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# Pt-modified molybdenum carbide for the hydrogen evolution reaction: From model surfaces to powder electrocatalysts

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## HIGHLIGHTS

- We investigate $Mo_2C$ catalysts modified by Pt for the hydrogen evolution reaction.
- Thin films of $Mo_2C$ supporting a Pt monolayer displayed activity similar to bulk Pt.
- Results from thin film surfaces were scaled to powder electrocatalysts.
- Pt-modified $Mo_2C$ powders showed high activity and stability.

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## ABSTRACT

This work explores the opportunity to substantially reduce the cost of hydrogen evolution reaction (HER) electrocatalysts by supporting one monolayer (ML) of platinum (Pt) on low-cost molybdenum carbide ($Mo_2C$) substrate. These efforts were primarily directed towards scaling a thin-film catalyst to high surface area particles. Electrochemical experiments investigated single-phase $Mo_2C$ thin films modified by different coverages of Pt for the HER. The ML Pt–$Mo_2C$ thin film showed Pt-like HER activity while displaying excellent stability under HER conditions. The promising results on thin films were then extended to more practical powder catalysts. Samples of various Pt loadings on $Mo_2C$ powders were synthesized using the co-impregnation method and were evaluated for HER activity. The ability to successfully link electrochemical activity on thin films and powder catalysts was thus demonstrated.

## 1. Introduction

Low- temperature water electrolyzers show promise as sources of hydrogen. For example, a proton exchange membrane (PEM) electrolyzer can produce $H_2$ at high levels of pressure and purity. As compared to traditional alkaline electrolyzers, a PEM cell does not contain a caustic liquid electrolyte that is difficult to transport. However, due to the acidic environment and need for high current density, PEMs utilize scarce and expensive precious metals such as platinum (Pt). With the demand for hydrogen and the extensive development of fuel cells and PEM electrolyzers, the global reserves of Pt are gradually decreasing. Therefore, it is necessary to search for alternative electrocatalysts that substantially decrease or eliminate altogether the amount of Pt, without losing the performance of conventional Pt electrocatalysts.

One method of minimizing Pt loading is to use metal carbides as support materials for one monolayer (ML) of Pt. Recent findings have shown that Pt monolayer supported on tungsten carbide (Pt/WC or $W_2C$) showed HER activity almost identical to that of Pt bulk foil [1]. However, the synthesis of WC requires extremely high temperatures that could promote the sintering of small WC particles into larger ones, decreasing the surface area [2]. Another metal carbide, molybdenum carbide ($Mo_2C$), can be synthesized at lower temperatures and thus has a higher surface area than WC. Recently, porous $Mo_2C$ catalysts were synthesized with a surface area of 94 $m^2\ g^{-1}$ and were active for the hydrodeoxygenation of C3 oxygenates to alkenes [3]. Additionally, $Mo_2C$ has shown to be a promising support material in both gas-phase and electrochemical systems [4,5]. Moreover, similar to WC, $Mo_2C$ is electrochemically stable at HER conditions in acidic solution [6,7]. Pt-modified Mo2C has previously been used as a catalyst for cellulose conversion to polyols [8] and the water-gas shift reaction [9]. Additionally, Pt/Mo2C was studied as an electrocatalyst for the oxygen reduction

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reaction [10]. This prior work makes $Mo_2C$ a promising material to support ML Pt as low-cost HER electrocatalysts.

There are two primary objectives in the current study. First, we seek to explore Pt-modified $Mo_2C$ HER catalysts by studying the deposition of sub-ML to ML amounts of Pt loadings on single-phase $Mo_2C$ thin films. Previously, HER activity was shown to be correlated to the hydrogen binding energy (HBE) in both monometallic and bimetallic alloys [11,12]. Materials such as the Pt-group metals have intermediate HBE values, which result in high HER activity. In the current study, electrochemical experiments were conducted to evaluate the activity and stability of single-phase $Mo_2C$ and ML Pt/$Mo_2C$ films. Polycrystalline $Mo_2C$ foils were synthesized using temperature programmed reaction with methane and hydrogen. Multiple coverages of Pt were deposited on the foils by physical vapor deposition (PVD). X-ray photoelectron spectroscopy (XPS) was used to verify the carbide stoichiometry and overlayer coverage of Pt. Electrochemical measurements such as linear sweep voltammetry (LSV) and chronopotentiometry (CP) were utilized to assess the activity and stability of the Pt/$Mo_2C$ electrocatalysts. Finally, XPS characterization was compared before and after electrochemical experiments to determine catalyst stability.

The second objective of this study is to scale up the ML Pt—$Mo_2C$ thin film system to more commercially viable powder electrocatalysts. The motivation for synthesizing catalysts in powder form is driven by their high surface area and ease of impregnation on carbon paper. HER measurements were conducted to compare samples of $Mo_2C$ with different loadings of Pt with 10 wt% Pt supported on high surface area carbon (Pt/C) to determine whether Pt—$Mo_2C$ powder showed good catalytic activity for HER in acidic environment as predicted from the results on ML Pt—$Mo_2C$ thin films.

## 2. Methods

### 2.1. Synthesis and characterization of Pt-modified $Mo_2C$ thin films

Polycrystalline Mo foils (Alfa Aesar, 99.95%, 0.1 mm) were rinsed with deionized (DI) water and methanol, and dipped in a 0.3 M NaOH solution for one minute (Fisher Scientific, 99.5%), which has been shown to remove surface oxides [7,13]. The treated foils were placed within a Lindberg furnace (model 55035) to synthesize $Mo_2C$ by direct carburization with methane ($CH_4$) and hydrogen ($H_2$) using flow rates of 33 and 122 sccm (molar ratio 21% and 79%), respectively. The high temperature synthesis step for $Mo_2C$ was carried out at 850 °C. At the end of the synthesis procedure, $H_2$ was fed for two hours to remove excess surface carbon, as previously verified using XPS [14]. The samples were then exposed to a mixture of 1% $O_2$ in 99% $N_2$ for three hours at room temperature to passivate the surface defects to prevent severe oxidation upon exposing $Mo_2C$ to atmospheric oxygen.

The $Mo_2C$ foils were rinsed with DI water, methanol, and dipped in a 0.3 M NaOH solution for one minute. Within ten minutes of ambient exposure, the samples were transferred into a PVD chamber with a base pressure of $1 \times 10^{-8}$ Torr. A 0.5 mm diameter tungsten filament with a 0.2 mm diameter Pt wire (Alfa Aesar, 99.9%) coiled around the filament was resistively heated to evaporate Pt on the $Mo_2C$ substrate. This thermal evaporation method has been commonly employed in the preparation of ML metal over carbide surfaces [15].

Once the Pt/$Mo_2C$ samples were synthesized, they were transferred into a Phi 5600 XPS chamber within ten minutes of ambient exposure. The XPS was calibrated using the reported binding energies of Au, Ag, and Cu reference thin films [16]. The Pt overlayer coverage was calculated using the inelastic mean free path (IMFP) values provided in Cumpson and Seah [17]. Further details can be found in previous publications [1,18]. After the electrochemical experiments, the samples were transferred into the XPS chamber within ten minutes of ambient exposure for further characterization.

### 2.2. Preparation and characterization of Pt/$Mo_2C$ powders

For each experiment, 20 μL of ink sample was dropped onto the center of a glassy carbon substrate. The ink was an aqueous suspension of ~2.6 mg of catalyst/mL of solvent produced by ultrasonically dispersing a metal loading of 0.0025, 0.005, 0.01, 0.02, 0.04, 0.06, 0.08, 0.1 (g of catalyst/g of support) for 1 h in deionized water. The catalyst was prepared by co-impregnating Pt metals on $Mo_2C$ immersed in an oil bath at a temperature of ~65 °C until all of the water was evaporated, followed by a 2 h calcination process at 290 °C in order to remove volatile fractions such as $NO_3^-$ from the respective precursors. Once the metal was uniformly dispersed in water solvent, the ink was dropped onto the glassy carbon electrode by forming a ring of droplets on the outside edge of the disk, and then filling the middle with the remainder of the ink. This procedure was calculated to yield a catalyst loading of 10 μg $cm^{-2}$ for a standard electrode geometric surface area of 0.196 $cm^2$. After the ink dried on the electrode, a single drop of Nafion was pipetted onto the catalyst and allowed to dry for a stronger binding between the catalyst and the surface of the electrode. Inductively coupled plasma (ICP) was used to test for dissolution of Pt/$Mo_2C$ powders from the disk into the electrolyte solution.

### 2.3. Electrochemical measurements

Electrochemical measurements were performed using a three-electrode glass cell containing 0.5 M sulfuric acid solution ($H_2SO_4$, Fisher Scientific, 96.9%) using a Princeton Applied Research Versastat 4 potentiostat. The solution was prepared with DI water purified to a resistivity above 17 MΩ-cm by a Barnstead NAN-Opure filtration system. Pt gauze (Alfa Aesar, 99.9%) was used as the counter electrode. Twenty-five cyclic voltammetry (CV) scans between 0 and 0.4 V vs NHE were used to clean and condition the Pt/$Mo_2C$ electrode surfaces, and scans in the range of 0–1.4 V were used to clean the Pt reference wire. LSV measurements from +0.1 to −0.4 V vs NHE at a sweep rate of 2 mV $s^{-1}$ were used to measure the HER activity by generating Tafel plots. LSV measurements were performed in Ar-purged solution with a saturated calomel electrode (SCE) used as the reference. Chronopotentiometry (CP) was used to measure the electrochemical stability of the samples over two hours of HER operation; alternating periods without current for five minutes and 10.0 mA $cm^{-2}$ for twenty-five minutes were used to simulate the intermittent operation typical of an electrolysis device. A Pt wire with $H_2$ bubbled through the solution to maintain saturation was used as an internal reference electrode for the CP experiments.

## 3. Results and discussion

### 3.1. Structure and activity of thin films

The Pt/$Mo_2C$ thin film system was first evaluated to determine its growth mechanism by using XPS. Fig. 1 shows the Pt coverage as a function of deposition time on a thin $Mo_2C$ film. The increase in Pt film thickness was linear with respect to deposition time, suggesting that Pt growth was layer-by-layer on $Mo_2C$. The layer-by-layer mechanism agrees with that seen previously for Pt on a WC substrate [1].

The Pt-modified $Mo_2C$ thin films, with different Pt coverages, were evaluated for HER activity. Fig. 2 shows a CV performed in Ar-