# Theoretical prediction and experimental verification of low loading of platinum on titanium carbide as low-cost and stable electrocatalysts

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A B S T R A C T

Titanium carbide (TiC) is electrochemically stable and can be synthesized with high surface area. It also has a strong affinity to platinum (Pt), making TiC an ideal support for low loading of Pt as a low-cost and stable electrocatalyst. Density functional theory (DFT) calculations were used to predict the hydrogen evolution reaction (HER) activity and the stability of monolayer (ML) Pt on TiC. The DFT prediction was verified experimentally on ML Pt/TiC thin film that showed comparable HER activity as bulk Pt. The HER activity of Pt/TiC thin film was then extended to Pt supported TiC powders with similar results. The combined theoretical and experimental results demonstrate the utilization of TiC as a support to significantly reduce the Pt loading required for the HER.

## 1. Introduction

Interest in the production and utilization of hydrogen as renewable energy source has led to the development of photoelectrochemical (PEC) cells, electrolyzers, and proton exchange membrane (PEM) fuel cells. These devices carry out either the hydrogen evolution reaction (HER) or the reverse reaction, hydrogen oxidation (HOR). The most active catalysts for HER and HOR under acidic conditions are the platinum (Pt)-group metals. However, the scarcity and high cost of Pt indicate that the current loading of Pt is a major hurdle for the large-scale production and use of these devices [1]. Dissimilarities in chemical properties between Pt and carbon, the standard support for the Pt catalysts, prevent the significant reduction in Pt loadings without compromise in activity [2].

Previous studies have taken advantage of the Pt-like bulk electronic and catalytic properties of tungsten carbide (WC) [3,4] as a support to significantly reduce the Pt loading for HER. This similarity allows for a stable monolayer (ML) of Pt to form on a WC support, resulting in similar HER activity as to bulk Pt [5,6]. The use of a Pt ML represents the minimum Pt loading as every Pt atom is theoretically being utilized as a catalyst. A drawback for using WC is that it requires high synthesis temperatures, leading to a low surface area material that is not desirable for realistic, highly active electrocatalysts.

The challenges in low surface area can be potentially solved by supporting ML Pt on titanium carbide (TiC). In addition to possessing similar Pt-like electronic properties as WC [7], TiC has a lower synthesis temperature that leads to smaller carbide particles and higher surface areas. For example, TiC powders can be commercially purchased with sizes of ∼30–50 nm [8], which are in the size range typically required for catalyst supports in PEM fuel cells. High surface area TiC has been synthesized with areas over 700 m² g⁻¹ [9]. Furthermore, TiC has been shown to be more stable under operational electrochemical conditions compared to Vulcan XC-72 [10] and other metal ceramics [11]. From an economic perspective, Ti is orders of magnitude more abundant than Pt in the earth crust. Currently, Pt production is five orders of magnitude lower than that of Ti and is dominated by a small number of countries, while Ti mineral production is spread among many countries [12]. This allows the availability of Ti metal to be more tolerant to geopolitical or economic issues. Consequently, the cost of Ti is orders of magnitude less expensive than Pt [13]. However, TiC has been largely ignored as a support compared to other metal carbides, such as WC or molybdenum carbide (Mo₂C), which could be because TiC was not as active as a stand-alone catalyst as WC or Mo₂C [11,14].

There are primarily two novel aspects for the current study: (1) The demonstration of TiC as a low-cost, stable, and high surface area support for low loadings of Pt for the HER and as a viable alternative to the conventional carbon support. (2) The correlation of DFT predicted activity and stability with experimental results of

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Pt supported on TiC thin films that are easily characterized and modified, and then with supported Pt/TiC powders that can be used realistically in a PEM device.

## 2. Experimental and theoretical methods

In the current study DFT calculations were used to predict the HER activity and stability based on the binding energy values. TiC films were synthesized, characterized with X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), and modified with ML Pt using physical vapor deposition (PVD). TiC powders were modified with Pt by the simple and widely used industrial technique, incipient wetness impregnation (IWI). The electrochemical stability and HER activity of TiC and Pt/TiC films and powders were characterized in 0.5 M sulfuric acid ($H_2SO_4$), using cyclic voltammetry (CV) and linear sweep voltammetry (LSV). XPS measurements were compared before and after electrochemical measurements to verify the stability of the Pt ML and TiC films.

### 2.1. Synthesis of TiC films

Polycrystalline 0.127 mm thick titanium foil (Alfa Aesar, 99.99+% pure) was rinsed in methanol, DI water, and sulfuric acid (Fischer Scientific, Certified ACS plus) to remove any impurities. The Ti foils were slowly heated in a tube furnace to 1273 K for 1 h in the presence of 21 vol% methane/79% hydrogen to carburize foils. After the carburization step, the furnace was cooled at 3.3 K min$^{-1}$ to 1123 K, and at this point, the methane was turned off, and the temperature was held constant for 15 min before cooling. After the furnace was cooled to below 303 K, the hydrogen flow was turned off and the TiC foils were passivated in 1% oxygen/99% nitrogen for 1 h before exposure to atmosphere. More information on synthesis of carbide foils can be found in literature [15].

### 2.2. Characterization of Pt on TiC thin films

The TiC thin films were loaded into an ultra-high vacuum (UHV) chamber with Pt PVD and XPS capabilities. The PVD of Pt was performed by evaporation of Pt wire wrapped around a resistively heated tungsten wire. XPS scans were measured using a Phi 5600 XPS system using an Al X-ray source. Symmetric XRD was performed with a Cu Kα X-ray source using a Phillips Norelco XRD diffractometer. SEM images were taken using a JSM 7400f SEM with a probe current of 10 μA and an accelerating voltage of 3 keV.

### 2.3. Pt IWI onto TiC powders

Pt/TiC powders were prepared via slurry method, using tetraamineplatinum(II) nitrate (Alfa Aesar, Premion) as a precursor. The precursor was dissolved in ~10 ml of DI water and added to TiC powder (Alfa Aesar, APS powder). The mixture was stirred and heated at 333 K in a silicon oil bath to allow for the slow evaporation of water. Once all the water was evaporated, the sample was slowly heated in a furnace to 373 K at a rate of 0.4 K min$^{-1}$ and further dried for 10 h. Finally, the sample was heated to 563 K at a rate of 0.8 K min$^{-1}$ and held for 2 h for calcination, which allowed for the decomposition of the Pt precursor.

### 2.4. Powder electrode preparation

For Pt/TiC samples and the 10% Pt/carbon black (Alfa Aesar), inks were typically prepared by dispersing Pt/TiC powder in 5 ml of 50 vol% isopropanol aqueous solution. The amount of catalysts was determined from the Pt loading of the catalyst, with 5 ml of

ink containing a total of 0.653 mg Pt. After being sonicated for ~60 min, 15 μL of ink was dropped on a glassy carbon electrode (5 mm diameter, Pine Research Instrumentation), corresponding to 10 μg cm$^{-2}$ of Pt on the electrode. The ink was evaporated in air at room temperature for 12 h.

### 2.5. Electrochemical measurements of thin films and powders

Electrochemical experiments were conducted at room temperature in a solution of 0.5 M $H_2SO_4$ that was saturated with $N_2$ or Ar for at least 40 min. Inert tape (3 M Electroplating tape 470) was used to cover the back and sides of the foils to give the foil a defined geometric area to the electrolyte. A Pt gauze was used as a counter electrode and a double-junction saturated mercury sulfate electrode (Pine Research Instrumentation) was used as a reference electrode. Polycrystalline Pt foil (Alfa Aesar, 99.99% pure) was sonicated in acetone and rinsed with DI water before use. The TiC foils and powders were conditioned by cycling 25 times between 0.05 and 0.4 V vs. normal hydrogen electrode (NHE) at a rate of 50 mV s$^{-1}$ before the linear sweep voltammetry (LSV) measurement, and Pt foil and 10% Pt/carbon were conditioned by cycling between 0.05 and 1.2 V vs. NHE at a rate of 50 mV s$^{-1}$ until steady state was reached. Tafel plots were generated from LSV scans that were recorded from 0.1 to −0.09 V vs. NHE for the foil samples and 0.1 to −0.4 V vs. NHE for the powder samples at a scan rate of 2 mV s$^{-1}$.

### 2.6. DFT calculations

Hydrogen binding energies were calculated on the Pt(111), TiC(111), and Pt/TiC(111) surfaces using DFT with the Vienna Ab-initio Simulation Package (VASP). The PW91 functional was utilized for electronic structure calculations [16–18]. A 3 × 3 fcc(111) unit cell was employed to represent the surfaces. These calculations were done with a 3 × 3 × 1 k-point mesh. The energy cutoff was 396 eV and calculations were spin-polarized. For the Pt(111) slab, four atomic layers were used, with the bottom two layers fixed and the top two layers allowed to relax. Lattice parameters for TiC(111) were taken from literature [19] and the slab was represented by three layers of TiC. Hydrogen binding energies were calculated by subtracting the clean slab and $H_2$ gas-phase energies from the slab-H total energy.

## 3. Results and discussion

### 3.1. Characterization of TiC films

The SEM image of the TiC film (Fig. 1a) shows that the surface is relatively rough. The 1273 K synthesis temperature is below the temperature required for polycrystalline TiC film to become dense and ductile [20], which could explain roughness shown in the SEM images. The ML Pt/TiC surface (Fig. 1b) does not show distinguishable particles, consistent with the formation of a thin Pt layer. Fig. 1c shows the XRD pattern of the synthesized TiC film, along with the labeled crystal facets of TiC from literature [ICDD 32-1383]. The primary facets are in the (200) and (220) planes, indicating that the surface is primarily low index planes. The XRD pattern shows that the film is phase-pure TiC with no bulk graphite, Ti metal, or oxide present.

The carbidic Ti/C atomic ratio of TiC near the surface is ~1, which was calculated from the Ti 2p and C 1s XPS peak areas (see Electronic Supplementary Information [ESI]). Fig. 1d shows the Pt 4f XPS spectra of unmodified TiC and ML Pt on TiC. The Pt 4f peak locations of the ML Pt are shifted by +0.3 eV compared to bulk Pt reported in literature [21]. Such a core level shift is likely