2012 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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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 2012) : 66%

- **Budget**
  - Total project funding:

  DOE share:$2,000,000

  Cost share: NA

  Received FY11: $250K
  - Funding Received (anticipated) FY12: $500K

- **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)
  - The Materials Foundry (materials synthesis and 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:
  - possess required surface area
  - foster high Pt utilization
  - exhibit enhanced Pt–support interaction
  - adequate electronic conductivity
  - corrosion resistance
  - synthesis method / procedure amenable to scale-up
  - reasonable synthesis costs

Relevance - Technical Targets

Original 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: Experimental Synthesis Methods

- Polymer assisted deposition (PAD) nitrides and sub-oxides of titania.
  - PAD precursor routes to produce ceramic materials with small average crystallite sizes determined via XRD and TEM.
  - Powders, bulk catalysts prepared by forming metal organic get followed by pyrolysis under controlled atmospheres.
  - Process produces ceramics with exceptionally small average crystallite sizes but at a not insubstantial penalty of residual carbon (reported last year).
- 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.
- Alternative synthetic methods (UNM)
  - Aerosol spray pyrolysis of alcohol or PAD solutions with addition of pluronic block co-polymers as templating agent followed by post-synthesis acid etch.
  - Focus shifter from conductive oxides studies to apply methods for nitrides and sub-oxides of titania this FY.

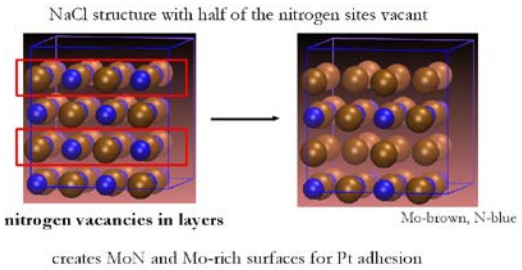
Approach: Focus on Select Support Candidate Materials

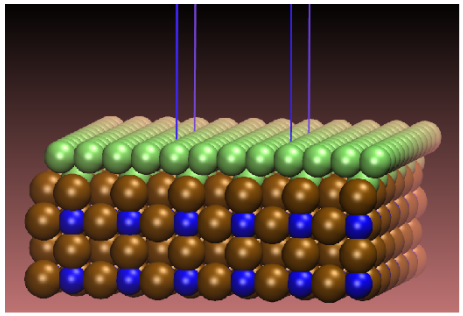
- Rare-earth hexa-borides via A-T-P; (No-Go)
- Conductive oxide supports via templated aerosols (UNM); (No-Go)
- Transition metal nitrides: Mo_2N; (Go)
  - Corrosion resistance, high electronic conductivity, catalytic properties
  - Computational studies show ©-Mo_2N surface heavily defected surface that promotes strong binding of Pt (FY11)
  - Thermal analysis studies supportive of modeling predictions
- Utilize carbon PAD process to prepare metal carbides: Mo_2C; (Go)
  - Deliberately push PAD reaction from nitride to carbide
- Titania and sub-stoichiometric titania (TiO_{2-x}); (Go)
  - Magnéli phase: high electronic conductivity, refractory, stable in acid media
  - Resistance to oxidation and demonstrated electro-catalytic activity for both hydrogen and oxygen / Pt
- Novel carbon/anatase composite via PAD approach (FY12)

Technical Accomplishments and Progress: Computational Studies Adhesion Energetics of Pt on Ceramic Supports (FY11)

- **Approach :**
  - Calculations to be performed using plane wave periodic density functional theory calculations (VASP software)
  - Construct structural models for phase – effect of non-stoichiometry and defect structures
  - Build model for dominant surfaces; determine most favorable binding sites for single and multiple Pt atoms on surfaces
  - Calculate trends in predicted over-potential for models

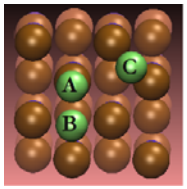
A structural model of γ-Mo_2N





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.

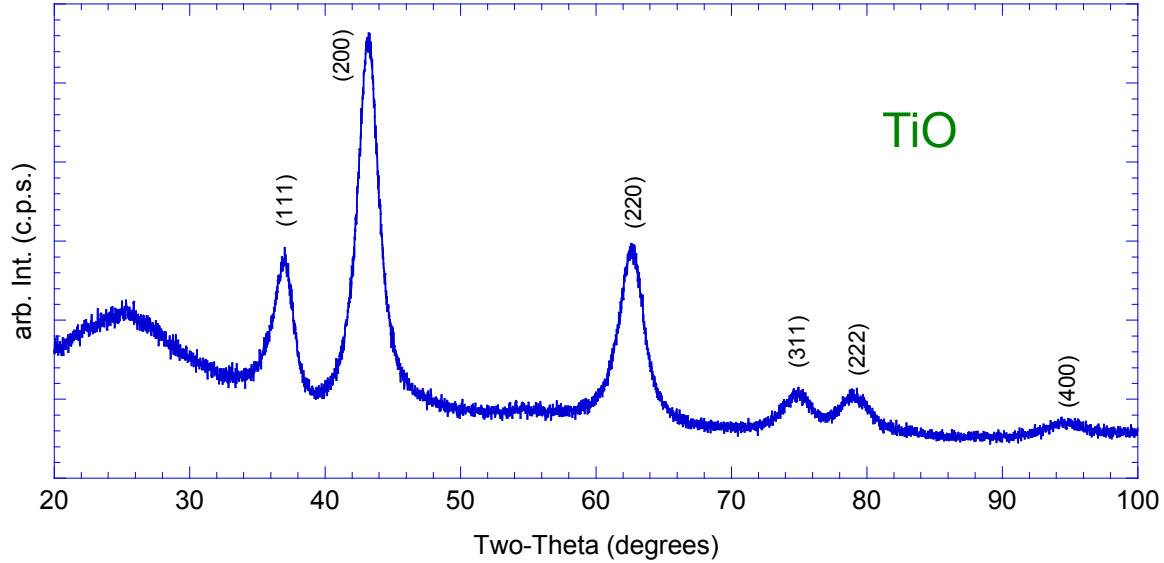


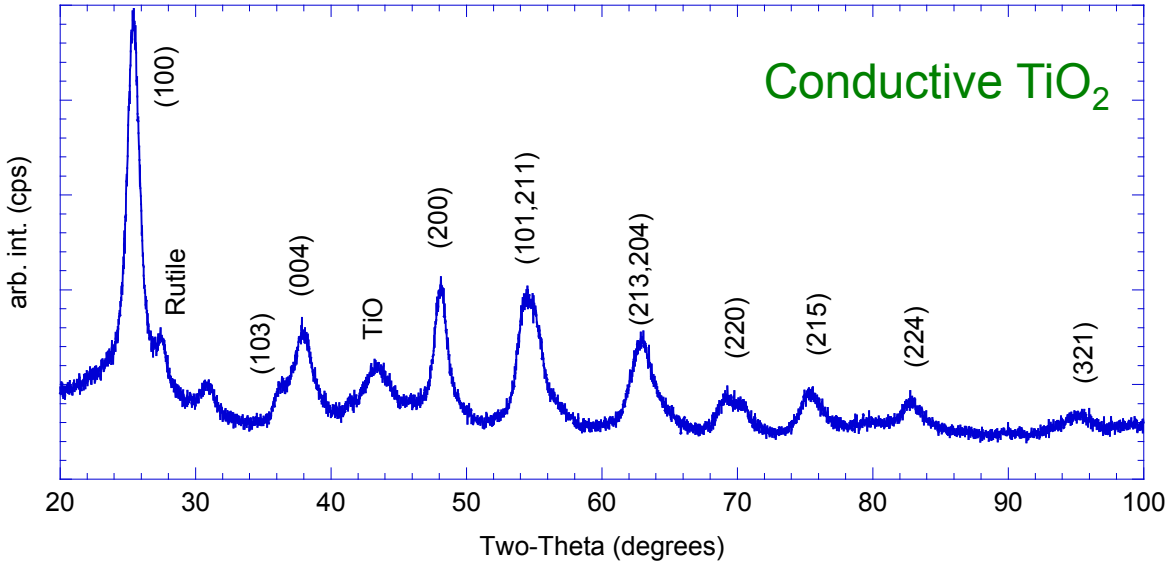
- identify most favourable sites for single Pt atoms
  B (4-fold) > C (bridge) > A (on-top)
- and construct a monolayer based on these results

- Initial CV ½ cell characterization (FY11)
- Thermal analysis (FY11)
- Studies of effect of residual carbon (FY11)
- MEA prep (FY12)
- Fuel cell performance testing (FY12)
- Durability testing (FY12)

Technical Accomplishments and Progress (FY11): 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.
  - Direct Ti_4O_7 synthesis not yet accomplished.
- Full profile analysis indicates average crystallite sizes 41-42Å for TiO and 81-82Å for "black" TiO_2 phase.
- BET surface areas: 230 to 260m^2/g

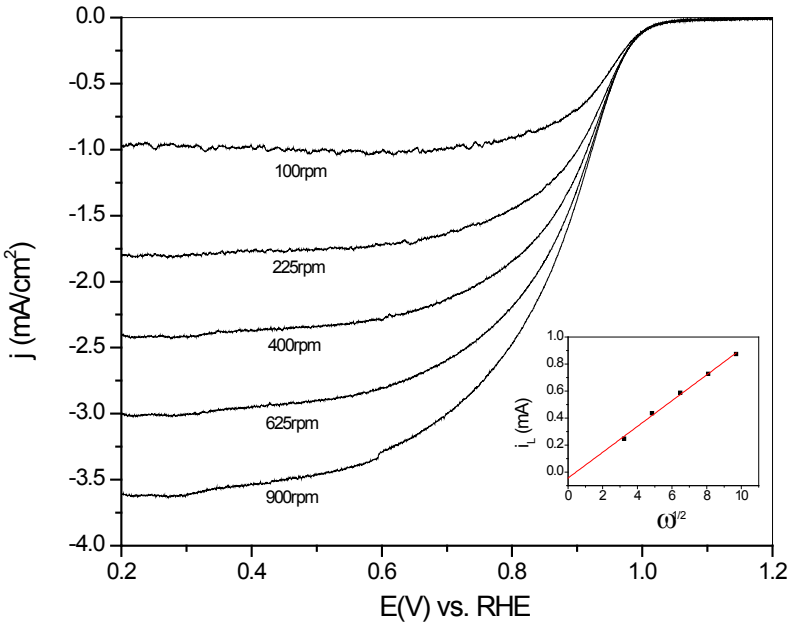


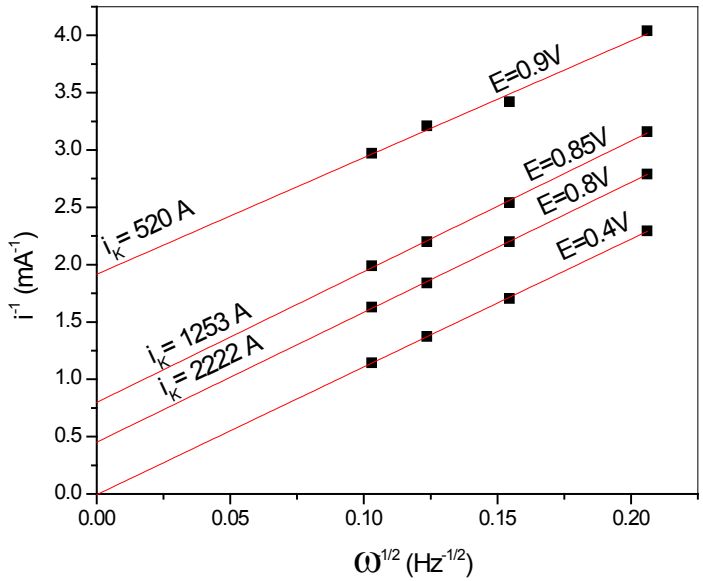


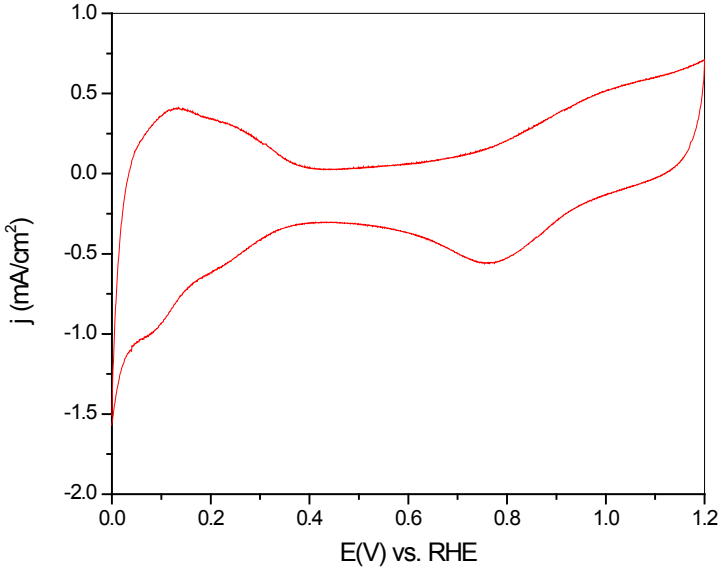
Approach: FY12 Milestones – Go and No/Go Decisions

- As of AMR meeting date: project is *on schedule* to meet 3rd year milestones and candidate materials have been selected for fuel cell testing, durability testing to compare with Pt/C.
- All Go/No-Go decisions for down-select of candidate materials scheduled in project have been made.
- Identified and studied carbon residues inherent by-product of the PAD approach – 2011 AMR. Effect on durability studied (FY12).
- Emphasis this FY on electrochemical characterization and durability testing of support materials (on-going throughout remainder of project).
- Ink, MEA prep, and fuel cell testing with Mo_2N, Mo_2C and titania supports began in FY12.
- Remainder of FY12 and FY13: support and MEA optimization, fuel cell testing, and durability studies.
- AST measurements in conjunction with DWG.

Technical Accomplishments and Progress FY12: 20%Pt/TiO_2(PAD)







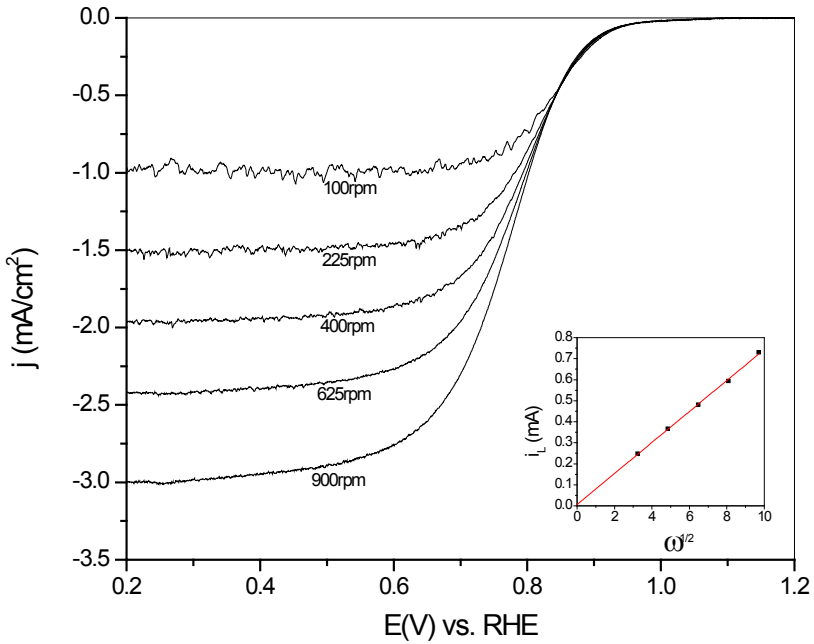
Conditions:

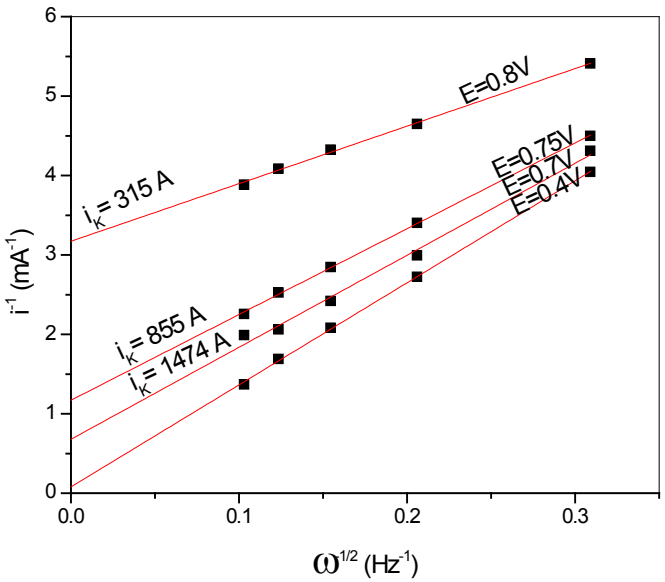
- Catalyst loading: 24μg Pt/cm^2
- RRDE: 0.1M $HClO_4$; scan rate 5mV/s
- CV: 0.1M $HClO_4$; scan rate 100mV/s

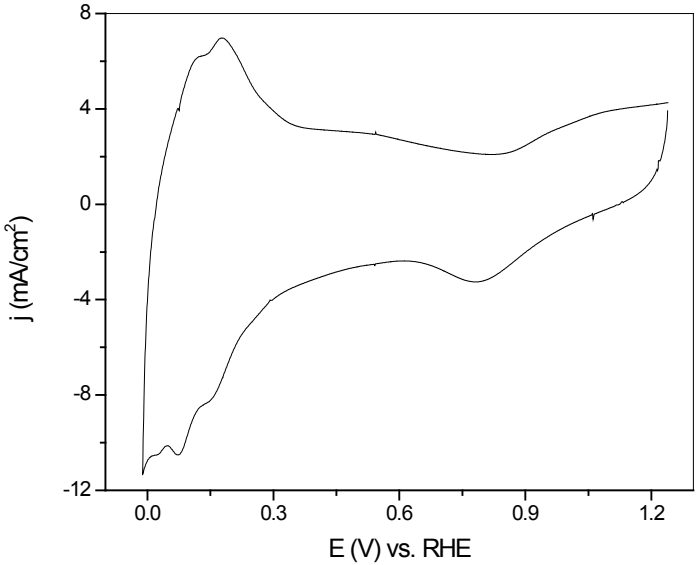
Results:

- Half wave potential: $E_{1/2}$=0.94V vs. RHE
- Kinetic current @0.8V : i_K= 2222A
- Number of electron (from Levich) = 4.0 e^-
- EASA = 57.5 m^2/g_{Pt}

Technical Accomplishments and Progress FY12: 20%Pt/TiO (PAD)







Conditions:

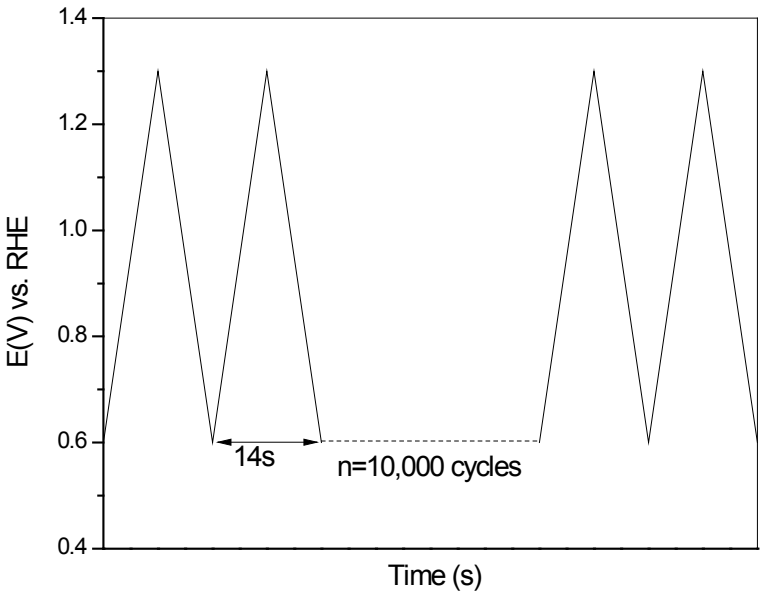
- Catalyst loading: 24μg Pt/cm^2
- RRDE: 0.1M $HClO_4$; scan rate 5mV/s
- CV: 0.5M H_2SO_4; scan rate 100mV/s

Results:

- Half wave potential: $E_{1/2}$=0.84V vs. RHE
- Kinetic current @0.8V : i_K= 315A
- Number of electron (from Levich) = 3.3 e^-
- EASA = 61 m^2/g_{Pt}

Technical Accomplishments and Progress FY12: Accelerated Stress Test (AST) Half Cell

Accelerated stress tests were conducted with the various ceramic supports in a half cell configuration to study their durability.



Conditions:

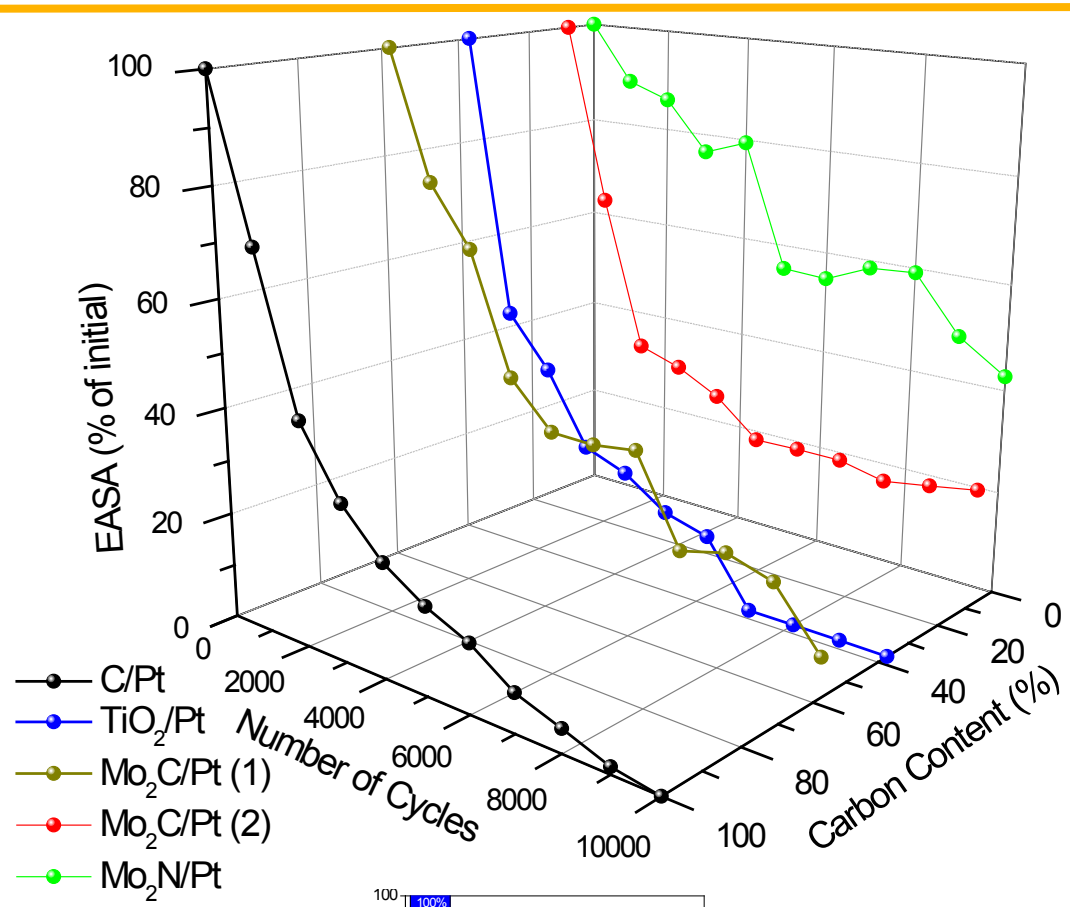
- Room temp. ~23°C
- Solution: de-aerated 0.1M $HClO_4$ in DI water
- Cycles: 10,000 between 0.6 and 1.3V vs. RHE
- ECSA meas. every 1000 cycles (cycling between 0.0 and 1.2V vs. RHE)

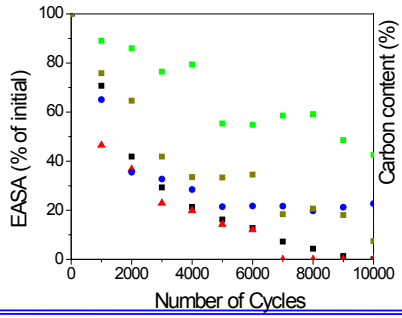
Motivation:

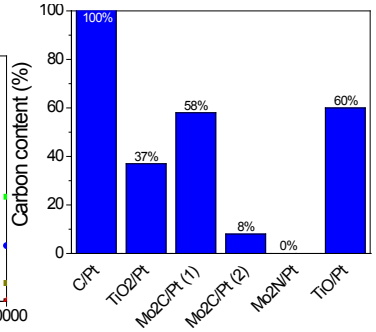
- The ceramic supports produced in this project should show superior stability when compared to common carbon supports.
- Half cell experiments allow one to isolate the new support from other parameters which may interfere with the experiment (by keeping the number of variables as low as possible).

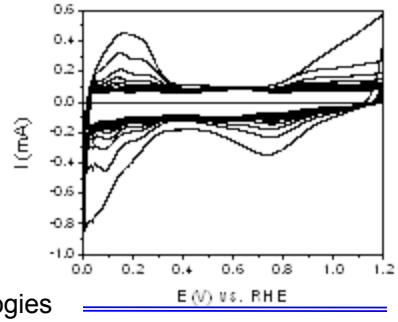
Technical Accomplishments and Progress FY12: Results of Initial AST

- AST's show that carbon supported catalyst loses its activity after 10,000 cycles.
- There is a correlation between the carbon content in the ceramic supports studied in this work and the loss of the activity.
- In order to make durable ceramic for fuel cells we need to get rid of all carbon.



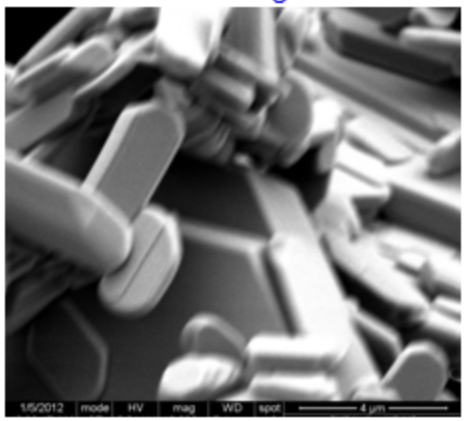


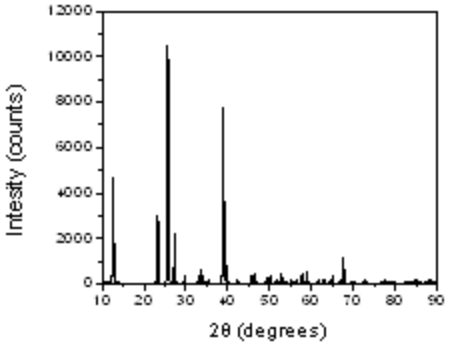




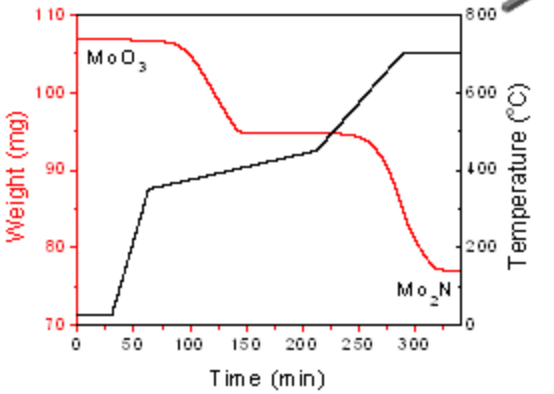
Technical Accomplishments and Progress FY12: Carbon free Mo_2N synthesis

MoO_3

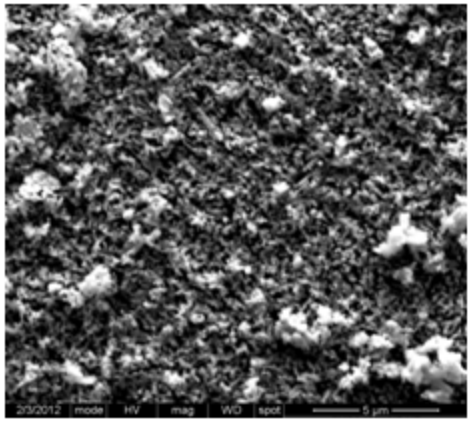


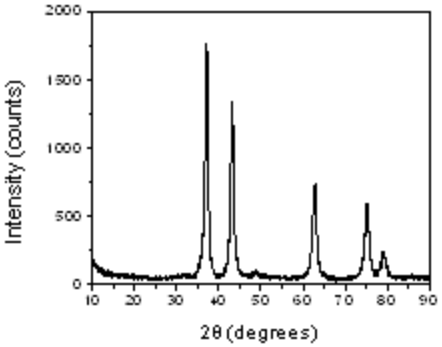


NH_3

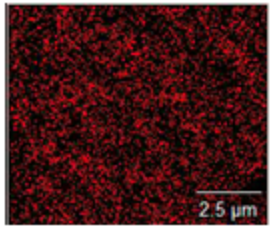


Mo_2N

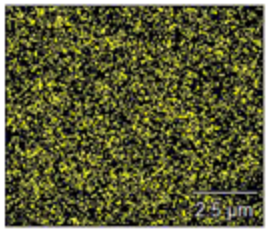




N



Mo



- We have started to synthesis carbon free Mo_2N according to known recipes from literature.
- One inherent problem with the known recipes is that they produce a relatively low surface area.
  - Supports (up to ~100 m^2/g).
- The crystallite size of the Mo_2N is dependent on the crystallite size of the MoO_3 precursor.
- The synthesis of nano-scale MoO_3 will be pursued via the PAD and aerosol processes.

Summary of Technical Progress FY12: Aerosol Synthesis of Mo_2N through Direct Nitridation and via Mesoporous Mo-oxide Formation

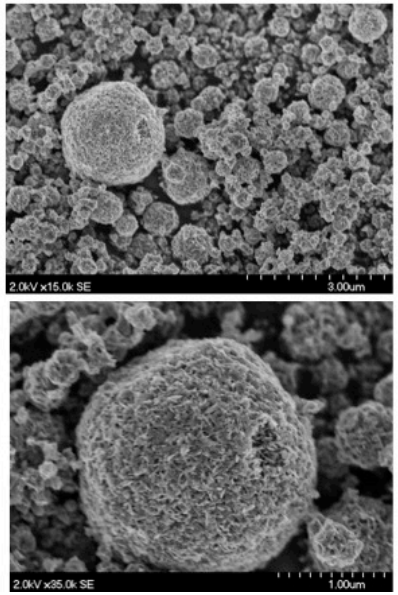
- UNM looking at synthesis of Mo_2N w/o residual carbon yet maintain surface area, etc.
  - Aerosol of aqueous ammonia molybdate+urea with N_2/7%H_2 carrier; 500-950°C not effective under these conditions
- Working on approach of aerosol mesoporous Mo-oxide synthesis using surfactant templating methods: applying early knowledge gained from Nb-Ru_yO_z support work.

Approaches to Aerosol Synthesis of Mesoporous Mo-Oxide

- Surfactant Templating Synthesis Approach
  - Precursor: aqueous Ammonium Molybdate Tetrahydrate ($(NH_4)_6Mo_7O_{24}$•$4H_2O$)
  - Air carrier gas
  - Surfactants
    - cetyltrimethylammonium bromide (CTAB)
    - Pluronic triblock copolymer (F127, P123)
  - Synthesis temperatures: 250°C, 350°C, 450°C
- Post processing (wash or calcination) to remove template

H_20 + F127 + EtOH + Ammonium Molybdate 450C

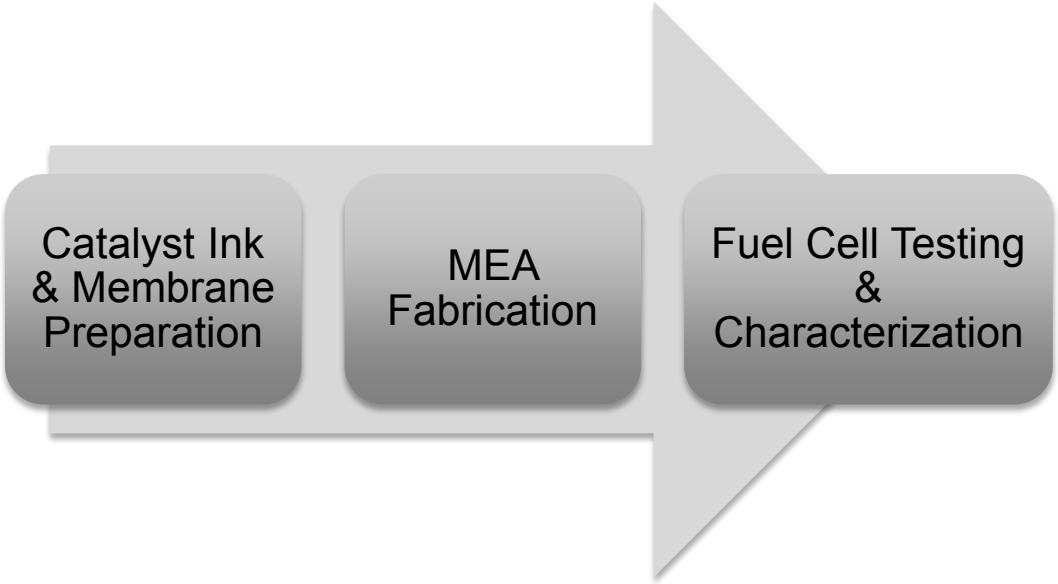
S.A. ~ (N/A)

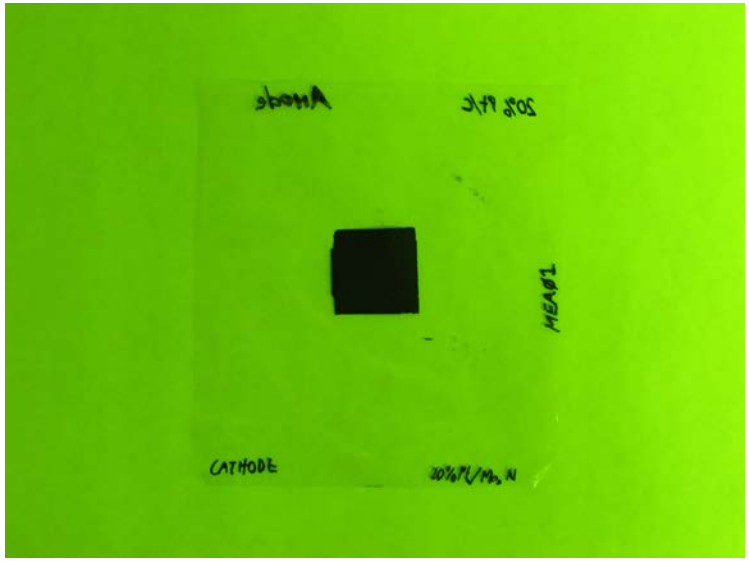


- One synthesis experiment conducted using Pluronic Block Copolymer (F127) Template ($EO_{106}PO_{70}EO_{106}$)
- Only characterization so far is SEM
- Very different morphology and microstructure than seem with CTAB – template here may be serving like polymer glue for oxide nanocrystals
- Need TEM/XRD on as-produced material, and full characterization after template removal

Operated by Los Alamos National Security, LLC for NNSA

Technical Accomplishments and Progress FY12: Fuel Cell Testing



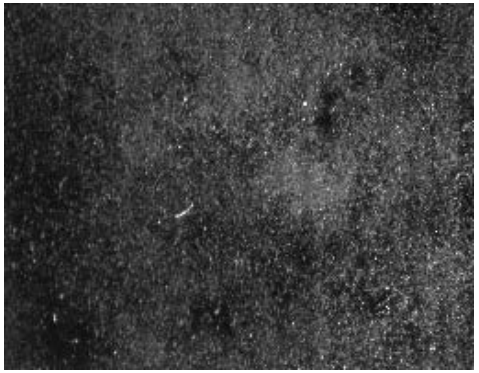


- Utilize LANL's standard ink formulation to compare with previously tested MEAs.
- Prepare MEAs with Hot-Press Decal Transfer Method to start (conventional Pt/C methods).
- Test MEAs in an operating fuel cell using identical test protocol (i.e. H_2/Air flow, Cell Temp, Pressure, and RH).
- Characterize using XRF, cyclic voltammetry, AC impedance, and VI curves.

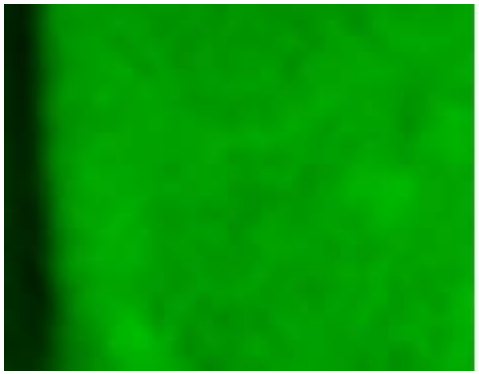
LANL standard hardware

Technical Accomplishments and Progress (FY12): MEA Preparation and Characterization

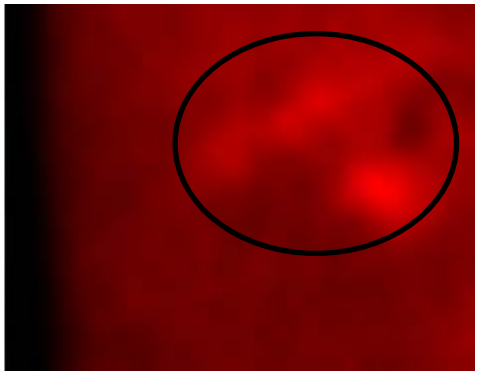
EDAX mapping and X-ray tomography of TiO_2/20%wt Pt ink before Fuel cell testing



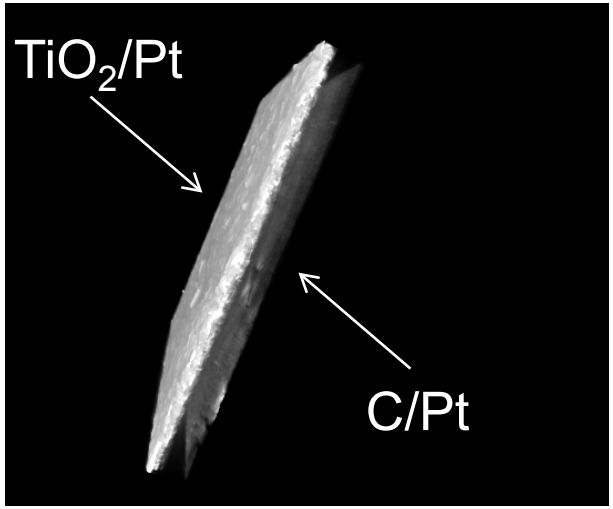
TiO_2/20% Pt

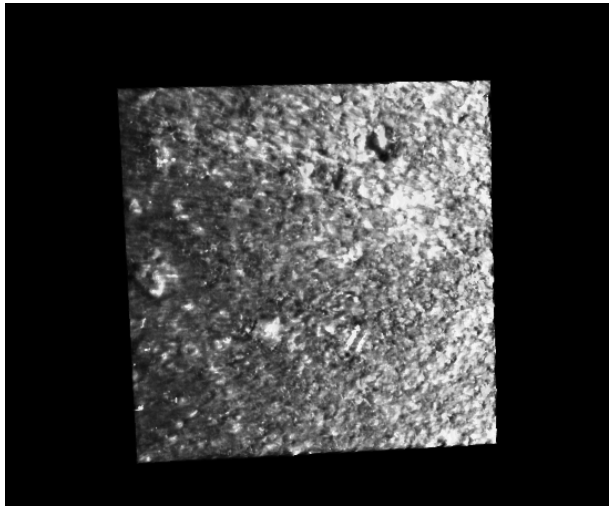


Pt mapping



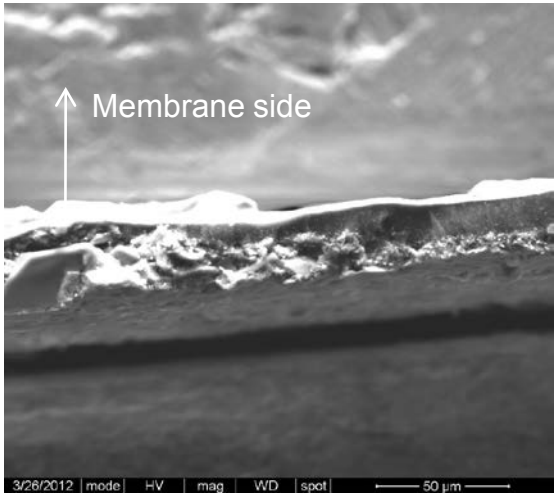
Ti mapping

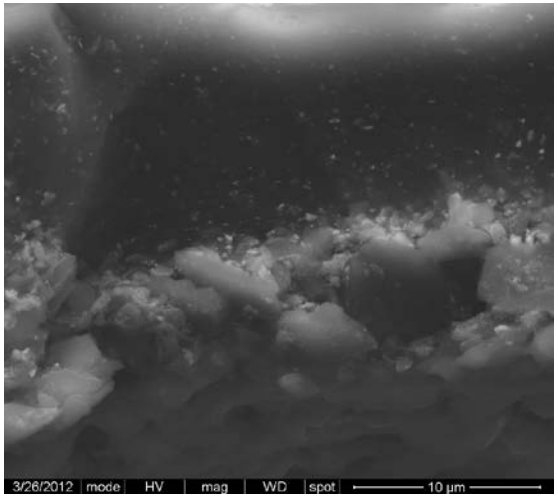


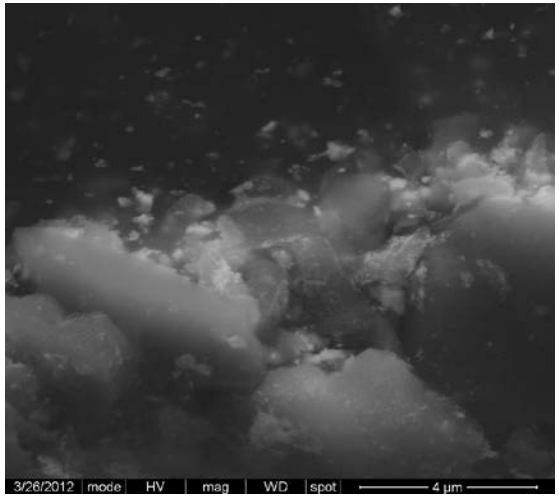


Pt is relatively well distributed, Ti is not well distributed. TiO_2/Pt thickness is relatively high.

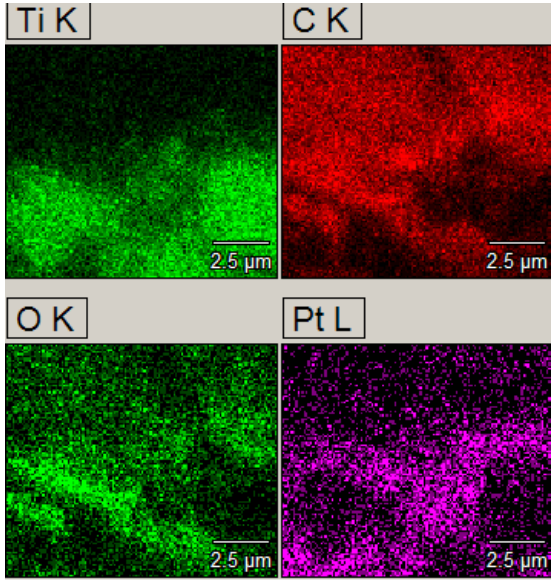
Technical Accomplishments and Progress FY12: SEM of the TiO_2/Pt Layer Cross Section



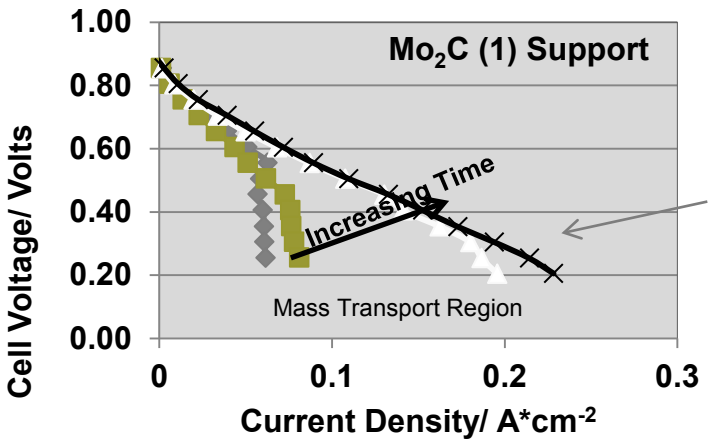




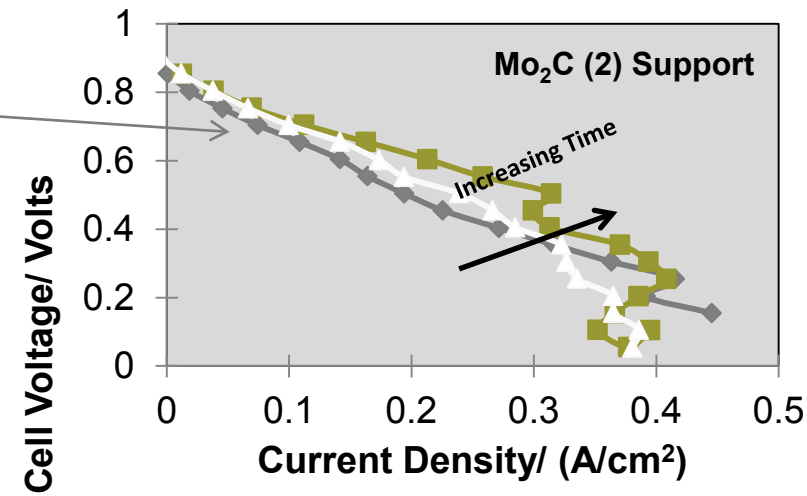
- MEA fabrication needs to be optimized
- Ti tends to separate from the carbon
- Pt seems to favor the Ti over the C
- The loss of carbon can result in the loss of all the support.



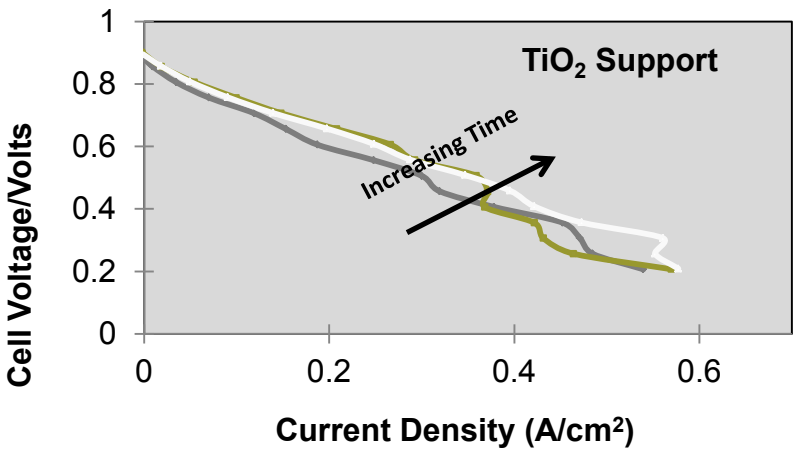
Technical Accomplishments and Progress FY12: Fuel Cell Testing

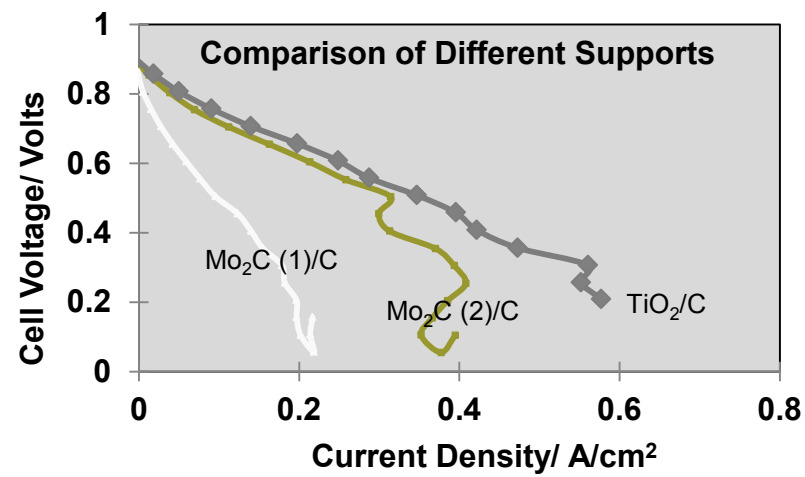


The **Mo_2C** support shows a gradual improvement over time, clearly in the mass transport region **(on the left),** but better processing led to an overall increase in performance **(on the right).**



Further improvements are anticipated through better understanding of support positioning within the electrode.

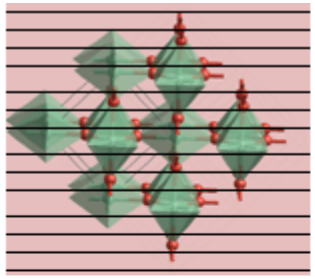




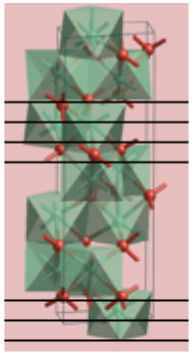
- The **TiO_2** support shows gains in the **kinetic region**
  - this points toward an increase in catalytic activity (possible through catalyst morphology, i.e. better gas access and/or three phase boundary)
  - and an increase over time along the polarization curve

- 5 cm^2 MEA: 0.2 ± 0.02 mg Pt/cm^2
- Cell Temp: 80°C, 100% RH, Back Pressure: 30 psig ,GDL: SGL 25BC, H_2/Air Flows: 160/550 sccm (fixed)
- VI's taken in ~ 24 hr increments

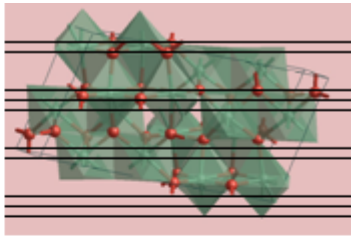
Technical Accomplishments and Progress FY12: Models for Magnéli phases, Ti_nO_{2n-1}; Calculated binding energies for Pt on <100> Ti_4O_7



TiO_2 rutile



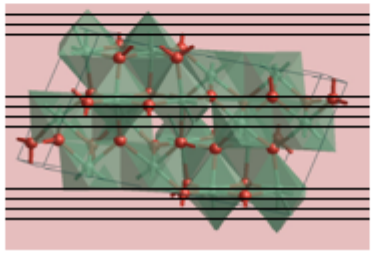
Ti_2O_3



Ti_4O_7

- Midway between TiO_2 and Ti_2O_3 structures
- Magnéli phases : regions of normal rutile structure with TiO_6 octahedra separated by crystallographic shear planes → unique surface structures
- Oxygen defects confined to planes
- First member of the series, Ti_4O_7, is best characterized

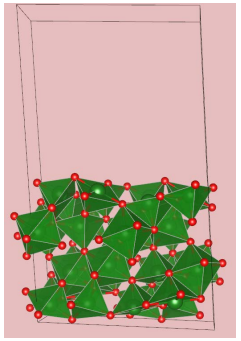
Surface models for Ti_4O_7



bulk

calibration: good reproduction of experimental bulk structure →

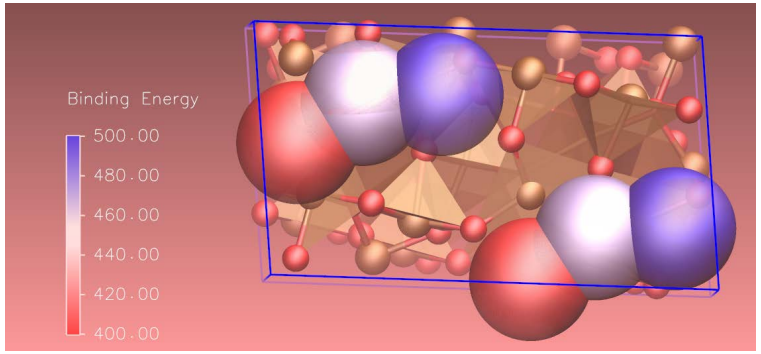
	a	b	c	α	β	γ
experiment	11.19	7.13	12.46	95.0	95.2	108.7
calculated	11.29	7.20	12.54	95.2	95.6	108.9

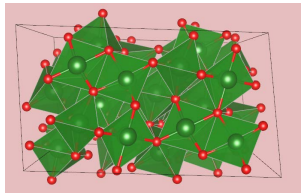


<100> side view

- Spheres are calculated binding sites for platinum on surface color coded by binding energy in $kJmol^{-1}$
- Three sites related to the symmetry of the surface, each less strongly bound that for Pt on Pt <111> (~630 $kJmol^{-1}$)
- Similar binding energies for other low index surfaces

Looking down on <100> surface





<100> top view

Proposed Future Work – FY12 Q4 and into FY13

- Characterization and testing of support materials (on-going throughout the entire project).
- Send samples to ORNL for TEM characterization.
- Send samples to UNM for XPS characterization.
- Continue fuel cell testing and lifetime-durability observations with Pt/Mo_2N-C (via PAD), Pt/Mo_2N, and TiO_2/C (via PAD).
- Continue durability testing both fuel cell and half cell.
- Optimization of MEA fabrication with ceramic supports.
- High surface area Mo_2N and TiO_{2-x} through aerosol synthesis route at UNM and characterization.
- Publications.

Summary of Technical Progress for FY12

- Electrochemical characterization including emphasis on durability studies has been increased in FY12 and will continue to be primary focus throughout the rest of year.
- Fuel cell testing under way with supports derived from PAD process and durability ½ cell studies started with Mo_2N derived from direct nitridation of MoO_3
- Return to work on titania supports – put on hold after FY11 Go decision to focus on Mo_2N support.
  - Modeling of Ti_4O_7 phase started although calculations suggest that Pt affinity not as good as Pt on defected Mo_2N surface.
- Ink formulation and MEA preparation started.
  - Established methods optimized for Pt/C need to be changed for ceramic supports.
- Fuel cell testing started in FY12.
- AST testing show correlation between durability and carbon content in the supports – ceramic supports with least carbon contamination show better durability.
- Catalyst and MEA optimization work on target for FY13.

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; Karen Armstrong
- Support Modeling; Neil Henson
- Fuel Cell Testing; Tommy Rockward

(Sub - University within DOE H_2 prg.)

- Conductive aerosol derived supports; Aaron Roy and Timothy L. Ward

(Sub – Fed. Lab. within DOE H_2 prg.)

- TEM Characterization; Karren More

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Technical Back Up Slides

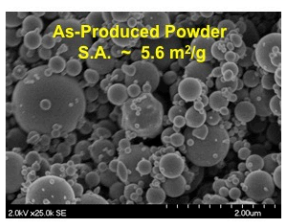
Technical Accomplishments and Progress FY12: Aerosol Development work at UNM - CTAB Templating

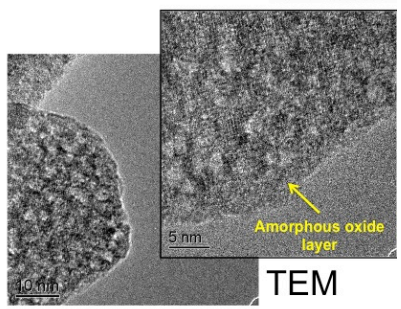
Approaches to Aerosol Synthesis of Mesoporous Mo-Oxide

- Surfactant Templating Synthesis Approach
  - Precursor: aqueous Ammonium Molybdate Tetrahydrate ($(NH_4)_6Mo_7O_{24}\bullet 4H_2O$)
  - Air carrier gas
  - Surfactants
    - cetyltrimethylammonium bromide (CTAB)
    - Pluronic triblock copolymer (F127, P123)
  - Synthesis temperatures: 250°C, 350°C, 450°C
- Post processing (wash or calcination) to remove template

H_20 + CTAB + Ammonium Molybdate 450 C

BET Surface Area
- as-produced 5.6 m^2/g
- after 2 wash: 10.7 m^2/g
- 400 C air calcine: 7.3 m^2/g



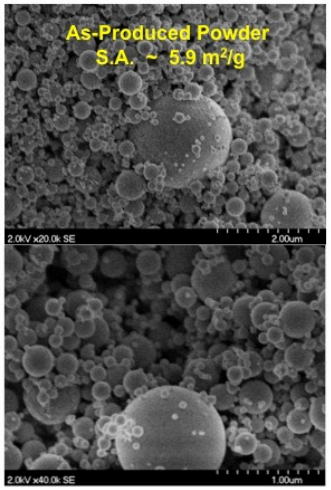


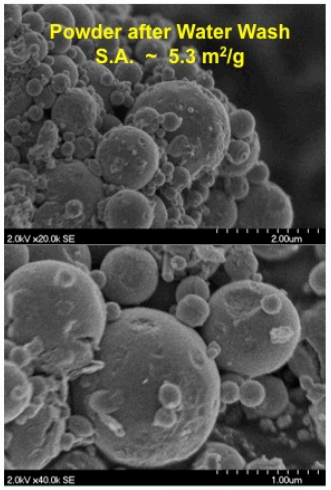
TEM

- TEM of as-produced powder shows lattice fringes (not identified yet) and apparent poorly ordered internal mesostructure
- would anticipate significant internal surface area if accessible after template removal
- water wash and air calcination has not provided large S.A. increase

H_20 + CTAB + Ammonium Molybdate 350 C

Some surface spalling apparent after washing, but no significant increase in BET surface area. Need to explore further.





Observations on CTAB Templating

- TEM on one sample indicates internal mesostructure, but without strong order – would expect reasonably high S.A (based other materials we have made) if it can accessed (need more TEM and other characterization)
- Water wash leads to some spalling and breakdown, but does not open up substantial surface area
- Calcination at 400 C did not open up much porosity
- Will try a higher T, but calcination may also promote S.A. loss by crystallization or sintering
- Also looking at an etching procedure followed by wash, based on appearance of amorphous oxide layer in TEM (also saw this in the Nb-O work)

Acknowledgments

- We wish to thank Nancy Garland and the U.S. DOE Hydrogen and Fuel Cells Program for providing funding for this work.