

Preparation and Properties of Poly (Methylene Blue) Composite Film

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Abstract

This paper aims to investigate the electro catalytic activities of poly (methylene blue) composite film. Modified graphite electrodes (Ni-Cu / poly methylene blue / graphite electrode) were examined for electro catalytic activities towards the oxidation of methanol in alkaline solutions. Poly methylene blue prepared electrochemically on the graphite electrode. Nickel and Copper ions are then scattered into the polymer film by immersion of the polymeric modified electrode in a stirred solution containing 0.7M NiSO₄.6H₂O and 0.05M CuSO₄.5H₂O. The morphologies and elemental ingredients of the film have inspected by scanning electron microscopy. The presence of Nickel and Copper in the composite film was then confirmed by x-ray diffraction Analysis. In cyclic voltammetry studies, in the presence of methanol Ni-Cu / poly methylene blue modified electrode shows a significantly higher response for methanol oxidation. The reaction followed a Cottrellian behavior under the chronoamperometry regime and the diffusion coefficient of methanol was obtained.

Keywords

PMB, Nickel, Copper, Catalytic Properties, X-ray Diffraction

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1. Introduction

In the past decades, conductive polymers nanocomposites have been studied extensively because of their useful properties and possible usage in many practical applications such as modified electrodes, charge storage devices, anti-corrosion coating, and electro catalyst for the electro-oxidation of small organic molecules in fuel cells [1-7]. Conductive polymers nanocomposites have many advantages because of their excellent conducting and mechanical properties and good adhesion to electrode substrates. There is a need to extend these studies to other polymers, such as poly methylene blue (PMB), which can be a suitable host material for catalyst micro- and nano- particles. Incorporating catalyst particles into a conducting polymer film will represent an attractive field of study due to improve the properties of polymers. There are some reports directed toward the study of the electro-oxidation reactions using these materials such as

formic acid [8-10], ethanol [11-12] and methanol [13-14]. Conducting polymers provide a suitable environment for metal nanoparticles to achieve high dispersion of metallic particles. The high porosity and extended structure of conducting polymers generate maximum number of catalytic centers available for the reacting species which improves the electro catalytic performance significantly. During the past few years, several studies dedicated to the electro-oxidation of alcohols on metals and their alloys incorporated into polymeric matrices have been reported [15-17]. It has been shown that modified electrodes act as effective catalysts for oxidation of alcohols [13-17]. Au-polyaniline nanocomposite was found to be the best electro-catalyst for ethanol oxidation reaction in alkaline medium by Pandey and Lakshminarayanan [18]. Jafarian and coworkers [19] have explored electro-oxidation of alcohols on nickel dispersed in poly-o-aminophenol on graphite electrode (GE) and found that the electro-oxidation of alcohols on graphite/ POAP/ Ni modified electrode is dominated by direct electro-oxidation

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with some contribution from Ni (II)/ Ni (III) couple.

There is still a need to compare electro catalytic activity of various combinations of polymers and metals. Here I study the electrochemical oxidation of methanol on Ni-Cu/ PMB nanocomposite modified electrode in alkaline medium.

2. Experimental

2.1. Material and Methods

All chemical used in this work were Merck products of analytical grade and used without further purification. Twice distilled water used to prepare all solutions. Electrochemical studies performed with an Autolab potentiostat / galvanostat (Metrohm, model 12/30/302, The Netherlands).

The three-electrode system consists of graphite rod (diameter 3mm) or Ni-Cu/ PMB nanocomposite modified graphite as working electrode, Ag/ AgCl/ KCl 3M as the reference electrode and a platinum wire as an auxiliary electrode. Scanning electron microscopy (SEM) carried out with (model KYKY-EM3200 China). All the experiments were carried out at $22 \pm 1^\circ\text{C}$.

2.2. Preparation of the Ni-Cu / PMB Film

Graphite electrode polished with $0.05 \mu\text{m}$ $\alpha\text{-Al}_2\text{O}_3$ on a piece of leather. It was first washed with distilled water and then rinsed ultrasonically in ethanol and water for 5 min. Poly methylene blue was deposited on the cleaned electrode by cyclic voltammetry at $-0.4 \sim 1.3 \text{ V}$ with $50 \text{ mv}^{-1}\text{s}$, from an aqueous solution containing 1 mM methylene blue, 0.05 M Sodium tetra- borate and 0.5 M KCl. To incorporate Ni (II) and Cu (II) ions into the PMB film, the freshly electropolymerized PMB/ GE was added to a stirred solution of 0.7 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.05 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ for 60min, respectively to form Ni-Cu/ PMB/ GE.

3. Results and Discussion

The SEM and EDS analysis of Ni-Cu/ PMB on GE surface is shown in figure 1. It is clear that the film is compact. The result of chemical composition analysis obtained by EDX revealed that the composite contains Ni and Cu. The SEM and EDS analysis shows the presence of Ni and Cu found at 0.5, 7.5, 8.1 and 0.8, 7.9, 8.8 keV, respectively. The EDS spectrum of the electrochemically prepared film shows signal peak of carbon (C) at 0.25 keV and oxygen (O) at 0.53 keV characteristic of the PMB polymer. The other peaks are related to graphite substrate and gold as coating the electrode.

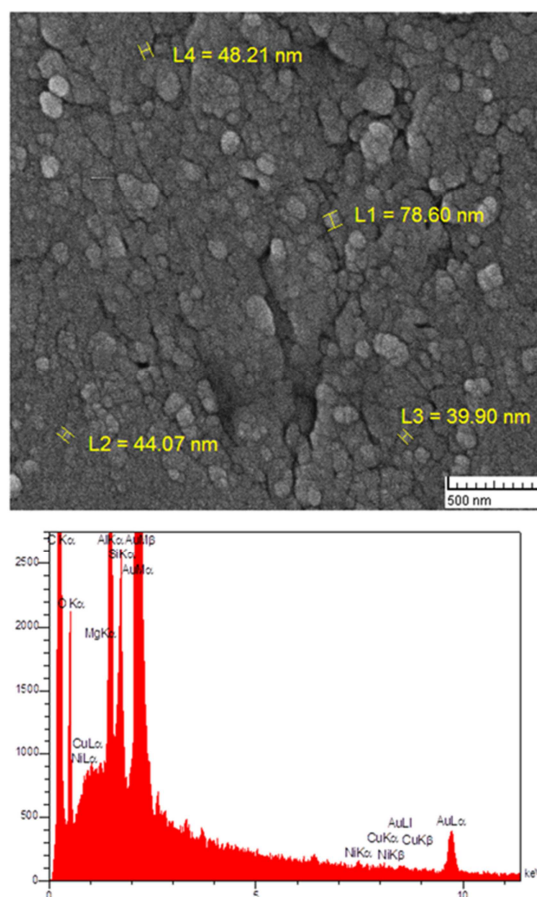


Figure 1. SEM and EDS analysis of Ni-Cu/ PMB.

X-ray diffraction (XRD) of Ni-Cu/ PMB and PMB which is in the range of $10^\circ < 2\theta < 100^\circ$ are shown in figure 2. Peaks centered at 44.5° , 52° , 78.2° and 98.4° are related to nickel and peaks at $2\theta = 42.6$, 51.60 and 74° are because of the electrodeposited Cu. Peaks at $2\theta = 19$, 22 , 24 and 38° are related to PMB. The other peaks are because of the carbon substrate. The grain size of the deposit has found to be about 9.5 nm , which estimated from the width at half height of most intense diffraction line by Scherer's equation [20].

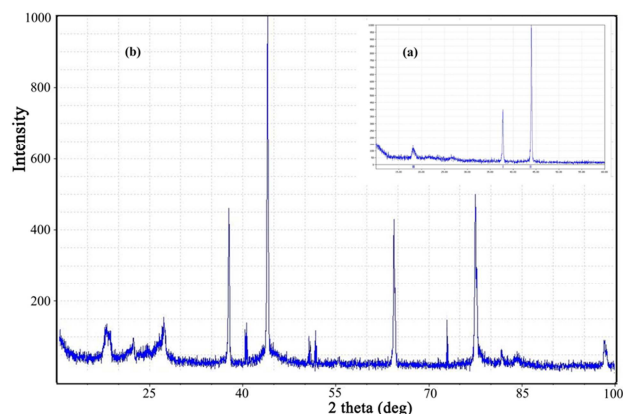


Figure 2. X-ray diffraction of: (a) PMB and (b) Ni-Cu/ PMB nanocomposite.

After incorporation of Ni (II) and Cu (II) ions into the PMB film, nickel and copper were accumulated by complex formation between Ni (II) and Cu (II) in solution and amines sites in the polymer backbone [21, 22] in a given time. Figure 3 shows polarization behavior of Ni-Cu/ PMB/ GE and PMB / GE in 0.1 M NaOH solution using cyclic voltammetry. Voltammograms have been recorded by cycling the potential between 0 and 0.6V at a potential sweep rate of 50 mv^{-1}s . A pair of redox peaks appeared at 400 and 320 mv / Ag/ AgCl are assigned to $\text{Ni}^{+2} / \text{Ni}^{+3}$ redox couple in alkaline media for Ni-Cu/ PMB/ GE.

These redox waves are related to the oxidation of Ni (OH)₂ to NiOOH and reduction of NiOOH to Ni (OH)₂, respectively [23-27]. It was observed (fig. 3) that neither oxidation nor reduction takes place on the PMB / GE.

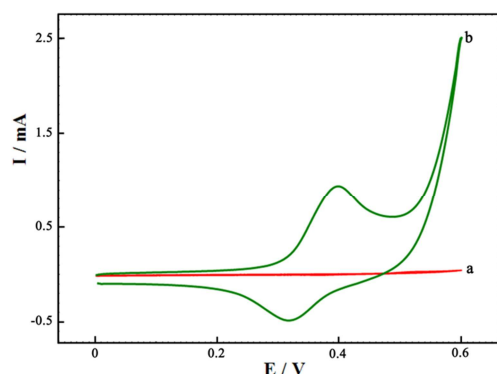


Figure 3. Electrochemical responses of electrodes: (a) PMB/ GE and (b) Ni-Cu/ PMB/ GE, in 0.1M NaOH solution, scan rate 50 mv^{-1}s .

Figure 4 shows the consecutive cyclic voltammograms (CV) of a Ni-Cu/ PMB/ GE in 1M NaOH solution at 50 mv^{-1}s sweep rate in order to enrich the accessible electroactive species [28-31].

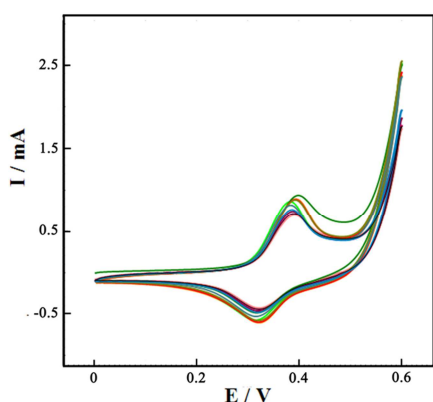


Figure 4. Consecutive cyclic voltammograms of a Ni-Cu/ PMB/ GE in 1M NaOH solution at 50 mv^{-1}s sweep rate.

Figure 5 presents the CVs of PMB/ GE (1) and Ni-Cu/ PMB/ GE (2) in the absence (a) and presence (b) of 0.05M methanol in 1M NaOH solution, respectively. We found that

there is no redox peaks in 1a and 1b plots, while plots 2a and 2b present the irreversible electro-oxidation of methanol following the oxidation peak of Ni (II) generating undisputable oxidation current.

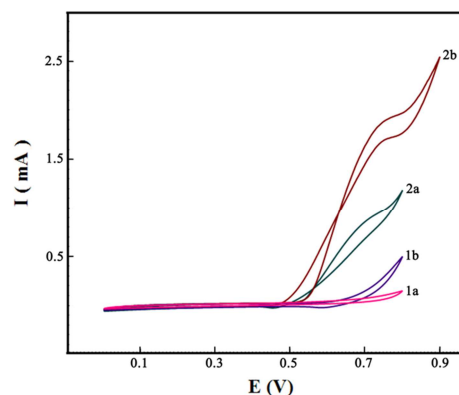


Figure 5. CVs of at PMB/ GE (1) and Ni-Cu/ PMB/ GE (2) in absence (a) and presence (b) of 0.05 M methanol, in 0.1 M NaOH at a scan rate of 10 mVs^{-1} .

Figure 6a shows CVs of Ni-Cu/ PMB/ GE in 1M NaOH solution at different concentrations of methanol (0.1-0.6 M) in a potential sweep rate of 10 mv^{-1}s . At Ni-Cu/ PMB/ GE, oxidation of methanol appeared as a typical electrocatalytic response. It is clear that, there is a linear relationship between the methanol oxidation peak current and concentration (fig 6b). Anodic current is linearly increased as methanol concentration increases. Therefore, catalytic electrooxidation of methanol on Ni-Cu / PMB / G electrode appears to be indisputable. It is proposed that this occurs because there is a dramatic increase in the surface area of the catalytic particles in the conductive polymer matrix.

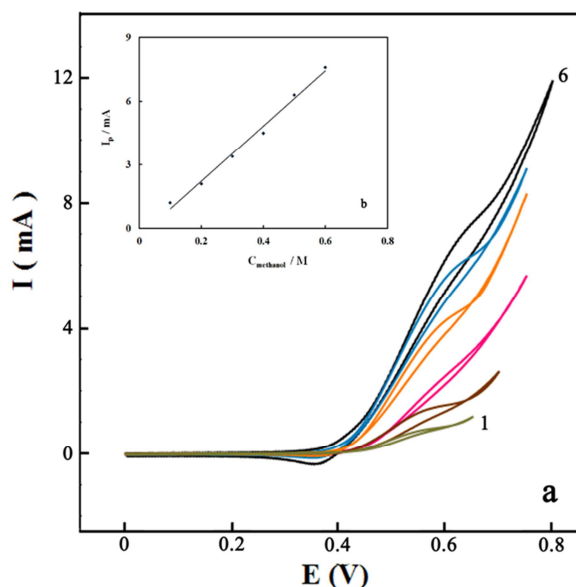
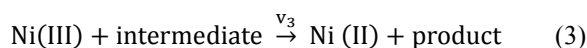
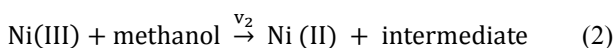
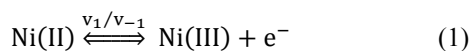


Figure 6. Cyclic voltammograms of Ni-Cu/ PMB/ GE in 1M NaOH solution at different concentrations of methanol (0.1-0.6M) in a potential sweep rate of 10 mv^{-1}s .

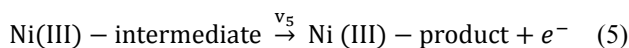
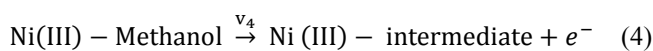
The larger methanol response at Ni-Cu / PMB / G electrode is due to the composite material which enhances the catalytic properties of nickel oxide and copper oxide through fine dispersion of the catalyst particles into the conductive polymer matrix to results in a drastic increase in surface area.

The decreased cathodic current in the reverse cycle, indicates that the rate determining step certainly involves methanol and that it is incapable of reducing the entire high valent nickel species formed in the oxidation. The electrocatalytic oxidation of methanol occurs not only in the anodic half cycle but also continues in the initial stage of the cathodic half cycle. Methanol molecules adsorbed on the surface are oxidized at higher potentials parallel to the oxidation of Ni (II) to Ni (III) species. The later process has the consequence of decreasing the number of sites for methanol adsorption. In addition, poisoning effect of reaction products or intermediates decrease the overall rate of methanol oxidation. Thus, the anodic current passes through a maximum as the potential is anodically swept. In the reverse half cycle, oxidation continues and its corresponding current goes through a maximum due to the regeneration of active sites for methanol adsorption as a result of the removal of adsorbed intermediates and products.

Based on our current work and the existing literature [28-32], the following mechanism is proposed for the electro-oxidation of methanol proceeding chemically and electrochemically:



Where Ni (III) species are reproduced by the power source. As an alternative [31], indeed the dominant route, methanol adsorbed on Ni (III) sites undergoes electro-oxidation according to the following mechanism:



Upon analysis of the results, it seems that a small part of the anodic current is due to reaction (2) and (3); however, the largest part in contributed by reactions (4) and (5). Figure 7a shows double steps chronoamperograms for the Ni-Cu/ PMB/ GE in 1 M NaOH solution in different concentrations of methanol (0, 0.1, 0.3, 0.5, 0.7, 0.9M) with an applied potential step of 420 and 340 mV, respectively. Plotting net current with respect to the inverse of the square root of time, current presents a linear dependency after removing the background (figure 7b). Dominating a diffusion controlled

process is obvious.

Using the slope of this line in Cottrell equation [33]:

$$I = nFAD^{1/2}C \times \pi^{-1/2}t^{-1/2} \quad (6)$$

The diffusion coefficient of methanol was found to be $4.8 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ in agreement with the cyclic voltammetry result. The current is also negligible when potential stepped down to 300 mV, suggesting the irreversibility of methanol oxidation process.

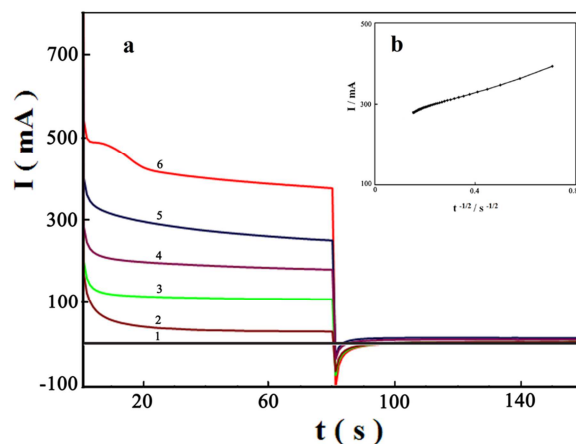


Figure 7. (a) Double steps chronoamperograms of Ni-Cu/ PMB/ GE electrode in 1 M NaOH solution with different concentrations of methanol of: (1) 0 M, (2) 0.1 M, (3) 0.3 M, (4) 0.5 M, (5) 0.7 M, (6) 0.9M. Potential steps were 420 mV and 340 mV, respectively, (b) Dependency of transient current on $t^{-1/2}$.

4. Conclusion

Here, I presented cyclic voltammetry technique for fabrication of Ni-Cu/ PMB composite on the GE and tested for electrooxidation of methanol in alkaline media. The morphology of the composite was analyzed using SEM images. The modified electrodes show electrocatalytic activity for the oxidation of methanol, while the GE presents no activity. More specifically, the response for methanol electrooxidation at the Ni-Cu/ PMB modified electrode is significantly larger than the response obtained for pure PMB. Electro-catalysis is enhanced by incorporation of Ni- Cu species into PMB film. The anodic peak currents for methanol oxidation at Ni-Cu/ PMB are linearly proportional with methanol concentration. Double steps chronoamperograms for the Ni-Cu/ PMB in the presence of methanol show irreversible process and the dominance of a diffusion controlled process is evident. The diffusion coefficient of methanol was found to $4.8 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$.

Acknowledgements

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