Influence of Composition and Morphology on Photo and Electrocatalytic Activity of Electrodeposited Pt/WO₃

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Introduction

Methanol oxidation, which is a multi-dehydrogenation process, has been strongly investigated for methanol-air fuel cells (DMFCs)[1-3]. However, the activities of commercial catalysts are still low. Platinum, a well-known catalyst for methanol oxidation, is easily poisoned by reaction intermediates. Intermediates such as CH_xO strongly adsorb on the platinum surface and permanently bind to the active site, thus preventing further reactions from taking place [4, 5]. To improve catalytic activity, platinum alloys, generally Pt-Ru, have been studied [6, 7]. Unfortunately, the alloy is electrochemically unstable because Ru dissolves at elevated potentials. In an attempt to increase the stability of methanol oxidation catalysts, a great number of researchers have investigated platinum or platinum alloys supported on metal oxides [8-10]. Shen and Tseung [11] reported that a Pt/WO₃ electrode showed promise as a catalyst for methanol oxidation – WO₃ can oxidize reaction intermediates, thus enhancing both the activity and stability of the catalyst. For this system, both the amount of platinum and the dispersion of platinum are of key importance.

WO₃ of several different crystal structures has been prepared by a variety of physical and chemical methods [12, 13]. Electrochemical deposition methods have also been used to synthesize WO₃ by dissolving Na_2WO_4 in sulfuric acid [14] or tungsten powder in hydrogen peroxide [15, 16]. The electrodeposition method has many advantages over other synthesis routes in terms of economics and flexibility for making large area WO₃ films. Pt and WO₃ can be electrochemically co-deposited using a hydrogen peroxide solution [17-19].

For the synthesis of Pt or Pt/WO₃ catalysts, we used four different methods: continuous electrochemical co-deposition, pulsed electrochemical co-deposition, serial electrochemical deposition (deposition of Pt on the surface of previously electrodeposited tungsten oxide), and electron beam evaporation of Pt on the surface of previously electrodeposited tungsten oxide. We addressed the following questions: 1) What is the role of tungsten oxide in methanol oxidation? 2) Can particle size and morphology of Pt/WO₃ be used to improve the catalytic activity for methanol oxidation? 3) What is the effect of the Pt/WO₃ ratio on the photocatalytic and electrocatalytic activity?

Experimental

E-beam evaporated Pt was fabricated in a Class 10,000 cleanroom environment. Electrodeposited tungsten oxides on Ti foil were placed in the high vacuum ($\sim 10^{-7}$ Torr) evaporation system and Pt was deposited at a rate of 1-1.5 Å/sec.

For the electrodeposition of tungsten oxide, the stabilized W-peroxo electrolyte was prepared by dissolving 1.83g of tungsten powder in 60ml of a 30% hydrogen peroxide solution. The excess hydrogen peroxide was subsequently decomposed with platinum black. The solution was diluted to 50mM with a 50:50 mixture of water and isopropanol. For the electrodeposition of platinum, 50mM chloroplatinic acid was used. For co-deposition of Pt/WO₃, the electrolyte consisted of 50 mM W-peroxo and various concentrations of chloroplatinic acid (1 mole % to 50 mole %), which allowed for control of the deposited Pt/WO₃ ratio. Both pulsed and continuous electrodeposition were used; electrochemical pulses were 5 msec in duration, and for series deposition, the Pt/WO₃ ratio was controlled by varying the deposition time of Pt on WO₃ from 5 min to 30 min. The cathodic-potentiostatic deposition was performed using a conventional three electrode system (EG&G 273A) with Pt as a counter electrode and SCE as a reference electrode.

Following synthesis, samples underwent more detailed quantitative analysis. Scanning electron microscopy (Philips, XL-30 ESEM-FEG) and electron stimulated energy dispersed x-ray spectroscopy (Princeton Gamma Tech, IMIX) were performed to give surface morphology and composition. X-ray diffraction (Scintag, X2) was used to examine the crystal structures. The amount of platinum was calculated using the weight of deposits and the Pt/WO₃ ratio determined from EDS.

The electrocatalytic activity of Pt/WO₃ was measured in a solution of 0.5M MeOH and 0.5M H_2SO_4. The measurements were carried out from 0 to 0.8V vs SCE at room temperature. Testing for zero bias photocurrent utilized an electrochemical cell described in detail elsewhere [17]. Electrolytes, either 0.1M sodium acetate or 0.5M methanol, were pumped automatically into the cell and the electrical current was measured while the surface was illuminated with a chopped light source (Oriel, Xe 150W, chopped at 100 Hz). Due to losses through the optical fiber, the light intensity incident on the sample was approximately 25 mW/cm².

Results and Discussion

As-deposited tungsten oxide films were confirmed to be amorphous. XRD confirmed that crystalline films were obtained after 450°C calcination in air. Prior to testing, all samples were calcined as such immediately after deposition.

E-beam evaporated Pt exhibited a very smooth and dense surface, while electrodeposited Pt had a very rough morphology. Generally, e-beam evaporation of metals at slow rates and at low pressure is conducive to layer-by-layer growth, which accounts for the smooth and dense film.

Fig. 1 shows SEM photographs of Pt/WO₃ films prepared by various electrochemical methods: pulsed co-deposition (a), continuous co-deposition (b), and series deposition (c). In the case of the continuous co-deposited Pt/WO₃ film, large distinct clusters of platinum particles were easily seen on the tungsten oxide surface.
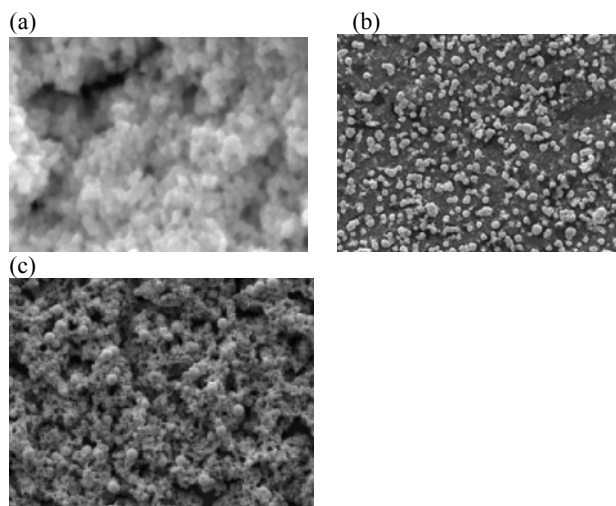

Figure 1. SEM photographs of (a)pulse elctrocodeposited Pt/WO₃, (b)continuous codeposited Pt/WO₃, and (c) series deposited Pt/WO₃. In all cases substrate was Ti foil.

When Pt was electrodeposited on the tungsten oxide (series deposition), spheres of Pt were observed on the tungsten oxide surface and the particles were much larger than those of tungsten oxide. When we pulse co-deposited Pt with WO_3, a very homogeneous phase was observed and the particle size was significantly smaller than that observed with the other two methods. Pulsed electrodeposition with short, high potential pulses can be used to nucleate particle growth at a higher number of sites than with lower voltage continuous deposition [20, 21].

Pt supported on different metal oxides has been studied for methanol oxidation, with certain catalysts showing higher activity than pure platinum [8, 9, 11]. However, in these references there was no mention of the absolute amount of platinum within the catalytic systems investigated. In each case, Pt is believed to be an active site for methanol oxidation, so the total platinum content of each catalyst must be known in order to accurately compare activities. To address this concern, we compared catalytic activities of Pt e-beam evaporated on WO_3 versus Pt evaporated on a Ti-foil substrate, Fig. 2.
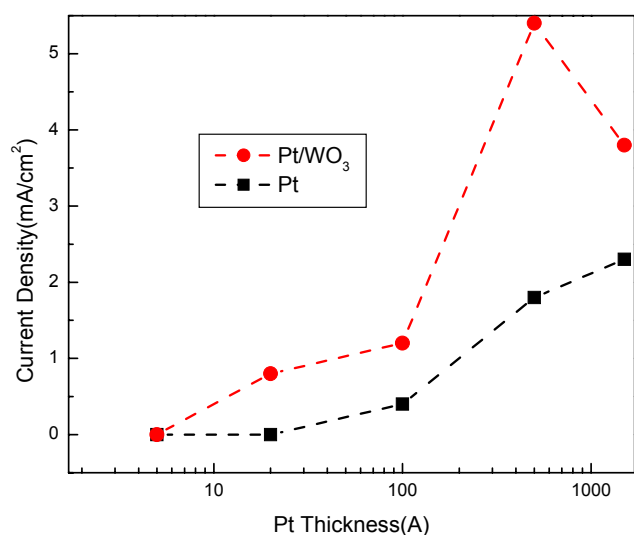

Figure 2. Current density for methanol oxidation of e-beam deposited Pt(square) and e-beam deposited Pt/WO_3(circle) as a function of thickness of Pt.

The two kinds of substrates were evaporated upon simultaneously to ensure the same Pt thickness, which was varied from 5 to 1500 Å. In case of Pt films on Ti foil, activity for methanol oxidation was observed only for Pt thickness of 100Å or greater. Activity increased with thicker films, with a limit of 2.7mA/cm^2 reached at a thickness of 1500Å. Tungsten oxide itself has no activity for methanol oxidation.. Methanol oxidation was observed with as little as 50Å of Pt deposited on the tungsten oxide, and activity increased with increasing Pt thickness up to 500Å, 5.4mA/cm^2. The catalytic activity of 1500Å Pt supported on WO_3 was lower than that of 500 Å Pt/WO_3, indicating that the thick Pt layer prevents exposure of WO_3 to the reactants, thus resulting in decreased catalytic activity. This reveals the importance of Pt-WO_3 interfaces for this reaction. One can observe that in every case, Pt deposited on tungsten oxide films showed higher current density for methanol oxidation than the same amount of Pt alone. We concluded that Pt/WO_3 is a better catalyst for methanol oxidation than pure platinum.

Electrodeposited Pt showed 25 times higher current density for methanol oxidation than e-beam deposited Pt. This result can be explained by the great difference of surface morphologies between the two samples. The surface of electrodeposited Pt was very rough and porous, while that of e-beam deposited Pt was smooth and dense. The rough morphology of electrodeposited films can be attributed to the mass transfer limitations of a solid-liquid interface during rapid deposition [22]. This yields a high surface area, leading to greater catalytic activity.

Table 1. Comparison of Catalytic Activities for Methanol Oxidation

Sample	Pt/WO_3	*Pt amount (mg)*	Catalytic activity (mA/cm^2.mg Pt)
Electrodeposited Pt	-	2.6	14.1
Series deposited Pt/WO_3	1.31	2.4	18.4
Continuous codeposited Pt/WO_3	1.42	2.9	17.4
Pulse codeposited Pt/WO_3	1.22	2.8	25.6

Catalytic activities for methanol oxidation were investigated for electrodeposited Pt/WO_3 films, Table 1. We prepared Pt/WO_3 films by three electrochemical methods: continuous co-deposition, pulsed co-deposition, and series deposition. The Pt/WO_3 film prepared by pulsed co-deposition showed the highest activity for methanol oxidation, 25.6 mA/(cm^2 mg Pt), Table 1.

The differences in catalytic activity observed for the three electrochemical methods of preparation can be attributed to their differences in surface morphology, Fig. 1. Large clusters of Pt were found to exist on the surface of the WO_3 films prepared by series deposition or continuous co-deposition. Pulsed co-deposited Pt/WO_3 films, meanwhile, exhibited great homogeneity and small particle size. These morphological features equate to a great number of Pt/WO_3 interfaces, which makes for a very effective methanol oxidation catalyst.
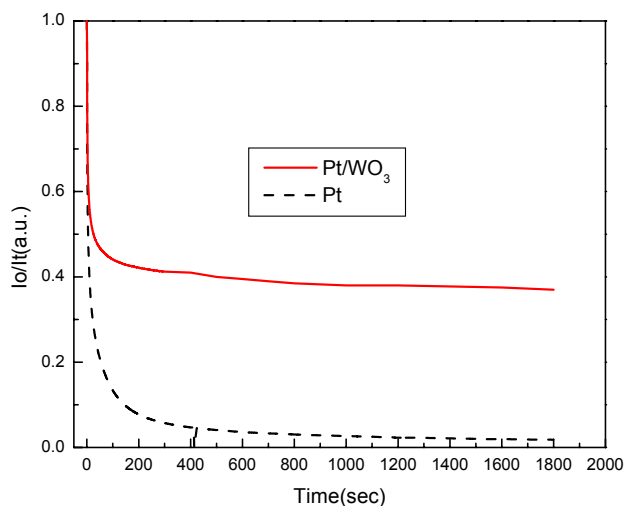

Figure 3. Current density with time on stream at 0.6V on Pt electrode(dashed line) and Pt/WO_3 electrode(solid line)

Long-term oxidation of methanol was performed at a constant potential of 0.6V for both electrodeposited Pt and pulsed co-deposited Pt/WO$_3$. As shown in Fig. 3, the pure Pt electrode suffered from rapid deactivation to less than 2% of its initial current density within 10 minutes, most likely due to heavy poisoning. The Pt/WO$_3$, however, demonstrated a relatively high current density. Although it dropped to approximately 40% of its initial value after 5 minutes, it remained steady at that level for the next half-hour, showing little sign of decay. We can conclude that the Pt/WO$_3$ system is much more active and stable than the Pt electrode. It is well known that partially dehydrogenated intermediates may act as poisons [4, 5, 11]. The presence of WO$_3$, a known oxidizing material, can remove such intermediates by dehydrogenation, resulting in an increase of both activity and stability.
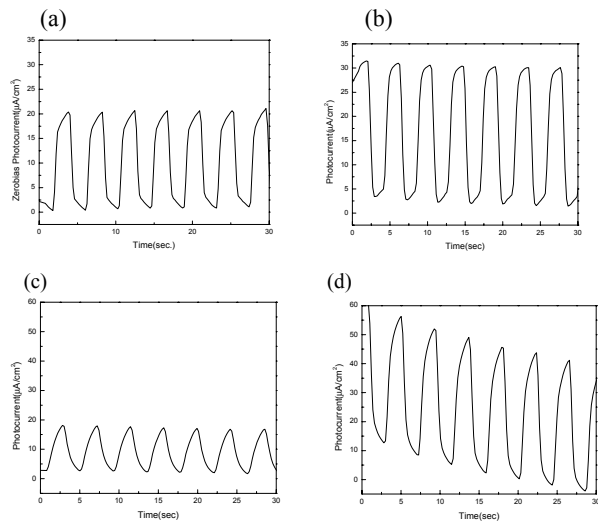

Figure 4. Zerobias photocurrents of WO$_3$(a, c) and 2.3% Pt/WO$_3$(b, d) in 0.1M sodium acetate electrolyte(a, b) or 0.5M methanol electrolyte(c, d).

Zerobias photocurrent was measured under chopped illumination for pure tungsten oxide and for 2.3% Pt doped tungsten oxide prepared by pulsed electrochemical co-deposition. Two different electrolytes were used – 0.1M sodium acetate solution (Fig. 8(a, b)) and 0.5M methanol (Fig. 8(c, d)). The measurement of zero bias photocurrent is an indirect means of screening for photocatalytic activity. Our previous work [19] showed that photoactive Pt/WO$_3$ could be obtained only when small amounts (below 5%) of highly dispersed platinum were added to tungsten oxide. Pt/WO$_3$ films with a large atomic ratio of platinum to tungsten tend to be photoinactive, presumably due to inhibited photon absorption. 2.3% Pt doped tungsten oxide showed higher photocurrent than pure tungsten oxide in both sodium acetate and methanol electrolytes.

Our results indicate that the requirements of an electrocatalyst are very different from those of a photocatalyst. A large atomic ratio of Pt to WO$_3$ yields a very effective electrocatalyst for methanol oxidation, whereas a low ratio of Pt to WO$_3$ is required for good photocatalysts.

Conclusions

Catalytic activity for methanol oxidation was investigated for different Pt doped tungsten oxide films synthesized by various methods based upon electrochemical deposition and electron beam evaporation. The electrocatalytic activity of these films depended significantly upon the method of preparation, which can be explained by the vastly different morphologies of the films. The Pt/WO$_3$ film prepared by pulsed electrochemical co-deposition showed highest activity for methanol oxidation. This film exhibited a very homogeneous phase, which makes for a great number of Pt/WO$_3$ interfaces, thus explaining its effectiveness. Pt/WO$_3$ samples were compared to pure Pt samples (each sample contained the same weight Pt), and it was found that Pt/WO$_3$ is much more stable and active for methanol oxidation than pure platinum. It was also found that the requirements for an electrocatalyst are very different from those for a photocatalyst. A large atomic ratio of Pt to WO$_3$ improves the electrocatalytic properties of the material for methanol oxidation, while materials with low ratio of Pt to WO$_3$ are good photocatalysts.

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