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Short Communication

Poly(1-Naphthylamine)-Nickel Modified Glassy Carbon Electrode for Electrocatalytic Oxidation of Formaldehyde in Alkaline Medium

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The electrocatalytic oxidation of formaldehyde on poly(1-naphthylamine)-nickel modified glassy carbon electrode (P(NA)-Ni/GCE) was developed. This involves in situ electropolymerization of 1-naphthylamine at glassy carbon electrode, which is following to the incorporation of Ni(II) to polymeric layer by immersion of modified electrode in 1.0 M nickel sulphate solution. The general electrochemical behavior was characterized by cyclic voltammetry and chronoamperometry methods in alkaline media. The results show that the (P(NA)-Ni /GCE system exhibits a significant electrocatalytic activity towards oxidation of formaldehyde. The effects of scan rate and formaldehyde concentration on the electrocatalytic oxidation of formaldehyde were also investigated at the surface of P(NA)-Ni/GCE. The diffusion coefficient ($D= 2.85\times10^{-4}$ cm^2 s^{-1}), and the transfer coefficient (α = 0.36) of formaldehyde were calculated.

Keywords: 1-Naphthylamine; Nickel oxyhydroxide; Formaldehyde; Sensor

1. INTRODUCTION

Recently, there has been an increasing interest in the development of fuel cells. The electrochemical oxidation of small organic molecules has been studied due to their potential utilization as fuels in energy conversion systems. Using formaldehyde (CH_2O) is a risk to human health. But recent data demonstrated that formaldehyde fuel cells are attractive alternatives for proton exchange membrane (PEM) fuel cells applications [1-3].

Pt and Pt alloys [4-6], copper and copper alloys [7-8], gold [9] and palladium nanoparticles modified electrode [10-12] have been studied as anode catalysts for the HCHO oxidation. However, precious metals (Pt, Pd, Au, etc.) are readily poisoned by adsorbed intermediates and lost their active sites. And the high cost and short supply of these metals makes it unsuitable for practical and industrial application [13]. Thus, a great deal of interest has been focused on an alternative metal (non-noble metal) while maintaining the high catalytic activity and less expensive materials as anodes for HCHO oxidation. Nickel is used extensively in numerous industrial applications due to its low cost and its surface oxidation properties [13]. And it is a useful catalyst to electrooxidation of methanol and formaldehyde in alkaline medium for long-term stability in alkaline solutions [14-18]. Owing to its controllable thickness, high conductivity and good stability, polymer modified electrode prepared by electropolymerization has been receiving extensive interest in the fields of chemical sensors [19, 20]. Moreover, polymer modified electrodes prepared by electropolymerization make the immobilization procedure of a nickel-based electrocatalyst very simple and reliable [13, 18].

In this work, we describe the synthesis of poly(1-naphthylamine) (P(NA)) composite film during the process of electropolymerization at glassy carbon electrode, which is following to the incorporation of Ni(II) to polymeric layer by immersion of modified electrode in 1.0 M nickel sulphate solution. Then, P(NA)-Ni modified electrode was used for electrooxidation of formaldehyde. The experimental data reveal that the modified electrode has a very high catalytic activity for formaldehyde.

2. EXPERIMENTS

2.1 Chemical reagents

1-naphthylamine (NA) was from Aladdin-Reagent Company (Shanghai, China). Sulfuric acid, sodium hydroxide and formaldehyde from Sinopharm Chemical Reagents Co., Ltd (China), and sulfuric acid was used as the supporting electrolyte. All reagents were of analytical-grade and used without any further purification. Aqueous solutions were prepared with redistilled water.

2.1 Instrumentation

Electrochemical experiments were performed with a CHI660D electrochemical workstation (Shanghai Chenhua Co., China) with a conventional three-electrode cell. A bare or poly(1-naphthylamine) - nickel modified glassy carbon electrode (φ=3mm) (P(NA)-Ni /GCE) was used as working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as reference electrode and auxiliary electrode, respectively.

3. RESULTS AND DISCUSSION

3.1. Electropolymerization of NA on GCE

Prior to preparation of the P(NA)/GCE, the glassy carbon electrode was prepared by polishing with 0.05 μm Gamma alumina slurry on microcloth pads to a mirror-like finish and rinsed with redistilled water. Subsequently, it was ultrasonicated thoroughly with HNO_3 (1:1, v/v), ethanol (1:1, v/v), and doubly distilled water. After pretreating, the glassy carbon electrode was cycled in 0.5 M H_2SO_4 with the potential range from -0.15 to +0.60 V at a scan rate of 100 mV/s until the reproducible background was obtained. Fig. 1 displays the cyclic voltammograms for the electrochemical polymerization of NA over the range of -0.15 to 0.60 V at 100 mV/s for 80 cycles continuously. During the polymerized process, it is clear that an anodic peak at 0.25 V corresponding to the oxidation of NA descended gradually with cyclic time increasing and trended to be stable after 30 scans. The gradually descended of the anodic peaks in the cyclic voltammogram indicated the gradually conversion of NA into its polymeric product on the surface of GCE.

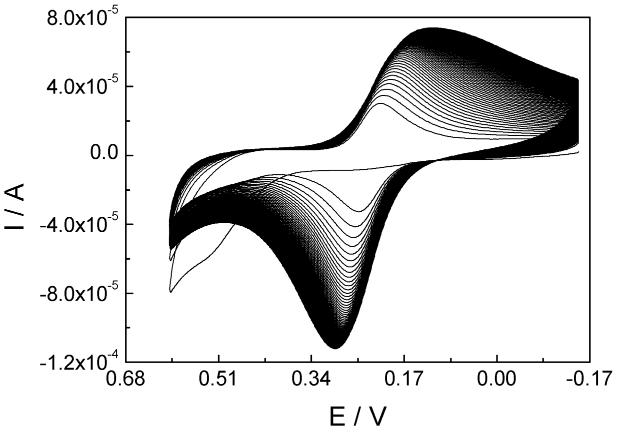

Figure 1. Cyclic voltammograms of polymerization of NA (5.0×10^{-4} M) in 0.5 M H_2SO_4 on GCE in the potential range from -1.0 to 2.0 V at a scan rate 100 mV/s. The cycling number is 25..

3.2. Incorporation of Ni(II) ions into P(NA) /GCE and the electrochemical behavior of P(NA)-Ni/GCE

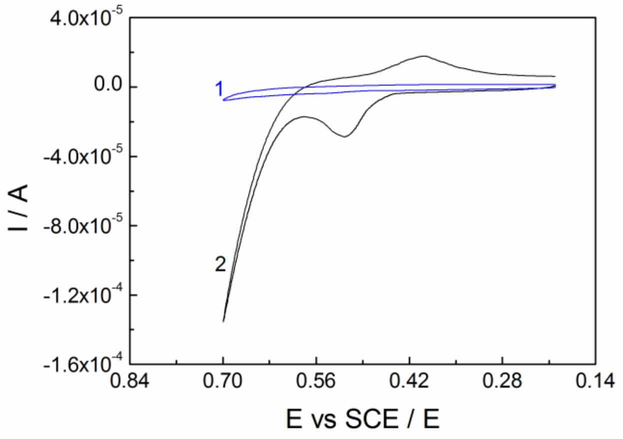

Figure 2. Cyclic voltammograms of (1) P(NA)/GCE and P(NA)-Ni/GCE in 0.1 M NaOH solution at potential scan rate of 20 mV s^{-1}.

In order to incorporate Ni(II) ions into polymeric film, the freshly P(NA)/GCE was placed in a well stirred 1.0 M $NiSO_4$ solution at open circuit for five minutes. Accumulation of nickel ions was carried out by complex formation between Ni(II) and amine sites in the polymer backbone onto GCE. The redox process of these modified electrode is expressed as :

$$Ni(OH)_2 + OH^- \longleftrightarrow NiOOH + H_2O + e^-$$

Fig. 2 shows the electrochemical response of P(NA) /GCE and P(NA)-Ni/GCE in 0.1 M NaOH solution. As it can be seen, whereas neither oxidation nor reduction took place on P(NA)/GCE a well defined stable redox peaks were observed for P(NA)-Ni/GCE in the potential ranges from 0.2 to 0.7 V vs. SCE. This phenomenon was attributed to the oxidation of Ni(II) to Ni(III) with a peak potential of 0.52 V and to the reduction of Ni(III) to Ni(II) with a peak potential of 0.40 V vs SCE.

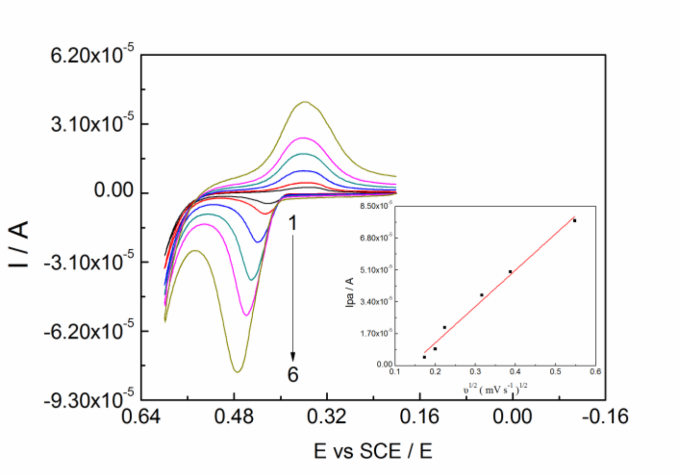

Figure 3. Cyclic voltammograms of P (NA)–Ni/GCE, at various scan rates: (1) 20, (2) 30, (3) 50, (4) 100, (5) 150, (6) 300 mV s^{-1}. (B) Plot of Ipa vs. $υ^{1/2}$.

Fig. 3 exhibits cyclic voltammograms of P(NA)–Ni/GCE in 0.1 M NaOH solution at different potential scan rate. The anodic peaks shifted to more positive potentials and the cathodic peaks moved to more negative potential values with the increasing scan rates. The results indicate a limitation in the charge-transfer kinetics, probably due to: (a) chemical interactions between the electrolyte ions and the modifier film, (b) dominance of electrostatic factors, (c) the lateral interactions of the redox couples present on the surface and/or (d) non-equivalent sites present in the film [18]. As can be seen in Fig. 3, a linear relationship ($I_p = 1.94\times10^{-4}\ υ - 2.65\times10^{-5}$, n=6, r=0.9939) was obtained between the peak current and the square root of the potential scan rate in the range of 0.03–0.3 V s^{-1}, which revealed that the oxidation of formaldehyde was a diffusion process. This limiting diffusion process may occur for the charge neutralization of the film during oxidation / reduction process.

3.3. Electrocatalytic oxidation of formaldehyde at the modified electrode

3.3.1. Cyclic voltammetric studies

The electrooxidation of formaldehyde was first studied at the surface of P(NA)/GCE and P(NA)-Ni/GCE by cyclic voltammetric experiments in 0.1 M NaOH. As it can be seen from fig. 4, formaldehyde oxidation at P(NA)/GCE take place near solvent oxidation discharge. The electrochemical response of P(NA)–Ni /GCE in alkaline media showed well defined anodic and cathodic peaks. In presence of formaldehyde a great enhancement of the anodic peak current was observed. This phenomenon is attributed to the production of $Ni(OH)_2$ and consumption of NiOOH, respectively. Moreover formaldehyde oxidation shifted to less positive potential. These results showed that the modified electrode has a high ability for formaldehyde oxidation and the following mechanism can be proposed for the mediated electrooxidation of formaldehyde at the surface of this modified electrode (Fig. 5).

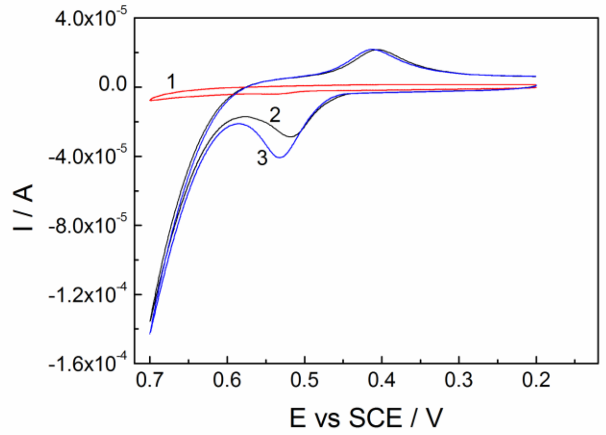

Figure 4. Cyclic voltammograms of (1) 3×10^{-5} M formaldehyde in 0.1 M NaOH solution at the surface of P(NA)/GCE, (2) 0.0 and (3) 3×10^{-5} M formaldehyde at the surface of P(NA)Ni/GCE at υ= 100 mV s^{-1}.

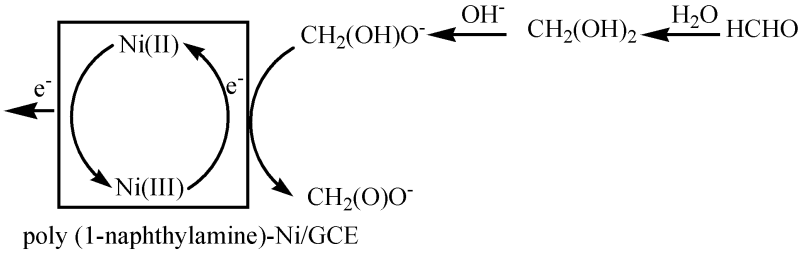

Figure 5. Representative schematic for mechanism of formaldehyde electrooxidation at the surface of P(NA)-Ni/GCE.

The effect of formaldehyde concentration was also investigated. The results indicated that the modified electrode can be an efficient catalyst for electrooxidation of formaldehyde. Furthermore, the effects of scan rate on the cyclic voltammograms of P(NA)-Ni/GCE in the presence of 3×10^{-5} M formaldehyde were studied (Fig. 6). As can be seen, the anodic peaks potential shifted to more positive potentials with increasing of potential scan rate. However the electrocatalytic oxidation current of formaldehyde linearly increased with the square root of potential scan rate (Fig. 6A), which demonstrates the reaction is diffusion controlled.

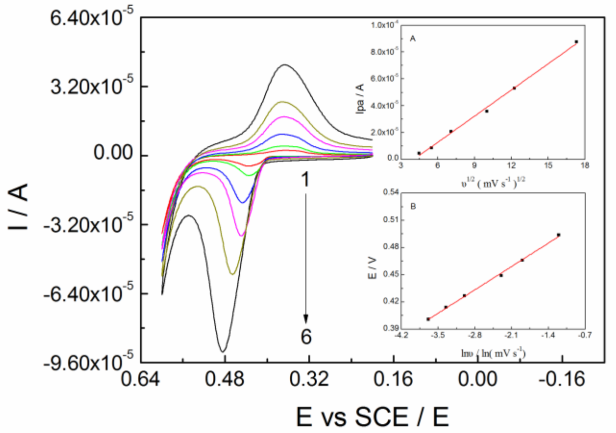

Figure 6. Cyclic voltammograms of the P(NA)-Ni/GCE in the presence of 3×10^{-5} M formaldehyde in 0.1 M NaOH solution at various scan rates: (1) 20, (2) 30, (3) 50, (4) 100, (5) 150, (6) 300 mV s^{-1}. (A) Plot of anodic peak current vs. $\upsilon^{1/2}$, (B) plot of Epa vs. ln υ.

The linear relation between peak potential and logarithm of scan rate can be expressed as *E*p (V) = 0.0394lnυ (V s^{-1}) + 0.5413 (n=6, r=9966). As for an irreversible electrode process, according to Laviron [21], *E*p is defined by the following equation:

$$E_p = E^{\theta'} + \frac{RT}{(1-\alpha)nF}\ln\nu \qquad (1)$$

where E_p is the peak potential (V vs. SCE), $E^{\theta'}$ is the formal potential (V vs. SCE), *R* is the universal gas constant (8.314 J K^{-1} mol^{-1}), *T* is the temperature (K), α (alpha) is the charge transfer coefficient for the oxidation step, *n* is the number of electrons involved in the rate determining step, *F* is the Faraday constant

(96,485 C mol^{-1}). So, from this we got the value of α to be 0.36.

3.3.2. Chronoamperometric studies

Double step chronoamperograms were recorded by setting the working electrode potential at desired values. Fig. 7A shows double step chronoamperogram of the modified electrode in the absence (a) and in the presence (b, c) of formaldehyde. The applied potential steps were 0.45 and 0.33 V vs. SCE in the anodic and cathodic direction, respectively. As can be seen, the forward and backward potential step chronoamperometry of the modified electrode in blank solution showed an almost symmetrical chronoamperogram with almost equal charge which is consumed for the oxidation and reduction of surface confined Ni(II)/Ni(III) sites. However, in the presence of formaldehyde, the charge value associated with the forward chronoamperometry, Q, is greater than of that observed for the backward, (Fig. 7B). These results indicate the electrocatalytic ability of this modified electrode for the oxidation of formaldehyde in alkaline media. Plotting of the net current as a function of the inverse square root of time, gives a linear relationship (Fig. 7C), resulting in a diffusion controlled process. The diffusion coefficient of formaldehyde can be obtained by using the slope of this straight line, according to Cottrell equation [22]:

$$I=\frac{nFAD^{1/2}C^{*}}{\pi^{1/2}}t^{1/2} \qquad (2)$$

where D is diffusion coefficient and C^{*} is the bulk concentration of formaldehyde. As can be seen in Fig.7C, a linear relationship between I and $t^{1/2}$ can be obtained after point-by-point background subtraction, and the regression can be expressed as $I=3.45\times10^{-6}\,t^{1/2}+3.65\times10^{-6}$ (C, $s^{1/2}$, r = 0.9999). Based on the slope of 3.45×10^{-6} C $s^{-1/2}$, it is calculated that D= 2.85×10^{-4} cm^{2} s^{-1}.

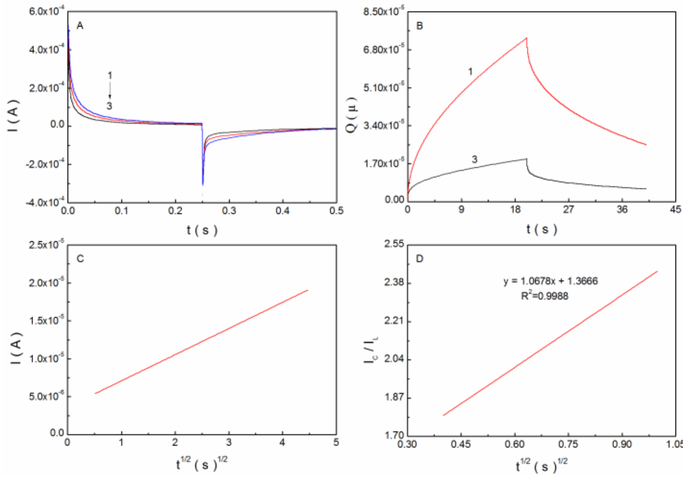

Figure 7. (A) Double step chronoamperograms of P(NA)-Ni/GCE in 0.1 M NaOH solution with different concentrations of formaldehyde: (1) 3.0×10^{-5}, (2) 1.0×10^{-5} and (3). 0.0 M (B) Plot of Q vs. t derived from the data of chronoamperogram of 1 and 3. (C) Plot of I vs. $t^{-1/2}$. (D) Plot of I_C/I_L vs. $t^{1/2}$ derived from the data of chronoamperogram of 3.

Chronoamperometry was also used for the evaluation of the catalytic rate constant according to [23]:

$$\frac{I_C}{I_L}=\gamma^{1/2}\pi^{1/2}=\pi^{1/2}(kC_0t)^{1/2} \qquad (3)$$

where I_C and I_L are the currents in the presence and in the absence of formaldehyde, $\gamma = kC_0t$ is the argument of error function, k is the catalytic rate constant (cm3 mol^{-1} s^{-1}), C_0 is the concentration of formaldehyde (mol cm^{-3}) in testing solution and t is elapsed time (s).

As can be seen in Fig.7D, the regression can be expressed as $\frac{I_C}{I_L} = 1.0678\, t^{1/2} + 1.3666$ ($s^{1/2}$, r = 0.9993). From the slope of the I_C/I_L vs. $t^{1/2}$ plot, the mean value of k for formaldehyde (0.01 M) was found to be 2.01×10^4 cm^3 mol^{-1} s^{-1}.

4. CONCLUSIONS

A novel electrode has been described herein, consisting of nickel ions loaded into a poly(N-methylaniline) modified carbon paste electrode by immersion of the polymeric modified carbon paste electrode in nickel sulphate solution. This modified electrode was found to be capable of catalyzing the electrooxidation of formaldehyde very efficiently. The oxidation of formaldehyde occurs at a potential where the oxidizing Ni(III) species are generated.

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