

Gold-Platinum Binary Nanocatalysts for Enhanced Ethylene Glycol Electro-oxidation

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Abstract

An enhanced electrocatalytic activity towards ethylene glycol electro-oxidation (EGO) in alkaline medium is observed at a glassy carbon (GC) electrode modified with Pt nanoparticles (nano-Pt) and Au nanoparticles (nano-Au). The electrocatalytic activity of the modified electrode towards EGO depends on the loading level and the deposition order of the catalyst layers atop the GC electrode surface. Several techniques including cyclic voltammetry (CV), field-emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS) are used to address the catalytic activity of the proposed catalyst and to reveal their surface morphology and composition, respectively. CV measurements showed that the GC electrode modified with nano-Pt and nano-Au, respectively (Au/Pt/GC electrode) supports an increase in the oxidation peak current (I_p) of EGO, that is, I_p is two times and a half larger than that obtained at Au/GC electrode, concurrently with a significant negative shift in the onset potential (E_{onset}) of EGO by $\cong 40$ mV. Moreover, this electrode showed a significant stability over a prolonged time of continuous electrolysis.

Keywords: Direct ethylene glycol fuel cells; Electrocatalysis; Pt nanoparticles; Au nanoparticles

I. INTRODUCTION

Sooner or later, the current storage of petroleum oil will be depleted. This fact had a great potential in the direction of the global interest to seek for alternative energy resources. In this regard, fuel cells appeared highly efficient and clean (low emissions) energy source which allow them to implement an environmentally-friendly electric power generation system without sacrificing efficiency. Fuel cells make an efficient utilization of fuels when compared to combustion-based technologies used in the current power plants and automotive applications. They also generate virtually no pollution such as nitrogen oxide (NO_x), sulfur oxide (SO_x), or particulate matter (PM₁₀) and dramatically reduced carbon dioxide emissions (CO₂). As well, fuel cells are not affected by the weather like wind turbines and solar power (Feliu and Herrero 2003, Hellman and van den Hoed 2007, Abdullah, Mohammad et al. 2009, Kirubakaran, Jain et al. 2009, Lee and Hung 2012).

Hence, the direct ethylene glycol fuel cell (DEGFC) has been studied in this investigation. It is a promising candidate, due to the ease handling and transporting of ethylene glycol as a liquid fuel in comparison to hydrogen gas fuel. Also DEGFC has a higher theoretical energy density (5.90 kWh⁻¹) if compared to the direct formic acid fuel cell (DFAFC, 2.086 kWh⁻¹) and direct methanol fuel cell (DMFC, 4.69 kWh⁻¹) (Zhu, Ha et al. 2004, Antolini and Gonzalez 2010, Serov and Kwak 2010, Yu, Krewer et al. 2010, Xin, Zhang et al. 2012).

Nano-Pt is considered the best electrocatalyst for ethylene glycol electrooxidation reaction (EGO) as it easily adsorbed and oxidized on its surface. However, EGO suffers from several difficulties, including the generation of various reaction intermediates which cause deterioration in the catalytic activity of the Pt as they block its active sites and lower the kinetics of EGO. So other catalyst has been used together with nano-Pt in order to suppress poisoning effects of the nano-Pt and enhance EGO (Demarconnay, Brimaud et al. 2007, Miyazaki, Matsumiya et al. 2011, Xin, Zhang et al. 2012, Kim, Kim et al. 2014).

In this investigation, the glassy carbon (GC) electrode has been modified by nano-Pt and nano-Au and its activity has been examined towards EGO in alkaline medium. The binary catalyst is fabricated electrochemically and is characterized by field emission scanning electron microscope (FE-SEM) and cyclic voltammetry (CV) techniques. The stability of the electrodes over prolonged time of electrolysis has been

examined using $I-t$ curves. The influence of the composition and order of deposition of the catalyst layers atop the GC electrode surface is addressed as well.

II. EXPERIMENTAL

All chemicals used in this work were of analytical grade and were used without further purification. All solutions were prepared using distilled water.

2.1. Measurements

A glassy carbon (GC) electrode with diameter =5 mm acts as a working electrode after cleaning by conventional procedures. Spiral platinum wire and Ag/AgCl/KCl (sat.) electrodes act as counter electrode and reference electrode, respectively. Using a Bio-Logic SAS potentiostat (model SP-150) operated by EC-lab software, the electrochemical measurements are performed in a conventional two-compartments-three-electrode electrochemical cell. The working (GC) and the counter (Pt spiral wire) electrodes are separated by a porous glass. The reference electrode (Ag/AgCl/KCl (sat.)) is separated from the working electrode by a salt bridge. The GC electrode is first cleaned by mechanical polishing using aqueous slurries of alumina powder (down to 0.06 μm).

2.2. Electrodes modification

Nano-Pt is electrodeposited atop the GC electrode from an acidic solution of 0.1M H_2SO_4 containing 2 mM $\text{H}_2[\text{PtCl}_6]$ by applying a potential step electrolysis technique from 1 to 0.1 V vs. Ag/AgCl/KCl (sat.) at various deposition charges ($Q= 4, 8, 12, 16, 20$ and 24 mC). On the other hand, nano-Au is electrodeposited from 0.1 M H_2SO_4 solution containing 1.0 mM $\text{Na}[\text{AuCl}_4]$, using potential step electrolysis from 1.1 to 0 V vs. Ag/AgCl/KCl (sat.) at various deposition charges ($Q= 4, 8, 12, 16, 20, 24$ mC). The binary modification of GC electrode by nano-Pt and nano-Au is achieved by the same method using different orders of depositions.

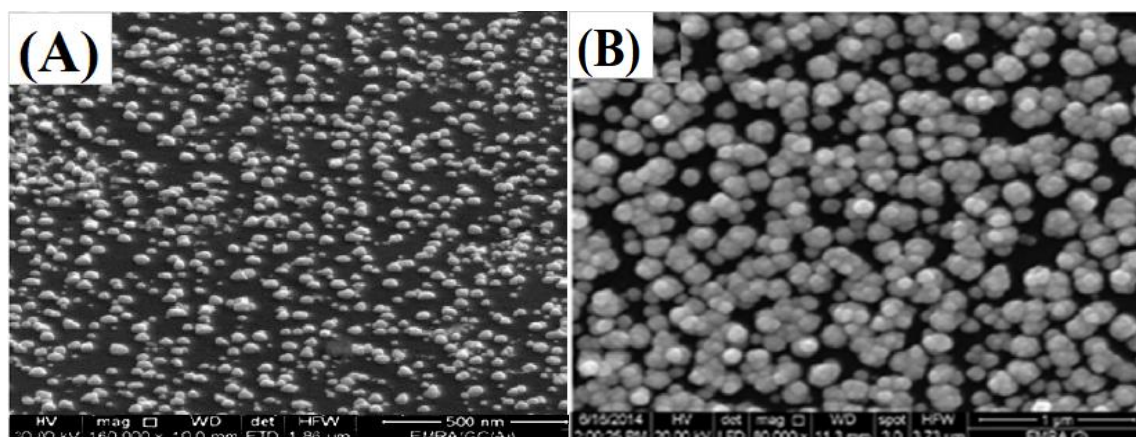
2.3. Materials Characterization

A field-emission scanning electron microscope (FE-SEM) (FEI, QUANTA FEG250) coupled with energy dispersive X-ray spectroscopy (EDS-EDAX genitive) is employed to disclose the morphology of the various modified GC electrodes and their surface composition, respectively.

III. RESULTS AND DISCUSSION

3.1. Characterization of Au/GC, Pt/GC, Pt/Au/GC, Au/Pt/GC electrodes

Fig. 1A shows FE-SEM images of Au/GC electrode, it reveals that grain shapes of nano-Au are formed with average particle size of ca. 80 nm. Whereas, at Pt/GC electrode (Fig. 1B), a larger agglomerates of nano-Pt are deposited onto the GC electrode with average size of ca. 100 nm. On the other hand, a binary structures of nano-Au and nano-Pt are electrodeposited onto the GC electrode in Fig. 1C and D with different sequence of deposition. They are electrodeposited in a porous texture that covers homogeneously the entire surface of GC electrode.



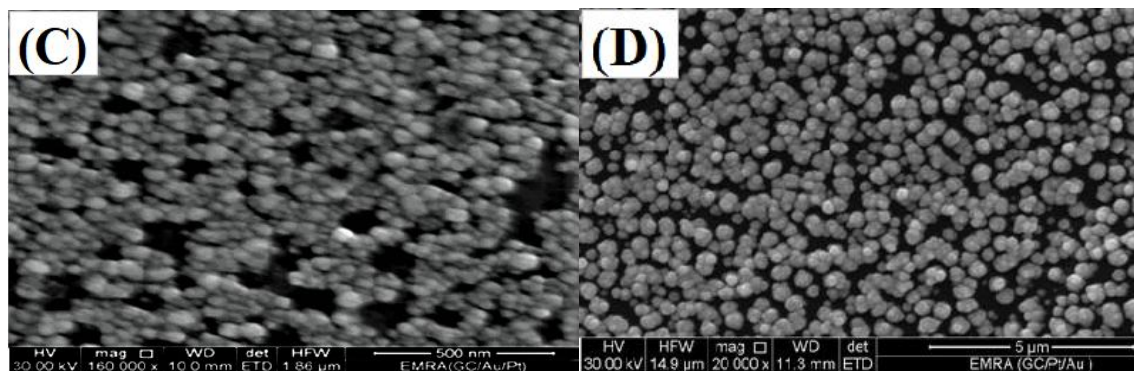


Figure 1. FE-SEM images of: (A) Au/GC, (B) Pt/GC, (C) Pt/Au/GC and (D) Au/Pt/GC electrodes. Nano-Pt, nano-Au are electrodeposited as described in the experimental section.

3.2. Electrocatalytic oxidation of ethylene glycol at the modified electrodes

Fig.2 shows CVs measured in 0.5 M NaOH solution containing 0.5 M EG at (a) Au/GC, (b) Pt/GC, (c) Pt/Au/GC and (d) Au/Pt/GC electrodes. We can observe that the lowest peak current (I_p) of EGO (at ca. -0.05 V) is obtained at Au/GC electrode (curve a). This may be attributed to the low activity of nano-Au towards ethylene glycol adsorption and oxidation.

However, the Pt/GC electrode (curve b) exhibited a higher activity towards EGO as an evident from the increase in I_p of EGO but it is lower than that obtained at Pt/Au/GC and Au/Pt/GC electrodes (curves c and d, respectively). The reason behind that is that nano-Pt is poisoned by the adsorption of several incompletely oxidized carbonaceous intermediates during EGO such as glycolaldehyde, glyoxal, glycolic acid, glyoxylic acid, and oxalic acid (Dailey, Shin et al. 1998, Demarconnay, Brimaud et al. 2007, Xin, Zhang et al. 2012, Matsumoto, Sadakiyo et al. 2014) and possibly COads (Dailey, Shin et al. 1998, Demarconnay, Brimaud et al. 2007, Xin, Zhang et al. 2012, Matsumoto, Sadakiyo et al. 2014) formaldehyde and formic acid (Dailey, Shin et al. 1998, Demarconnay, Brimaud et al. 2007, Xin, Zhang et al. 2012, Matsumoto, Sadakiyo et al. 2014) which consequently reduces the available surface of Pt and deteriorates its catalytic activity.

On the other hand, upon the binary modification of GC electrode with nano-Pt and nano-Au (curves c and d), I_p of EGO at Pt/Au/GC electrode is almost doubled upon the modification of the Au/GC electrode with nano-Pt (curve c). As well, I_p of EGO at Au/Pt/GC electrode (curve d) is about two times and a half of that obtained at Au/GC electrode (curve a). We wish here to emphasize that the adsorption of CO on Pt surface requires the existence of three adjacent Pt sites (with a definite atomic spacing), and any interruption in this continuity may impede or prevent its adsorption (Cuesta, Escudero et al. 2009). In this regard, the modification of GC substrate with nano-Au before or after the deposition of nano-Pt in the Pt/Au/GC and Au/Pt/GC electrodes is intended to interrupt the Pt atoms contiguity required for CO adsorption. We should also point here to the importance of nanoparticles order of deposition towards the enhancement of EGO as revealed from the highest I_p of EGO obtained at Au/Pt/GC (curve d) electrode when compared to Pt/Au/GC electrode (curve c).

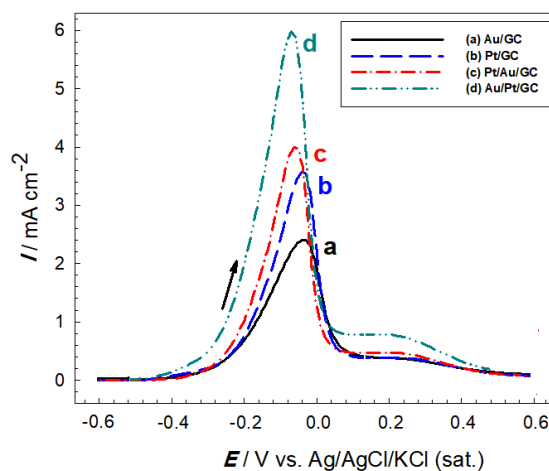


Figure 2. Linear sweep voltamograms (LSVs) obtained at (a) Au/GC, (b) Pt/GC, (c) Pt/Au/GC and (d) Au/Pt/GC electrodes in 0.5 M NaOH solutions containing 0.5 M ethylene glycol. Scan rate = 50 mVs^{-1} . Nano-Pt, nano-Au are electrodeposited as described in the experimental section.

3.3. Effect of ageing

Fig. 3 shows current transients ($I-t$) recorded for EGO at (a) Au/GC, (b) Pt/GC, (c) Pt/Au/GC and (d) Au/Pt/GC electrodes at a constant potential of -200 mV vs. Ag/AgCl/KCl (sat.) for 3hr of continuous electrolysis. The stability of the first three electrodes deteriorates with time to different extents. On the other hand, the highest oxidation current is obtained at Au/Pt/GC electrode (curve d) which is maintained at high value for 3hr of oxidation. This reflects the high stability and tolerance of this electrode against the poisoning intermediates. The high stability obtained at this electrode is believed to originate from the reinforcement of nano-Au to the mechanical stability of the nano-Pt at the electrode surface.

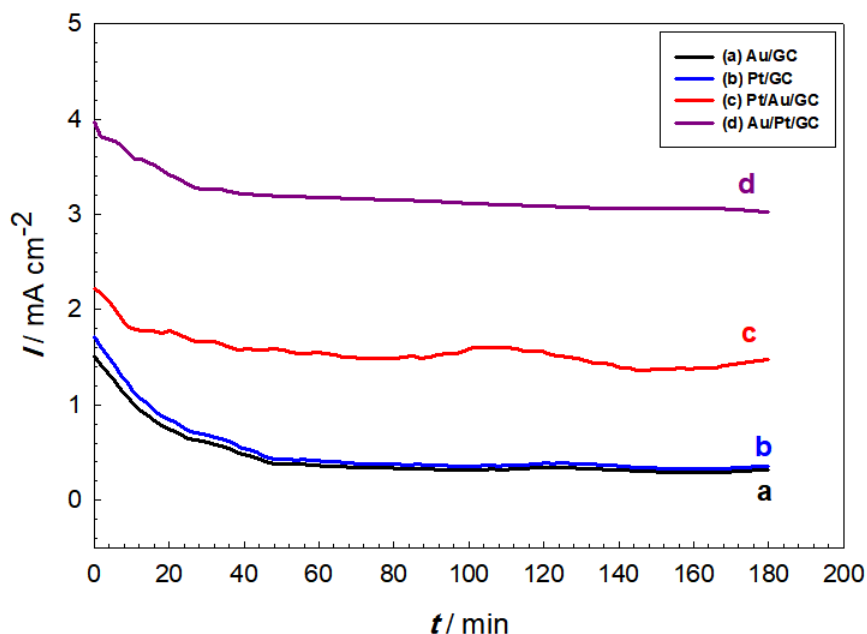


Figure 3. Current transients ($I-t$) obtained during EGO (at -0.2 V vs. Ag/AgCl/KCl (sat.)) at (a) Au/GC, (b) Pt/GC, (c) Pt/Au/GC and (d) Au/Pt/GC electrodes in 0.5 M NaOH solutions containing 0.5 M EG.

IV. CONCLUSION

The current study introduces efficient nanostructured modified GC anodes for EGO in alkaline medium. The catalyst layers composition and sequence of deposition greatly affects EGO. The highest enhancement for EGO is achieved at Au/Pt/GC electrode, where nano-Pt was first electrodeposited followed by nano-Au electrodeposition. At this electrode I_p of EGO is two times and a half of that obtained at Au/GC electrode. The enhancement in the catalytic activity is most likely originated from the interruption of the Pt atoms contiguity required for CO poison adsorption.

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