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.N.3 Engineered Nano-Scale Ceramic Supports for PEM Fuel Cells

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Subcontractors:

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Start Date: September 2009

Project End Date: 2013

Objectives

- Develop a ceramic alternative to carbon material supports for a polymer electrolyte fuel cell cathode.
- Ceramic support replacement for carbon must:
 - Have enhanced resistance to corrosion and Pt coalescence.
 - Preserve positive attributes of carbon such as cost, surface area, and conductivity.
 - Be compatible with present membrane electrode assembly (MEA) architecture and preparation methods.
- Ceramic properties goals:
 - Surface area suitable for high fuel cell performance
 - High Pt utilization with enhanced Pt-support interaction to resist Pt loss
 - Adequate electronic conductivity
 - Corrosion resistance
 - Synthetic methods amenable to scale-up
 - Reasonable synthesis costs

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Durability: Pt sintering, corrosion loss, effects from load-cycling and high potential.
- Cost: Better Pt utilization balanced by cost difference of new support vs. carbon.
- Performance: Pt sintering, corrosion loss, and loss of electro-active surface area.

Technical Targets

- Precious metal loading (0.2 mg/cm²)

- Cost (<\$3/kW)
- Activity (0.44 A/mg_{Pt} @ 0.9 V_{iR-free})
- Electrocatalysis support loss (<30 mV after 100 hrs @ 1.2 V)
- Electrochemical surface area loss (<40%)

Accomplishments in 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 exhibiting Pt nano-raft structures shows both enhanced activity and durability compared to commercially sourced Pt/XC-72 catalysts.
- Pt imbedded into/onto the support during synthesis process more durable and active for ORR compared catalysts prepared by 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 further development work.
- Initial loading levels lead to cathode microstructures that impedance analysis indicates impacting performance.
 - Obvious mass transport issues identified, and cross-over, but not loss of kinetics.
- Focus made on understanding results from first fuel cell test.
- Remainder of project will concentrate on application of AST protocols to fuel cells with to validate that durability seen in ½ cell measurements carries over to fuel cell.

Introduction

Development of electronically conductive ceramic materials is of fundamental importance to a wide variety of applications.¹⁻⁴ One application of particular interest is proton exchange membrane fuel cells (PEMFC)⁵, where strong oxidizing conditions exist, especially in the cathode.⁶⁻⁸ The reaction that takes place in the cathodic side of PEMFCs is the oxygen reduction reaction (ORR) which is considered to be kinetically sluggish⁹ and thus, it is catalyzed, usually by platinum nano-particles.¹⁰ Due to the high cost of such catalysts¹¹, and in order to maintain their optimized nano-crystallite structure, they are normally supported on a relatively cheap, electronically conductive, porous, high surface area support. Most of the electrode support materials used in fuel cells today are carbon based¹² which are highly sensitive to corrosive conditions and thus corrode under normal fuel cell operating conditions.⁷ This leads to processes that can be detrimental to the fuel cell and is manifested in the form of loss of surface area, impediment of mass transport and loss of catalyst activity due to sintering or dissolution. The direct consequence of these effects is the loss of the overall fuel cell power output overtime and shortening their lifetime; both make this technology less attractive to industry. In order to make PEMFCs more viable, it is necessary to extend their lifetime and reliability by improving the catalyst support.

New materials, which are electronically conductive and are corrosion resistant, are also important to other technologies such as metal-air batteries.

Various ceramic materials have been proposed over the years as a replacement for the commonly used carbon supports. These include titanium oxides¹³, molybdenum nitride^{14,15}, and tungsten oxide.¹⁶ While there are numerous studies investigating the catalytic activity of molybdenum carbide, the performance and durability of this material as a catalyst support has not been extensively studied. In this work, several support candidates have been investigated as potential non-carbon supports. In this final year for this particular project, molybdenum nitride and molybdenum carbide show promise. However, one Pt-molybdenum carbide system was identified in this work that exhibits exceptional stability and potential for high activity and performance and all of the FY13 work was concentrated on this non-carbon support catalyst. We

propose the use of molybdenum carbide supporting Pt nano-raft structures as a possible support for catalyst for use in fuel cell cathodes.

Approach

At the end of FY12, $\frac{1}{2}$ cell testing using an accelerated stress test (AST) indicated that samples prepared using polymer assisted deposition (PAD) exhibited compromised durability because of the significant amount of residual carbon remaining in the sample post synthesis. Since we showed in $\frac{1}{2}$ cell characterization in FY12 that the Pt/Mo₂C/C exhibited activity that was actually better than commercial Pt/XC-72 catalysts of the same Pt loading, we looked at new synthetic approaches to eliminate excess C contamination in the catalyst. Two new approaches were investigated to prepare the Pt/Mo₂C. A novel catalytic synthesis of Pt/Mo₂C, from a physical mixture of precursors, led to the production of unique platinum structures: Nano-rafts, containing less than six atoms of Pt on a molybdenum carbide support. The Materials Foundry of Monterrey CA invented this particular synthetic approach. A second approach was investigated in parallel at UNM using a novel synthesis method, which focuses on the controlled decomposition of magnesium containing precursors under syngas to yield a high surface β -Mo₂C phase. A newly developed Pt-Mo salt has been prepared by adding chloroplatinic acid hydrate to a solution of (NH₄)₂Mg(MoO₄)₂. A precipitate is formed from the solution by using ammonium hydroxide, which produces an insoluble salt containing platinum, magnesium, and molybdenum. The molybdenum salt is then reacted in syngas at elevated temperature producing a solid solution of Pt and β -Mo₂C as well as MgO, which serves as a sacrificial support.

Results

Transmission electron microscope (TEM) was used to further characterize the Pt imbedded Mo₂C prepared by the Materials Foundry. The sample was composed of two agglomerate morphologies (1) spongy-porous and (2) sheet-like. The spongy-porous agglomerates are comprised of a 'skeleton' of nano-crystalline Mo₂C that forms interlocking flat-sheets (Fig. 1a) and nanowires (Fig. 3b and c) and large sheets (Fig. 3d) that are thin and comprised of densely packed nano-crystalline Mo₂C. The Pt is homogenously dispersed throughout the Mo₂C support and could be seen in the high-angle annular dark field (HAADF) STEM image (Fig. 2), where the brighter "islands" distributed on the Mo₂C surface are small clusters (nano-rafts) of Pt atoms. These nano-rafts are composed of three to six atoms of Pt. These structures are not Pt nano particles and are not crystalline. This supports the previous observation made using XRD, where Pt was not detected once it was imbedded in the Mo₂C.

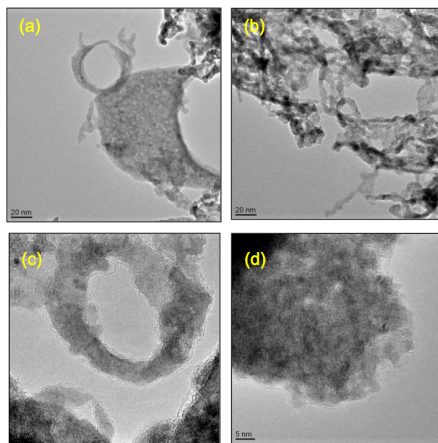


Figure 1. TEM images of (a) sheets of nano-crystalline Mo₂C, (b&c) nano-wires of Mo₂C, and (d) large sheets of densely packed Mo₂C.

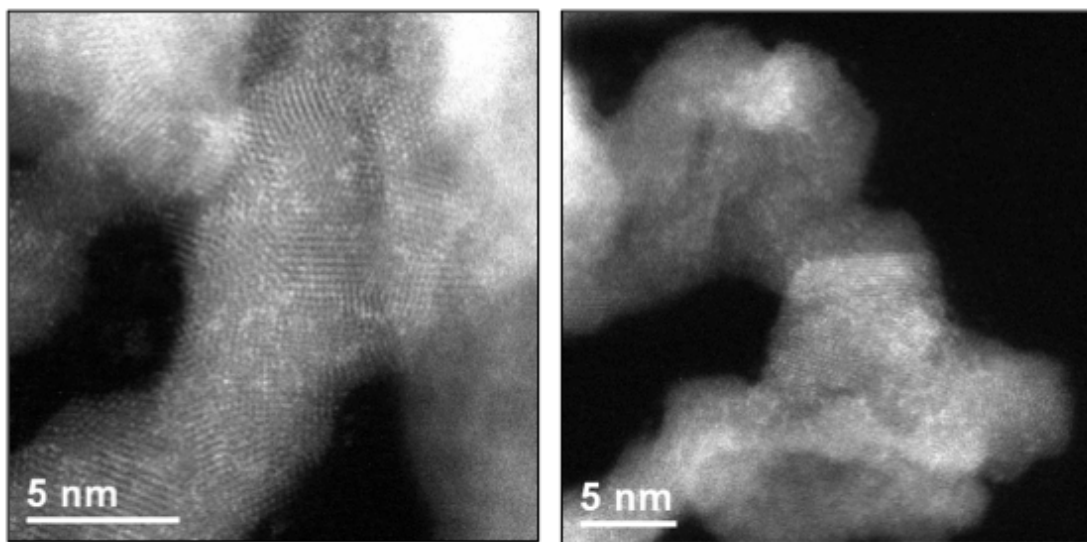


Figure 2. High-angle annular dark field (HAADF) transmission electron microscopy images taken at Oak Ridge National Laboratory of Pt nano-raft structures created on Mo₂C support in-situ.

Suspensions of nano-rafts and a commercially available Pt/XC-72 in 0.05%_{wt} Nafion in isopropanol were prepared and 30 ml were deposited on the glassy carbon disk of an RRDE electrode and were let dry overnight. Figure 3 shows the RDE results obtained with nano-rafts and Pt/XC-72 at 900 rpm and 5 mV s⁻¹. From these results, the half wave potential for ORR with nano-rafts is 0.92 V vs. RHE, whereas with the carbon supported Pt, the measured half wave potential is 0.89 V vs. RHE. A difference in onset potentials was also observed and was found to be 1.11 V and 1.04V vs. RHE for the nano-rafts and Pt/XC-72, respectively. The reaction seems to be predominantly a four-electron reduction of oxygen to water in both cases, as insignificant amounts of peroxide were formed and detected by the Pt ring on the RRDE electrode (not shown). The limiting current correlates to a 3.6 electron process according to the value obtained from the Levich equation. This is in agreement with the peroxide detected on the ring. The activity per mass unit of Pt was calculated from the RRDE data. The mass activity of the nano-rafts and Pt/XC-72 was plotted versus the potential (Fig. 3b). It is apparent that the nano-rafts are superior to the commercially available platinum on carbon per mass unit as the mass activity of the nano-rafts reaches 290 A g_{Pt}⁻¹ whereas the Pt/XC-72 is only 190 A g_{Pt}⁻¹ at 0.9 V vs. RHE. These results can be interpreted in two ways. First, the utilization of the Pt on in the nano-rafts is higher than on carbon, due to the simple sheet-like morphology of the rafts, which leaves all Pt atoms exposed (100% dispersion) In contrast on carbon particles form and the dispersion is generally not more than 10%. And second, The Pt in nano-rafts is chemically modified due to strong interaction with the Mo₂C. This chemical modification increases the ORR of Pt in nano-rafts relative to Pt on carbon. These are not mutually exclusive explanations, so both may play a role in the enhanced activity of Pt in nano-rafts.

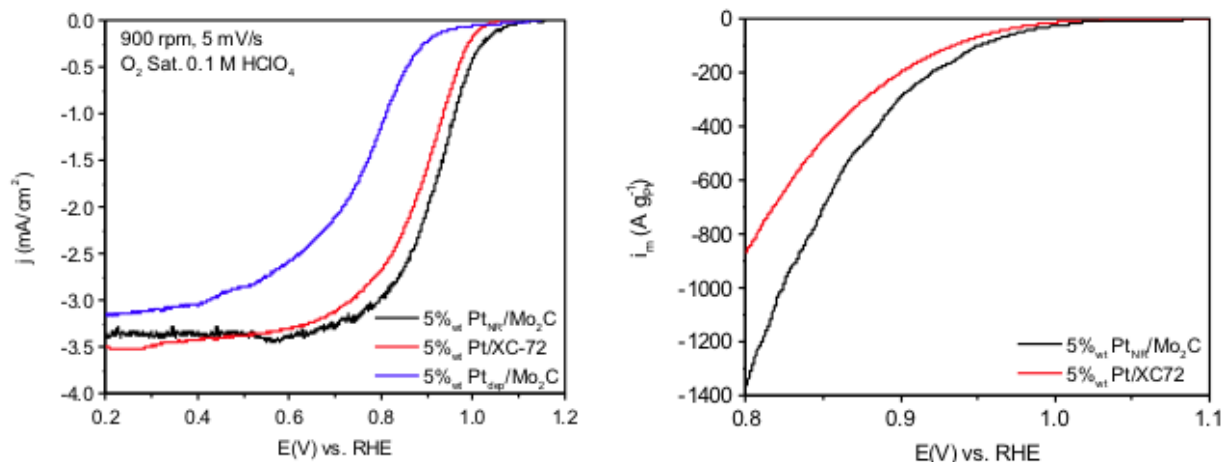


Figure 3. RDE electrochemical $\frac{1}{2}$ cell characterization of Pt nano-raft/Mo₂C (black curve) compared to commercial Pt/XC-72 (red curve) and to Pt-Mo₂C prepared by an incipient wetness approach (blue curve).

In order to evaluate the Pt-ceramic support catalysts prepared in this work, a $\frac{1}{2}$ cell accelerated stress protocol (AST) was designed and shown to significantly degrade commercial Pt/XC-72 catalysts in a reasonable amount of time (e.g. < 24 hrs and 5000 cycles). This protocol proved to be a useful tool to test more durable ceramic supports as well. The AST was conducted at 23°C in de-aerated 0.1M HClO₄ cycling between 0.6V vs. RHE to 1.3V vs. RHE in 14 s for 5000 cycles. Figure 4 shows the results of applying this AST to Pt/C and several supports prepared in this project over the past 4 years. The two most durable supports are Pt nano-raft/Mo₂C and the carbon-free Mo₂N with Pt deposited onto the support post synthesis. Note that the nano-raft Pt Mo₂C is superior to the Mo₂C with Pt applied post support synthesis losing less than 10% of initial EASA over 5000 cycles.

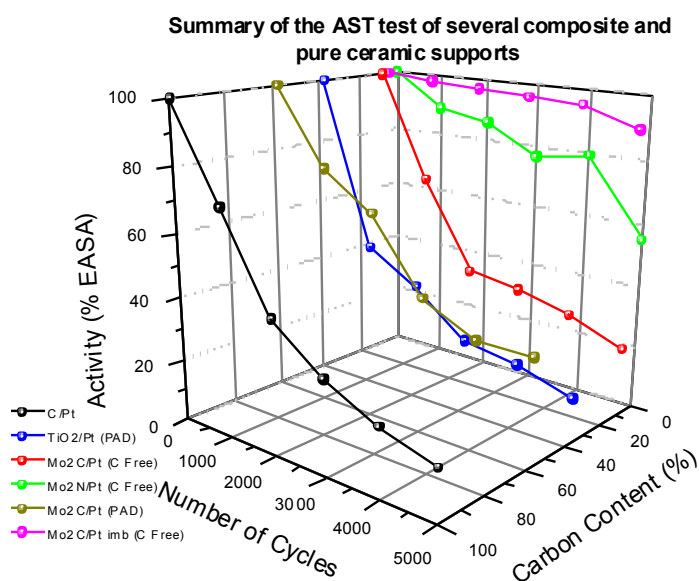


Figure 4. Results of the application of LANL ceramic support durability AST for: a commercial Pt/XC-72 fuel cell catalyst, PAD-prepared TiO₂/C and Mo₂C/C, Mo₂N prepared by conventional solid-state synthesis, and Pt-Mo₂C (Pt applied to support post support synthesis) and nano-raft

Pt/Mo₂C prepared by the Materials Foundry.

XPS analysis on the nano-raft Pt/Mo₂C sample supports the results from this durability AST experiment. The interactions of the platinum nano-rafts with the Mo₂C support were studied at UNM using X-ray photoelectron spectroscopy (XPS) and were compared to those of a platinum on carbon electro-catalyst such as XC-72. Conventional Pt on C have three types of Pt present with metallic Pt being the dominant. In comparison, the Pt nano-raft Mo₂C showed no metallic Pt that is not interacting with the carbide support. There were some small amounts of oxidized Pt (approx. 18.6%) but the major species observed were Pt associated with carbon. The Mo 3d spectra showed binding energies of Mo mostly (e.g. 70%) associated with carbide indicating small amounts of surface oxidation (e.g. 30%). The Pt 4f and C 1s spectra for Pt nano-rafts on Mo₂C reveals the electronic structure of platinum is significantly impacted by the support. On Mo₂C the bond between Pt and C was found to be of a complexing type that is generally associated with organometallic compounds. These results will be presented in more detail in a publication that is currently nearing completing.

The difference in bond types between Pt on XC-72 and Pt on Mo₂C would suggest durability differences and these data are in agreement with the results from the AST experiments and Figure 4 above. On XC-72, 23% of the Pt is bound to a mixture of graphitic and amorphous carbon. Durability studies suggest this bond is weak and allows platinum to migrate and sinter¹⁷. In contrast, as confirmed by XPS, on Mo₂C there is no 'free' Pt that is not interacting with the support. Thus XPS measurements determined that Pt on Mo₂C is stabilized against sintering due to interaction between platinum and carbon in the crystalline lattice in the support.

New, larger quantity samples were provided by the The Materials Foundry to prepare electrode inks for fuel cell investigations. Standard 5cm² decals were prepared using ink methods commonly employed in the preparation of fuel cells using conventional, commercial Pt/C catalysts. XL100 membranes were used and loadings were adjusted at 0.2 mg_{Pt}/cm² on the cathode using the Pt nano-raft Mo₂C catalyst (5wt% Pt); excessively thick cathodes were required (areas as thick as 70 – 100 μm were observed in cross-section SEM analysis.) Electrode thicknesses of such magnitude may induce mass transport problems. Another area of concern was that the hot pressing, decal transfer methods may not be suitable due to the hardness of the support and membrane piercing was a concern. This last concern may have been realized because several of the initial membranes quickly formed holes during initial fuel cell testing. The initial MEA exhibited crossover issues and local membrane thinning that lead to hole formation and failure. Figure 5a shows the initial results of testing the second membrane and after three consecutive 1.2V 24hr holds. Figure 5b and c show the impedance data for this fuel cell after initial break-in and after the three 24hr 1.2V holds. These data show that initially the charge transfer region decreased as did the voltage but after 190 hr of operation and three consecutive 24hr voltage holds, the charge transfer region remained unchanged while the onset of mass transport became more pronounced. This indicated the electrode kinetics were stable to the voltage holds. The lower OCV was attributed to higher hydrogen crossover consistent with evidence of membrane thinning from SEM cross-section imaging. Post mortem investigations using XRD analysis of cathode catalyst showed no evidence of Pt coalescence – in fact, no diffraction peaks associated with Pt were observed at all – however, some molybdenum oxide was evident in the XRD pattern. More fuel cell testing and optimization of the ink, Pt/Mo₂C catalyst, and study of break-in procedure optimization, and fuel cell durability testing will be required.

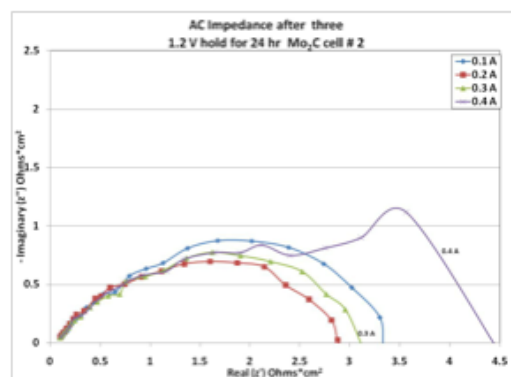
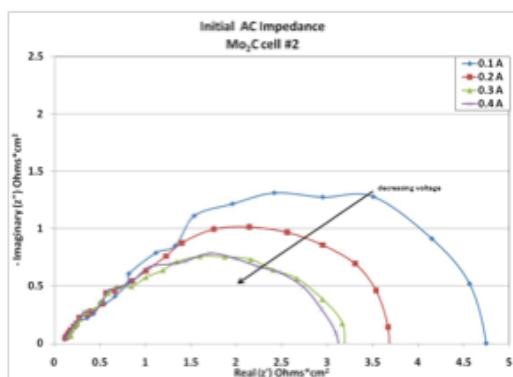
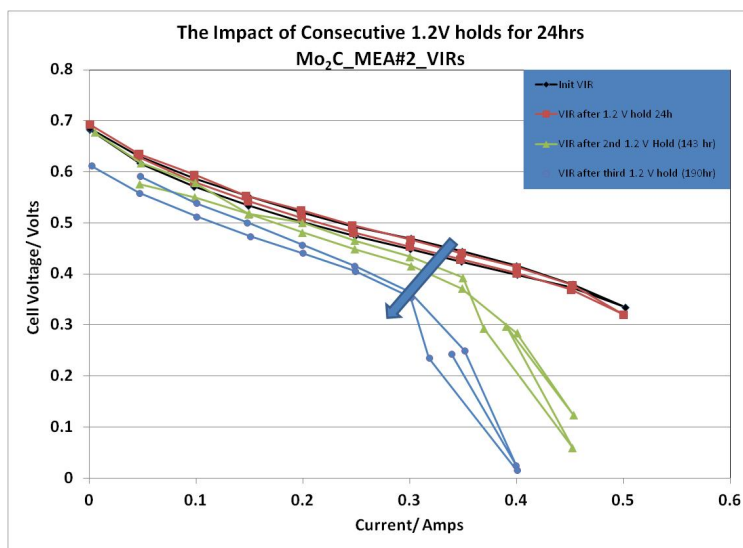


Figure 5. First fuel cell testing results using MEAs prepared with Pt/Mo₂C cathode catalyst synthesized using materials provided by The Materials Foundry. 5 cm²; Cathode: 5%Pt/Mo₂C 0.2mg_{Pt}/cm²; Anode 20%Pt/XC-72 0.2 mg_{Pt}/cm²; R.H. 100%, 30 psig H₂/air 160/550 sccm.

The new synthetic approach invented by The Materials Foundry is limited in control over support surface area, which may impact catalyst optimization. Moreover, Intellectual Property considerations limit information that may be shared by this company with LANL and the fuel cell community. The University of New Mexico has been working on non-carbo thermal moly carbide synthetic approaches to prepare nano-raft structures (confirmation through TEM and XPS analysis) without excess, residual carbon. Their task will enable greater scientific investigation and optimization of this unique and desirable catalyst system. One approach, using a sacrificial anode support (SAS) uses a specially prepared Mg-molybdate precursor that when reacted with CO and H₂ leads to the formation of MgO and Mo₂C. The MgO serves to prevent agglomeration and sintering of the carbide and may be easily removed by an HCl etch post synthesis. Particle sizes between 25 and 100nm have been prepared and surface areas higher than 50 m²/g have been prepared with no excess, residual C. Several approaches to Pt incorporation have been tested and high Pt dispersions (confirmed by XRD and TEM in the near future) have been achieved. Electrochemical $\frac{1}{2}$ cell and fuel cell testing have commenced at the time of this report's preparation and initial electrochemical results strongly suggest that the at least some characteristics of the nano-raft Pt structures have been prepared using these approaches however, TEM characterization at ORNL will be necessary.

Last, the computational work produced results that are supportive of the evidence of enhanced durability seen in the data above. A (100) MoC_{0.5} surface model was created and a layer of Pt atoms were placed on the surface using a simple structural model. The Pt-Pt bond distance on the carbide surface was calculated to be 3.0Å and this value indicates a forced registry is taking place on the surface of the support. The Pt-Pt bond distance on a Pt/C is typically in the range of 2.80Å on a Pt(111) surface for comparison. The d-band center energy of Pt atoms on the moly carbide surface was calculated to be -2.42eV and this value is lower when compared to -1.88eV from recent computations performed for Pt(111) surfaces. In the remaining time for this project, we hope to calculate over-potentials and effect of support on Pt solubility. In summery, the modeling results, XPS spectra, and electrochemical characterization are all in agreement.

Conclusions

- Molybdenum carbide - carbon composite was successfully synthesized using the LANL PAD technique.
 - The resulting MoC_{0.56}/C was predominately composed of 1nm crystallites of cubic phase MoC_{0.56} (56.1%) and amorphous carbon (40.7%).
 - Platinum was deposited on the MoC_{0.56}/C and confirmed to be uniformly distributed by the small and uniform crystallite size measured with XRD.
- The Pt on MoC_{0.56}/C composite support showed enhanced ORR catalytic activity when compared to Pt on carbon.
- A ½ cell accelerated stress test (AST) was developed and tested to ascertain effectiveness as a measure to test a Pt/ceramic support's resistance to corrosion and Pt loss
 - AST shown to effectively kill commercial Pt/XC-72 catalysts in a reasonable amount of time (e.g. 5000 cycles in less than 24 hours). Complete loss of ECSA in a commercial Pt/XC-72 demonstrated in 10000 cycles.
- Presence of carbon in PAD prepared samples impacted durability and offsets benefits of enhanced activity.
- New methods were explored to prepare Pt deposited, carbon free Mo₂C catalysts that lead to discovery of unique properties of Pt Nano-raft structures placed onto Mo₂C surfaces.
 - Presence of Pt-nanoraft structures confirmed using ORNL HAADF STEM imaging.
- The Pt nano-raft structures supported on Mo₂C show enhanced catalytic activity when compared to Pt on carbon or Pt deposited onto Mo₂C post synthesis of ceramic support. E_{1/2} is 0.92V vs. RHE and onset potential is 1.11V vs. RHE compared to 0.89V and 1.04V respectively for commercial Pt/XC-72.
 - Mass activity for new Pt Nano-raft/Mo₂C at 0.9V vs. RHE is 290 A/g_{Pt} compared to 190 A/g_{Pt} for commercial Pt/XC-72.
- AST ½ cell testing performed Pt Nano-raft/Mo₂C catalyst show that this catalyst is significantly more durable than commercial Pt/XC-72 catalyst.
 - Pt/XC-72 losses approx. 90% of ECSA after 5000 cycles compared to approx. 10% loss for Pt Nano-raft/Mo₂C catalyst.
 - AST also showed that Pt Nano-raft/Mo₂C is also significantly more durable than Pt/Mo₂C catalysts prepared where Pt disposition occurs post support synthesis.
 - This fact indicates unique properties associated with the Pt and its interaction with the support with synthesis that forms nano-raft structures.
- XPS investigations combined with modeling results support enhanced Pt-support interactions, which was one of the objectives of the project.
 - 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.
 - Pt on Mo₂C shows no metallic Pt that is not interacting with the support. Major Pt species associated with carbon.
- Initial fuel cell testing with nano-raft catalysts combined with fuel cell AST protocol immediately suggested stable electrode kinetics but un-optimized Pt loadings lead to overly thick cathodes that created mass transport limitations.
 - No evidence in XRD of Pt coalescence and particle growth post AST.

Future Directions

- Understand source of activity and origin of enhanced durability of the Pt nano-raft structures.
- Optimization of ink and method of MEA preparation.
- In conjunction with increased fuel cell testing activity, improve initial performance and perform more durability testing.
- Scale-up of batch size and optimization of support surface area.
- Correlate studies of ½ cell, fuel cell, and XPS results with increase number of samples and optimize Pt loading.
- Scale up for Pt Nano-raft/Mo₂C catalysts produced numerous samples with varying activity, surface properties. Correlate activity data to surface properties.
- Understand degradation mechanisms through durability testing / bulk quantities and recovery of fuel cell materials.

Collaboration and Coordination with Other Institutions

- Los Alamos National Laboratory (LANL)
- Oak Ridge National Laboratory (ORNL)
- University of New Mexico (UNM)
- The Materials Foundry (TMF)

FY13 Publications/Presentations

- K. Blackmore, L. Elbaz, E. Brosha, A. Burrell, and T. M. McCleskey, “Nano-scale Titania Ceramic Supports for PEM Fuel Cells,” *J. Mater. Res.* **27** no. 15 (2012).
- L. Elbaz, C. Kreller, N. Henson and E.L. Brosha, “Molybdenum Carbide-Carbon Composite Support for Oxygen Reduction Catalysts”, submitted to the Journal of Power Sources.
- L. Elbaz and E.L. Brosha, “Accelerated Stress Tests in Half-Cell for Catalysts Supports for Polymer-Electrolyte-Membrane Fuel Cells”, in preparation.
- L. Elbaz, K. More, K. Artyushkova, N. Henson, Jonathan Phillips and E. L. Brosha, “Evidence of Enhanced Electrocatalytic Activity of Molybdenum Carbide Supported Platinum Nano-Rafts”, in preparation.
- A. Roy, A. Serov, E. Brosha, P. Atanassov, and T. Ward, “Synthesis and Characterization of High Surface Area Mo₂N as a Durable Support for Electrocatalysts, in preparation, *Am. Chem. Soc., Div. Energy Fuels*, 2013.
- A. Roy, U. Martinez, P. Atanassov, E. Brosha, and T. Ward, “Highly Dispersed Pt on Mo₂C: Durable Catalyst for Oxygen Reduction Reaction,” 224th Meeting of the ECS, San Francisco, CA, October 2013.
- L. Elbaz and E. L. Brosha,” Development of Ceramic Supports for Polymer Membrane-Electrolyte Fuel Cells,” Electrochemistry Israel, Ben Ilam University, June 2013.

- L. Elbaz, J. Phillips, N. Henson, and E. Brosha, "Molybdenum Carbide as Support for Platinum Catalysts for Oxygen Reduction in Fuel Cells," PRIME 222nd Meeting of the Electrochemical Society, Honolulu HI, October, 2012.
- M. Sykora, A. Mueller, C. Kreller, E. Brosha, and F. Garzon, "Synthesis and Characterization of Molybdenum Nitride for Electrosynthesis Applications" PRIME 222nd Meeting of the Electrochemical Society, Honolulu HI, October, 2012.
- L. Elbaz, T. Rockward, N.J. Henson, K. Artyushkova, K. More, J. Phillips, and E.L. Brosha," Evidence of Enhanced Activity on In-situ Formed Pt Nano-rafts on Molybdenum Carbide Support," 224th Meeting of the ECS, October 2013.

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Figure Captions

Figure 1. TEM images of (a) sheets of nano-crystalline Mo₂C, (b) & (c) nano-wires of Mo₂C, and (d) large sheets of densely packed Mo₂C.

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Figure 4. Results of the application of LANL ceramic support durability AST for: a commercial Pt/XC-72 fuel cell catalyst, PAD-prepared TiO₂/C and Mo₂C/C, Mo₂N prepared by conventional solid-state synthesis, and Pt-Mo₂C (Pt applied to support post support synthesis) and nano-raft Pt/Mo₂C prepared by the Materials Foundry.

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