

V.A.6 Engineered Nano-Scale Ceramic Supports for PEM Fuel Cells

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Project Start Date: September 2009

Project End Date: 2013

Overall 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.

Fiscal Year (FY) 2013 Objectives

- Perform accelerated stress test (AST) ½ cell electrochemical experiments on ceramic support candidates.
- Fabricate 5-cm² MEAs and test in fuel cell.
- Perform fuel cell durability tests on MEAs using ceramic support on cathode.
- Validate ceramic support fuel cell AST in ½ cell and fuel cell against commercial Pt-carbon catalyst.

Technical Barriers

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

- (A) Durability: Pt sintering, corrosion loss, effects from load-cycling and high potential.
- (B) Cost: Better Pt utilization balanced by cost difference of new support vs. carbon.
- (C) 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%)

FY 2013 Accomplishments

- Ceramic supports for proton exchange membrane fuel cell (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 commercially sourced Pt/XC-72 catalysts.
- Pt imbedded into/onto the support during the synthesis process makes the catalyst more durable and active for the oxygen reduction reaction (ORR) compared to catalysts prepared by post-synthesis Pt disposition.
- Fuel cell testing for durability has started in FY 2013.

- 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 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 PEMFCs [5], where strong oxidizing conditions exist, especially in the cathode [6-8]. The reaction that takes place on the cathodic side of PEMFCs is the ORR which is considered to be kinetically sluggish [9] and thus, it is catalyzed, usually with platinum nano-particles [10]. Due to the high cost of such catalysts [11], 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-based [12] 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 oxides [13], 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 FY 2013 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 catalysts for use in fuel cell cathodes.

APPROACH

At the end of FY 2012, ½-cell testing using an 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 ½ cell characterization in FY 2012 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 the University of New Mexico 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 (Figure 1a) and nanowires (Figures 1b and c) and large sheets (Figure 1d) that are thin and comprised of densely packed nano-crystalline Mo₂C. The Pt is homogeneously dispersed throughout the Mo₂C support and could be seen in the high-angle annular dark field (HAADF)

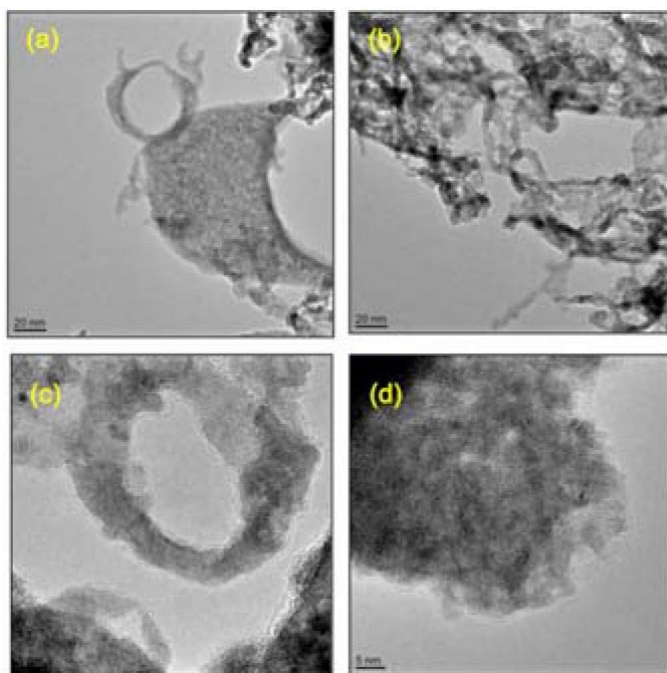


FIGURE 1. TEM images of (a) sheets of nano-crystalline Mo_2C , (b and c) nano-wires of Mo_2C , and (d) large sheets of densely packed Mo_2C .

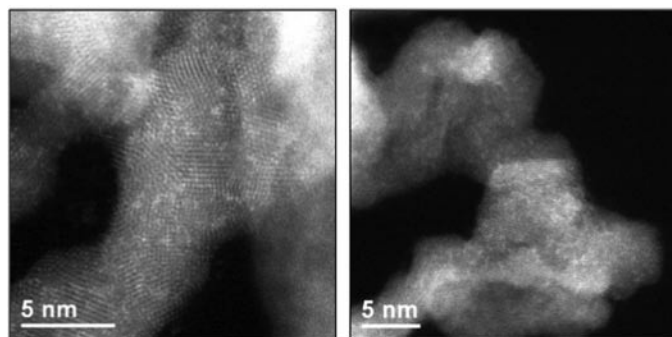


FIGURE 2. HAADF transmission electron microscopy images taken at Oak Ridge National Laboratory of Pt nano-raft structures created on Mo_2C support in situ.

scanning transmission electron microscope (STEM) image (Figure 2), where the brighter “islands” distributed on the Mo_2C 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 nanoparticles and are not crystalline. This supports the previous observation made using X-ray diffraction (XRD), where Pt was not detected once it was imbedded in the Mo_2C .

Suspensions of nano-rafts and a commercially available Pt/XC-72 in 0.05%_{wt} Nafion® in isopropanol were prepared and 30 μl were deposited on the glassy carbon disk of an rotating ring disc electrode (RRDE) electrode and were let to dry overnight. Figure 3 shows the rotating disk electrode (RDE) results obtained with nano-rafts and Pt/XC-72 at

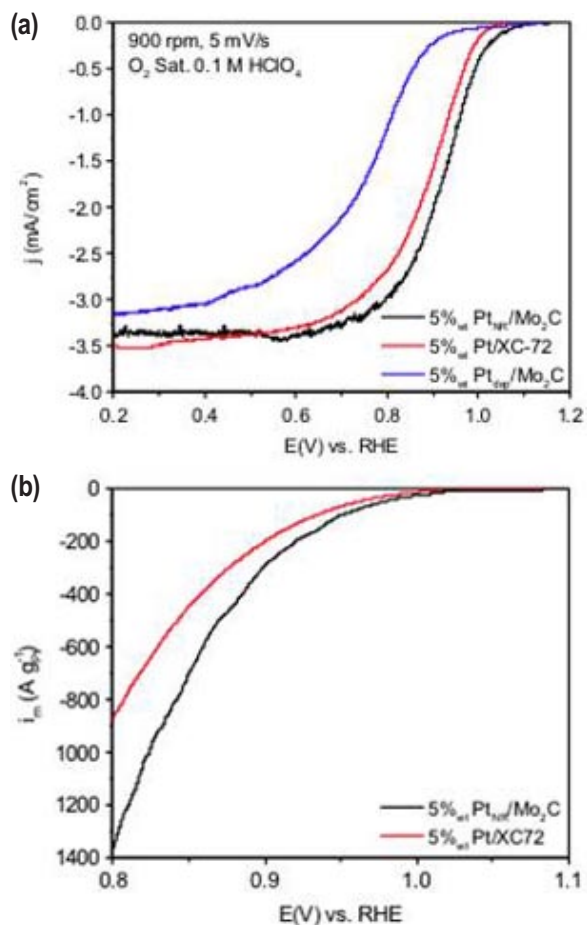


FIGURE 3. RDE electrochemical $\frac{1}{2}$ cell characterization of Pt nano-raft/ Mo_2C (black curve) compared to commercial Pt/XC-72 (red curve) and to Pt- Mo_2C prepared by an incipient wetness approach (blue curve).

900 rpm and 5 mV s^{-1} . From these results, the half wave potential for ORR with nano-rafts is 0.92 V vs. the reference hydrogen electrode (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 1.04 V 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 (Figure 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 $290 \text{ A g}_{\text{Pt}}^{-1}$ whereas the Pt/XC-72 is only $190 \text{ A g}_{\text{Pt}}^{-1}$ 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 Mo_2C . 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.

In order to evaluate the Pt-ceramic support catalysts prepared in this work, a $\frac{1}{2}$ cell AST was designed and shown to significantly degrade commercial Pt/XC-72 catalysts in a reasonable amount of time (e.g. <24 hrs and 5,000 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 0.1 M HClO_4 cycling between 0.6 V vs. RHE to 1.3 V vs. RHE in 14 s for 5,000 cycles. Figure 4 shows the results of applying this AST to Pt/C and several supports prepared in this project over the past four years. The two most durable supports are Pt nano-raft/ Mo_2C and the carbon-free Mo_2N with Pt deposited onto the support post synthesis. Note that the nano-raft Pt Mo_2C is superior to the Mo_2C with Pt applied post support synthesis losing less than 10% of initial electrochemically active surface area over 5,000 cycles.

XPS analysis on the nano-raft Pt/ Mo_2C sample supports the results from this durability AST experiment. The interactions of the platinum nano-rafts with the Mo_2C support were studied at UNM using X-ray photoelectron spectroscopy (XPS) and were compared to those of 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 Mo_2C showed no metallic Pt that is not interacting with the carbide support. There were some small amounts of oxidized Pt (approximately 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 Mo_2C reveals the electronic structure of platinum is significantly impacted by the support. On Mo_2C 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 Mo_2C would suggest durability differences and these data are in agreement with the results from the AST experiments and Figure 4. 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 sinter [17]. In contrast, as confirmed by XPS, on Mo_2C there is no 'free' Pt that is not interacting with the support. Thus XPS measurements determined that Pt on Mo_2C 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 5-cm² 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 Mo_2C catalyst (5 wt% 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 1.2 V holds for 24 hr each. Figures 5b and c show the impedance data for this fuel cell after initial break-in and after the three 24-hr 1.2 V holds. These data show that initially the charge transfer region decreased as did the voltage but after 190 hr of operation and three consecutive 24-hr voltage holds, the charge transfer region remained unchanged while the onset of mass transport became more pronounced. This indicated the electrode kinetics were

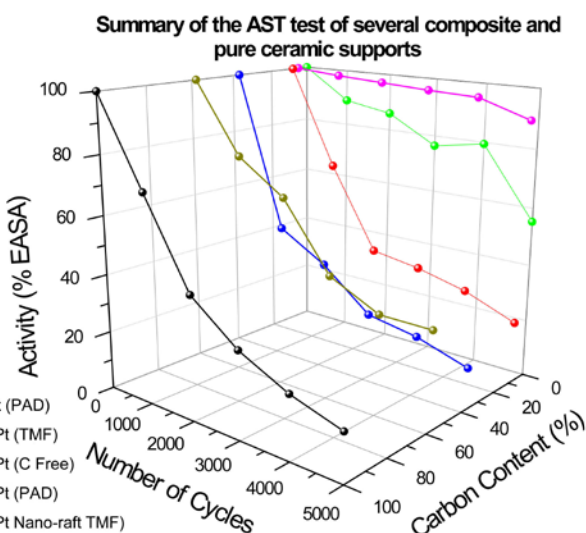


FIGURE 4. Results of the application of LANL ceramic support durability AST for: a commercial Pt/XC-72 fuel cell catalyst, PAD-prepared TiO_2/C and $\text{Mo}_2\text{C}/\text{C}$, Mo_2N prepared by conventional solid-state synthesis, and Pt- Mo_2C (Pt applied to support post support synthesis) and nano-raft Pt/ Mo_2C prepared by The Materials Foundry.

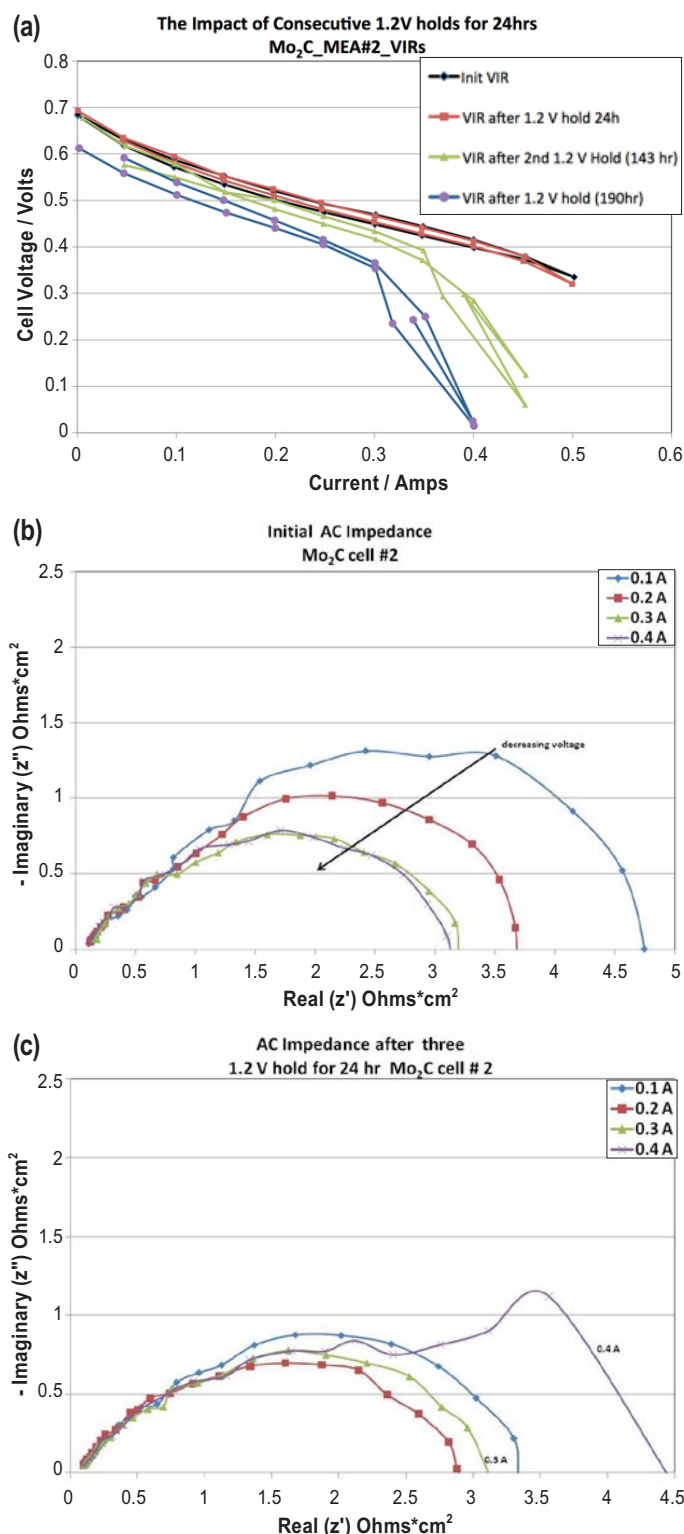


FIGURE 5. Figure 5. First fuel cell testing results using MEAs prepared with Pt/Mo₂C cathode catalyst synthesized using materials provided by The Materials Foundry. 5 cm²; Cathode: 5% Pt/Mo₂C 0.2 mg_{pt}/cm²; Anode 20% Pt/XC-72 0.2 mg_{pt}/cm²; relative humidity 100%, 30 psig H₂/air 160/550 sccm: (a) voltage-current-resistance curves (initial, and after 1st, 2nd, and 3rd 1.2 V holds ea. 24 hours), (b) initial AC impedance response at 0.1–0.4 A, and (c) AC impedance response 0.1–0.4 A after 1st 1.2 V 24-hour hold.

stable to the voltage holds. The lower open-circuit voltage 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.

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 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 100 nm 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 ½ 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 -2.42 eV and this value is lower when compared to -1.88 eV 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 summary, 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 $\text{MoC}_{0.56}/\text{C}$ was predominately composed of 1-nm crystallites of cubic phase $\text{MoC}_{0.56}$ (56.1%) and amorphous carbon (40.7%).
 - Platinum was deposited on the $\text{MoC}_{0.56}/\text{C}$ and confirmed to be uniformly distributed by the small and uniform crystallite size measured with XRD.
- The Pt on $\text{MoC}_{0.56}/\text{C}$ composite support showed enhanced ORR catalytic activity when compared to Pt on carbon.
- A $\frac{1}{2}$ -cell 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. 5,000 cycles in less than 24 hours). Complete loss of ECSA in a commercial Pt/XC-72 demonstrated in 10,000 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 Mo_2C catalysts that lead to discovery of unique properties of Pt nano-raft structures placed onto Mo_2C surfaces:
 - Presence of Pt nano-raft structures confirmed using ORNL HAADF STEM imaging.
- The Pt nano-raft structures supported on Mo_2C show enhanced catalytic activity when compared to Pt on carbon or Pt deposited onto Mo_2C post synthesis of the ceramic support. $E_{1/2}$ is 0.92 V vs. RHE and the onset potential is 1.11 V vs. RHE compared to 0.89 V and 1.04 V, respectively for commercial Pt/XC-72:
 - Mass activity for new Pt nano-raft/ Mo_2C at 0.9 V vs. RHE is 290 A/g_{Pt} compared to 190 A/g_{Pt} for commercial Pt/XC-72.
- AST $\frac{1}{2}$ -cell testing performed on a Pt nano-raft/ Mo_2C catalyst shows that this catalyst is significantly more durable than the commercially available Pt/XC-72 catalyst:
 - Pt/XC-72 losses approximately 90% of ECSA after 5,000 cycles compared to approximately 10% loss for Pt nano-raft/ Mo_2C catalyst.
 - AST also showed that Pt nano-raft/ Mo_2C is also significantly more durable than Pt/ Mo_2C catalysts prepared when Pt disposition occurs post support synthesis.
 - These data indicate 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 binding energy is shifted to higher energies for the Mo_2C support compared to XC-72.
 - Pt on Mo_2C 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.
- Optimize ink and method of the 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 $\frac{1}{2}$ cell, fuel cell, and XPS results with increase number of samples and optimize Pt loading.
- Scale up for Pt nano-raft/ Mo_2C 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)

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2. 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.
3. L. Elbaz and E.L. Brosha, "Accelerated Stress Tests in Half-Cell for Catalysts Supports for Polymer-Electrolyte-Membrane Fuel Cells", in preparation.
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