Journal of Materials Science and Chemical Engineering, 2016, 4, 97-105
Published Online February 2016 in SciRes. http://www.scirp.org/journal/msce
http://dx.doi.org/10.4236/msce.2016.42011

Electrocatalytic Oxidation of Methanol on Glassy Carbon Electrode Modified by Metal Ions (Copper and Nickel) Dispersed into Polyaniline Film

Asmea Khouchaf*, Driss Takky, Mohammed El Mahi Chbihi, Said Benmokhtar

Department of Chemistry, Faculty of Sciences, Laboratory of Chemistry and Physics of Materials LCPM, University of Casablanca, Casablanca, Morocco
Email: *asmea.khouchaf@gmail.com

Received 24 October 2015; accepted 21 February 2016; published 25 February 2016

Abstract

Polyaniline film was prepared by using the repeated potential cycling technique in an acidic solution at the surface of glassy carbon electrode. Then transition metal ions of Ni and Cu were incorporated to the polymer by immersion of the modified electrode. A comparative study of the electrocatalytic oxidation of methanol is made in NaOH, on Ni and Cu on polyaniline film covered glassy carbon electrode (Ni-PANI-GC, Cu-PANI-GC) at 25˚C. Catalytic activity for the oxidation of methanol was studied by using cyclic voltammetry.

Keywords

Methanol, Polyanilne, Cyclic Voltammetry, Electrocatalytic Oxidation

1. Introduction

Direct methanol fuel cells (DMFC) are the promising power sources for applications such as electric vehicles and electronic portable. Methanol as a fuel has numerous advantages such as low operating temperature, easy transportation and fuel storage, high-energy efficiency, low exhaustion and fast start-up [1] [2].

The electrooxidation of methanol on platinum and a variety of other metals has been the subject of numerous studies. In order to improve the activity of methanol electrooxidation, types of mono-metallic electrodes [3]-[8], bimetallic [9]-[17] or multimetallic [18]-[25] are directly used to oxidize methanol. Besides, these electrodes are

*Corresponding author.

How to cite this paper: Khouchaf, A., Takky, D., Chbihi, M.El.M. and Benmokhtar, S. (2016) Electrocatalytic Oxidation of Methanol on Glassy Carbon Electrode Modified by Metal Ions (Copper and Nickel) Dispersed into Polyaniline Film. *Journal of Materials Science and Chemical Engineering*, **4**, 97-105. http://dx.doi.org/10.4236/msce.2016.42011

first incorporated in the aniline polymer before using. Moreover the synergy effect of different electrodes was scrutinized [26]-[31].

Conductive polymers are important materials because of their specific properties, simple preparation and possible application to electrochemical energy conversion. The conducting polymers used are mainly polyaniline [32]-[41] poly(2-Methoxyaniline)-sodium dodecyl sulfatecomposite [42], poly(2-aminodiphenylamine) [43], poly(vinylferrocene) [44], poly(1,5-diaminonaphthalene) [45], polyindoles [46] and poly(o-aminophenol) [47] [48]. Polymers are usually used as matrix to incorporate noble metal [49] [50] and no noble metal [34] [43] [45] catalysts in the electrooxidation of methanol. Polyaniline (PANI) is one of the best candidates because it can easily be prepared on the electrode substrate as a homogeneous and strong adherent film with a high surface area and good stability in acid media.

In the present work, in order to investigate the effect of PANI nanofibers in methanol electrooxidation reaction, two types of anode, Ni and Cu, were prepared and investigated by cyclic voltammetry.

2. Experimental

Electrochemical experiments were carried out with a voltalab potentiostat (model PGZ 100) by the general purpose electrochemical systems data processing software (Voltamaste 4). All electrochemical measurements were conducted in a three-compartment electrochemical cell with platinum as the counter electrode; a silver/silver chloride reference (Ag/AgCl/KCl) as the reference electrode, and carbon glassy electrode was used as the working electrode.

The solutions were prepared using Double-distilled water, super pure NaOH, H_2SO_4, $CuSO_4$, 5 H_2O, $NiSO_4$, 6 H_2O and $C_6H_5NH_2$ of analytical grade. (Ag/AgCl/KCl) electrode was served as reference electrode. Potentials in this paper were reported versus the (Ag/AgCl/KCl) scale. The solution was deaerated by bubbling pure N_2 gas before experiment, and kept a flux of N_2 over it during measurements to prevent possible interference of oxygen and impurities from the atmosphere. All tests were performed at 25˚C.

3. Results and Discussion

3.1. Preparation of PANI/CG Electrode

Previously polyaniline films were obtained at the surface of Au, Pt, and CP electrodes [51]-[53]. In this work, electropolymerization at the surface of GC using consecutive cyclic voltammetry (for 15 cycles) between −0.2 and 1.2 V at 50 mVs^{-1} was performed in sulfuric acid solution 0.5 M containing 0.1 M $C_6H_5NH_2$ (**Figure 1**). As can be seen, the electrooxidation of aniline starts at 0.97 V in the first cycle and produces the first layer of po-

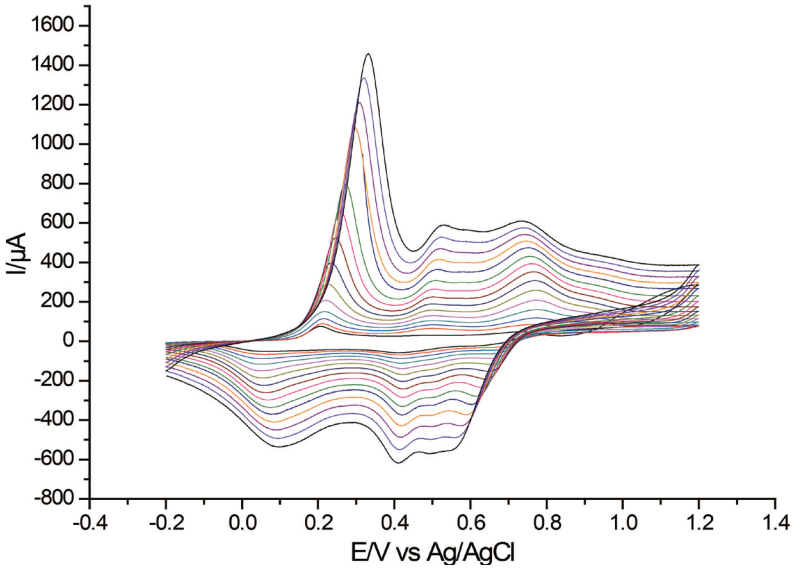


Figure 1. Series of CV during 15 potential cycles between −0.2 and 1.2 V in a 0.5 M H_2SO_4 solution containing 0.1 M Aniline at a glassy carbon electrode, scan rate 50 mVs^{-1}.

lyaniline. Subsequent cycles indicate a successive growth of the polyaniline film as evidenced by the increase in the redox current. Two redox couples are readily apparent with E values of 0.20 and 0.76 V in the CV.

3.2. Preparation of Cu-PANI-GC

The electrodeposition of Cu was performed in a solution of 0.25 M $CuSO_4$ + 0.1 M H_2SO_4, and the applied potential and time were optimized as −0.175 V and 30 min, respectively.

Figure 2(A) shows cyclic voltammograms of Cu/PANI/CGE in 0.1 M NaOH solution at a scan rate of 10 mVs^{-1}. The voltammogram is in good agreement with those reported in literature [26] [31]-[34] [36], some redox transitions appeared and were indicated by I-III. From the cyclic voltammogram depicted in this figure and the literature [54]-[56], peak a at less than −0.5 V vs. Ag/AgCl may be attributed to the electrosorption of oxygen, peak b is attributed to the Cu/Cu(I) redox couple, peak c attributed to the Cu/Cu(II) as well as Cu(I)/Cu(II), Peak d to Cu/CuII (soluble species), peak e is associated with the formation of Cu(III) species, It has been proposed that Cu(III) species are more easily formed, and indeed detected, at high hydroxide concentration. In our case, the oxidative wave for the formation Cu (III) species may be under the rising portion of the current at about 0.57 V. and peaks f, g and h the cathodic half cycle are assigned to the reduction of Cu(I) to Cu, Cu(II) to Cu(I) and Cu(III) to Cu(II) respectively.

In the presence of 0.5 $mol \cdot l^{-1}$ methanol **Figure 2(B)**, there is augmentation of currents at potentials corresponding to redox reactions involving low oxidation states of Cu (peaks c, d) and peak e was replaced by a remarkably high anodic peak resulting from oxidation of methanol. The onset potential of the electrocatalytic oxidation appeared at 0.57 V vs Ag/AgCl.

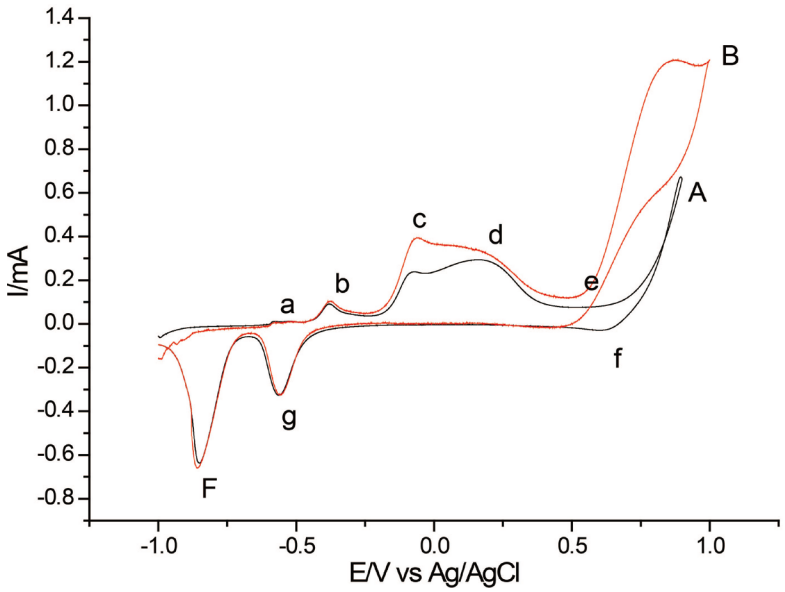


Figure 2. Typical cyclic voltammogram of Cu-PANI-CGE in 0.1 M NaOH solution in the absence (A) and presence (B) of 0.5 M methanol, scan rate 10 mVs^{-1}.

3.3. Effect of Methanol Concentration

Figure 3 shows the behavior of this modified electrode in the presence of different methanol concentrations of 0.1 M NaOH at the scan rate of 10 $mV \cdot s^{-1}$, respectively. It is clearly observed that upon increasing methanol concentration its oxidation develops in the region of the electrochemical formation of Cu(III). Thus, it is likely that the Cu(III) species is the active moiety which efficiently speeds up the oxidation of methanol. The oxidation current density increases with increasing methanol concentration and levels off at concentrations higher than 0.5 M.

3.4. Preparation of Ni- PANI-GC

In order to prepare the Ni-PANI composite, a freshly electropolymerized CGE was placed at open circuit in an

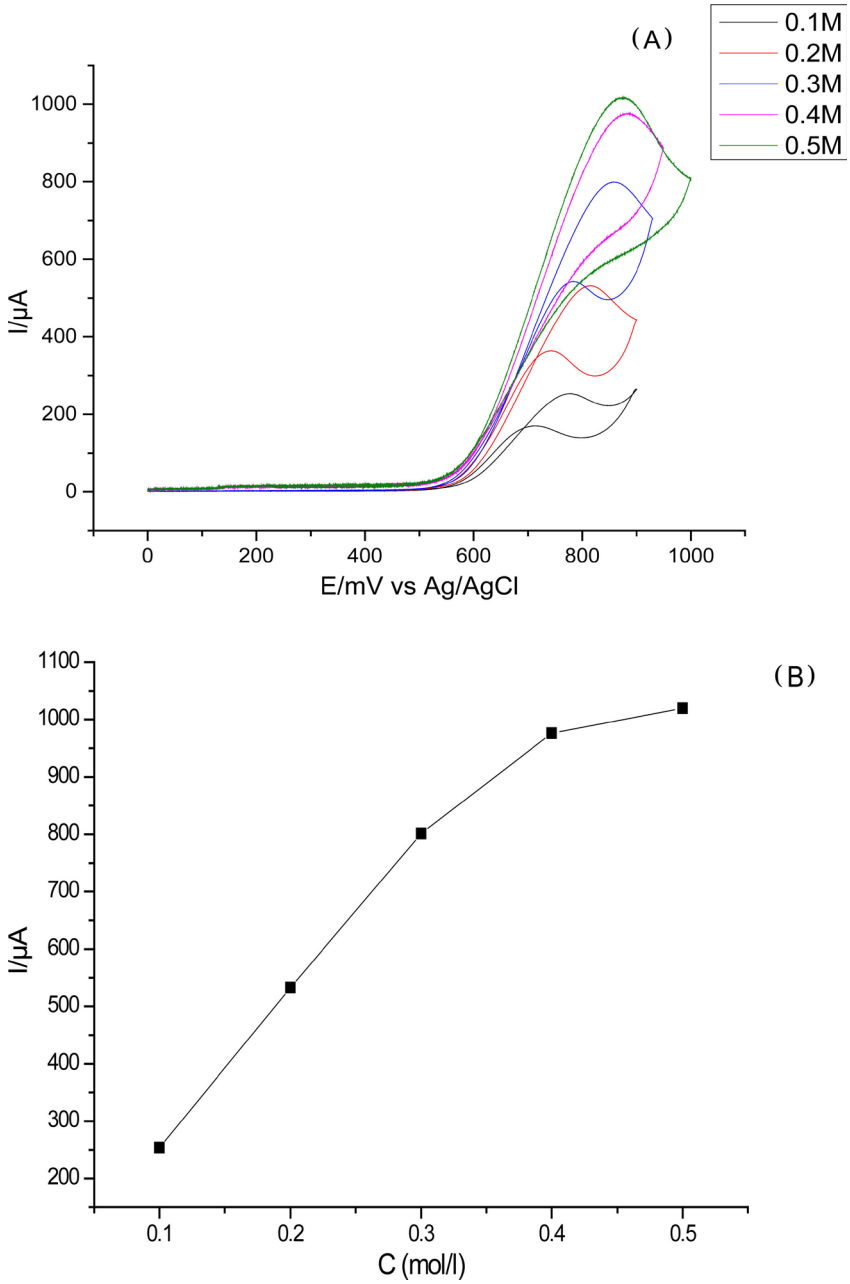


Figure 3. (A) Current-potential curves of 0.1 M NaOH solution with different concentrations of methanol 0. 1 - 0. 5 M at the Cu-PANI-GC at scan rate of 10 mVs^{-1}. (B) Plot of the dependence of methanol oxidation peak current on the methanol concentration.

aqueous 0.1 M H_2SO_4 solution of 0.2 M $NiSO_4$. The accumulation of nickel was conducted by complex formation between Ni(II) and amine sites in the polymer backbone. After incorporating Ni ion into the polymer using the procedure discussed above, the polarization behavior was examined in 0.1 M NaOH for Ni/PANI/CGE using cyclic voltammetry. Voltammograms were recorded by cycling the potential between 0 and 0.7 V at 10 mVs^{-1} until a stable voltammogram was obtained. **Figure 4(A)**, from this figure it can be seen that a well redox pair was observed on the Ni-PANI-CGE when the potential was cycled between 0.0 and 0.7 V, which was related to the oxidation of Ni(II) to Ni(III) with a peak potential of 0.46 V and reduction of Ni(III) to Ni(II) with a peak potential of 0.38 V. Our results show that methanol can be effectively catalyzed on the surface of Ni-PANI-CGE **Figure 4(B)**.

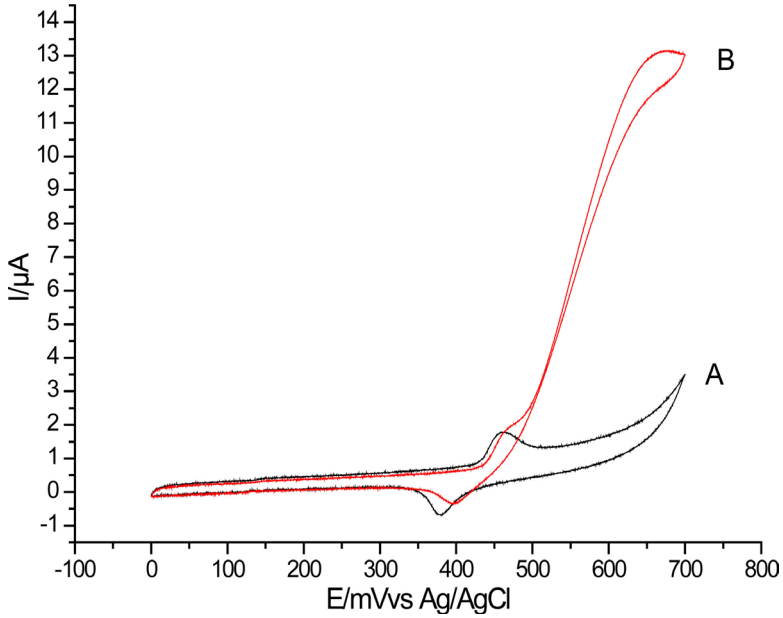
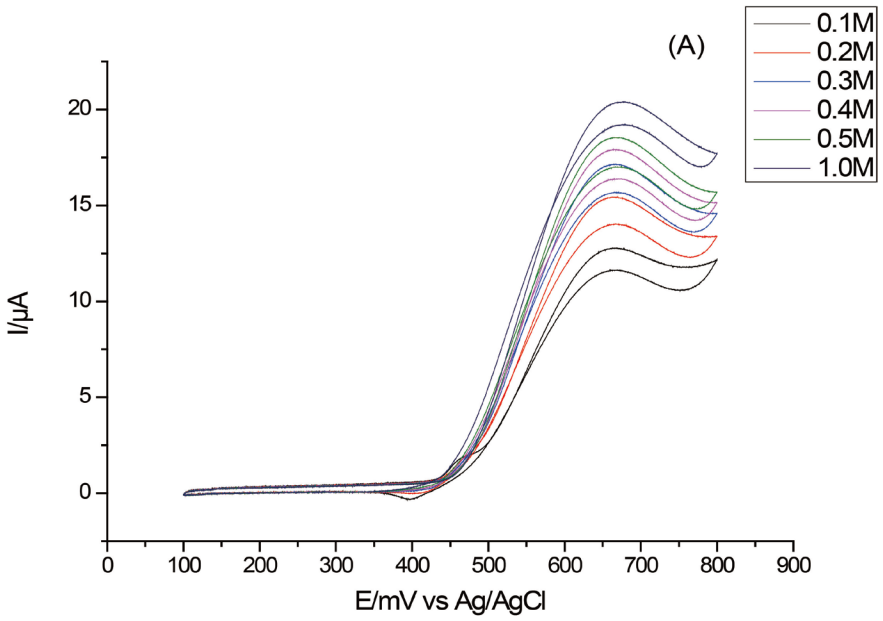


Figure 4. Electrochemical responses of Ni-PANI-GC in 0.1 M NaOH solution with scan rate of 10 mVs^{-1} to: (A) 0.0 M, (B) 0.1 M methanol.

3.5. Effect of Methanol Concentration

Figure 5(A) presents the effect of various methanol concentrations on the electrooxidation current at the Ni-PANI-GCE. As shown in this figure, when the excessive concentrations are added, the oxidation peak currents increase. The anodic current in the positive sweep was proportional to the concentration of methanol, and any increase in the concentration of methanol caused an almost proportional linear enhancement of the anodic current **Figure 5(B)**. Moreover, in the presence of methanol, the onset potential of the Ni(II) moiety oxidation shifted to a positive value and enhanced upon increasing the concentration of methanol. In fact, this indicated a strong interaction of methanol with the surface already covered by nickel species. This indicates that methanol is oxidized by active nickel. The electrocatalytic oxidation of methanol occurs not only in the anodic but also continues in the initial stage of the cathodic half cycle.



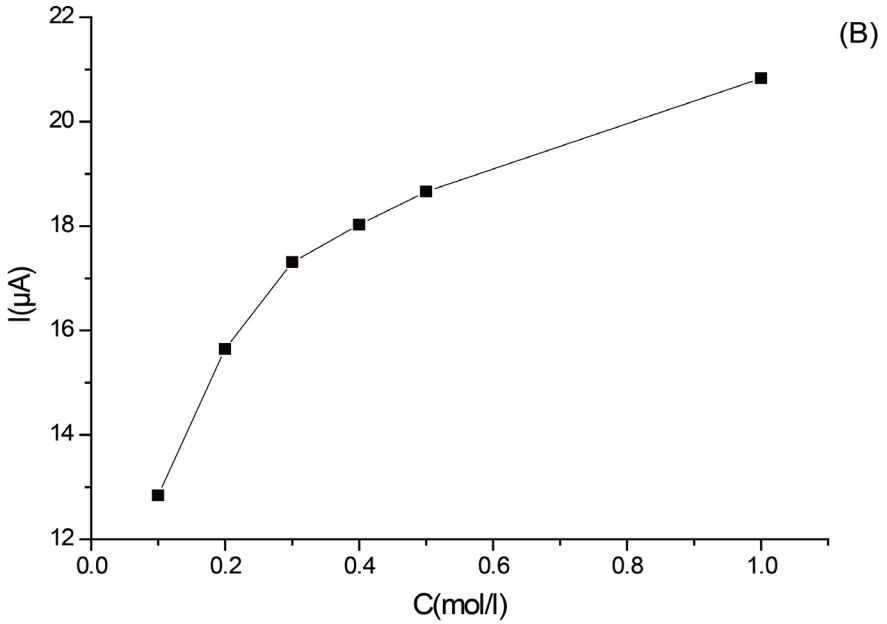


Figure 5. (A) Current-potential curves of the Ni-PANI-CGE for electrocatalytic oxidation of methanol at the scan rate of 10 mVs^{-1} in 0.1 M NaOH solution with different concentrations of methanol: 0.1 - 1 M, respectively. Inset (B) represents the dependence of methanol oxidation peak current on the methanol concentration.

4. Conclusion

In this work, we have shown the advantageous features of carbon glassy technology, polymer modification and dispersion of metallic particles into an organic polymer. The experimental results described show that glassy carbon electrodes which are modified with Ni and Cu on polyaniline film are useful for the electrooxidation of methanol in alkaline medium using CV method. The response for methanol electro-oxidation at the Cu-PANI-GC electrode is significantly larger than the response obtained for Ni-PANI-GC electrode.

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