Understanding the Effects of Surface Chemistry and Microstructure on the Activity and Stability of Pt Electrocatalysts on Non-Carbon Supports

Principal Investigator: William E. Mustain

Department of Chemical & Biomolecular Engineering
University of Connecticut
191 Auditorium Rd., Unit 3222
Storrs, CT 06269-3222

DOE Program Manager: Raul Miranda
Phone: (301) 903-8014
Email: raul.miranda@science.doe.gov

Objectives

The objective of this DOE/BES sponsored research is to use Pt nanoparticles supported on several carbon and non-carbon supports to elucidate the effects of the chemical composition and microstructure of the electrocatalyst support on the activity, stability and utilization of supported Pt clusters. The overall goal of this work is to develop the tools needed to design novel electrocatalysts that have ultra-low Pt content and excellent electrochemical stability. The work in this program is organized across 3 themes:

I.   Elucidating the Role of Support Surface Chemistry on the Structure and Activity of Supported Pt

II.   Understanding the Influence of Carbon Support Adatoms on Electrochemical Stability

III.   Rational Design of the Catalyst-Support Microstructure

Technical Barriers

Use of intrinsically unstable materials: Due to the weak interaction between all known carbon-black catalyst support materials and Pt clusters and the thermodynamic instability of carbon at elevated surface potentials, it is currently in question whether the continued investigation of carbon black support materials will lead to high stability electrocatalysts. The weak interaction and support dissolution leads to catalyst agglomeration during operation and severe reduction in the number of electrochemically active sites, drastically lowering the reaction rate with time. Also, though Pt alloy electrocatalysts have shown enhanced activity for the ORR, they suffer from low chemical stability in acidic environments, such as the PEMFC cathode, due to leaching of the alloyed metal. Also, there is no evidence in the literature that alloying Pt has any appreciable effect on cluster agglomeration. Therefore, alloying does not address the fundamental issue with PEMFC catalysts: cluster stability.

Lack of guiding principles for catalyst and support design: Carbon offers many properties that make it nearly ideal for electrochemical applications including: i) tolerance to acidic and alkali media; ii) high electronic conductivity; iii) low cost; and iv) complex microporous structure, yielding high specific surface area and facile mass transport. Despite this, little is known about how the balance between porosity, microstructure, and surface chemistry of the support influences the dispersion of Pt, its utilization, and the mass transport of both reactants and products within the catalyst. This limited information regarding the catalyst support and its role in PEMFC performance has translated to non-carbon supports as well, which has stunted the advance and implementation of next-generation materials in PEMFCs. Therefore, a fundamental, systematic study carefully controlling the catalyst support porosity, microcrystallinity and surface chemistry is desperately needed.

Abstract

In the first 2 ½ years of this project, we have clearly shown that the electrocatalyst support has an impact on the activity and stability of Pt through at least two different mechanisms: 1) Electron transfer between the catalyst and support that shifted the binding energy of oxygen to more positive potentials, leaving a clean Pt surface for the ORR; and 2) Lattice matching, which led to preferential faceting of Pt (111), which has a very high ORR activity. In fact, preferential faceting and strong bonding between the catalyst and support led to a Pt/ITO catalyst with a specific activity of 750 $\mu A/cm^2_{Pt}$ and mass activity of 621 mA/mg_{Pt} (both exceed 2015 DOE targets) with no measurable reduction in activity over 1000 accelerated degradation cycles between 0.0V and 1.4 V. vs. NHE. Pt/WC also showed improved activity compared to Pt/C, though surface oxidation and dissolution led to low catalyst life. However, we were also able to report, for the first time, a detailed mechanism for the electrochemical dissolution and instability of WC and WO_3 in acid media. In addition, using templated carbon, we have found that pore sizes < 5 nm are not useful for ORR electrocatalysts. We have also found that having an amorphous support nanostructure significantly improves the Pt utilization. In addition, we found that doping carbon-based supports with surface N functional groups improves the stability of the carbon relative to commercial carbon and allows for very small Pt particle sizes (< 2 nm) even at very high Pt loading (50 wt%). This combination led to Pt/N-OMC (OMC = ordered mesoporous carbon) catalysts with better activity and stability than commercial Pt/C (BASF). We also found during degradation testing of the N-OMC that it has very high double layer capacitance for its surface area

(156 F/g; 25.1 μF/cm^2) and is competitive with commercial carbons for supercapacitor applications. Most importantly, our initial work has validated our overall approach, allowed us to develop reliable experimental protocols, has used fundamental discoveries to make contributions to real devices and has led to interesting new questions that will be the subject of our work moving forward.

Progress Report

To date, our team focused our efforts in two key areas: surface chemistry and microstructure. With regards to the surface chemistry work, we have started developing a fundamental understanding to learn if and how the support surface can influence the electrocatalytic activity of supported Pt nanoparticles. Also of great interest here was the ability of the support to dictate the dispersion and stability of supported Pt. Most of the work in this area was accomplished using non-carbon support materials (with Pt/Vulcan acting as our control material): WC/WO$_3$, Indium-Tin Oxides and TiAlN. Our microstructural work focused on using a silicate templating approach to control the pore size of an ordered mesoporous carbon (OMC). Carbon was selected due to its ease in preparation and similarity of its surface composition and bonding to the control material. We also developed a template modification technique to control the homogeneity and structural order of the OMC. In the following sections, it is impossible to provide all the work that was done; for this, we would like to invite readers to visit our publications and feel free to contact us with any questions.

High Activity, High Stability Pt/Sn-doped Indium Oxide Electrocatalysts for the ORR

We studied indium-tin oxides over a very broad range of composition, from 1% indium in tin oxide, which had rutile crystal structure with inserted In^{3+} to 1% Sn in indium oxide, which had a bixbyite cubic structure. We found that 5% Sn in indium oxide possessed the highest ORR activity and excellent stability. We will focus on the 5% Sn-In$_2$O$_3$ results here, which was reported in the Journal of the American Chemical Society [Publication 3], which will be denoted as ITO below.

The specific and mass activity of Pt supported on ITO was considerably higher than Pt/C. The Pt/ITO catalyst exhibited a specific activity of 0.750 $\pm$ 0.04 mA/cm2 at 0.9 V, which was 3 times greater than that of Pt/C (0.235 0.01 $\pm$ mA/ cm2). After normalization to the loading amount of Pt metal, the mass activity of Pt/ITO catalyst was found to be 621 $\pm$ 31 mA/mgPt, which was

4 times greater than that of Pt/C (156 $\pm$ 9 mA/mgPt) and far exceeded the 2015 DOE goal for Pt mass activity of 440 mA/mgPt. Characteristic voltammograms for Pt/ITO at various rotation rates are presented in Figure 1a. The higher specific activity of the Pt/ITO was found to be a result of synergistic effects between the surface Sn of ITO and the supported Pt NPs. Perhaps the most significant impact of the ITO was the preferential exposure of {111} facets on the Pt NPs on Pt/ITO compared to Pt NPs supported on carbon black, which typically contain mostly {100} facets. Interestingly, the Pt and ITO seemed to have similar cubic lattice spacing, which resulted in continuous lattice fringes from the ITO substrate to supported Pt particles, indicating that the Pt was grown epitaxially on the ITO surface The ORR activity on low-index crystallographic facets of Pt in a nonadsorbing electrolyte such as perchloric acid is known to increase on the order of Pt(100) $\ll$ Pt(111) < Pt(110), with a minor difference in catalytic activity between Pt(111) and Pt(110). This difference in ORR activity most likely arises from the structure-sensitive inhibiting effect of OH$_{ad}$ species on Pt(hkl), which blocks the active site for O$_2$ adsorption
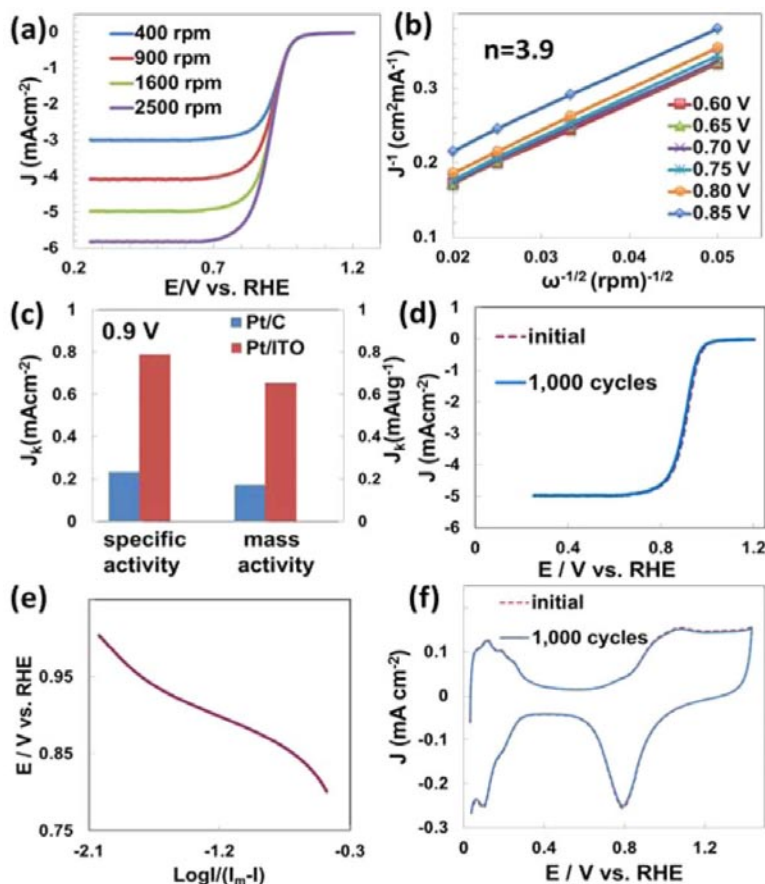

FIGURE 1. (a) Polarization curves for Pt/ITO. (b) Koutecky-Levich plots for the ORR on Pt/ITO. (c) measured specific and mass activity of Pt/ITO and its comparison to Pt/C. (d) ORR stability of Pt/ITO over 1000 Cycles. (e) ORR Tafel plot for Pt/ITO. (f) Voltammetry stability for Pt/ITO.

and thus retards the ORR kinetics. The Pt/ITO catalyst also showed excellent ORR stability over 1000 cycles between 0 and 1.4 V vs. NHE (Figure 1d) and excellent retention in the electrochemically active area during cycling (Figure 1f).

Pt Nanoparticles Supported on WC and WO$_3$

Our interest in WC as an electrocatalyst support for Pt was born out of several papers in the recent literature that claimed that WC promoted the electrocatalytic activity of Pt for several reactions, including the ORR. However, none of the authors at that time were able to provide an adequate explanation, though it was noted that near the Fermi level, Pt and WC have similar electronic structures, which could allow for electron transfer between the catalyst and support, particularly when adsorbates approach the Pt surface. Another key limitation of the literature was that many authors failed to report the surface state of the WC and only reported one scan for the WC surface. This left significant doubt as to the real role of the WC surface state and its stability in highly acidic media at ORR relevant potentials.

One of the most significant findings of this study was that the ORR on Pt is enhanced by the presence of the WC support [Publication 7]. In fact, the onset potential for Pt/WC was higher than Pt/Vulcan (Pt/C) and that the ½ wave potential was shifted positive. The root cause for this was suggested by theTafel slope where a 120 mV/decade slope was observed over the entire potential window, up to 0.9V. This is an important finding since bulk Pt and Pt/C both typically show two Tafel slopes in this region: i) 120 mV/decade < ~0.7V vs. NHE where the Pt is nearly oxide free; and ii) 60 mV/decade > ~ 0.7 V vs. NHE where the surface coverage of oxygen on Pt is very high. The presence of only the 120 mV/decade Tafel slope for Pt supported on WC suggests that the WC support suppressed oxide formation on the Pt nanoparticles. Unfortunately, the enhancement was short-lived [Publication 5]. After the Pt/WC catalyst

was cycled between 0.0 V and 0.8 V vs. NHE, we observed significant degradation in both the electrochemical response and the physical structure of the support and severe agglomeration of Pt. Extensive studies with both WC and WO$_3$ supports showed that Pt is very strongly bound to WC initially and Pt/WC shows excellent stability at potentials < 0.8 V vs. NHE. However, as the potential approaches 0.8 V vs. NHE, the WC is rapidly oxidized to WO$_2$, which we found by XPS. Finally, the WO$_3$ chemically reacts in the highly acidic environment to form tungsten bronze, H$_x$WO$_3$, which is water soluble. The solubility of the bronze physically isolates the Pt nanoparticles, which migrate and agglomerate into large superclusters.

Nitrogen-Doped Ordered Mesoporous Carbon

We also evaluated the influence of surface functional groups (primarily nitrogen and oxygen) on carbon and its microcrystallinity on the dispersion and activity of supported platinum particles [Publications 1-2, 9-13]. We prepared the carbon supports using an amorphized silicate template. The carbons were made by modifying SBA-15, filling the template with pyrrole, polymerization and carburization at various temperatures between 800°C and 1400°C to control the length of the graphitic domains and nitrogen content. The carbons are denoted as CPPy-X, where X is the heat treatment temperature in Celsius. The PSD profile of all of CPPy-X carbons were similar, signifying that the temperature treatment did not change their pore structure. The SBET and V$_{tot}$ of all samples were within 5%. The SBET of CPPy-1000 was 593 m^2/g and its V$_{tot}$ was 0.78 cm^3/g. We also performed extensive XRD and RAMAN analysis, which showed that, generally, the length of the graphitic domains of the carbon increased with temperature; however, this did not change the overall structure of the material. However, XPS showed significant changes in surface composition among CPPy-X samples. The atomic (at) % of C, N and O were determined
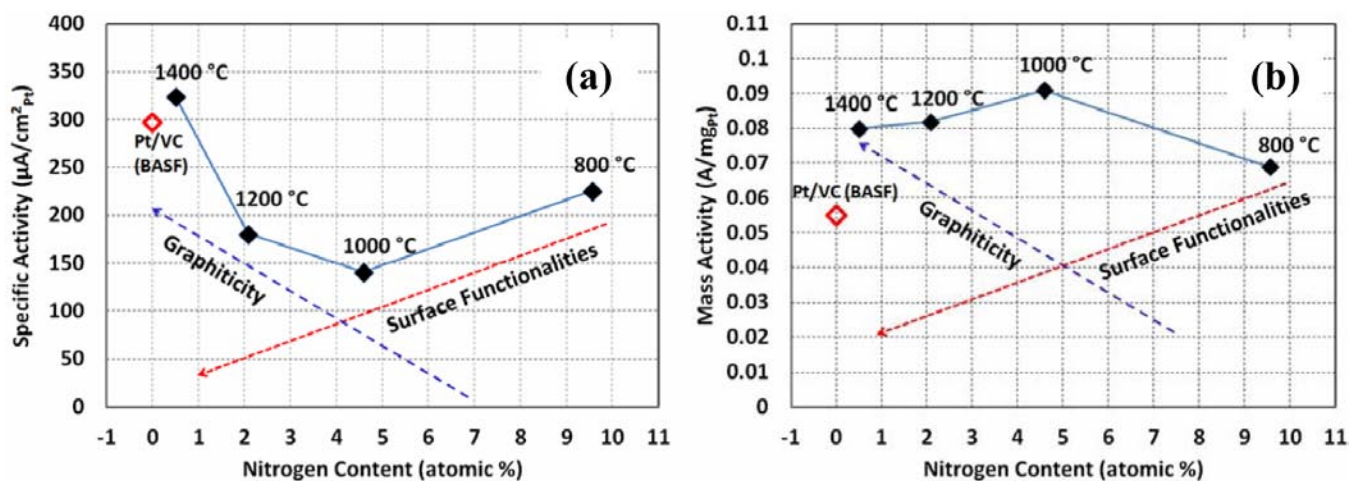

FIGURE 2. Trends in the specific (a) and mass (b) activity of Pt supported on N-functionalized carbon.

from C 1s, N 1s and O 1s peaks of full survey spectra. The nitrogen content decreased from 10.5 at % (800 °C) to 0.5 at % (1400 °C) while the oxygen content decreased from 8.4 at % (800 °C) to 0.3 at % (1400 °C). In fact, at 1400 °C, the nitrogen and oxygen contents were within the error limit of XPS (< 1%).

50 wt% of Pt was deposited onto the CPPy-X supports without pre-activation (i.e. boiling in acid to increase the number of oxygen functionalities). Without such pre-activation, Pt NPs on CPPy-X were expected to be clustered, especially at high loadings such as 50 wt% which was the target loading in this work. High resolution TEM images of Pt/CPPy -800 and Pt/CPPy -1000 showed a uniform Pt NPs particle size distribution. However, particles in Pt/CPPy -1000 were larger than that of Pt/CPPy-800. Indeed, the average size of Pt NPs was 3.7 nm on Pt/CPPy -1000 while it was 1.5 nm on Pt/CPPy-800. Compared to Pt/CPPy-800 and Pt/CPPy-1000, agglomeration could be observed in Pt/CPPy-1200 and Pt/CPPy-1400 despite their high surface areas. However, the size of Pt NPs on Pt/CPPy-1200 and Pt/CPPy-1400 were 2.9 and 3.3 nm, respectively. We found that a very intricate mechanism of Pt NPs nucleation and growth existed on Pt/CPPy-X which warrants additional study.

The ORR activity of the Pt/CPPy-X electrocatalysts was determined by CV between 0.2 and 1.1 V vs. NHE. Overall, we found that the nitrogen content played a far more significant role in the ORR activity than the surface oxygen groups and some interesting trends were observed. The trends in the specific and mass activity of Pt are shown in Figures 2a and 2b, respectively. The specific ORR activity of supported Pt initially decreased with increasing N content, as the particle size decreased. However, after a minimum at 5% N, the specific activity again increases, which is very surprising since the Pt dispersion was enhanced with excess N, which gave the smallest Pt particle sizes. We would normally

have expected the specific activity to further drop. The enhancement in specific activity suggests some interaction between Pt and the N groups, which needs to be understood. We have done some preliminary XAS work and have observed some variation of shape in the secondary peaks of the high energy (EXAFS) region, which suggests some electronic interaction between Pt and the functional groups. We expected the unusually high specific activity with small particle size to yield very high mass activity catalysts, however, we found that the Pt in the carbon pores were generally inaccessible, leading to very low electrochemically active area (only 31 m^2/g). Mechanisms to improve the accessibility of the nanosized Pt also require additional study.

Future Directions

Our future work with ITO and WC supports will focus on improving their long-term stability. We will also further study how the faceting of the non-carbon catalyst support influences how the Pt nanoparticles grow and some of our future work will be targeted in this area as well on model surfaces. We will also investigate new geometries to shield carbide-based supports from the electrolyte as well as the deposition of monolayer thickness Pt films. We will also investigate coupling a new physics-based model with a genetic algorithm to evaluate their performance with the goal of predicting novel catalyst layer microstructures.

Publication list (including patents) acknowledging the DOE grant or contract

1. Shrestha, Sujan; Asheghi, Sasha; Timbro, Jeffrey; Mustain, William E., "Effects of Pore Structure in Nitrogen Functionalized Mesoporous Carbon on Oxygen Reduction Reaction Activity of Platinum Nanoparticles.", *Carbon*, Accepted, In Press.

2. Shrestha, Sujan; Asheghi, Sasha; Timbro, Jeffrey; Morse, Nicholas; Mustain, William E., "Temperature Controlled Surface Chemistry of Nitrogen Doped Mesoporous Carbon and Its Influence on Pt ORR Activity", *Appl. Catal. A*, Accepted.

3. Liu, Ying; Mustain, William E., "High Stability, High Activity Pt/ITO Oxygen Reduction Electrocatalysts", *J. Am. Chem. Soc.*, 2013, **135** (2), 530.

4. Liu, Ying; Mustain, William E., "Evaluation of Tungsten Carbide as the Electrocatalyst Support for Platinum Hydrogen Evolution/Oxidation Catalysts", *Int. J. Hydrogen Energy*, 2012, **37**, 8929.

5. Liu, Ying; Shrestha, Sujan; Mustain, William E., "Synthesis of nano-size tungsten oxide and its evaluation as an electrocatalysts support for oxygen reduction in acid media", ACS Catalysis, 2012, **2**, 456.

6. Shrestha, Sujan; Liu, Ying; Mustain, William E., "Electrocatalytic Activity and Stability of Pt clusters on State-of-the-Art Supports: A Review, 2011, **53**, 256.

7. Liu, Ying; Mustain, William E., "Structural and Electrochemical Studies of Pt Clusters Supported on High Surface Area Tungsten Carbide for Oxygen Reduction", *ACS Catalysis*, 2011, **1**, 212.

8. Shrestha, Sujan; Mustain, William E., "Properties of Nitrogen-Functionalized Ordered Mesoporous Carbon Prepared Using Polypyrrole Precursor", *J. Electrochem. Soc.*, 2010, **157**, B1665.

9. Shrestha, Sujan; Morse, Nicholas; Mustain, William E., "Effect of Surface Chemistry on Double Layer Capacitance of Nitrogen Doped Ordered Mesoporous Carbon", Submitted for Review.

10. Shrestha, Sujan; Asheghi, Sasha; Timbro, Jeffrey; Mustain, William E., "Influence of Pore Structure of N-Doped Mesoporous Carbon in PEM Fuel Cells", *ECS Trans.*, 2013, 50 (2), 1287.

11. Shrestha, Sujan; Asheghi, Sasha; Timbro, Jeffrey; Lang, Christopher M.; Mustain, William E., "ORR and Fuel Cell Performance of Pt Supported on N-Functionalized Mesoporous Carbon", *ECS Trans.*, 2011, **41**(1), 1183.

12. Shrestha, Sujan; Mustain, William E., "Pt Nanoparticles Supported on Nitrogen Functionalized Ordered Mesoporous Carbon", *ECS Trans.*, 2010, **33**(1), 293.

13. Shrestha, Sujan; Mustain, William E., "Electrochemical Studies of N-functionalized Mesoporous Carbon", *ECS Trans.*, 2010, **28**(23), 27.