# Electro Oxidation of Methanol at Pt/Au/Sn Triplet Electrode

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#### Abstract

**Objectives**: To find a novel and a cheap anode for direct methanol fuel cell that resists the poisoning by carbon monoxide produced inside the cell. **Methods/Statistical Analysis**: We prepare triplet electrode by using electrodeposition technique in nano-scale to improve the overall electro-catalytic properties of anode towards electrochemical oxidation of methanol. **Findings**: The prepared nano-anode is better than the traditional electrode Pt/Au because the triplet anode Pt/Au/Sn give higher current density in low over potential. **Application/Improvements**: There exist many applications of this triplet nano-anode in portable devices, cars, vehicles, airplanes and space shuttles.

**Keywords:** Cyclic Voltammogram (CV), Direct Methanol Fuel Cell (DMFCs), Electrochemical Oxidation, Methanol, Scanning Electron Microscope, Triplet Electrode

### 1. Introduction

Methanol fuel cells are very important because they are potentially highly efficient and clean energy systems with technological applications<sup>1,2</sup>. There is many improvements that have been made in the performance of DMFCs<sup>3,4</sup> but still not widespread applied. The limitations mainly arise from electrocatalytic activity of both anode<sup>5-7</sup> and cathode<sup>8,9</sup> catalysts, and high cost of anode specially Pt. Therefore, much effort has been devoted to increase the performance of the catalysts<sup>10–13</sup>. Now, more attention paid on bimetallic anode<sup>14,15</sup> because they have better catalytic activity than the separate metals<sup>16–18</sup>. The platinum modified by gold electrode, has high catalytic activity towards methanol oxidation<sup>19–24</sup>. Gold has uniform coverage on Pt, so decreases Pt dissolution during methanol oxidation<sup>25</sup>.

Moreover, Au increases the catalytic activity that involves the tolerance of adsorbed poisonous species and a change in electronic band structure to modify the strength of the surface adsorption<sup>26</sup>. The Pt–Au catalysts have superior CO oxidation activity and CO tolerance ability in comparison with their separate metal<sup>27-29</sup>. In this study we test triplet electrode of Pt/Au/Sn nanoparticles for electrooxidation of methanol in fuel cell.

# 2. Experimental Techniques

#### 2.1 Solutions

We used double distilled water for preparation of the electrolytes solutions and ultra pure chemicals: sulfuric acid (BDH), sodium bicarbonate (BDH), methanol (Merck), stannous sulfate (Merck), and gold trichloride (Merck). We purged ultra-pure nitrogen for all electrolytic solutions.

#### 2.2 Instrumentation and Cell

We used Saturated Calomel Electrode (SCE) as a reference electrode and a gold wire as a counter electrode. All electrochemical measurements are done by using three compartment electrochemical cell.

Electrochemical measurements were performed using a potentio glvanostate model Wenking PS 95.

Samples for TEM examined by using a JEOL 2010 transmission electron microscopy operated at 200 kV.

#### 2.3 Preparation of Working Electrode

#### 2.3.1 Preparation of Pt Modified Au Electrode

The steady state of Pt electrode was checked by cyclic voltammetry in  $0.1M H_2SO_4$ , Au nano-particles was deposited from  $10^{-3}M AuCl_3$  in  $0.1M H_2SO_4$ .

The electrode position process was performed by cycling the Pt substrate between -0.25V to 1.15V/SCE using nano-membrane. The modified electrode, referred as Pt-Au electrode, was checked by cycling the electrode in  $0.1M \text{ H}_2\text{SO}_4$ .

#### 2.3.2 Real Surface Area Determination

Pt surface area  $(S_{pt})$  determined from the hydrogen adsorption/desorption region<sup>30,31</sup> in the voltammogram of platinum in 0.1 M sulfuric acid Figure 1. The percentage of Pt to Au determined from the hydrogen region according to the following equation

 $%Pt = (Q^{H}_{Pt/Au} / Q^{H}_{Pt}) \times 100$ 



**Figure 1.** Cyclic voltammogram of Pt electrode in 0.1 M  $H_2SO_4$ . Scan rate 50 mV s<sup>-1</sup>.

Where  $Q^{H}_{Pt}$  and  $Q^{H}_{Pt/Au}$  are the charges for hydrogen adsorption in the absence and the presence of deposited gold.

#### 2.4 Cyclic Voltammetry

The experiments were performed according to the following procedure:

- The steady state cyclic voltammogram of platinum was recorded in supporting electrolyte.
- Metal ion solution was added to the electrolytic solution to prepare the desired metal ion concentration and a new voltammogram was recorded.
- The required amount of the methanol was introduced to the cell and the steady-state voltammogram was recorded.

## 3. Results and Discussion

#### **3.1 TEM Analysis**

Figure 2(a) demonstrates the distribution of gold nanoparticles on platinum. Figure 2(b) shows the composition of Pt-0.5Au TEM images. In the Pt/Au nanoparticles, the high coverage and similar surface particle coverage. The Au nanoparticles dispersed very well on Pt.

The decreased widths of distributions indicate that no new additional nucleation goes on platinum during the formation of Pt/Au nanoparticles.

#### 3.2 Oxidation of Methanol on Au@Pt Anode in 0.1M Sodium Bicarbonate

Figure 3 shows the dependence of peak current density on the composition of Pt-Au electrodes. As can be shown from this Figure the best composition is 40% Au. This activity due to the synergistic effect<sup>32–36</sup>.

# 3.3 Platinum/Gold/Sn<sub>ad-atoms</sub> Modified Electrodes in NaHCO<sub>3</sub>

Figure 4 represents the effect of  $10^{-5}$ M Sn<sup>2+</sup> on the voltammograms of Au@Pt. As shown from this figure the upd process of Sn in 0.1M NaHCO<sub>3</sub> begins at 0 V/ SCE. Its re-dissolution occurs mainly in a single peak at -0.05V/SCE.



Figure 2. TEM images for (a) Pt/ 0.4Au nanoparticles. (b) Pt/ 0.5 Au nanoparticles.



**Figure 3.** Dependence of the peak current density on the Pt region on the alloy compositions for Pt/Au in 0.5 M  $CH_3OH + 0.1 M NaHCO_3$ .

## 3.4 Oxidation of Methanol at Platinum/ Gold/Sn<sub>ad-atoms</sub> Anode in NaHCO<sub>3</sub>

Figure 5 shows the oxidation of methanol at Pt/Au/Sn anode. We found that Sn ions increase the catalytic activity of Pt/Au electrode at all metal concentrations accompanied by a shift of the peak potential by around 140 mV to the positive direction.



**Figure 4.** Cyclic voltammogram of Pt/40% Au in 0.1 M NaHCO<sub>3</sub> in absence (solid line) and presence (dashed line)  $10^{-5}$  M Sn<sup>+2</sup>. Scan rate 50 mV s<sup>-1</sup>.



**Figure 5.** Cyclic voltammogram of Pt/ 40% Au in 0.5 M  $CH_{3}OH + 0.1 M NaHCO_{3}$  in absence. (a) and presence of. (b)  $10^{-7} M.$  (c)  $10^{-5} M.$  (d)  $10^{-3} M.$  (e)  $10^{-2} M$  of  $Sn^{+2}$ . Scan rate 50 mV s<sup>-1</sup>.

### 4. Discussion and Conclusion

We can use the following equation to demonstrate the effect of metal ions on Pt/Au electrode :

 $Au-Pt_{(subs)}$ - $[RCHOH]_{ads} + Au-Pt_{(subs)}$ - $M(OH)_{ads} = products$ 

where M is the metal and (subs) is the substrate. Hence, the catalytic properties of Sn on the methanol oxidation can be demonstrated by the modification of both  $\theta_0$  and  $\theta_{0H}$  as follow:

• If the foreign metal is easily oxidized than platinum,  $\theta_{OH}$  has satisfied values at potentials more negative than Pt anode. Hence, there is acceleration in methanol electrochemical oxidation according to the bi-functional theory.

On the basis of ligand effect theory, the properties of platinum anode in presence of Sn ions cannot be overcame.

• If Sn ions are not easily oxidized than Pt, both  $q_{OH}$  and  $q_{O}$  decreases due to the insufficient Pt surface sites towards methanol electrooxidation.

The catalytic activity of Pt/Au/Sn triplet electrode can be explained by the combination of both bifunctional theory of electro catalysis which explain the role of metal adatoms as in the above two points (1 and 2).

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