Tailor-Tuned Nanoparticle-Based CoOx/Pd Electrocatalyst for the Direct Glycerol Fuel Cell

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Abstract. A glassy carbon (GC) electrode decorated with an efficient nanoparticle-based electrocatalyst of palladium (nano-Pd) and cobalt oxide (nano-CoOx) is electrochemically prepared and examined towards glycerol electro-oxidation (GO) for direct glycerol fuel cell (DGFC) applications. The activity of the tailored electrode toward GO depends on the catalyst components and loadings onto the GC surface. Cyclic voltammetry (CV) technique is used to evaluate the electrocatalytic activity of the introduced catalyst toward GO. Field-emission scanning electron microscope (FE-SEM) and X-ray diffraction (XRD) are used to disclose the morphology and the crystallographic structure of the surface, respectively. CV measurements depict that the oxidation peak current ($I_p$) of GO obtained at CoOx/Pd/GC electrode (where nano-Pd is first electrodeposited at GC surface followed by nano-CoOx deposition) is almost double the value obtained at Pd/GC electrode (where nano-Pd is electrodeposited at GC surface), concurrently with a significant cathodic shift in the onset potential ($E_{onset}$) of GO $\approx$ 80 mV. As well, CoOx/Pd/GC electrode shows a good stability towards GO with continuous electrolysis. It also shows an enhanced catalytic activity towards other alcohols oxidation (i.e., methanol and ethylene glycol) when compared to Pd/GC electrode.

1. Introduction
Direct liquid fuel cells (DLFCs) are recently considered promising candidates for the renewable energy source [1]. They have several advantages over the hydrogen fuel cells; e.g., (a) the higher energy output, (b) the easy handling, transportation, and storage [2-4]. Later on, many researches focused on the development of the direct methanol fuel cell (DMFC) and the direct formic acid fuel cell (DFAFC), however, they are still encountering many challenges such as the volatility, toxicity and low stability of the oxidation current due to the intermediates poisoning effects [1, 2]. Hence, glycerol as a nano-volatile and non-toxic biomass product, having an elevated boiling point and high theoretical energy output, seems a promising fuel for the DLFCs [5, 6]. Glycerol electro-oxidation (GO) will generate both; electricity and useful products with a high demand for the market, such as tartaronic acid, mesoxalate, dihydroxyacetone, dihydroxyacetone, and glycolic acid.

Pt and Pd are considered the best electrocatalysts for GO as glycerol is easily adsorbed and oxidized at their surfaces, however, the production of poisoning intermediate species block their active sites and lower the kinetics of GO [7-10]. Hence, in this study to solve the problem of catalyst poisoning, we introduce a binary nano-catalyst of Pd and CoOx for GO. The addition of nano-CoOx (transition metal oxide) to nano-Pd is due to the availability of unpaired d-orbitals in its electronic configuration which provides better adsorption and facilitate the charge transfer during GO [11, 12].
Hence, nano-CoOx redox transformation is introduced to enhance GO and provide high tolerance to the main catalyst (i.e., nano-Pd) towards the poisoning intermediates.

2. Experimental

2.1. Electrodes, measurements and modification

A GC (d = 3.0 mm) electrode acted as a working electrode at which NPs are deposited after its cleaning by conventional methods [13]. The GC was first polished using slurries of aqueous fine alumina powder then rinsed with distilled water. Ag/AgCl/KCl (sat.) and spiral Pt wire acted as reference and counter electrodes, respectively. The potentials were set versus the reversible hydrogen electrode (RHE). The chemicals used were of analytical grade and the solutions were prepared using distilled water.

Biologic potentiostat operated with EC-lab software was used to perform the electrochemical measurements. The onset potential \( E_{\text{onset}} \) of GO was measured at the two modified GC electrodes at a current density of 250 mA cm\(^{-2}\). As well, current densities were calculated according to the real surface area of nano-Pd.

The electrodeposition of nano-Pd onto the GC surface was performed using chronoamperometry technique at 0V vs. Ag/AgCl/KCl (sat.) with various loading levels (charges, \( Q \)) from 0.1 M H\(_2\)SO\(_4\) solution containing 2.0 mM PdCl\(_2\). The optimum loading level of nano-Pd was found to be 7.25 mC (equivalent to 4 µg). On the other hand, nano-CoOx (with an optimum surface coverage, \( \theta_{\text{CoOx}} = 20\% \)) electrodeposition onto Pd/GC electrodes was performed using cyclic voltammetry technique (potential range between -1.1 and 1.2 V vs. Ag/AgCl/KCl) in 0.1 M phosphate buffer solution (PBS, pH=7) containing 1mM CoCl\(_2\) (scan rate = 0.1 V s–1) [11, 12].

2.2. Materials characterization

In order to disclose the morphology of Pd/GC and CoOx/Pd/GC electrode’s surfaces, field-emission scanning electron microscope (FE-SEM) was used. X-ray diffraction, XRD was used to reveal the crystallographic structure of the deposited nano-catalysts (i.e., nano-Pd and nano-CoOx)

3. Results and discussion

3.1. Electrochemical and Materials characterization

The electrochemical characterization of the electrodes was performed to track the minute amounts of the electroactive species which could not be detected by common material characterization methods. CVs of Pd/GC and CoOx/Pd/GC electrodes in 0.1 M KOH solution is shown in Fig. 1 (curves a and b, respectively). The characteristic redox phases transformation of nano-CoOx could only be detected in alkaline media as it dissolve in acidic media. Fig.1, curve a shows the characteristic CV of the nano-Pd surface, where the Pd oxide formation peak appears between 0.8 and 1.6 V and the Pd oxide reduction peak appears at ca. 0.6 V. As well, the Hydrogen adsorption/desorption (H\(_{\text{ads/des}}\)) peaks appear between 0.1 and 0.3 V. In general, the charge associated with the reduction of nano-Pd oxide was used to calculate the real surface area of nano-Pd surface, from which the surface coverage (\( \theta \)) of the deposited nano-CoOx onto nano-Pd surface was calculated. In Fig.1, curve b, Pd/GC electrode is further modified by nano-CoOx (i.e., CoOx/Pd/GC). We can observe a decrease in the intensity of Pd oxide reduction peak upon nano-CoOx deposition which reflects a partial Pd surface coverage (\( \theta \)) by nano-CoOx. In addition, three oxidation peaks are observed in the anodic potential scan in a potential range (1.1 to 1.6 V) corresponding to nano-CoOx sequential transformation from low to high oxidation states (i.e., Co(OH)\(_2\), CoOOH, and, CoO\(_2\)) [7, 11, 14, 15]:

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\begin{align*}
3\text{Co(OH)}_2 + 2\text{OH}^- & \rightarrow \text{Co}_3\text{O}_4 + 4\text{H}_2\text{O} + 2\text{e}^- & e^-_{\text{rev}} = -0.292 \text{ V} \\
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} & \rightarrow 3\text{CoOOH} + \text{e}^- & e^-_{\text{rev}} = 0.122 \text{ V} \\
\text{CoOOH} + \text{OH}^- & \rightarrow \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^- & e^-_{\text{rev}} = 0.462 \text{ V}
\end{align*}
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On the other hand, we can observe reduction peaks of CoOOH and CoO\(_2\) in the same potential range during the cathodic potential scan [7, 11, 14, 15].
Figure 1. CVs measured in 0.1 M KOH solution at (a) Pd/GC and (b) CoOx/Pd/GC electrodes. Potential rate = 0.1 V s$^{-1}$.

FE-SEM images of Pd/GC and CoOx/Pd/GC electrodes are disclosed in Fig. 2, A and B, respectively. The figure confirms that the catalysts cover homogeneously the entire surface of the GC substrate and that they are deposited in the nano-size.

Figure 2. FE-SEM images of (A) Pd/GC and (B) CoOx/Pd/GC electrodes.

Fig. 3. shows the XRD patterns of Pd/GC (curve a) and CoOx/Pd/GC (curve b) electrodes. It shows the crystalline orientation of nano-Pd and nano-CoOx phases at the GC electrode surface. Fig. 3, curve a shows the diffraction peaks at 2$\theta$ of ca. 25° related to C(002) facet of the carbon and the diffraction peaks at 2$\theta$ of 39.7°, 43.2°, 67.2° and 78° related to Pd(111), Pd(200), Pd(220) and Pd(311) planes of Pd face centered cubic (fcc), respectively [16, 17]. Moreover, XRD pattern of CoOx/Pd/GC is shown in the same figure (curves b), we can observe the same diffraction peaks of the carbon substrate and nano-Pd in addition to nano-CoOx diffraction peaks which are detected at 2$\theta$ of ca. 32°, 37°, 39°, 45°, 56°, 60°, and 67° and corresponding to Co(220), Co(311), Co(222), Co(400), Co(422), Co(511), and Co(440) facets of CoOx spinel, Co$_3$O$_4$ [18-21].
3.2. Glycerol and other alcohols electro-oxidation

The electrocatalytic activities of GO at Pd/GC and CoOx/Pd/GC electrodes are depicted in Fig. 4A (curves a and b, respectively). The CV illustrates that CoOx/Pd/GC electrode provides a peak current ($I_p$) value, 1.7 times, of that provided at Pd/GC electrode together with a favourable cathodic shift in the onset potential ($E_{onset}$) of GO ~80 mV (c.f. Table 1). This points to the role of nano-CoOx in mediating GO at Pd/GC electrode through its redox transformation and highlight the synergistic effect of the binary catalyst. Moreover, the binary catalyst (CoOx/Pd/GC electrode) supported methanol (MeOH) and ethylene glycol (EG) electrooxidation as shown in Fig. 4B. In Fig. 4B (curves a, and a'), $I_p$ of methanol electro-oxidation at CoOx/Pd/GC is 1.8 times of that obtained at Pd/GC electrode. As well, $I_p$ of EG electro-oxidation at CoOx/Pd/GC is 1.6 times of that obtained at Pd/GC electrode (4B curves b, and b'). See also Table 1.

In addition, the binary catalyst (CoOx/Pd/GC) showed a good stability towards GO (see Fig. 5) with continuous oxidation. The figure depicts that the current obtained at CoOx/Pd/GC surface (Fig.5, curve b) remained at a high value over an extended time of electrolysis compared with that obtained at Pd/GC electrode (Fig.5, curve a). This confirms the good tolerance of CoOx/Pd/GC surface against the poisoning intermediates.

![Figure 3. XRD patterns of (a) Pd/GC and (b) CoOx/Pd/GC electrodes.](image)

**Figure 3.** XRD patterns of (a) Pd/GC and (b) CoOx/Pd/GC electrodes.

![Figure 4. (A) CVs obtained at (a) Pd/GC and (b) CoOx/Pd/GC in 0.1 M KOH solution containing 0.3 M glycerol. (B) LSVs obtained at Pd/GC (a, b, c) and CoOx/Pd/GC (a’, b’, c’) electrodes in 0.1 M KOH solutions containing 0.3 M MeOH (a’, a’), 0.3 M EG (b, b’), and 0.3 M glycerol (c, c’). Potential rate = 0.05 Vs$^{-1}$.)](image)

**Figure 4.** (A) CVs obtained at (a) Pd/GC and (b) CoOx/Pd/GC in 0.1 M KOH solution containing 0.3 M glycerol. (B) LSVs obtained at Pd/GC (a, b, c) and CoOx/Pd/GC (a’, b’, c’) electrodes in 0.1 M KOH solutions containing 0.3 M MeOH (a’, a’), 0.3 M EG (b, b’), and 0.3 M glycerol (c, c’). Potential rate = 0.05 Vs$^{-1}$.
Figure 5. Current transients ($I$-$t$, at $E_{1/2} = 0.7$ V vs. RHE) obtained at (a) Pd/GC and (b) CoOx/Pd/GC electrodes in 0.1 M KOH solution containing 0.3 M glycerol.

Table 1. Variation of the oxidation peak current ($I_p$/mA cm$^{-2}$), onset potential ($E_{onset}$), and catalytic enhancement factor ($E.F.$) for MeOH, EG, and glycerol electro-oxidation at various electrodes (nano-Pd, 4.0 μg and 20% CoOx) in 0.3 M MeOH, 0.3 M EG, and 0.3 M glycerol solutions (pH=12).

| Electrode     | Fuel     | $I_p$/mA cm$^{-2}$ | $E_{onset}$/V (vs. RHE) | $E.F.$ |
|---------------|----------|--------------------|-------------------------|--------|
| Pd/GC         | MeOH     | 6.0                | 0.45                    | ----   |
|               | EG       | 11.0               | 0.47                    | ----   |
|               | Glycerol | 12.5               | 0.48                    | ----   |
| CoOx/Pd/GC    | MeOH     | 11.0               | 0.37                    | 1.8    |
|               | EG       | 18.0               | 0.39                    | 1.6    |
|               | Glycerol | 21.5               | 0.40                    | 1.7    |

4. Conclusions
The binary catalyst of CoOx/Pd/GC (where nano-Pd was first electrodeposited at GC surface followed by nano-CoOx electro-deposition) was an efficient catalyst towards methanol (MeOH), ethylene glycol (EG), and glycerol electrooxidation. The peak current ($I_p$) of glycerol electro-oxidation obtained at its surface was about two times of that obtained at Pd/GC electrode surface in 0.3 M glycerol solution besides a negative shift in the onset potential ($E_{onset}$) of GO = 80 mV. The same observation was detected for MeOH and EG electro-oxidation when comparing CoOx/Pd/GC with Pd/GC electrodes. Nano-Pd acted as the main catalyst for MeOH, EG, and glycerol electro-oxidation, while nano-CoOx was mediating the oxidation reaction through its redox transformations between the various oxidation states. In addition, CoOx/Pd/GC showed a good stability towards glycerol electro-oxidation over extended time of oxidation when compared to Pd/GC electrode.

5. References
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