2013 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

Fuel Cell Technologies Office

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Overview

Timeline

- Project start : September 2009
- Project end : September 2013
- Percent complete (as of May 2013) : 92%

Budget

- Total project funding:
 - DOE share \$2,000,000
 - Cost Share: NA
- Received FY12: \$500K
- Funding Received (anticipated) FY13: \$500K

<u>Technical Barriers Addressed</u>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 ECSA)

Partners

- LANL (Project Lead)
- UNM
- ORNL
- The Materials Foundry

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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





Approach: Experimental Synthesis Methods

- New synthesis method developed at The Materials Foundry at end of FY12
 - Loosely based on Rapid Expansion Synthesis (RES) method (patent pending) developed for this project in FY11 by Dr. Jonathan Phillips.
 - Mechanical mixtures of moly and Pt sources with urea are rapidly heated to induce reaction commensurate with expansion in sample volume in a controlled atmosphere.

Polymer assisted deposition (PAD) of molybdenum carbide

- PAD precursor routes to produce ceramic materials with small average crystallite sizes (determined via XRD and TEM) and potential for high surface areas.
- Process produces ceramics with exceptionally small average crystallite sizes but at a not insubstantial penalty of residual carbon.
- 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 Pt adhesion energies and nature of binding sites.
- Alternative synthetic approaches (UNM); attention to scale up
 - Continue non-PAD bulk and aerosol approaches to nitride and carbide synthesis.



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Approach: Focus on Select Support Candidate Materials and Synthesis Approach

- Rare-earth hexa-borides via plasma torch; (No-Go)
- Conductive oxide supports via templated aerosols (UNM); (No-Go)
- Utilize PAD process to prepare metal carbides: Mo₂C; (No-Go end of FY12)
 - Deliberately push PAD reaction from nitride to carbide
 - Substantial amount of residual carbon remaining in sample shown to negatively impact support durability in AST ¹/₂ cell testing.
- Conductive carbon/anatase composite via PAD approach (No-Go end of FY12)
 - Presence of carbon from PAD significantly impacts durability.
- Transition metal nitrides: Mo₂N; (Go FY12)
 - Mo₂N found to be 2nd most durable support in AST ½ cell testing but complicated surface properties and susceptibility to surface oxidation raises some doubts about longevity in FC.
- Mo₂C and Pt/Mo₂C preparation via new synthetic methods developed at TMF
 - ORNL TEM analysis revealed highly dispersed Pt Nano-raft structures
 - Advantages in activity and durability readily apparent
 - Highly resistant to, or different degradation mechanism than for commercial Pt/XC-72 (AST)
 - Experimental confirmation about impact of synthesis approach on durability



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Technical Accomplishments and Progress: Support Durability Testing Results of Go-selected Materials (FY12)









- Durability protocol a useful tool to test more durable ceramic supports for PEMFCs.
- The LANL AST used has been shown to effectively degrade Pt/carbon in reasonable experiment time.
- Half cell experiments allow 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): Cubic Mo₂C prepared using a synthesis approach

- Mo₂C and (5 wt% Pt)/Mo₂C obtained from Dr. Jonathan Phillips and The Materials Foundry using new approach developed as an outgrowth from previous work associated with this project.
- Samples sent to Dr. Karren More at ORNL for TEM analysis.
- Like PAD process, high dispersions of Pt possible during formation of support, but....
- ... unlike PAD process, little excess carbon residue present in samples and samples are electrocatalyticaly active <u>as-prepared</u>.





TEM images of (a) sheets of nano-crystalline Mo_2C , (b & c) nano-wires of Mo_2C , and (d) large sheet of densely packed Mo_2C .



Technical Accomplishments and Progress (FY12): Issues Immediately Identified Regarding MEA Preparation with New Supports













- As of AMR meeting date: project is on schedule to meet 4th year milestones and ink, MEA optimization, and fuel cell testing (durability) is underway.
- All Go/No-Go decisions for down-select of candidate materials scheduled in project have been made (FY12).
- Identification of a ceramic support candidate that electrochemical measurements, durability testing and modeling results agree is a viable candidate.
- Ceramic support AST for a simple ½ cell testing protocol used that effectively kills Pt/XC-72 commercial catalysts in a reasonable experiment time.
- Emphasis this FY on fuel cell durability testing and electrochemical characterization of catalyst materials.
- Fuel cells prepared and tested and subjected to high potential holds to study impact on un-optimized cathodes.



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Technical Accomplishments and Progress FY13: Synthesis of carbonfree Mo₂C w/wo Pt (The Materials Foundry)



- After numerous iterations of trying to get rid of the excess carbon in Mo₂C (via the PAD process and others), The Materials Foundry (led by Dr. Jonathan Phillips) was successful at synthesizing a Mo₂C free of excess carbon.
- A simple, one step synthesis of Mo₂C was conducted in solid phase.
- Molybdenum metal precursor was mixed with solid urea and heated to 700°C under reducing atmosphere w/wo platinum salt to give Mo₂C w/wo Pt.

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* RA: Reducing atmosphere such as ammonia or hydrogen

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Technical Accomplishments and Progress FY13: Electrochemical Performance of Pt-imbedded Mo₂C

- Pt (5 wt%) imbedded Mo₂C showed highly dispersed Pt (XRD).
- Carbon-free Mo₂C, with and without 5% Pt incorporated in precursor;





- XRD Analysis shows cubic Mo₂C with very little excess carbon visible in XRD trace. **a** = 4.225 Å
- Avg. crystallite size determined by full profile fitting ca. 22 Å
- No evidence in XRD data to indicate presence of Pt



Technical Accomplishments and Progress FY13: Mo₂C/Pt Morphology

- From SEM pictures, the Mo₂C is composed of two different morphologies:
 - large chunks of agglomerated Mo₂C crystals.
 - 2) Nano-wires of Mo_2C .
- The composition of the newly synthesized Mo₂C was measured using EDAX and support the stoichometry and lack of excess carbon.
- 4.8 wt% Pt was detected using EDAX and confirmed with XRF.







Technical Accomplishments and Progress FY13: Mo₂C/Pt Morphology

Characterized by two agglomerate morphologies (TEM image): (1) spongy-porous (yellow) and (2) sheet-like (blue)





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Technical Accomplishments and Progress FY13: Mo₂C/Pt Morphology

Pt is homogeneously dispersed on the Mo_2C crystallite surfaces as single atoms and as 3-6 atom clusters/rafts, *not* as Pt nanoparticles.

- TMF Pt Nano-raft (5 wt%) / Mo₂C
- High-angle annular dark field (HAADF) STEM images taken by Oak Ridge National Lab.





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Technical Accomplishments and Progress FY13: Mo₂C/Pt XPS Results

- XPS data were collected at UNM and compared to Pt/XC-72.
- XPS data clearly shows different Pt spectra than for Pt on carbon and suggest enhanced Pt-support interaction compared to Pt/XC-72.
- Pt BE is shifted to higher energies for the Mo₂C support compared to XC-72.
- Typical Pt catalysts supported on C, see metallic Pt around 71 eV and Pt-C around 71.5 eV.
- Pt on Mo₂C show no metallic Pt that is not interacting with the support. Major Pt species associated with carbon.
- No Pt carbide detected (71.1 eV); bonding characteristics between Pt and C are of complexing type such as in organometallic compounds.

High resolution XPS Pt 4f and C 1s spectra for Pt on Mo₂C and Pt on XC-72





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- Mo is present as carbide (70%) with rest as mixture of Mo IV and Mo VI oxides.
- Surface oxidation is consistent with air exposure post synthesis.
- Bond of Pt to either free C or to carbon in molybdenum carbide would appear at he same BE in the Pt spectra.
- TGA analysis (bulk) post removal of phys-adsorbed species shows little excess/free carbon so the Pt – carbon association is entirely with the support.





* "Evidence of Enhanced Electrocatalytic Activity of Molybdenum Carbide Supported Platinum Nano-rafts," L. Elbaz, N.J. Henson, K. Artyushkova, K. More, J. Phillips, and E.L. Brosha, *in preparation* (2013).



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Technical Accomplishments and Progress FY13: Surface passivation

- Prior to AST's, the supports are cycled for ~100 times (0-1.2V vs. RHE @ 100mv/s) until reaching a steady state.
- The Pt/Mo₂C CVs show an oxidation process occurring during this pre-treatment. This
 oxidation is presumed to form a thin oxidized layer on the surface of the support, and
 passivating it.
- The support does not seem to lose its electronic conductivity since the surface at the pointof-contact of the support particles is not oxidize nor the core of the particles.



Technical Accomplishments and Progress FY13: Mo₂C/Pt Activity



- The Nano-rafts show enhanced catalytic activity when compared to Pt on carbon or deposited on Mo₂C (post support synthesis). E_{1/2} is 0.92 and 0.89 V vs. RHE and onset potential is 1.11 and 1.04 V vs. RHE for Nano-rafts and Pt/XC-72 respectively.
- The reaction is predominantly 4 electron reduction to water as insignificant amounts of peroxide were detected (<1%) using RRDE. The limiting current correlates to 3.6 electron process according to the Levich equation.
- The mass activity at 0.9V vs. RHE is 290 and 190 A g⁻¹_{Pt} for Nano-rafts and Pt/XC-72, respectively.





Technical Accomplishments and Progress FY13: Mo₂C/Pt Durability

- The presence of excess carbon is detrimental to the durability of the support.
- When compared to Pt deposited on carbon-free Mo₂C, the Nano-rafts on the same support seem to be significantly more durable.
- Carbon-free Mo₂N is still a good candidate. May show even better durability w/ Pt Nano-rafts.
- Pt/XC-72 losses ~90% of its activity after 5000 cycles whereas the Nano-rafts are losing less than 10%.







Technical Accomplishments and Progress FY13: Fuel Cell Testing Experimental Set-up



- Fuel Cell: 5 cm² Active Area
- Gas Diffusion Media: SGL 24 BC
- H₂/Air: 160/550 sccm fixed
- Back pressure: 30 psig
- Relative Humidity: 100 %
- Cathode: 5%Pt/Mo₂C (Nano-raft); 0.2mg_{Pt}/cm²
- Anode: 20%Pt/XC72; 0.2 mg_{pt}/cm²
- Concerns at onset or work:
- Electrode thickness may induce mass transport and catalyst access issues.
- Hot-pressing may not be suitable due to the hardness of the support (i.e. piercing of the membrane).

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Technical Accomplishments and Progress FY13: Fuel Cell Testing

- Initial hold 24 hr at 1.2V was tolerated but subsequent 1.2V hold induced losses that were readily apparent in the mass transport region of the IV.
- AC Impedance data support this finding.

LANL standard hardware







- 1st MEA (back-up technical slides) exhibited cross-over issues and local membrane thinning leading to hole formation and failure.
- Initial performance and impedance data of MEA#1 similar before loss but with higher OCV (back-up technical slides).

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Technical Accomplishments and Progress FY13: Fuel Cell Testing; Impedance Results



- Initially the CTR decreased as did the voltage.
- After 190 hours of operation and three consecutive 24h voltage holds at 1.2V, the CTR remained unchanged, while the onset of mass transport became more pronounced.
- This indicates that the electrode kinetics are stable to voltage hold.
- The lowering of the OCV was attributed to higher H₂ cross-over.
- The decrease in performance over time is solely attributed to mass transfer for both samples.





Technical Accomplishments and Progress FY13: Fuel Cell Testing, SEM Cross-section of MEA post operation





Thickness of cathode varies from 20 μ m to as much as 70 μ m.



Technical Accomplishments and Progress FY13: Fuel Cell Testing, MEA Post-mortem

- General observations point to need to change ink/MEA preparation using ceramic supported catalyst. Must address:
- Cathode thickness
- Cathode density high porous cathode microstructure of Pt/C catalysts plays important role leading to reduced mass transport losses and is lacking here
- Support uniformity: Presence of inhomogeneity / 2nd phases









Technical Accomplishments and Progress FY13: Fuel Cell Testing, MEA Post-mortem, cont'd





- Back-scatter imaging and EDS analysis shows formation of oxide within cathode post multiple 24hr 1.2 V holds.
- Oxide layer identified at membrane/cathode interface as well as areas away from interface with agglomerates of oxide located well away from the interface.
- XRD of catalyst recovered from cathode show MoO₃ but <u>no Pt</u>.



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Summary of Technical Progress FY13: New routes to Mo₂C

- TMF Pt Nano-raft structures created in-situ with Mo₂C support formation introduced us to a new material with improved durability.
- Unlike PAD-prepared Mo₂C, little residual C but at expense of surface area.
- New method developed for this project: Alternative precursors and Sacrificial Anode Support (SAS)
- Aerosol method possible for greater control of Mo₂C microstructure
- Can Pt Nano-raft structures be replicated using synthesis methods to increase SA?



 $SA \sim 28 m^2/g$

- synthesis temperature
- Lower T_{synthesis} with greater H₂ concentration will lead to smaller particles and higher surface area

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Technical Accomplishments and Progress FY13: Modeling Results

- (100) MoC_{0.5} surface model
- Layer of Pt atoms was created on (100) using simple structural model
- The Pt-Pt distance on carbide structure is 3.0Å indicating forced registry with the surface of the support.
- Pt-Pt distance for Pt/C: typically 2.80Å on Pt (111) surface
- The d-band center energy for Pt atoms on this surface is -2.42 eV, lower when compared to -1.88 eV from recent work on Pt (111) surfaces.
- Calculations of over-potentials and effect of support on Pt solubility next.

 $MoC_{0.5}$ (100) Pt model (a) top view and (b) side view.

Mo = brown C = green

(a)



Pt = black

"Molybdenum Carbide-Carbon Composite Support for Fuel Cell Catalysts," I. Elbaz, C. Kreller, N. Henson, and E. Brosha, Journal of Power Sources, Spring 2013.

Summary of modeling work: Agreement with experimental observations and XPS data.

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Summary of Technical Progress for FY13

- Ceramic supports for PEMFC cathode catalysts have been identified in this project and tested for enhanced ½ cell durability compared to commercial Pt/XC-72 catalysts.
 - A novel Mo₂C support utilizing Pt Nano-raft structures shows both enhanced activity and durability compared to Pt/XC-72 catalysts.
- Pt imbedded into/onto the support during synthesis process more durable and active for ORR compared to post synthesis Pt disposition.
- Fuel cell testing for durability has started in FY13.
 - Initial performance indicates optimization of catalyst and method of MEA fabrication will require work.
 - Initial loadings and cathode microstructure lead to undesirable performance.
 - Obvious mass transport issues identified, cross-over, but not loss of kinetics
- Focus on understanding cause of degradation in first fuel cell test.
- Remainder of project will focus on application of AST protocols to fuel cells with to validate that durability seen in ½ cell measurements carries over to fuel cell.
 - In parallel with improving fuel cell performance by changing MEA to accommodate ceramic support.



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Modeling

Fuel cell

- Understand source activity and enhanced durability of Pt Nano-raft structures.
- Optimization of ink and MEA preparation. Continue FC durability testing.
- Improve fuel cell performance!
- Scale-up of batch size and optimization of support surface area and Pt loading.
- Understand degradation mechanisms through durability testing / bulk quantities and recovery of fuel cell materials.
- Extend synthetic approach to other ceramics that may have been dismissed from prior work.



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Collaborations / Distribution of Technical Personnel



- Materials characterization: XRD, XRF and thermal analysis; Eric Brosha (PI)
- Electrochemical characterization; Lior Elbaz
- Support Modeling; Neil Henson
- Fuel Cell Testing, MEA and ink preparation; Tommy Rockward



- Conductive aerosol derived supports; Aaron Roy, Alexey Serov, Plamen Atanassov, and Timothy L. Ward
- > XPS Characterization; Kateryna Artyushkova



> TEM Characterization; Karren More





Technical Back Up Slides



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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



XPS Speciation data Pt Nano-raft Mo₂C



C and Pt speciation for Pt on Mo₂C and Pt on XC72 samples

	Mo ₂ C	Mo-C	C gr	C-C	C*	C-O	соон	sate	llites	Pt	Pt-C	PtO
	282.0	283.4	284.3	285.1	286.0	287.0	288.5	290.0	291.3	71.1	71.8	72.8
Pt Mo ₂ C	11.1	19.5	38.2	14.9	9.4	2.9	4.0				81.4	18.6
Pt XC72	0.0	1.5	50.0	23.6	9.8	5.1	5.0	3.6	1.5	67.3	23.5	9.2



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2-pt Support Resistivity Measurements

- Measurements of support resistivity have been made since project began.
- Data are always presented compared to Vulcan[®] XC-72R for the same measurement.
- Better, more precise measurement method adopted last year.
- Quick screening possible.
- Still requires a certain minimum amount of sample that precludes tracking changes in resistivity with ¹/₂ cell durability experiments.
- Ideal for samples recovered from Au-boat bulk CV experiment to be performed in near future.

Sample	ρ (ohm•cm)			
Mo ₂ C/5Pt _{em} (RES)	0.27			
Mo ₂ C (RES)	0.18			
$Mo_2N_{(TGA)}$ 90b	0.27			
$Mo_2N_{(TGA)}$ 82c	0.35			
UNM –B-MoO ₂ /MoN	0.47			
UNM –B-Mo ₂ N _{1-x}	0.43			
Vulcan [®] XC-72R	0.60			







 First MEA failed due to hole burning through membrane.
 Similar mass transport issues seen in 2nd MEA.





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AC Impedance measured over time: 1st prepared Pt/Nano-raft Mo₂C MEA



Results indicate:

- 1) Initially the CTR decreased until 0.6 A, the onset of Mass transport
- After 100 hours, the CTR remained unchanged, while the onset of mass transport begins at 0.5 A
- 3) This indicates that the electrode kinetics are stable









Technical Accomplishments and Progress FY13: Modeling Mo₂C

- Calculations were performed using generalized gradient approximation (GCA) to density functional theory (DTF) with Perdew-Burke-Emzerhof (PBE) exchange –correlation functional implemented in the VASP
 - K-point Monkhorst-Pack mesh of the 1st Brillouin zone ranging between 2x2x2 (bulk) and 2x2x1 (surface)
- Mo₂C represented as MoC_x (X<1) reflecting a significant number of carbon vacancies
- The binding of Pt and reaction of surface intermediates in the ORR, were studied by building surface models using bulk structure starting points.
- Mo terminated (100) surface
- AIM: assess the strength of the Pt-support cohesive interaction compared to Pt (111) & calculate shift in d-band center for Pt mono-layer





Construction of a structural model for MoC_{0.5}



Model slightly over-estimates experimentallydetermined cell parameter <2%. ave. Mo-C distance 2.12 Å.

Predicts the material to be a metal with dband center of -1.39 eV.







$MoO_{3} + H_{2}O_{2} \longrightarrow H_{2}O \cdot MoO_{3} + \frac{1}{2}O_{2}$ $H_{2}O \cdot MoO_{3} + MO \longrightarrow \underline{M(MoO_{4})} + H_{2}O$

• Molybdate salts can be made by etching metal oxides in molybdic acid

Metal cations with high oxidation potentials

may favorably influence the reaction kinetics

 $H = O = H_2O \cdot MOO_3$ $H = O = H_2O \cdot MOO_3$ $H = O = H_2O \cdot MOO_3$

Sacrificial Anode:





Operated by Los Alamos National Security, LLC for NNSA

 \bullet

Aerosol Synthesis





Larger Aerosol Particles are required to retain spherical character Aerosol pre-forming of molybdate appears to minimize sintering

SA ~ 30 m²/g









- High surface area Mo₂C can be produced by SAS method in syngas
- Optimizing $T_{synthesis}$ and $[H_2]$ will lead to shorter grain size and higher sufrace area Mo_2C
- *Minimization of residual carbon can be controlled kinetically*
- Potential aerosol synthesis can be employed to obtain greater control of Mo₂C micro-structure



