

Electrocatalytic Activity of NiOx Nanostructured Modified Electrodes Towards Oxidation of Small Organic Molecules

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Abstract Nickel oxide nanostructured modified platinum nanoparticles (PtNPs) supported in glassy carbon electrode (NiOx/Pt/GC) was used as an effective anode for formic acid (FA), methanol (ME) and ethanol (ET) electrooxidation in 0.3 M NaOH solution. GC surface was fabricated with NiOx nanostructured and Pt nanoparticles electrochemically. The modified electrodes were characterized using cyclic voltammetry (CV) and scanning electron microscopy (SEM). The catalytic improvement observed at NiOx/Pt/GC electrode for FAO, MEO, and ETO was not only confined in the large increase of the oxidation current but also in a negative shift in the onset potential of the oxidation reactions. The influence of temperature on the oxidation current was investigated and the apparent activation energy, E_a , for each fuel was calculated at a specific potential. Furthermore, NiOx/Pt/GC electrode showed a satisfactory stability for FAO, MEO, and ETO in 0.3 M NaOH solution.

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1 Introduction

Fuel cells (FCs) have received increasing attention in many applications due to their unique advantages such as high efficiency, renewable, clean and low emissions energy resources. The use of H_2-O_2 as a fuel in FCs presents some significant drawbacks related to their transportation and storage [1–4]. In this context, small organic molecules which rich with hydrogen start to replace H_2 fuel. Of these, formic acid (essential anodic reaction of direct formic acid fuel cell; DFAFC) [2] methanol (vital anodic reaction of direct methanol fuel cell; DMFC) [3] and ethanol (the main anodic reaction of direct ethanol fuel cell; DEFC) [4] appeared promising in terms of the ease handling, transporting and storage in addition to their interesting oxidation efficiency.

The mainly used anodes in fuel cells are Pt and Pt-based materials. These catalysts have been one of most expensive materials in the fabrication of components for FCs. The generation of several poisoning intermediates at the anode during the fuel electrooxidation induces a considerable reduction in the electrocatalytic activity of the anode. The modification of Pt with metal oxide (e.g., MoOx, MnOx, SnOx, TaOx, NiOx or NbOx) is a possible way to modify the electrocatalytic properties of Pt in order to overcome poisoning and to reduce the cost of the catalyst considerably [2–4].

Herein, the possibility of the fabrication of Pt and NiOx binary catalysts on the GC electrode by electrodeposition as a highly active catalyst for FA, ME and ET oxidation in alkaline medium was investigated. Scanning electron microscopy (SEM), cyclic voltammetry (CV) and chronoamperometry techniques are used to characterize and measure catalytic activity of the prepared electrodes towards FA, ME and ET electrooxidation.

2 Experimental

GC ($d = 3.0$ mm and its area is 0.07 cm²) served as a working electrode. A spiral Pt wire and an Ag/AgCl/KCl (sat.) are used as counter and reference electrodes, respectively. Conventional method used to cleaning the working electrode and its modification with Platinum nanoparticles (PtNPs) and NiOx were described elsewhere [2]. Electrochemical measurements were performed in a conventional two-compartment three-electrode glass cell at various temperature using an EG&G potentiostat (model 273A) operated with Echem 270 software. A field emission scanning electron microscope (FE-SEM, QUANTA FEG 250) is employed to evaluate the electrode's morphology. The electrocatalytic activity of the modified GC electrodes with Pt and NiOx nanoparticles toward FA, ME and ET oxidation was examined in a solution of 0.3 M NaOH containing 0.3 M FA, ME and ET, respectively. All chemicals (analytical grades) are used without further purification. Current densities calculated on the basis of the real surface area of Pt. The surface

coverage (θ) of NiOx on Pt/GC electrode was estimated from the decrease of the peak current intensity at ca. -0.32 V corresponding to the reduction of the Pt surface oxide formed during the anodic scan (surface coverage of NiOx ≈ 25 %) (Fig. 1d) [2].

3 Results and Discussions

3.1 Materials and Electrochemical Characterization

Figure 1 shows FE-SEM images of Pt/GC (a), NiOx/Pt/GC (b). CVs of Pt/GC (c) and NiOx/Pt/GC (d) electrodes in 0.3 M NaOH solution at scan rate 200 mVs^{-1} , respectively. Figure 1a depicts that, round-shape Pt nanoparticles with uniform size of ca. 100 nm are observed. At the NiOx/Pt/GC electrode (Fig. 1b), a flower-like Pt and Ni nanostructures are obtained with a significantly larger average particle size

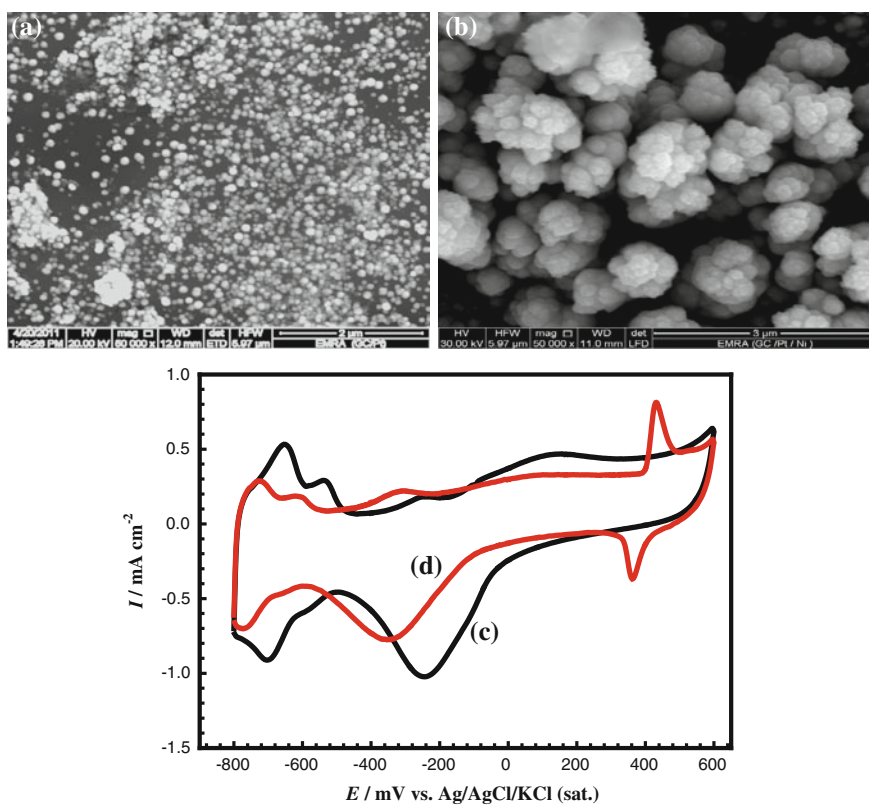


Fig. 1 FE-SEM micrographs obtained for Pt/GC (a), NiOx/Pt/GC (b). CVs of Pt/GC (c) and NiOx/Pt/GC (d) electrodes in 0.5 M NaOH at scan rate 200 mV s^{-1} , respectively

compared with Fig. 1a. Pt/GC electrode gives a characteristic CV response of the polycrystalline bulk Pt surface (Fig. 1c) [2]. On the other hand, the modification of the Pt/GC electrode with NiOx (Fig. 2d) resulted in a new noticeable changes in the characteristic CV including decrease in the intensity of the Pt oxide reduction peak (at ca. -0.34 V) along with a decrease in the current intensity of the $H_{ads/des}$ peaks (in the potential region from -0.6 to -0.8 V). In addition, a redox pair is appeared at ca. 0.45 V corresponding to the Ni(II)/Ni(III) reversible transformation [2].

3.2 Electrocatalytic Activity Toward FAO, MEO and ETO

Figure 2 shows CVs obtained at Pt/GC (a, c and e) and NiOx/Pt/GC (b, d and f) electrodes for FAO, MEO and ETO, respectively in 0.3 M NaOH solution. Figure 2a shows the typical CVs of FAO at Pt/GC electrode (where two oxidation peaks are observed in the forward direction which are corresponding to the direct oxidation of FA to CO_2 (at ca., 0.23 V, desired one) and CO oxidation (ca., 0.65 V) which resulted from non-faradic dissociation of FA (indirect FA oxidation, undesired pathway) [2]. Interestingly, on the modification of Pt/GC electrode with NiOx (Fig. 2b) a significant enhancement of direct oxidation pathway current (I_p^d) with a concurrent suppression of indirect oxidation pathway current (I_p^{ind}) is observed, indicating that the direct pathway is enhanced and CO tolerance increase [2].

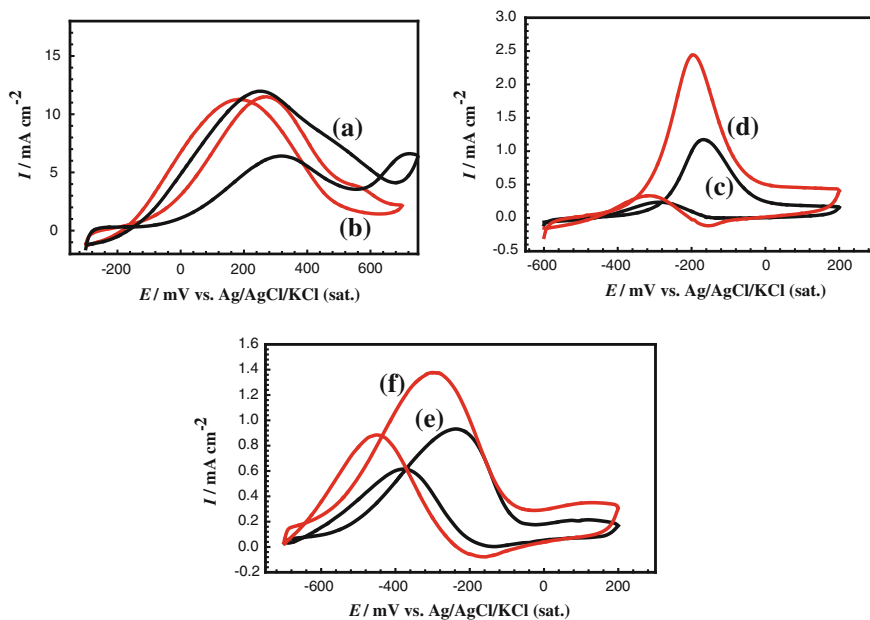


Fig. 2 CVs for Pt/GC (a, c and e) and NiOx/Pt/GC (b, d and f) electrodes in 0.3 M NaOH containing 0.3 M FA (a, b), ME (c, d) and ET (e, f) oxidation measured at 200 $mV s^{-1}$, respectively

Figure 2c–f shows CV for MEO and ETO at Pt/GC and NiOx/Pt/GC electrodes, respectively. Inspection of Fig. 2c, e discloses the presence of anodic peaks (I_f) at ca. -190 and -235 mV at the Pt/GC electrode for ME and ET, respectively. Another backward anodic peak (I_b) appears, which was assigned to the oxidation of the incompletely oxidized species formed in the forward scan (e.g., CO) at the freshly reduced PtO surface. This figure shows also that, the modification of Pt with NiOx causes a negative shift in the onset potential of alcohol oxidation in comparison with Pt/GC electrode concurrently with a significant increase in the oxidation peak current (I_f). The enhanced activity of NiOx/Pt/GC for alcohol oxidation in alkaline media can be attributed to the synergistic role of Pt and nickel oxides/hydroxides in the catalytic enhancement. The poisoned Pt nanoparticles surface with CO_{ad} can be regenerated via the mediated oxidation of CO_{ad} with nickel oxides/hydroxides on the catalyst surface [3, 4].

3.3 Stability of the Binary Catalyst

The steady state behavior for the oxidation of the FA, ME and ET are studied using chronoamperometric measurements at different potentials according to the oxidized fuel. Figure 3a–f shows the I - t plots measured at Pt/GC (a, c and e) and NiOx/Pt/GC (b, d and f) electrodes in

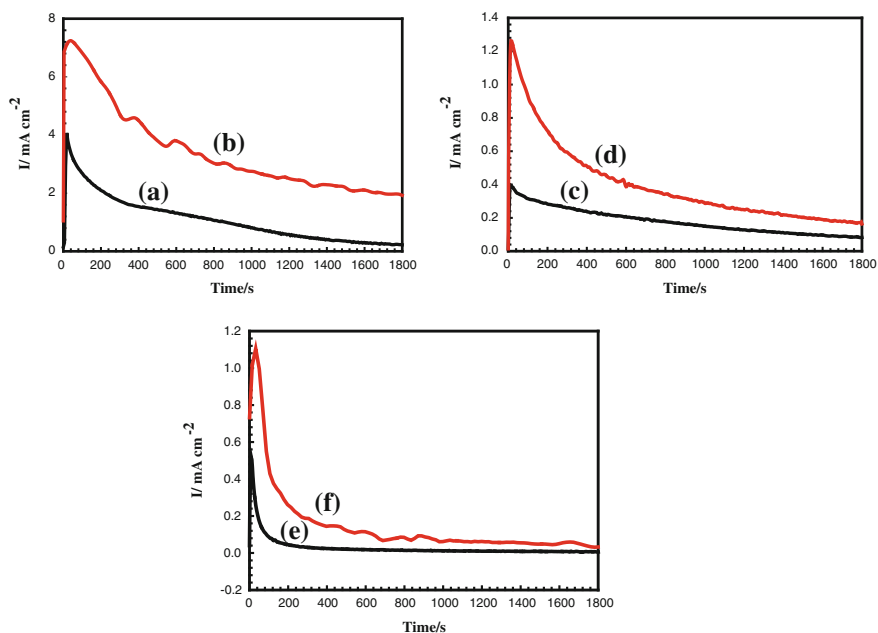


Fig. 3 I - t transient measured for Pt/GC (a, c and e) and NiOx/Pt/GC (b, d and f) electrodes in 0.3 M NaOH containing 0.3 M FA (a, b), ME (c, d) and ET (e, f), respectively

(b, d and f) electrodes in 0.3 M NaOH containing 0.3 M FA, ME and ET at 0.3, -0.2 and -0.35 V respectively. For FAO (Fig. 3a, b) NiOx/Pt/GC electrode supports a higher current density than Pt/GC electrode over the employed electrolysis time, the decay in current might be due to accumulation of CO at the electrode surface with the time [2]. Similarly, the same behavior is observed for ME (Fig. 3c, d) and ET (Fig. 4e, f) at Pt/GC and NiOx/Pt/GC electrodes [3, 4].

3.4 Effect of Temperature

Temperature is one of the most important factors affecting the catalytic activity of catalysts according to Arrhenius equation. In this regard we aim to study the effect of solution temperature on the oxidation of FA, ME and ET at Pt/GC and NiOx/Pt/GC electrodes. Figure 4 shows LSVs response for FA, ME and ET oxidation at NiOx/Pt/GC in 0.3 NaOH containing 0.3 M of each fuel at different temperatures (insets show a representative Arrhenius plot for the oxidation of 0.3 M of each fuel in 0.3 M NaOH at Pt/GC (dashed) and NiOx/Pt/GC (solid) line). Inspection of this figure reveals that, an increase of the oxidation current with temperature up to 60 °C occurs, reflecting a more favorable kinetics for the oxidation of the three fuels at the

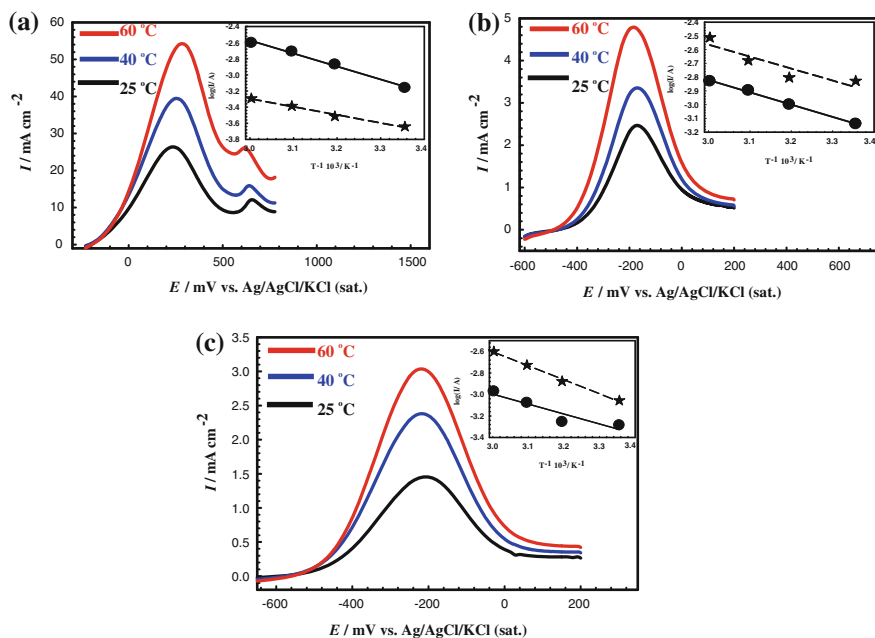


Fig. 4 LSVs for FA (a), ME (b) and ET (c) oxidation at NiOx/Pt/GC in 0.3 NaOH at different temperatures at scan rate 200 mV s⁻¹. Insets show a representative Arrhenius plot for the oxidation of each fuel at Pt/GC (dashed) and NiOx/Pt/GC (solid) line

proposed electrode. The values of the apparent activation energy (E_a) are calculated by plotting the current (I) at a specific potential as a function of T . From the analysis of Fig. 4 insets E_a is calculated to be 19.136, 16.665 and 24.867 kJ/mole at Pt/GC electrode and 30.725, 17.151 and 17.664 kJ/mole at NiOx/Pt/GC electrode for FA, ME and ET, respectively. And these values are comparable to that reported in literature for FA, ME and ET oxidation [4–6].

4 Conclusions

In summary, nickel oxide (NiOx) and platinum nanoparticles (Pt) are supported on GC electrode electrochemically and characterized using CV and FE-SEM. NiOx/Pt/GC in comparison with Pt/GC electrode shows high catalytic activity for the oxidation of (FA, ME and ET). In fact, NiOx could acts as a catalytic mediator which facilitates the charge transfer during the oxidation process and/or providing the oxygen species necessary for promoting the oxidative removal of the poisoning species produced during the reaction. The influence of temperature on the catalytic activity of the proposed electrodes towards FA, ME and ET is also tested. Furthermore, the NiOx/Pt/GC electrode shows a acceptable stability for FAO, MEO, and ETO when used in constant potential applying (chronoamperometry) which makes it more attractive for fuel cell applications.

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