Platinum nanoparticles-cobalt oxide nanostructures as efficient binary catalyst for ethylene glycol electro-oxidation

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Abstract

An enhanced electrocatalytic activity towards ethylene glycol oxidation reaction (EGO) in alkaline medium is observed at a glassy carbon (GC) electrode modified with a nanoparticle-based binary catalyst composed of Pt (nano-Pt) and cobalt oxide (nano-CoOx). The electrocatalytic activity of the modified electrodes towards EGO depends on the loading level as well as the composition of the catalyst layer 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 CoOx/Pt/GC electrode (with nano-Pt; furnished at the base and nano-CoOx; the topmost layer) support the largest increase in the oxidation peak current (Ip) of EGO, that is, Ip is two times larger than that obtained at Pt/GC electrode, concurrently with a significant negative shift in the onset potential (Eonset) of EGO by ≅ 170 mV. Moreover, this electrode showed a significant stability over a prolonged time of continuous electrolysis.

Keywords: Direct alcohol fuel cell, Electrocatalysis, Platinum nanoparticles, Transition metal oxides

1. INTRODUCTION

The expected upcoming shortage of fossil fuels and the affirmed restrictions to reduce CO₂ emissions that typically emerged to society with burning fossil fuels have stimulated a global
interest to secure alternative clean and efficient energy resources for next generations. In this regard, fuel cells appeared highly efficient, clean (little emissions), reliable, longlasted, easily moved, and economic [1, 2].

Of these, the direct ethylene glycol fuel cell (DEGFC) 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 l\(^{-1}\)) if compared to the direct formic acid fuel cell (DFAFC, 2.086 kWh l\(^{-1}\)) and direct methanol fuel cell (DMFC, 4.69 kWh l\(^{-1}\)) [3-7].

Pt-based electrocatalyst has been investigated for ethylene glycol electrooxidation reaction (EGO). However, EGO suffers from several difficulties, including the generation of various reaction intermediates which cause deterioration in the catalytic activity of the anode as they block the active sites of Pt and lower the kinetics of EGO. So it was necessary to search for efficient modifiers to Pt-based electrocatalysts in order to suppress poisoning effects of the anode and enhance EGOH [8-11].

The current investigation concerns with the modification of glassy carbon (GC) electrode with Pt nanoparticles (nano-Pt) and metal oxide nanoparticles (nano-NiOx or nano-MnOx or nano-CoOx) for EGO in alkaline medium. The binary catalyst is fabricated electrochemically and is characterized by FE-SEM, EDS and CV. The influence of the composition of the catalyst layer atop the GC electrode surface is addressed.

2. EXPERIMENTAL

All chemicals used in this work were of analytical grade and were purchased from Merck, and Sigma Aldrich, and were used without further purification. All solutions were prepared using distilled water.

2.1. Measurements

Electrochemical measurements were performed using a Bio-Logic SAS potentiostat (model SP-150) operated with EC-Lab software. An electrochemical cell with a three-electrode configuration was used in this study. A platinum spiral wire and an Ag/AgCl/KCl (sat.) were employed as counter and reference electrodes, respectively. All potentials will be presented with respect to this reference electrode. The working electrode was glassy carbon (d = 3 mm) and was cleaned by mechanical polishing with aqueous slurries of successively finer alumina powder (down to 0.06 µm) then washed thoroughly with distilled water.

2.2. Electrode’s modification

The modification of the GC electrode with nano-Pt is achieved by applying a potential step electrolysis from 1 to 0.1 V vs. Ag/AgCl/KCl (sat.) for various durations in an aqueous solution of 0.1 M H\(_2\)SO\(_4\) containing 2.0 mM H\(_2\)[PtCl\(_6\)]. Whereas the modification of the surface of the Pt-modified GC electrode with nano-NiOx is achieved in two sequential steps; first, Ni is deposited by a potentiostatic electrolysis at −1.0 V in 0.1 M acetate buffer solution (ABS, pH = 4.0) containing 1 mM Ni(NO\(_3\))\(_2\) for different durations. Next, a passivation step of Ni is performed in 0.1 M phosphate buffer solution (PBS, pH = 7) by cycling the potential between −0.5 and 1 V for 10 cycles
at a potential scan rate of 0.2 V s\(^{-1}\) \cite{12, 13}. The modification of the Pt/GC electrode with nano-MnOx is performed by cycling the potential between 0 and 0.4 V vs. Ag/AgCl/KCl (sat.) for several cycles at 0.02 V s\(^{-1}\) in 0.1 M Na\(_2\)SO\(_4\) containing 0.1 M Mn(CH\(_3\)COO)\(_2\) \cite{14, 15, 16} resulting in different surface coverages ($\theta$) of nano-MnOx at the Pt surface. The further modification of the Pt/GC electrode with nano-CoOx is achieved by cycling the potential for several cycles at a potential scan rate of 0.1 V s\(^{-1}\) between \(-1.1\) and 1.2 V vs. Ag/AgCl/KCl in 0.1 M phosphate buffer solution (PBS, pH 7) containing 1 mM CoCl\(_2\) \cite{16}.

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.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of Pt/GC, NiOx/Pt/GC, MnOx/Pt/GC, CoOx/Pt/GC electrodes

Fig. 1A shows FE-SEM images of Pt/GC electrode, it reveals that grain shapes of nano-Pt are formed with average particle size of ca. 100 nm. Whereas, at NiOx/Pt/GC electrode (Fig. 1B), the large agglomerates of nano-NiOx partially deposited atop the nano-Pt and concealed its grained shape. On the other hand, at MnOx/Pt/GC electrode (Fig. 1C), nano-MnOx was electrodeposited at Pt/GC electrode and at the bare portion of the GC electrode as well. At CoOx/MnOx/Pt/GC electrode (Fig. 1D), the nano-CoOx is electrodeposited in a porous texture onto Pt/GC electrode surface. This texture partially covers homogeneously the entire surface of Pt/GC electrode.
Fig.1. FE-SEM images of: (A) Pt/GC, (B) NiOx/Pt/GC, (C) MnOx/Pt/GC and (D) CoOx/Pt/GC electrodes. Nano-Pt, nan-NiOx, nano-MnOx and nano-CoOx were electrodeposited as described in the experimental section.

EDS spectrum of CoOx/Pt/GC electrode is shown in Fig.2. The appearance of the characteristic peaks of Pt and Co confirms the coexistence of the catalysts’ ingredients at the electrode surface and assists in the calculation of their relative surface composition (see Fig. 2 and the table inserted therein).

Fig.2. EDS spectrum of nano-Pt and nano-Co electrodeposited onto the GC surface for CoOx/Pt/GC electrode. Nano-Pt and nano-CoOx are electrodeposited as described in the experimental section.

3.2. Electrocatalytic oxidation of ethylene glycol at the modified electrodes

EGO in NaOH solution at Pt/GC, NiOx/Pt/GC, MnOx/Pt/GC and CoOx/Pt/GC electrodes has been studied. It was found that:
1) EGO at Pt/GC electrode as ethylene glycol is easily adsorbed and oxidized at the platinum surface (Fig. 3a); however, this oxidation is with low oxidation peak current ($I_p$) when compared to the other modified electrodes.

2) At NiOx/Pt/GC electrode, at the same conditions, the oxidation peak current ($I_p$) at NiOx/Pt/GC is enhanced (Fig. 3b). That's to say that the redox transition of nickel species from Ni(II) to Ni(III) occurs, then in a following step ethylene glycol is oxidized on the modified surface (according to the Fleischmann mechanism [14-18] via the following reactions:

\[
\text{Ni(III)} + \text{ethylene glycol} \rightarrow \text{intermediate} + \text{Ni(II)} \quad (1)
\]

\[
\text{Ni(III)} + \text{intermediate} \rightarrow \text{product} + \text{Ni(II)} \quad (2)
\]

3) At MnOx/Pt/GC electrode (Fig. 3c), EGO further enhanced as the $I_p$ of EGO increased when compared to NiOx/Pt/GC electrode. That is to say Mn(IV) is oxidized to Mn(V), then, in a following chemical step, ethylene glycol is oxidized according to the following equations [14-16, 19-23];

\[
\text{Mn(V)} + \text{ethylene glycol} \rightarrow \text{Mn(IV)} + \text{products} \quad (3)
\]

4) Interestingly, at CoOx/Pt/GC electrode (Fig. 3d), the highest enhancement of EGO was achieved when compared to that obtained at Pt/GC, NiOx/Pt/GC and MnOx/Pt/GC electrodes. It’s obvious that the catalyst composition dramatically affects the performance of the catalyst. At CoOx/Pt/GC electrode, $I_p$ of EGO is two times larger than that obtained at Pt/GC electrode, concurrently with a significant negative shift in the onset potential ($E_{\text{onset}}$) of EGO by $\approx 170$ mV. The great response to EGO at CoOx/Pt/GC electrode may be attributed to that nano-CoOx can provide two routes for EGO arise from the two redox transformations of nano-CoOx (Co(II)/Co(III) and Co(III)/Co(IV)) which efficiently enhance the charge transfer of EGO according to the following equations [14-16, 24-27];

\[
3 \text{Co(OH)}_2 + 2 \text{OH}^- \rightarrow \text{Co}_3\text{O}_4 + 4 \text{H}_2\text{O} + 2 \text{e}^- \quad e_{\text{rev}}^\circ = -0.292 \text{ V} \quad (4)
\]

\[
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \rightarrow 3 \text{CoOOH} + \text{e}^- \quad e_{\text{rev}}^\circ = 0.122 \text{ V} \quad (5)
\]

\[
\text{CoOOH} + \text{OH}^- \rightarrow \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^- \quad e_{\text{rev}}^\circ = 0.462 \text{ V} \quad (6)
\]
Fig.3. Linear sweep voltamograms (LSVs) obtained at (a) Pt/GC, (b) NiOx/Pt/GC, (c) MnOx/Pt/GC and (d) CoOx/Pt/GC electrodes in 0.5 M NaOH solutions containing 0.5 M ethylene glycol. Scan rate = 50 mVs⁻¹. Nano-Pt, nano-NiOx, nano-Mn and nano-CoOx are electrodeposited as described in the experimental section.

4. CONCLUSION

The current study introduces efficient nanostructured modified GC anodes for EGO in alkaline medium. The catalyst composition dramatically affects EGO. The highest enhancement for EGO is achieved at CoOx/Pt/GC electrode, where nano-Pt was first deposited followed by nano-CoOx deposition. At this electrode $I_p$ of EGO is two times of that at Pt/GC electrode. The enhancement in the catalytic activity is most likely originated from a catalytic mediation by nano-NiOx, nano-MnOx and nano-CoOx during EGO in such a way facilitating the charge transfer and/or removing the poisoning intermediates.

REFERENCES