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Enhanced Electro-Oxidation of Methanol at Pt-Au Nanocatalyst for Direct Methanol Fuel Cells

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ABSTRACT

In this investigation, a Pt-Au nanocatalyst prepared by the co-electrodeposition of Pt (PtNPs) and Au (AuNPs) nanoparticles is assembled onto a glassy carbon (GC) electrode for efficient methanol oxidation (MO). Several molar ratios between PtNPs and AuNPs have been used and the corresponding catalytic activity towards MO is tracked. The Pt1:Au1 catalyst showed the highest catalytic activity (5 times higher oxidation peak current (I_p) and a 126 mV negative shift in the onset potential (E_{onset}) toward MO). The catalyst's morphology, composition and activity are investigated and the enhancement mechanism is recognized.

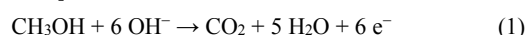
Keywords

Fuel cells; Methanol oxidation; Poisoning; Pt-Au; Co-electrodeposition.

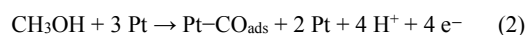
1. INTRODUCTION

Today, fuel cells (FCs) have received a huge interest as a high efficiency and ecofriendly energy conversion technology [1-4]. Of which, direct liquid fuel cells (DLFCs) is recently under deep investigation, because of their advantages over hydrogen-fed polymer electrolyte membrane fuel cells (PEMFCs) which use hydrogen as their fuel [5-7]. Due to the ease of handling, storing, transporting, and higher energy density as compared to hydrogen, methanol as an inexpensive liquid fuel has drawn researchers attention for direct methanol fuel cells (DMFCs) [8, 9].

DMFCs is a clean, efficient, easily-operated energy conversion technology that could be incorporated in many applications, such as vehicles, cellular phones, and laptop computers [2]. However, Pt which is the most commonly used anodic catalyst for methanol oxidation (MO) is unfortunately poisoned by the reaction intermediates [10, 11]. Generally, on Pt-based catalysts, the direct MO in alkaline solutions produces CO_2 according to the following equation [12, 13];



At the same time, the formation of poisonous intermediates as CO is possible (equation 2). This causes a severe drawback in the catalytic performance of the catalyst toward MO [13].



To solve this big problem, the Pt could be modified with other metal and/or metal oxides that limit the adsorption of these poisoning intermediates on its surface [14-22]. Specifically, Au-Pt systems were investigated as promising electrocatalysts for MO because of their high activity and high CO tolerance [11, 23-25].

In this investigation, a simple methodology for the fabrication of a "simultaneously co-electrodeposited" PtNPs and AuNPs binary catalyst is suggested for efficient "less-poisoned" MO. This methodology ensures a proper homogeneity of PtNPs and AuNPs with the use of a less loading of these precious metals. This study is willing to optimize molar ratios of PtNPs and AuNPs to achieve the highest catalytic activity toward MO. With the inspection of the catalyst's morphology and composition together with catalytic data of MO, the origin of catalytic enhancement could be expected.

2. EXPERIMENTAL

All the chemicals used in this investigation were of analytical grade and used without prior purification. A glassy carbon (GC, $d = 5.0 \text{ mm}$) rod served as the working electrode after subjecting to a conventional cleaning procedure; a mechanical polishing with aqueous slurries of successively finer alumina powder (down to 0.06 mm) followed by a thorough washing with second distilled water. A spiral Pt wire and saturated calomel electrode (SCE) were respectively employed as the counter and reference electrodes. Potentials will always be displayed in reference to SCE.

The "simultaneous co-electrodeposition" of PtNPs and AuNPs onto the GC electrode with several molar ratios was carried out in $0.1 \text{ M Na}_2\text{SO}_4$ containing $2.0 \text{ mM H}_2[\text{PtCl}_6] + 2.0 \text{ mM HAuCl}_4$ solution at -0.2 V .

In order to recognize easily the electrode with its appropriate deposition condition, a system of abbreviations was settled to distinguish the molar ratios of Pt^{4+} and Au^{3+} in the deposition bath. For example, when the molar ratio of Pt^{4+} and Au^{3+} in the deposition bath was 1:1, the catalyst will be abbreviated as Pt1:Au1.

Current densities were always calculated on the basis of real surface areas of working electrodes employing a reference value

of $420 \mu\text{C cm}^{-2}$ [26]. The electrocatalytic activity toward MO was studied in an aqueous solution of 0.3 M Methanol (pH = 3.5) while the pH was controlled by a dilute solution of sodium hydroxide.

Electrochemical measurements were performed at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$) in a two-compartment three-electrode glass cell (home-made) using a Bio-Logic SAS potentiostat (model SP-150) operated with EC-Lab[®] software.

A field emission scanning electron microscope, FE-SEM, (QUANTA FEG 250) coupled with an energy dispersive X-ray spectrometer (EDS) was employed to reveal the electrode's morphology and the relative composition of the catalyst components.

3. RESULTS AND DISCUSSION

3.1 Electrochemical characterization

Figure 1 shows cyclic voltammograms (CVs) measured in 0.5 M H_2SO_4 at 100 mVs^{-1} for the entire set of prepared catalysts. Figure 1a corresponding to the Pt1:Au0 electrode (only PtNPs is electrodeposited at GC electrode) depicts a typical performance of a clean polycrystalline Pt electrode in acidic conditions [27]. The Pt oxidation extending over a potential range from 0.7 to 1.5 V together with characteristic PtO reduction peak at ca. 0.3 V could be observed. Additionally, the hydrogen adsorption/desorption ($H_{\text{ads/des}}$) peaks appeared between -0.35 to 0.0 V.

When PtNPs was simultaneously deposited with AuNPs (with increasing the molar ratio of Au^{+3} in the deposition bath) onto the GC electrode (Figs. 1 b-f), the intensities of the Pt/PtO and $H_{\text{ads/des}}$ peaks got lowered in addition to the appearance of a new cathodic peak at ca. 0.8 V which corresponding to the Au oxide reduction [28, 29]. The systematic decrease of the Pt/PtO and $H_{\text{ads/des}}$ peaks and increase in the Au oxide reduction peak verify the successful deposition of AuNPs together with PtNPs.

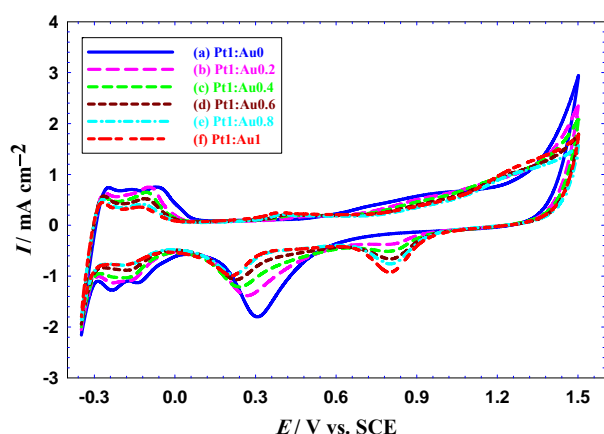


Figure 1. CVs measured in 0.5 M H_2SO_4 for a GC electrode modified with molar ratios of PtNPs : AuNPs of (a) 1:0, (b) 1:0.2, (c) 1:0.4 (d) 1:0.6, (e) 1:0.8, and (f) 1:1. Scan rate = 100 mV s^{-1} .

3.2 Materials characterization

Morphologically, Fig. 2 shows FE-SEM images of the GC tip modified with Pt1:Au0 (image a) and Pt1:Au1 (image b). Image a depicts a semi-spherical lumps of PtNPs with an average particle

size of ca. 95 nm. This morphology kept as it was, although shrunken (ca. 40 nm), for PtNPs in in image b with AuNPs deposited in a bigger (ca. 105 nm) nanospheres. The difference in the electronic conductivity of GC and AuNPs may also impact the exchange current density of deposition to alter the particle size.

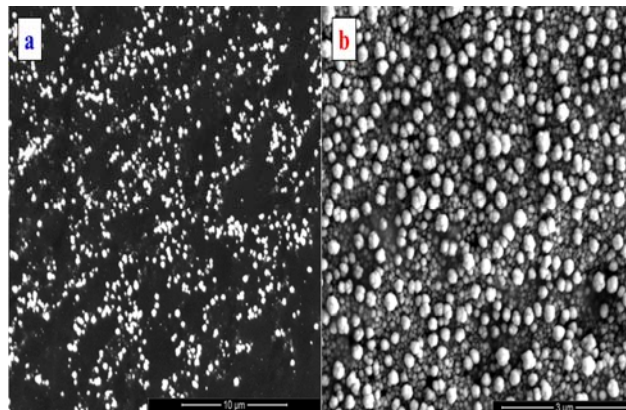


Figure 2. FE-SEM images of (a) Pt1:Au0 and (b) Pt1:Au1 simultaneously electrodeposited at a GC tip.

Also, the EDS spectra of the Pt1:Au0 (Fig. 3a) and Pt1:Au1 (Fig. 3b) catalysts confirmed the successful deposition of the different ingredients (PtNPs and AuNPs) onto the GC electrode and assisted in predicting their relative ratios.

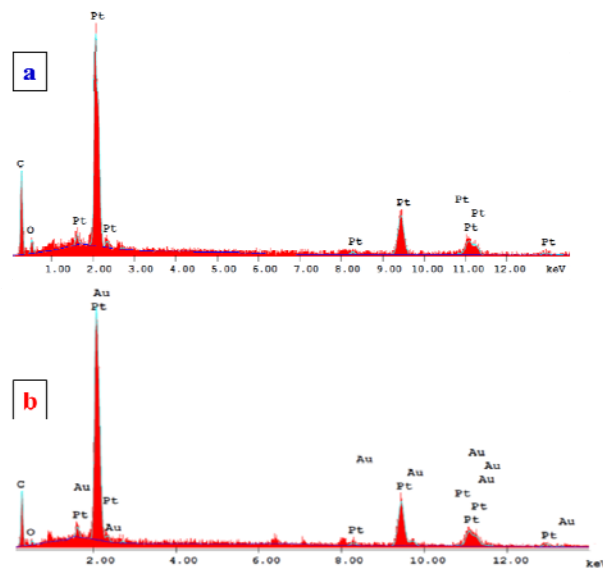


Figure 3. EDS analysis of (a) Pt1:Au0 and (b) Pt1:Au1 simultaneously electrodeposited at a GC tip.

3.3 Electrocatalysis of MO

Figure 4 displays positive-potential going linear sweep voltammograms (LSVs) measured in 0.1 M NaOH solution containing 0.3 M methanol at 100 mV s^{-1} for the entire set of prepared catalysts (Fig. 4 a-f). As clearly shown in Fig. 4a (Pt1:Au0), the smallest oxidation current density (at ca. -0.08 V) was observed for MO. This is likely because the poisoning effect with several intermediates such as ($-\text{CH}_2\text{OH}$, $=\text{CHOH}$, $\equiv\text{COH}$, CO, and HCOOH), which consume an appreciated part of the Pt surface, deteriorating its catalytic activity [12, 13].

Surprisingly, when PtNPs were simultaneously deposited with AuNPs (with increasing the molar ratio of Au³⁺ in the deposition bath) onto the GC electrode (Figs. 4 b-f), the I_p could be observed to increase systematically reaching 5 times higher, concurrently, with a negative shift by 126 mV in the E_{onset} of MO in case of Pt1:Au1 catalyst. This shows the preminance of AuNPs addition that thought to lower the poisoning occurring at the catalyst surface through the ensemble/third body mechanism which suggests the distortion of the Pt atoms contiguity by AuNPs and thus could lead to minimizing the adsorption of the poisoning species at its surface [2, 3]. Table 1 summarizes the electrochemical data from Fig. 4.

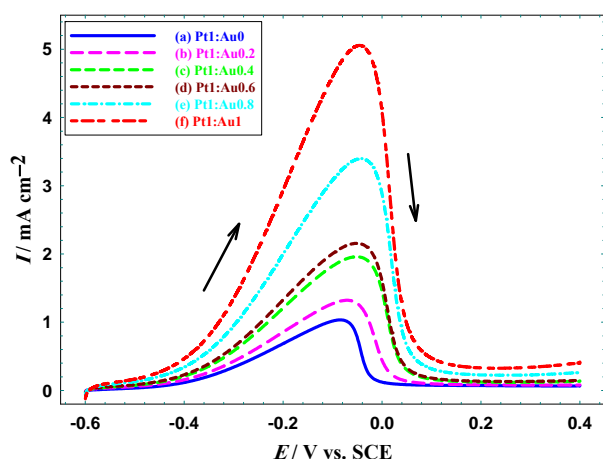


Figure 4. LSVs for MO in 0.1 M NaOH solutions containing 0.3 M methanol (pH = 3.5) for a GC electrode modified with molar ratios of PtNPs : AuNPs of (a) 1:0, (b) 1:0.2, (c) 1:0.4 (d) 1:0.6, (e) 1:0.8, and (f) 1:1. Scan rate = 100 mV s⁻¹.

Table 1. A summary of the electrochemical data extracted from Fig. 4.

Catalyst	I_p / mA cm ⁻²	Enhancement factor ($I_{p(modified)} / I_{p(bare)}$)	E_{onset} / mV
Pt1:Au0	1.00	----	-353
Pt1:Au0.2	1.33	1.33	-377
Pt1:Au0.4	1.96	1.96	-403
Pt1:Au0.6	2.17	2.17	-413
Pt1:Au0.8	3.39	3.39	-452
Pt1:Au1	5.08	5.08	-479

Furthermore, the catalyst's stability is as important as its activity from an industrial perspective. To compare the stability of the Pt1:Au1 (Fig. 5b) catalyst with that of the Pt1:Au0 (Fig. 5a) one, CV measurements of MO were carried out for 100 cycles and the corresponding I_p was recorded. Interestingly again, the Pt1:Au1 catalyst showed a higher stability in terms of a lower current decay (29% for Pt1:Au1 vs. 75% for Pt1:Au0). This shows once more the importance of AuNPs addition to PtNPs in the proposed catalyst.

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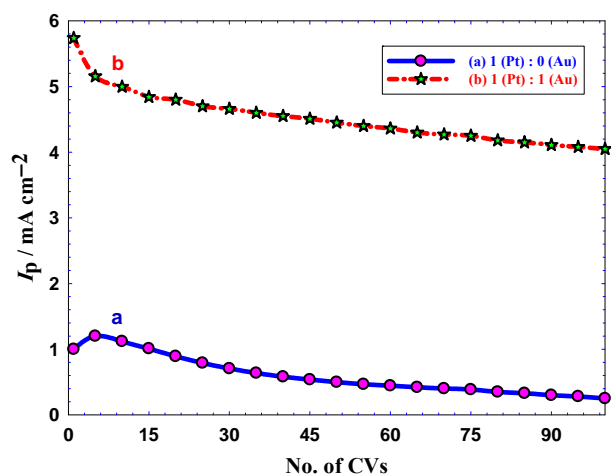


Figure 5. Stability measurement (I_p vs. No. of cycles) for MO at a glassy carbon electrode modified with molar ratios of PtNPs : AuNPs of (a) 1:0 and (b) 1:1. N.B. MO was measured as in Fig. 4.

4. CONCLUSION

An efficient catalyst fabricated by the co-electrodeposition of PtNPs and AuNPs onto a GC electrode has been indorsed for MO. The molar ratio between PtNPs and AuNPs influenced greatly the catalytic activity toward MO. The Pt1:Au1 catalyst showed the highest catalytic activity in terms of 5 times higher I_p , and a negative shift by 126 mV in the E_{onset} of MO. Additionally, it showed a higher stability in terms of a lower current decay (by 46%) compared with Pt1:Au0 catalyst. The enhancement is thought to be originated from mitigating the adsorption of the poisoning species at the Pt surface through the ensemble/third body effect.

5. ACKNOWLEDGMENTS

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