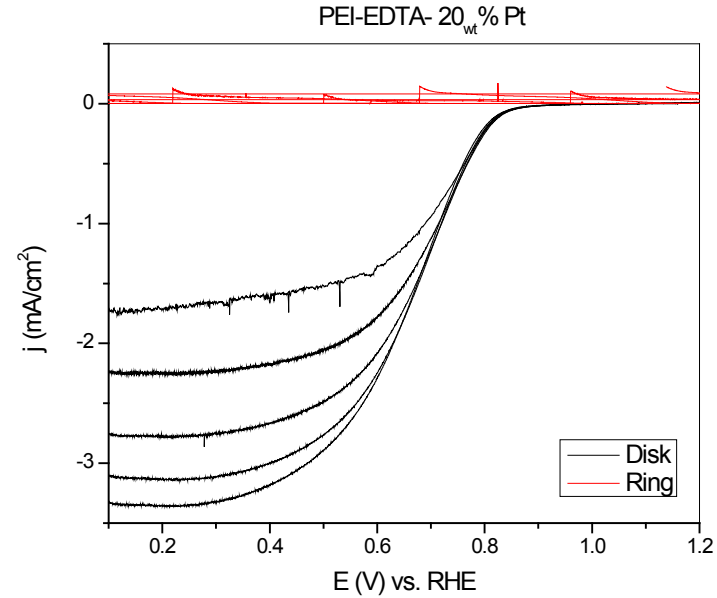


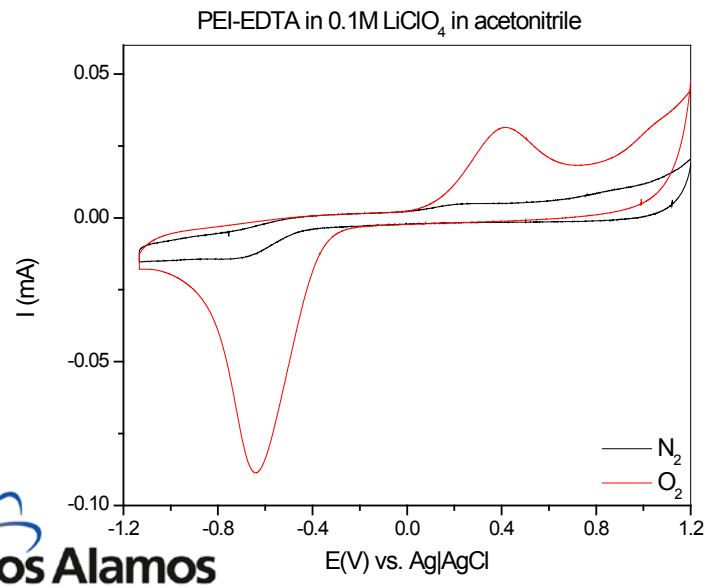


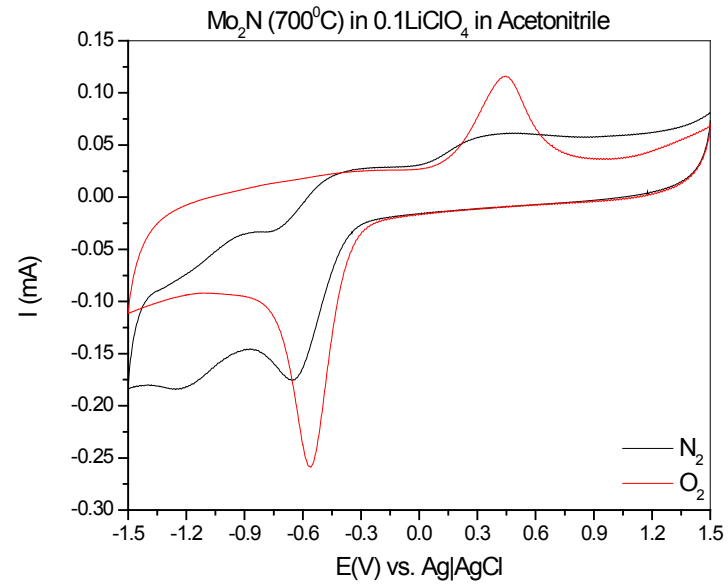


CV and RRDE Characterization : pyrolyzed PEI-EDTA + Pt

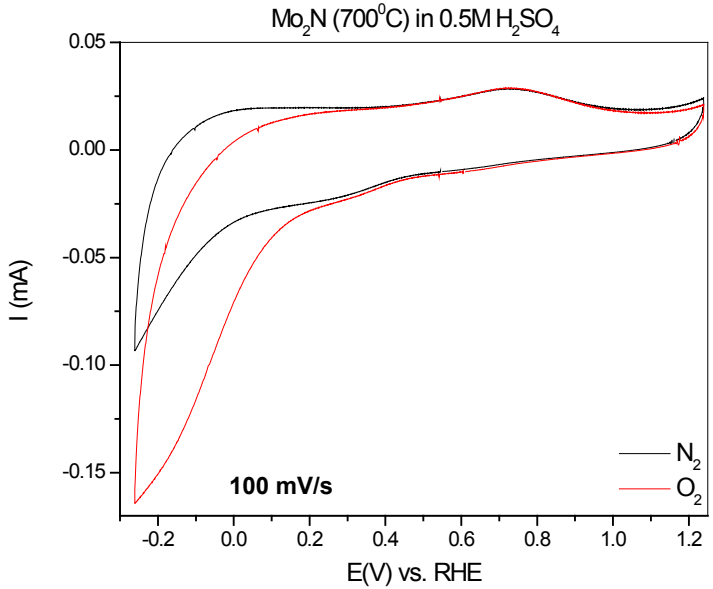


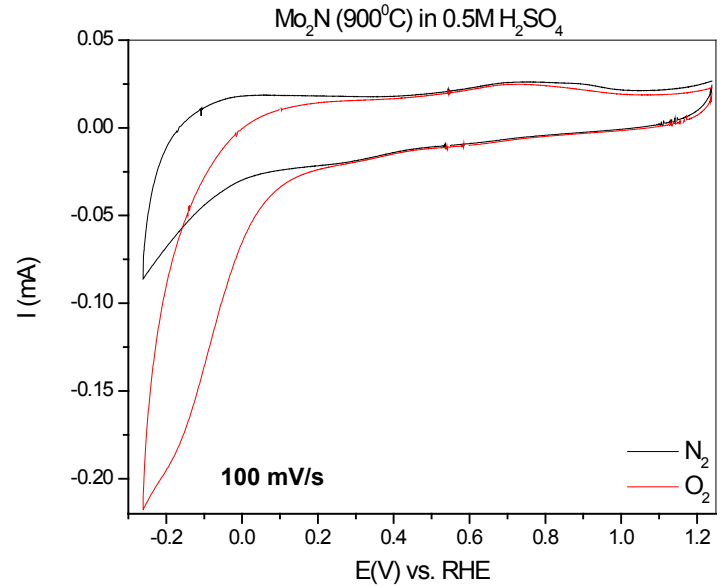
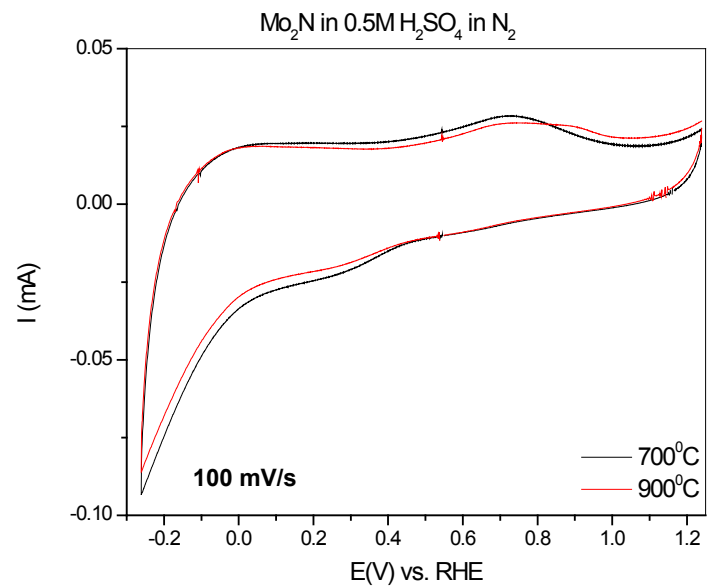






Technical Accomplishments and Progress: Mo_2N – Electrochemical Characterization Indicates Stable Support/Improved from FY10





- The electrochemistry of the heat treated Mo_2N was studied in 0.5M H_2SO_4.
- The Mo_2N devoid of Pt catalyst shows no activity toward ORR.
- The support shows stability in acidic medium (no effect was observed while running multiple CV's with the support).