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Cyclic voltammetry and X-ray photoelectron spectroscopy studies of electrochemical stability of clean and Pt-modified tungsten and molybdenum carbide (WC and Mo_2C) electrocatalysts

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ABSTRACT

The electrochemical stability of tungsten carbide (WC), Pt-modified WC, molybdenum carbide (Mo_2C), and Pt-modified Mo_2C has been examined using an *in situ* electrochemical half-cell in combination with X-ray photoelectron spectroscopy (XPS). The WC surface, created via the carburization of a tungsten foil, was electrochemically stable to ~0.8 V with respect to the normal hydrogen electrode (NHE) when exposed to dilute sulfuric acid. At higher potentials, XPS confirmed the surface oxidation of WC to form W_xO_y species. The deposition of submonolayer coverage of Pt on the WC surface increased the region of stability of WC, extending the onset of catalyst oxidation to ~1.0 V (NHE). These results suggest that both WC and Pt/WC have the potential to be used as anode electrocatalysts. In contrast, both Mo_2C and Pt-modified Mo_2C underwent oxidation at ~0.4 V (NHE), indicating that molybdenum carbides are not stable enough for applications as anode electrocatalysts.

1. Introduction

This work is a continuation to a series of surface science and electrochemical studies attempting to evaluate the feasibility of using tungsten and molybdenum carbides as anode electrocatalysts for direct methanol fuel cell (DMFC) [1–7]. DMFC anodic chemistry requires the oxidation of methanol and the decomposition of water to produce protons, electrons, and gas-phase CO_2 [8]. In addition to meeting these requirements, a desirable DMFC electrocatalyst must remain stable under the relatively harsh environment at the anode. Currently, the Pt/Ru bimetallic catalyst is the most effective anode electrocatalyst for DMFC [9–11]. Although the Pt/Ru bimetallic system exhibits desirable stability and electrochemical activity under anodic conditions, both Pt and Ru are expensive due to limited supplies. In addition, strong chemisorption of CO on Pt and Ru makes the electrocatalyst susceptible to CO poisoning, blocking the active sites for methanol oxidation. Consequently, discovery of less expensive and more CO tolerant alternatives to the Pt/Ru catalysts would help facilitate the commercialization of DMFC.

A large body of literature exists on the possibility of using transition metal carbides to mimic the catalytic properties of Pt-group metals [12–18]. In particular, there have been many studies on tungsten and molybdenum carbides since Levy and Boudart suggested that WC displayed Pt-like behavior in several catalytic reactions [18]. There have also been many recent studies to utilize supported tungsten carbides as alternative electrocatalysts [5,6,19–29].

The earlier papers of this series examined the surface reactions of methanol, water, and CO on carbide-modified tungsten and molybdenum single crystal and polycrystalline surfaces, with and without submonolayer coverages of Pt [1–5,7]. The carbide surfaces showed high activity toward the dissociation of methanol and water, as well as a relatively low desorption temperature of CO at around 330 K, suggesting that tungsten and molybdenum carbides would be potential electrocatalysts to replace Pt/Ru for DMFC. Recent cyclic voltammetry (CV) and chronoamperometry (CA) measurements confirmed that tungsten monocarbide (WC) and Pt-modified WC were active for the electrooxidation of methanol [6].

One of the critical issues in using carbides as alternative electrocatalysts is their stability within an electrochemical environment. In particular, it is very important to understand whether the carbides are oxidized after electrochemical measurements. Although X-ray photoelectron spectroscopy (XPS) has been used to determine the oxidation state of tungsten or molybdenum after electrochem-

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ical study, the samples in these previous studies were exposed to air between the electrochemical and XPS measurements, making it difficult to determine whether the oxidation occurred in air or during electrochemical evaluation. The focus of the current study is to clarify the uncertainties in the electrochemical stability of tungsten and molybdenum carbides using an *in situ* three-electrode half-cell that was connected via a gate valve to a UHV system containing XPS. This system allowed for surface characterization of carbides and Pt-modified carbides, both before and after CV measurements, without exposing the carbide electrode surfaces to air. Such measurements remove the potential complication due to air oxidation and therefore should provide conclusive evidence on the electrochemical stability of carbides.

2. Experimental

2.1. Techniques

The XPS measurements were performed in a UHV system equipped with an ESCALAB MK2 by VG Scientific Ltd, as described previously [6]. An Al Kα X-ray source of 1486.6 eV was used as the excitation source. All scans were performed with an anode potential of 12 kV and an emission current of 20 mA. The concentric hemispherical analyzer was mounted at 54.7° with respect to the X-ray source and XPS scans were taken under a vacuum condition of approximately 1×10^{-8} Torr.

The CV measurements were performed using a three-electrode electrochemical half-cell, consisting of a counter (auxiliary) electrode, a reference electrode, and a working electrode. As shown in Fig. 1, the half-cell assembly was attached to the UHV chamber via a gate valve. Implementation of the load lock transfer system between the electrochemical half-cell and the UHV chamber eliminated exposure of the sample to air during and after CV measurements. The counter electrode of the electrochemical half-cell was 99.99% pure Pt gauze, 0.1 mm thick with a surface area of approximately 15 cm^2. The reference electrode was a saturated calomel electrode ($Hg/Hg_2Cl_2/KCl$), which was measured to be 0.241 V with respect to the normal hydrogen electrode (NHE). The working electrode, typically a metal foil with a surface area of 1 cm^2, was the electrocatalyst (WC or Mo_2C with or without Pt modification) under investigation. The working electrode was spot welded onto a stainless steel feedthrough, allowing only the electrocatalyst to come in contact with the electrolyte of the electrochemical half-cell. The stainless steel feedthrough was connected to a Princeton Applied Research model 263A potientostat/galvanostat that controlled the potentials of the electrodes. The half-cell used 0.05 M H_2SO_4 as an electrolyte that was continuously pumped in a closed loop at ~10 ml min^{-1} from a 2.0-L glass vessel. A linear potential sweep between the working electrode and reference electrode, from −0.09 V to the desired potential then back to −0.09 V with respect to the NHE at 100 mV s^{-1}, was performed using the potentiostat.

To eliminate exposure of the sample to air during CV measurements and sample transfer to and from the XPS chamber, a typical experiment proceeded as follows, similar to that developed by Goodman and coworkers [30] and Stuve and coworker [31]. The metal carbide surface was first prepared and characterized using XPS in the UHV chamber. The sample was then positioned in the load lock chamber under vacuum and separated from the UHV chamber by closing a gate valve. The pressure inside the load lock chamber was raised to 1 atm using 99.999% purity N_2 and the gate valve was opened between the load lock chamber and electrochemical half-cell, which was pre-evacuated and backfilled with 99.999% purity N_2. The electrochemical half-cell was raised to allow the meniscus of the electrolyte to contact the surface of the sample. The electrolyte/fuel mixture was then pumped through the cell at 10 ml min^{-1} from a 2-L reservoir, which was purged with N_2. By raising the electrochemical half-cell, the tip of the Luggin-Haber capillary attached to the reference electrode was also brought near the surface, allowing CV measurements to be performed. Following CV measurements, the electrochemical half-cell was retracted, the gate valve to separate the load lock chamber from the electrochemical half-cell was closed, and the load lock chamber was evacuated to UHV conditions. Finally, the gate valve to the UHV chamber was opened and post-CV characterization was performed using XPS.

2.2. Preparations of clean and Pt-modified WC and Mo_2C thin films

To create the WC or Mo_2C thin films, a polycrystalline metal foil (either W or Mo) was carburized by decomposition of ethylene over a hot filament and deposition of the carbon on the metal surface, followed by annealing the sample to 1200 K. Prior to carburization, the surface of a 1 cm × 1 cm × 0.05 mm metal foil (99.9+% purity purchased from Aldrich Chemical Company Inc.) was cleaned by cycles of Ar^+ bombardment at 300 K (sample current ~5 μA, acceleration potential 4 kV) followed by flashing to 1200 K in vacuum. This 10-min cycle was generally repeated 2 times. XPS analysis after the cleaning cycles showed no detectable amount of impurities on the W or Mo surface. To carburize the clean W or Mo surface, 1.0×10^{-4} Torr of ethylene was decomposed using a hot filament sputter gun with 0.5 kV bias potential for 10 min. The surface was then annealed to 1200 K to form a carbide film. Several cycles of carburization were used to assure the formation of carbide films. XPS analysis revealed the characteristic carbidic carbon 1s feature at ~282.7 eV and an atomic C/W ratio of 1.0 (or C/Mo ~ 0.5) with no detectable impurities.

The Pt-modified surfaces were prepared via the evaporation of elemental Pt onto the clean carbide thin film [6]. The deposition of Pt was achieved by resistively heating a tungsten filament that was wrapped with a thin wire of 99.99+% pure Pt. The Pt evaporation source was contained within a tantalum shield, which had an aperture to direct Pt onto the carbide thin film surface without contaminating the entire UHV chamber. The metal thin film was maintained at 300 K during deposition followed by annealing to 600 K for 1 min after Pt deposition. The surface coverage of atomic Pt was estimated based on the Pt(4f)/W(4f) or Pt(4f)/Mo(3d) XPS ratio along with the standard XPS sensitivity factors as described elsewhere [32]. The calculations took into consideration screening of the W or Mo XPS signal by the surface Pt atoms and the contribution of the signal from metal layers in the bulk. After the Pt deposition rate was established based on the monolayer (ML) Pt layer on the clean metal foil, a similar deposition rate was used to form Pt-modified WC or Mo_2C surfaces with controlled amounts of Pt, ranging from 0.8 ML (monolayer) to 1.2 ML.

3. Results

3.1. Characterization of WC thin film

3.1.1. XPS and XRD results

Fig. 2 compares the W 4f and C 1s XPS spectra of a polycrystalline tungsten foil before and after the formation of the WC thin film. The WC film is characterized by tungsten $4f_{7/2}$ and $4f_{5/2}$ features at 31.6 and 33.7 eV, and a carbidic C 1s feature at 282.7 eV. There are no other impurities, such as oxygen or sulfur (spectra not shown), on the WC surface. The comparison of the W 4f region also shows that binding energies of the two W 4f features increase by about ~0.3 eV from clean W to WC, suggesting that the oxidation state of W is slightly higher upon the formation of WC.