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

Mohamed Abdelfattah Ibrahim¹² and Ali Moulahi¹
¹Department of Chemistry, Al-Wajha University College, University Of Tabuk, Tabuk, Saudi Arabia; science1712@gmail.com, mohamedfattah2002@yahoo.com
²Department of Chemistry, Faculty of Science, El-Arish University, North Sinai, Egypt

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 applications¹². There is many improvements that have been made in the performance of DMFCs³⁴ but still not widespread applied. The limitations mainly arise from electrocatalytic activity of both anode⁵⁷ and cathode⁸⁹ catalysts, and high cost of anode specially Pt. Therefore, much effort has been devoted to increase the performance of the catalysts¹⁰¹³. Now, more attention paid on bimetallic anode¹⁴¹⁵ because they have better catalytic activity than the separate metals¹⁶¹⁸. The platinum modified by gold electrode, has high catalytic activity towards methanol oxidation¹⁹²⁴. Gold has uniform coverage on Pt, so decreases Pt dissolution during methanol oxidation²⁵.

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 adsorption²⁶. The Pt–Au catalysts have superior CO oxidation activity and CO tolerance ability in comparison with their separate metal²⁷²⁹.

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 glyvanostate 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 H₂SO₄, Au nano-particles was deposited from 10⁻³M AuCl₃ in 0.1M H₂SO₄.

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 H₂SO₄.

2.3.2 Real Surface Area Determination

Pt surface area (Sₚₚ) determined from the hydrogen adsorption/desorption region 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

\[ \%\text{Pt} = \left(\frac{Q^H_{\text{Pt/Au}}}{Q^H_{\text{Pt}}}\right) \times 100 \]

Where \( Q^H_{\text{Pt}} \) and \( Q^H_{\text{Pt/Au}} \) 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.

3.3 Platinum/Gold/Sn ad-atoms Modified Electrodes in NaHCO₃

Figure 4 represents the effect of 10⁻³M Sn⁺⁺ on the voltammograms of Au@Pt. As shown from this figure the upd process of Sn in 0.1M NaHCO₃ begins at 0 V/ SCE. Its re-dissolution occurs mainly in a single peak at -0.05V/SCE.
3.4 Oxidation of Methanol at Platinum/Gold/Sn\textsubscript{ad-atoms} Anode in NaHCO\textsubscript{3}

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.
4. Discussion and Conclusion

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

\[
\text{Au-Pt}_{\text{(subs)}} \cdot [\text{RCHOH}]_{\text{ads}} + \text{Au-Pt}_{\text{(subs)}} \cdot \text{M(OH)}_{\text{ads}} = \text{products}
\]

where M is the metal and \text{(subs)} is the substrate. Hence, the catalytic properties of Sn on the methanol oxidation can be demonstrated by the modification of both \(\theta_O\) and \(\theta_{OH}\) 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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6. References

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