

# Structure-Property Relationship in Metal Carbides and Bimetallic Alloys

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## Objectives

The main objective of the current DOE-sponsored research is to correlate the structure-property relationship in metal carbides and bimetallic alloys, with the aim of replacing or substantially reducing the loading of Pt-group metals in catalysis and electrocatalysis. It is well known that the electronic and catalytic properties of transition metals can be modified by alloying either with carbon to form carbides or with another metal to produce bimetallic alloys. The carbide and bimetallic materials are excellent model systems to demonstrate the feasibility of tuning the catalytic activity, selectivity, and stability as alternative electrocatalysts to replace Pt-group metal catalysts.

## Technical Barriers

Fuel cells, electrolyzers, and photoelectrochemical cells are electrochemical devices that are commonly regarded as core technologies in a clean energy future. Central to the operation of all of these devices are electrocatalysts, which mediate charge transfer processes between the electrolyte and device electrodes with minimal losses in efficiency. Unfortunately, many state-of-the-art catalysts used in these technologies are comprised of expensive Pt-group metals. The high prices and limited supplies of these precious metals create potentially prohibitive barriers to market penetration and scale-up production of devices requiring large catalyst loadings.

## Abstract

In the current presentation we will discuss the utilization of metal-modified carbides as potentially low-cost electrocatalysts for several reactions, including hydrogen evolution reaction (HER) and alcohol oxidation. For example, by depositing one monolayer (ML) of Pt on a tungsten monocarbide (WC) substrate, the ML Pt/WC electrocatalysts show similar HER activity as bulk Pt, demonstrating the possibility of significantly reducing the Pt loading. The Pt/

WC catalyst also shows enhanced CO-tolerance over Pt for alcohol oxidation. We will also present our recent results on alternative electrocatalysts using other monolayer metals (Pd, Cu) and on other metal carbide substrates ( $W_2C$ ,  $Mo_2C$ , and TiC).

## Progress Report

When powered by renewable energy sources, such as wind- or solar-based technologies, the generation of hydrogen from the electrolysis of water represents a means to produce a high energy density, mobile energy carrier without any associated carbon dioxide emissions. At low temperatures, this process can take place in a variety of electrochemical devices ranging from high-current density polymer electrolyte membrane (PEM) electrolyzers to low-current density, solar-driven photoelectrochemical cells (PECs). For all of these water-splitting applications, the choice of the HER catalyst employed at the cathode can have a profound influence on the cost, lifetime, and efficiency of the device. Pt is a very active and commonly used HER catalyst, but its high cost and limited world-wide supply make its use a barrier to mass production of  $H_2$  by water electrolysis. One approach to overcoming the challenges associated with Pt HER catalysts is to increase the surface to bulk atomic ratio of Pt, allowing for a lower metal loading to be used without compromising electrolysis efficiency. At present Pt electrocatalysts are typically in the form of supported nanoparticles, in which most Pt atoms are located within the particle core where they are screened from being involved in the electrochemical reaction. During the past funding cycle we explored the lower limit of Pt loading by utilizing nearly all Pt atoms in the form of an atomic layer, or monolayer (ML), on low-cost tungsten monocarbide (WC) and other carbide substrates. Although Pt is still utilized, this ML Pt-WC electrocatalyst structure approaches the lower limit of Pt loading. By using a low cost support material such as WC, the ML Pt-WC structure offers great potential to drive down catalyst costs for various clean technology devices.

The main reason for choosing WC as the substrate is largely due to the fact that WC often shows "Pt-like" properties, as demonstrated by both our group and other researchers. There is a general agreement in the literature that WC has similar bulk electronic properties to Pt, but there is notable deviation in surface properties. These differences in surface electronic properties, which ultimately determine how a surface interacts with reactants, are small enough to translate into similar catalytic behavior for some reaction systems, but not for others, including most electrochemical applications. During the past funding cycle we have attempted to overcome the short-comings of pure WC

catalysts by modifying the WC surface with ML amounts of Pt. The hypothesis is that replacement of all but the top ML of bulk Pt catalysts with an electronically similar “Pt-like” WC core will result in a ML Pt-WC surface that should have electronic and catalytic properties more similar to Pt than WC. The significance of this concept is that it predicts that ML Pt-WC will exhibit catalytic activity that is comparable, though not identical, to bulk Pt catalysts while making full use of every Pt atom. A further expectation that follows from the similar electronic properties of Pt and WC is that they should intuitively result in good adhesion between the Pt ML and WC surface, suppressing the tendency for the Pt ML to agglomerate into bulk Pt particles that would lead to a reduction in catalytic activity.

In order to probe the electronic similarities of ML Pt-WC and bulk Pt catalysts, DFT calculations were used to determine the binding energies of reactant molecules that are relevant to key electrochemical applications. For example, we compared the binding energies for hydrogen (relevant to HER activity), oxygen (relevant to the oxygen reduction reaction (ORR) activity of polymer electrolyte membrane fuel cells), and methoxy (related to the direct methanol fuel cell (DMFC) activity) for Pt(111), WC(0001), and ML Pt-WC(0001) surfaces. These binding energies are chemical descriptors that are related to the HER, ORR, and DMFC activities, respectively. Previous work has shown that the hydrogen, oxygen, and methoxy binding energies all correlate strongly with the surface d-band density of states (DOS). It is well known that the distribution of the surface d-band DOS, approximated by the d-band center, plays a crucial role in determining how a surface interacts with adsorbed atoms and molecule. Our results show that the bare WC(0001) surface binds all three adsorbates much more strongly than Pt(111), but modification of the WC(0001) surface with 1 ML of Pt shifts all three binding energies to values that are similar to Pt. For the most simple adsorbates, hydrogen and oxygen, the calculated binding energies on ML Pt-WC(0001) are nearly identical to Pt(111), suggesting that ML Pt-WC should show similar HER and ORR activities to Pt. In comparison, it is seen that there is still a notable difference in the binding energy of the slightly more complex methoxy intermediate, suggesting different DMFC activity for ML Pt-WC and Pt. These predictions have been verified experimentally in our subsequent studies.

Based on DFT predictions of similar hydrogen binding energy on ML Pt-WC(0001) and Pt(111), we have evaluated the activity of ML Pt-WC for HER, which is the cathodic reaction that produces  $H_{2(g)}$  during water electrolysis and is one of the most fundamental and commonly studied electrochemical reactions. To test these predictions, the HER activity of sub-ML to ML amounts of Pt on WC thin films was compared to a Pt foil sample by carrying out linear sweep voltammetry in 0.5 M  $H_2SO_4$  at room temperature. Our results show that the HER activity of the bare WC

surface is much lower than that of the Pt foil, but the addition of one ML of Pt to WC results in a surface with HER activity comparable to the bulk Pt foil. This finding is in excellent agreement with DFT predictions based on the expected correlation between hydrogen binding energy and HER activity, and demonstrates the potential of using ML Pt-WC to drastically decrease Pt loading for the HER application. Furthermore, the ML Pt-WC surfaces show excellent stability due to the strong binding between surface Pt atoms and the WC substrate.

In order to extend the promising results on thin films to real world applications, it is important to synthesize and evaluate core-shell Pt-WC catalysts in the powder form. The synthesis of ML Pt-WC powder catalysts is challenging, and until our recent study no established methods exist. Physical vapor deposition (PVD) has been shown to successfully produce monolayers on planar substrates, but PVD is a line-of-sight technique, and therefore, not applicable to particle substrates. To demonstrate the proof-of-principle, we explored the atomic layer deposition (ALD) of Pt over WC particles. The HER activity of the resulting core-shell Pt-WC particles was evaluated using similar methods for the thin film catalysts. Our results show that, as Pt coverage on WC increases to an equivalent of 1 ML, the value for HER activity of Pt-WC approaches that of 10 wt% Pt/C. Although an ideal single ML of Pt is not produced on the WC powder using ALD, the presence of a thin Pt layer on the WC substrate is sufficient to achieve HER activities that are comparable to the conventional Pt/C catalysts. The Pt wt% for each of the ALD Pt-WC catalysts was determined from atomic absorption spectroscopy (AAS) measurements. The Pt loading in the Pt-WC sample is determined to be about a factor of ten less than the 10 wt% Pt/C catalyst, confirming the possibility of substantially reducing the Pt loading while achieving HER activity similar to pure Pt catalysts.

In addition to the ML Pt/WC catalysts, several other metal-carbide modified systems, including ML Pt on  $W_2C$ ,  $Mo_2C$  and  $TiC$ , have been evaluated for HER activity. These results demonstrate the possibility of extending knowledge learned from WC to other metal carbide substrates.

## Future Directions

We plan to further unravel the structure-property relationship in carbide and metal-modified carbide catalysts, with a special focus on the fundamental understanding of using metal-modified carbides as electrocatalysts. We plan to search for metal-modified carbides as efficient electrocatalysts, using combined theoretical and experimental approaches to identify descriptors for predicting HER catalysts; the promising metal-modified carbides will also be evaluated for HER activity and stability in the presence of impurity ions that are typically present in tap water. We will also explore the utilization of metal-modified carbides

as electrocatalysts for CO<sub>2</sub> reduction based on our hypothesis that the CO-tolerant nature of metal-modified carbides should make them more active and stable than currently leading Pt- and Cu-based electrocatalysts.

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