



Effect of pretreatment atmosphere on the particle size and oxygen reduction activity of low-loading platinum impregnated titanium carbide powder electrocatalysts



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HIGHLIGHTS

- Low-loading Pt/TiC synthesized from impregnation shows high ORR activity.
- The atmosphere during thermal pretreatment affects the Pt particle size and the ORR specific activity.
- Pretreatment of Pt/TiC in H₂ leads to smaller Pt particle size and higher ORR activity.
- A surface oxide layer forms on TiC powder after calcination of Pt/TiC in air and results in lower ORR activity.

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ABSTRACT

Low-loading Pt supported on TiC powder catalysts were synthesized by an impregnation method. After the Pt(NH₃)₄(NO₃)₂ precursor was impregnated onto the TiC support, different pretreatment atmospheres were used to study the influence on Pt dispersion, surface composition, and catalytic activity towards oxygen reduction reaction (ORR). Direct reduction of the Pt precursor in hydrogen led to small Pt particles with an average size of ~2.2 nm and superior ORR activity at low overpotential compared to commercial Pt/C. However, calcination of the Pt precursor in air resulted in larger Pt particles with an average size of ~6.7 nm and lower ORR specific activity. The decrease in ORR activity was primarily attributed to the surface oxidation of the TiC support during calcination. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) confirmed that the TiC powder was oxidized when the catalyst was calcined in air. The finding reported here demonstrates the importance of pretreatment atmosphere for synthesizing Pt-modified transition metal carbides as highly active electrocatalysts.

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1. Introduction

The need for active, stable, and inexpensive electrocatalysts has generated interest in high surface area supports that can decrease the use of precious metals without compromise in activity [1]. Transition metal carbides (TMCs) are one promising class of support materials, which often show similar chemical and electronic properties to Pt-group metals [2]. Many transition metal carbides exhibit high chemical stability, resistance to corrosion and poisoning, and high electric conductivity [3]. As

summarized in recent reviews [3,4], many recent studies have utilized low-loading platinum supported on transition metal carbides as electrocatalysts for various applications, such as the hydrogen evolution reaction (HER) [5,6] and oxygen reduction reaction (ORR) [7].

Our group has previously reported that a monolayer of Pt on titanium carbide (TiC) thin film exhibited similar HER activity as bulk Pt, which was attributed to similar hydrogen binding energies between Pt/TiC and Pt from density functional theory (DFT) calculations [8]. This result was extended to Pt supported TiC powders which showed same activity as a much higher loading of Pt supported on carbon powder, the conventional electrocatalyst used in a PEM fuel cell and electrolyzer [8]. TiC is an attractive catalyst support because it can be synthesized at a relatively low

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temperature that results in a high surface area, which is necessary for commercial use [9]. Additionally, TiC is useful as a support for low loading Pt compared to carbon because TiC can stabilize Pt, preventing Pt agglomeration that leads to the loss of active Pt surface area exhibited on carbon [1] and [10]. DFT calculations of binding energies of Pt–Pt, Pt–C and Pt–TiC showed that a Pt atom is more stable to bond to a TiC surface rather than to another Pt atom, while a Pt atom is more favorable to bond to another Pt atom rather than to graphite [8]. Lastly, it has been demonstrated that TiC is electrochemically stable over a wide range of pH, thus is a suitable support for many electrochemical reactions [11]. This includes the oxygen reduction reaction (ORR), which occurs under conditions that are generally too oxidizing for most other transition metal carbides.

While TMCs are promising supports for Pt-group metals, currently there is a lack of detailed studies of optimal conditions on the synthesis of low loadings of Pt supported on TMC powders. Generally, supported metal powder catalysts can be synthesized from several methods including impregnation, reductive deposition precipitation, colloidal precipitation, and electrodeposition [12]. For high metal loadings, colloidal precipitation [12] or chemical reduction [13] methods are often preferred in order to achieve high dispersion and precise control over the size of the metal nanoparticles. Previous studies of Pt supported on TiC and its derivatives, such as titanium oxycarbides or $Ti_3C_2X_2$ ($X = OH, F$), utilized chemical reduction [14,15] or electrodeposition [16] to synthesize relatively high-loading Pt catalysts. However, for lower metal loadings, impregnation is favored because it is a direct and low-cost synthesis method.

The impregnation method must be followed by a thermal pretreatment to decompose the metal precursor. The pretreatment parameters such as temperature and gaseous atmosphere, e.g., oxidizing or reducing, affect the surface composition, morphology, and catalytic performance of the metal catalysts [17,18]. Additionally, thermal pretreatment in oxygen-containing environment can lead to surface oxidation of the transition metal carbide support [19]. In such case, the resulting Pt particles are supported on a transition metal oxide shell encapsulating a metal carbide core, rather than just the metal carbide itself. Consequently, the surface electronic properties and metal-support interaction deviate from the behaviors of the oxide-free support [20,21].

The main focus of this study was to synthesize and demonstrate the catalytic activity of low-loading Pt supported on TiC powder, and to explore how the thermal decomposition atmosphere of Pt precursor affects the ORR activities. Specifically, Pt precursor was impregnated on TiC powders and decomposed under three different gas-phase conditions: Air (oxidizing environment), hydrogen (reducing environment), and a successive sequence of air and hydrogen (oxidizing followed by a reducing environment). The Pt modified TiC powders were characterized with X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). Copper underpotential deposition (UPD) was used to determine the electrochemically active surface area of Pt/TiC. The ORR was used as a probe reaction to test the activities of the synthesized powders. Results indicate that pretreatment atmosphere greatly influences the catalytic activity by affecting the surface oxidation and Pt particle size. Pt/TiC powders synthesized under a reducing environment, without leading to excess surface oxidation of the TiC support, demonstrate high ORR activity. In contrast, Pt/TiC powders calcined in air show a surface oxide layer and a poor Pt dispersion, which adversely affect the ORR activity of the catalysts. Although the study is carried out on TiC, the general findings of the effect of pretreatment procedures should be useful for synthesizing low loadings of Pt on other transition metal carbide supports.

2. Experimental methods

2.1. Synthesis

TiC powder (30–50 nm APS Powder, S.A. $35\text{--}45\text{ m}^2\text{ g}^{-1}$) was purchased from Alfa Aesar and used as received. The TiC powder was impregnated with Pt (1.75 wt%) by using 0.018 M tetraammineplatinum(II) nitrate ($Pt(NH_3)_4(NO_3)_2$) as a precursor dissolved in deionized water. The slurry was stirred at room temperature for 12 h to ensure the adsorption of precursor onto the TiC surface, and the solvent was slowly evaporated at $55\text{ }^\circ\text{C}$ for ~ 12 h. The solid product was further dried in air by increasing the temperature to $100\text{ }^\circ\text{C}$ at a rate of $0.4\text{ }^\circ\text{C min}^{-1}$ and drying at $100\text{ }^\circ\text{C}$ for 10 h. After the solid product was cooled and finely ground, three different pretreatment methods were used to decompose the adsorbed Pt precursor. For the first method, the product was calcined in air. The powders were heated at a rate of $2.0\text{ }^\circ\text{C min}^{-1}$ to $290\text{ }^\circ\text{C}$ and held at $290\text{ }^\circ\text{C}$ for 2 h [22]. The catalyst produced from this method will be referred to as Pt/TiC(Air) for the remainder of this manuscript. For the second method, the dried product was directly reduced under hydrogen at a flow rate of 100 sccm (standard cubic centimeter per minute) in a quartz tube furnace. The temperature was increased to $310\text{ }^\circ\text{C}$ at a ramp rate $1.0\text{ }^\circ\text{C min}^{-1}$, and then held at $310\text{ }^\circ\text{C}$ for 5 h. After the furnace cooled to room temperature, the powder was passivated under an atmosphere of 99% N_2 and 1% O_2 (total flow rate 20 sccm) for 1 h. The catalyst produced from the second method will be referred to as Pt/TiC(H_2). For the third method, the dried product was first calcined in an identical manner to the first method. After the calcination, it was successively reduced in hydrogen at $310\text{ }^\circ\text{C}$ for 3 h and passivated at room temperature in a similar manner to the second method. The catalyst produced from this method will be referred to as Pt/TiC(Air| H_2).

2.2. Material characterization

For surface composition studies, XPS measurements were performed with a Phi 5600 XPS system using an Al X-ray source. For the bulk crystallographic information, powder XRD was performed using a PANalytical X'Pert diffractometer with a $Cu\ K\alpha$ radiation at 45 kV and 40 mA. TEM measurements were obtained employing a JEOL JEM-2010F using an accelerating voltage of 200 kV.

2.3. Electrode preparation

For each Pt/TiC catalyst ink and unmodified TiC, 78 mg of the catalyst was dispersed in 5 mL of ethylene glycol and sonicated for at least 40 min. A total of 30 μL of ink was deposited onto a glassy carbon electrode (0.196 cm^2 , Pine Research Instrumentation) by pipetting of 10 μL ink onto the electrode and subsequent drying in air at $100\text{ }^\circ\text{C}$ three times. For Pt/TiC catalysts, the final platinum loading on the glassy carbon electrode was $0.041\text{ mg cm}^{-2}_{\text{disk}}$. For reference, commercial 40% Platinum on Vulcan XC-72 carbon (Premetek) ink was prepared by mixing 3.4 mg of Pt/C catalyst in 5 mL of ethylene glycol and depositing on the glassy carbon electrode in an identical manner. After the Pt/TiC and Pt/C inks were dried completely, 3 μL of $\sim 5\%$ Nafion 117 solution (Sigma–Aldrich) was dropped on top of the electrodes to act as a binder [23].

2.4. Electrochemical characterization

A standard three-electrode setup was used for all electrochemical characterization. Along with the prepared working electrodes, a saturated calomel electrode (SCE, Pine Research Instrumentation) was used as the reference electrode and a Pt wire (Alfa Aesar, 99.99%) was used as the auxiliary electrode. For

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