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Article

Synergistic effect of cobalt and copper on a nickel-based modified graphite electrode during methanol electro-oxidation in NaOH solution

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ABSTRACT

The electrocatalytic oxidation of methanol was studied over Ni, Co and Cu binary or ternary alloys on graphite electrodes in a NaOH solution (0.1 mol/L). The catalysts were prepared by cycling the graphite electrode in solutions containing Ni, Cu and Co ions at cathodic potentials. The synergistic effects and catalytic activity of the modified electrodes were investigated by cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). It was found that, in the presence of methanol, the modified Ni-based ternary alloy electrode (G/NiCuCo) exhibited a significantly higher response for methanol oxidation compared to the other samples. The anodic peak currents showed a linear dependency on the square root of the scan rate, which is a characteristic of a diffusion controlled process. During CA studies, the reaction exhibited Cottrellian behavior and the diffusion coefficient of methanol was determined to be $6.25 \times 10^{-6} \text{ cm}^2/\text{s}$ and the catalytic rate constant, K , for methanol oxidation was found to be $40 \times 10^7 \text{ cm}^3/(\text{mol} \cdot \text{s})$. EIS was used to investigate the catalytic oxidation of methanol on the surface of the modified electrode.

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1. Introduction

At present, the ever-increasing use of energy, and especially of fossil fuels, is a major source of air pollution. As a result, there is a search for alternatives to fossil fuels, and fuel cells have attracted much attention due to their minimal pollutant emissions. Fuel cells are currently used in a wide range of portable, stationary and transport applications, and direct methanol fuel cells (DMFCs) are a particularly promising clean, portable power source. As such, DMFCs have received considerable interest with regard to applications in automobiles and portable consumer electronics [1] as well as other mobile and stationary devices [2,3]. This is because of their high efficiency,

very low emissions and potential to act as renewable fuel sources with fast and convenient refueling, simple operation and ease of fuel storage and distribution. In addition, the low operating temperature of a DMFC (typically $<95^\circ\text{C}$) allows for easy start-up and rapid responses to changes in the load or operating conditions [2–4]. A considerable number of studies have been devoted to the electrocatalytic oxidation of methanol, which is of paramount importance in the development of DMFCs [5]. One approach to the design of DMFCs is to use alkaline solutions [6], since there are many associated advantages, such as increased efficiency [6,7], a wider selection of possible electrode materials, almost no sensitivity to surface structures and negligible poisoning effects [8,9]. However, because the

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kinetics of methanol oxidation are generally unfavorable, a catalyst is required to improve the oxidation efficiency. Electrocatalysts based on Pt [10–12] and Pt alloys [13–18] have been developed and used as anode catalysts for methanol oxidation in DMFCs [19], and have been shown to exhibit good activity for methanol oxidation. Unfortunately, these materials are too expensive for practical applications. Therefore, many attempts have been made to examine the catalytic activity of less expensive metals, such as nickel-based electrodes. The electrocatalytic oxidation of methanol by transitional metal based catalysts and metal-free carbon materials has been investigated by several researchers [20–27], most of whom have found enhanced activity of binary electrocatalysts during methanol oxidation compared with that of pure metals [28,29]. At present, many researchers are investigating the electrocatalytic activity for methanol oxidation in the presence of Ni-based ternary alloys that present higher activity for methanol oxidation than platinum [30], thus suggesting their applicability as DMFC electrocatalysts.

In the present study, we investigated the activity of a modified Ni-based ternary alloy graphite electrode (G/NiCuCo) and the associated synergistic effects on the electrocatalytic oxidation of methanol in alkaline solution. In addition, the electrocatalytic activity was compared with that of a Ni-based binary alloy. The addition of Co and Cu to modify the electrocatalyst had the aim of improving the methanol oxidation performance. It is believed that optimization of the composition of a Ni-based electrocatalyst containing Cu and Co via combinatorial electrochemistry is crucial to commercializing DMFCs. In the present work, we examined the electrochemical activity of Ni-based ternary alloy catalysts during methanol oxidation and reported the electrocatalytic properties of the modified electrode for the electro-oxidation of methanol.

2. Experimental

Nickel sulfate, copper sulfate, cobalt chloride, sodium hydroxide, hexacyanoferrate and methanol were all Merck products of analytical grade and were used without further purification. All solutions were made with distilled water. Modified electrodes were prepared by first polishing the graphite rods with emery papers of different grades until a mirror surface was obtained. In a typical experiment, the deposition of the ternary alloy on the graphite electrode was accomplished by repetitive scanning (40 cycles) of the electrode in a solution of soluble salts over the cathodic potential range of 0 to -1 V vs. Ag/AgCl, followed by repetitive scanning (60 cycles) over the anodic potential range of 0 to 1 V vs. Ag/AgCl in a NaOH solution. A scan rate of 100 mV/s was applied in both processes.

Electrochemical studies were carried out in a conventional three-electrode cell powered by an electrochemical system consisting of an EG&G model 273 potentiostat/galvanostat and a Solartron model 1255 frequency response analyzer. The system was run by a PC using the M270 and M398 commercial software packages via a GPIB interface. For impedance measurements, a frequency range of 100 kHz to 10 MHz was employed with an AC voltage amplitude of 5 mV. Fitting of exper-

imental impedance spectroscopy data to the proposed equivalent circuit was performed using the ZView software package. Ag/AgCl-saturated KCl, a graphite rod and a modified graphite rod with a geometric area of 0.11 cm^2 were employed as the reference, counter and working electrodes, respectively. All experiments were carried out at $298 \pm 2\text{ K}$. A JEOL JXA-840 scanning microanalyzer was used to examine the topography of the G/NiCuCo catalyst.

3. Results and discussion

3.1. Scanning electron microscopy (SEM) of graphite electrodes

SEM images of the surfaces of the unmodified graphite (A) and an electrodeposited G/NiCuCo modified electrode (B) are presented in Fig. 1. As can be seen, the unmodified graphite electrode (Fig. 1(a)) had a much smoother morphology, whereas grains of the deposited film are clearly seen on the surface of the electrode. It is also evident that the film coverage is almost uniform, indicating that the catalyst film covered the entire surface of the graphite electrode. The films were found to be fairly compact with virtually no pores or cavities.

3.2. Electrochemical oxidation of methanol on the G/NiCuCo-modified electrode

Figure 2 shows the cyclic voltammograms of bare graphite and G/NiCuCo electrodes. The oxidation of methanol was first studied over the bare graphite electrode and, as can be seen, the addition of methanol (0.5 mol/L) to the alkaline solution had no effect on the electrochemical response, meaning that the methanol was not oxidized. Several peaks are seen in both the anodic and cathodic half cycles of plot (b1). Peak I_a corresponds to the overlapped anodic peaks of Ni and Co species, while peaks I_c and II_c in the cathodic half cycle are related to the reduction of Cu species and a combination of Ni and Co species, respectively. In plot (b2), an increase in the anodic current density of the G/NiCuCo electrode is observed subsequent to the addition of methanol to the supporting electrolyte. In fact, this electrode shows remarkable electrocatalytic activity toward the oxidation of methanol. The more pronounced response of the modified electrode is due to the enhancement of the catalytic properties of the electrode by the composite material. It should be noted that plot (b2) also indicates the irreversible electro-oxidation of methanol.

Fig. 1. SEM images showing the surface morphology of (a) unmodified graphite and (b) G/NiCuCo modified electrode.

Fig. 2. Cyclic voltammograms of (a) bare graphite and (b) G/NiCuCo-modified electrode in the absence (1) and presence (2) of methanol (0.5 mol/L) in a NaOH solution (0.1 mol/L). Scan rate = 100 mV/s.

The inset to Fig. 2 shows that the reduction peak potential of the G/NiCuCo in the absence of methanol appears at 0.40 V vs. Ag/AgCl while, in the presence of methanol, this potential is located at 0.14 V. This shift of approximately 0.26 V demonstrates the catalytic activity of G/NiCuCo during methanol oxidation.

To investigate the current density increases resulting from surface or catalytic effects, CV was performed in $\text{Fe}(\text{CN})_6^{4-}$ solution (0.1 mol/L), using a bare electrode as well as G/Ni or G/NiCuCo-modified electrodes. Fig. 3 illustrates the reversible reactions associated with the oxidation/reduction of $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$, as evidenced by the anodic and cathodic peaks, respectively. Here it is evident that the same current density is obtained from the G/Ni and G/NiCuCo-modified electrodes and also with the bare graphite electrode. This is attributed to the negligible increase in the surface area of the modified electrode. For this reason, the remarkable increase in the anodic current density of the G/NiCuCo catalyst (plot (b2) in Fig. 2) is obviously related to the electrocatalytic effect. It is important to note that the electro-oxidation of methanol over Ni-based mod-

Fig. 3. Cyclic voltammograms of (1) bare graphite, (2) G/Ni, and (3) G/NiCuCo-modified electrodes in $\text{Fe}(\text{CN})_6^{4-}$ (0.1 mol/L). Scan rate = 100 mV/s.

ified electrodes has been shown to follow the Fleischmann mechanism [20,31].

3.3. Comparing electrochemical oxidation of methanol over pure metals and Ni-based binary and ternary alloy-modified graphite electrodes

Figure 4 shows the cyclic voltammograms obtained of different electrodes. The enhanced electro-catalytic activity of the binary electrocatalysts during methanol oxidation is evident when compared with that of the pure metals. The Ni-based ternary alloy electrode also shows a significantly higher response for methanol oxidation compared to the pure metals and binary alloys. Finally, the oxidation of methanol over the G/NiCuCo-modified electrode generates less over potential with respect to the other modified electrodes.

In recent studies, Jafarian et al. [32,33] have reported the electrocatalytic oxidation of methanol over a Ni-Cu alloy electrode and a polyNiTCPP-modified glassy carbon electrode. Comparing the catalytic activity of the present Ni-based ternary alloy-modified electrode with their reported results shows that the G/NiCuCo electrode is a more effective catalyst for the electro-oxidation of methanol. In Fig. 5, the anodic current density of the electro-oxidation of methanol with the modified electrode (Fig. 5(3)) indicates a pronounced electrocatalytic effect. Furthermore, superior results were obtained when applying a lower concentration of the electrolyte (NaOH, 0.1 mol/L) compared with the use of NaOH solution (1 mol/L, Fig. 5(2)).

Figure 6 presents double step chronoamperograms of different electrodes obtained by setting the working electrode potential in two steps. The applied potential of the first and second steps corresponded to the methanol oxidation and cathodic peaks of each sample. In the first step, the oxidation potentials of the Co, Cu, Ni, CuCo, NiCo, NiCu and NiCuCo-modified electrodes were 0.770, 0.820, 0.885, 0.930, 0.995, 1.1 and 1.4 V vs. Ag/AgCl, respectively. The current values were negligible in the second step, in which the applied cathodic potential was

Fig. 4. Cyclic voltammograms obtained from (1) G/Cu, (2) G/Co, (3) G/Ni, (4) G/CuCo, (5) G/NiCo, (6) G/NiCu, and (7) G/NiCuCo-modified electrodes in the presence of methanol (0.5 mol/L) in NaOH (0.1 mol/L). Scan rate = 100 mV/s.

Fig. 5. Anodic currents during the oxidation of methanol on (1) GC/polyNiTCPP, (2) Ni-Cu alloy (NCA), and (3) G/NiCuCo in the absence (black bar) and presence (pink bar) of methanol (0.5 mol/L) in NaOH solution (0.1 mol/L). Scan rate = 100 mV/s.

Fig. 6. Double step chronoamperograms of (1) G/Co, (2) G/Cu, (3) G/Ni, (4) G/CuCo, (5) G/NiCo, (6) G/NiCu, and (7) G/NiCuCo-modified electrodes in the presence of methanol (0.5 mol/L) in NaOH (0.1 mol/L).

approximately 0.4 V vs. Ag/AgCl. These results imply that irreversible electro-oxidation occurred. Fig. 6 also shows that the current density obtained when using the Ni-based binary alloy was higher than that generated by the pure metals, while the Ni-based ternary alloy produced the highest value. Therefore, the G/NiCuCo-modified electrode is a promising candidate for future electrocatalytic methanol oxidation investigations.

To verify these results, the Nyquist diagrams of the pure metals and binary and ternary alloys were acquired in methanol (0.5 mol/L) at a DOffset potential equal to that of the corresponding methanol oxidation peak of each sample. From Fig. 7, it is evident that the pure metals showed the highest resistance values together with the lowest current densities, while the ternary alloy exhibited the lowest resistance and highest current density. These data are in good agreement with the chronoamperograms and cyclic voltammograms.

3.4. Effect of scan rate

The effects of the scan rate on the CV results obtained from

Fig. 7. Nyquist diagrams of (1) G/Co, (2) G/Cu, (3) G/Ni, (4) G/CuCo, (5) G/NiCo, (6) G/NiCu, and (7) G/NiCuCo-modified electrodes in the presence of methanol (0.5 mol/L) in NaOH (0.1 mol/L).

the G/NiCuCo electrode in NaOH (0.1 mol/L) are shown in Fig. 8 at various potential sweep rates from 10 to 1000 mV/s. As the scan rate increases, the cathodic and anodic current densities increase and the potential of the anodic peak shifts to more positive values, showing that an irreversible electrode reaction is taking place on the G/NiCuCo electrode surface. The peak currents are proportional to the sweep rate in the range of 10 to 60 mV/s (Fig. 8(b)), demonstrating the electrochemical activity of the surface redox couple [34]. The value of I^* , the surface coverage of the redox species (mol/cm²), may be obtained from the slope of each line [34] via the following equation:

$$I_p = \frac{n^2 F^2}{RT} \Gamma^* \nu \quad (1)$$

where ν is the potential sweep rate. Taking the average of both cathodic and anodic results, a I^* value of approximately 2.82×10^{-8} mol/cm² was derived. At higher potential sweep rates, this dependency has a square root form (Fig. 8(c)), signi-

Fig. 8. (a) Typical CV data obtained from a G/NiCuCo electrode in NaOH (0.1 mol/L) at potential sweep rates of 10, 20, 30, 40, 50, 60, 100, 200, 400, 600, 800, and 1000 mV/s, and the relationships of anodic and cathodic peak currents to (b) the sweep rate at lower values (10–60 mV/s) and (c) the square root of the sweep rate at higher values (100–1000 mV/s).

fying the dominance of diffusion controlled processes. At higher potential sweep rates, the linear relationship observed between I_p and $\nu^{1/2}$ also implies that the electrochemical reaction is a diffusion-controlled process.

3.5. Effect of methanol concentration

Figure 9 summarizes the behavior of the modified electrode in NaOH solution (0.1 mol/L) in the presence of various concentrations of methanol at a scan rate of 100 mV/s. In this figure, the growth of the anodic peak is considerable and the negligible cathodic peak in the presence of methanol is attributed to an irreversible oxidation process. It can be seen that the anodic peak current density increases with increasing methanol concentration, but plateaus at a concentration of 0.3 mol/L (Fig. 9(b)). In this process, methanol molecules adsorbed on the electrode surface are oxidized, decreasing the number of sites available for subsequent adsorption. Eventually, the overall rate of methanol oxidation decreases and the anodic current density remains constant due to saturation of the surface sites. Higher methanol concentrations, thus lead to more pronounced passivation of the electrode surface. The oxidation of methanol involves both the adsorption of reactant/intermediate species or methanol oxidation products and the formation of a passive, nonconductive layer of oligomeric products resulting from the oxidation process on the electrode surface. In the reverse half cycle, the oxidation continues and the corresponding current density goes through a maximum due to the regeneration of active sites for the adsorption of methanol. It is important to note that the modified electrode functions as a stable electrocatalyst because the current density from the electro-oxidation of methanol was found to be almost constant over 50 cycles. This result indicates that methanol reacts at the electrode surface without generating a poisoning effect. In fact, the modified electrode was found to function over the course of several weeks without the need to renew the electrode surface.

Fig. 9. (a) Cyclic voltammograms obtained from the G/NiCuCo electrode in NaOH (0.1 mol/L) at (1) 0.1, (2) 0.2 and (3) 0.4 mol/L methanol concentrations (scan rate = 100 mV/s). (b) The dependency of the anodic peak current on the methanol concentration.

3.6. Chronoamperometric measurements

Chronoamperometry was also employed to investigate the electro-oxidation of methanol over the G/NiCuCo-modified electrode. Fig. 10(a) shows double step chronoamperograms obtained by setting the working electrode potential to 1.4 (first step) and 0.394 V (second step) vs. Ag/AgCl for the modified electrode in the absence (1) and presence (2–6) of methanol in NaOH solution (0.1 mol/L) containing various concentrations of methanol. The potential of the first step is related to the methanol oxidation peak and the potential of the second step is related to the cathodic peak of the G/NiCuCo alloy. As can be seen, upon increasing the methanol concentration, the current densities increase and the chronoamperograms correspond to cyclic voltammograms.

A plot of the net current with respect to the inverse of the square root of time, obtained by removing the background current density, indicates a linear relationship (Fig. 10(b)). Using the slope of this line in the Cottrell equation [34]:

$$I = nFAD^{1/2}C\pi^{-1/2}t^{-1/2} \quad (2)$$

The diffusion coefficient of methanol was determined to be 6.25×10^{-6} cm²/s. This result indicates that the transient current must be controlled by a diffusion process. The transient current results from the catalytic oxidation of methanol and thus the current density increases as the methanol concentration is raised. The current density was also found to be negligible when the electrolysis potential was increased to a value of 0.394 V vs. Ag/AgCl, implying irreversible electro-oxidation. Chronoamperometry can also be used for the evaluation of the catalytic rate constant [34], using the equation:

$$I_c/I_L = \pi^{1/2}k^{1/2}t^{1/2} = \pi^{1/2}(kc_0t)^{1/2} \quad (3)$$

where I_c and I_L are the currents in the presence and absence of methanol, k is the catalytic rate constant, c_0 is the bulk concentration of methanol and t is the elapsed time. Based on the slope of a plot of I_c/I_L against $t^{1/2}$, presented in Fig. 10(c), the mean value of k was determined to be 40×10^7 cm³/mol·s.

3.7. Electrochemical impedance spectroscopy

Figure 11(1) presents the Nyquist diagrams of the G/NiCuCo electrode obtained at various concentrations of methanol at the DC offset potential of the oxidation peak. In Fig. 11(1), two slightly depressed capacitive semicircles can be seen: a small one in the high frequency region and a large one in the low frequency region. The semicircle in the high frequency region exhibits a slight decrease in diameter while the other shows a steady decrease, indicating that this semicircle corresponds to the methanol electro-oxidation. The semicircle in the high frequency region likely results from a combination of charge transfer resistance and double layer capacitance. The low frequency semicircle is attributed to the adsorption of reaction intermediates on the electrode surface. Increasing methanol concentrations decrease the resistance and thus increase the current density, a trend that agrees with the chronoamperograms and CV data. Bode-phase plots for the same samples are shown in Fig. 11(2). Two peaks are observed in the

Fig. 10. (a) Double step chronoamperograms obtained from a G/NiCuCo electrode in NaOH solution (0.1 mol/L) with different methanol concentrations. (1) 0.0; (2) 0.1; (3) 0.2; (4) 0.3; (5) 0.4; (6) 0.5 mol/L. Potential steps were 1.4 and 0.394 V, respectively. (b) Dependency of the transient current on $t^{-1/2}$ and (c) dependency of I_e/I_o on $t^{1/2}$.

Fig. 11. (a) Nyquist and (b) Bode-phase plots for the G/NiCuCo electrode in NaOH solution (0.1 mol/L) with varying methanol concentrations. (1) 0.1; (2) 0.2; (3) 0.3; (4) 0.4; (5) 0.5 mol/L. A DC potential of 1.4 V vs. Ag/AgCl was applied.

Bode plots, corresponding to the depressed semicircles in the Nyquist plot.

An equivalent circuit compatible with these results is presented in Scheme 1. In this circuit, R_1 and CPE_1 are the solution resistance and the constant phase element, respectively, while CPE_2 represents the double layer capacitance. To corroborate the equivalent circuit, the experimental data were fitted to the circuit and the circuit elements were obtained. Table 1 summarizes the values of the equivalent circuit elements obtained by appropriate fitting of the experimental results (such that the

Scheme 1. Equivalent circuit compatible with the Nyquist diagrams in Fig. 9 for methanol electro-oxidation on the G/NiCuCo electrode.

Table 1

EIS parameters for electro-oxidation of different concentrations of methanol over the G/NiCuCo electrode in NaOH solution.

C_{meth} (mol/L)	R_s (Ω/cm^2)	R_{ct} (Ω/cm^2)	CPE_{dl} (mF/cm ²)	n_1	R_{ads} (Ω/cm^2)	CPE_{ads} (mF/cm ²)	n_2
0.1	61.50	6.0	0.653	0.85	109.1	1.537	0.85
0.2	62.79	5.8	0.643	0.79	53.74	0.961	0.91
0.3	63.15	5.4	0.611	0.75	47.84	0.847	0.89
0.4	62.89	5.0	0.309	0.82	45.73	1.020	0.86
0.5	63.11	4.8	0.350	0.85	45.50	0.915	0.86

mean errors of the fitted values were less than 5%) for different concentrations of methanol.

4. Conclusions

In the present study, modified electrodes were prepared by cycling in the cathodic region. The results showed that the modification of nickel by copper and cobalt enhances its electro-catalytic activity while the graphite electrode itself presents no activity. The G/NiCuCo-modified electrode behaves as an efficient catalyst for the electro-oxidation of methanol in alkaline media. In the presence of methanol, a Ni-based ternary alloy-modified electrode shows a significantly higher response for methanol oxidation compared with those obtained from pure metals or binary alloys. Therefore, the Cu and Co have a synergistic effect on the modified Ni-based electrode. The surface coverage, diffusion coefficient and rate constant were found to be 2.82×10^{-8} mol/cm², 6.25×10^{-6} cm²/s and 40×10^7 cm³/(mol·s), respectively.

Nomenclature

- V Potential sweep rate, mV/s
 Γ^* Surface coverage of the redox species, mol/cm²
 D Diffusion coefficient, cm²/s
 K Catalytic rate constant, cm³/mol

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Graphical Abstract

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A G/NiCuCo electrode exhibited the highest electrocatalytic activity among a series of modified electrodes. A comparison of the catalytic activity of this device with previously reported results shows that G/NiCuCo is a superior catalyst system for the oxidation of methanol.

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NaOH溶液中Ni基石墨修饰电极上甲醇电氧化过程中钴与铜的协同效应

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摘要: 在NaOH溶液(0.1 mol/L)中考察了Ni, Co和Cu二元和三元合金修饰的石墨电极上甲醇电氧化反应性能。采用循环伏安法、计时电流法和电化学阻抗谱(EIS)等技术研究了修饰电极的催化活性和协同效应。这些催化剂在含有Ni, Cu 和Co离子溶液的阴极电位上反复浸渍石墨电极制得。结果表明, 在甲醇存在下, Ni基三元合金修饰电极(G/NiCuCo)对甲醇氧化反应的响应值明显高于其它样品。阳极峰值电流与扫描速率的平方根呈线性关系, 表明该过程受扩散控制。在CA区域, 该反应遵循Cottrellin特性, 甲醇扩散系数为 $6.25 \times 10^{-6} \text{ cm}^2/\text{s}$ 。甲醇氧化反应速率常数为 $40 \times 10^7 \text{ cm}^3/(\text{mol} \cdot \text{s})$ 。另外, 采用EIS研究了修饰电极表面上甲醇催化氧化反应。

关键词: 甲醇电氧化; 电催化; 协同效应; 镍; 修饰电极

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