

Electrocatalytic oxidation of ethylene glycol at surface of modified carbon paste electrode with poly (*N,N*-dimethyl aniline)/Ni-Co

Banafsheh Norouzi,^{a*} Mahbobeh Ahangarian^a and Mehdi Norouzi^b

^aDepartment of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran

^bFaculty of Chemistry, Islamic Azad University, Tehran North Branch, Tehran, Iran

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Abstract: The electrooxidation of ethylene glycol (EG) on modified carbon paste electrode with poly (*N,N*-dimethyl aniline)(SDS) (CPE/PDMAN-SDS) with different proportions of Ni (II) and Co (II) in 1 M NaOH was studied by cyclic voltammetry. The results show that formed layers at the surface of the electrodes behave as an efficient electrocatalyst for the oxidation of EG in alkaline medium via the Ni (III) and Co (III) species. These modified electrodes exhibit high electrocatalytic activity and stability in alkaline solution, showing oxidation peaks at low potentials with high current densities. The effects of various parameters such as potential scan rates, EG concentration and the supporting electrolytes on the electrooxidation of EG are also investigated.

Keywords: Electrocatalytic oxidation; Ethylene glycol; Nickel-cobalt; Alkaline medium.

Introduction

Direct methanol fuel cells (DMFCs) are promising electrochemical power sources for mobile, stationary and portable applications, and the electrocatalytic oxidation of methanol has been studied extensively. However, methanol has several disadvantages such as high toxicity and flammability, low boiling point and the tendency to pass through the fuel cell membrane due to its small molecular size. As a result, attempts have been made to find alternative fuels to methanol. Electrocatalytic oxidation of EG has received increased interest due to its low toxicity, high boiling point, high energy density and relatively high reactivity [1-3].

Pt-based electrodes such as Pt, Pt nanoparticles and Pt-M bimetallic nanoparticles are mainly used in the reaction [4-7]. A parallel pathway mechanism has been proposed for the reaction [4, 5], which involves the partial oxidation of EG without c-c bond breaking in one pathway, and breaking of the c-c bond with subsequent formation and oxidation of CO_{ads} in the

second pathway. Intermediates and products such as glycolic acid, oxalic acid, formic acid and carbon dioxide are formed in the reaction.

Since platinum is susceptible to poisoning during the electrocatalytic oxidation of organic compounds, de Lima et al. [8] reported that the catalytic activity of PtRu/C for the electrocatalytic oxidation of EG increases with the Ru content, Demarconnay et al. [7] reported that PtPd/C and PtBi/C catalysts exhibit higher reactivity than pure platinum towards EG oxidation.

Though significant progress has been achieved in EG oxidation, further investigation and improvement in the field (such as improved reactivity and stability of the electrodes) remains necessary. The development of highly effective electrode materials is one key factor. The electrocatalytic activity of Ni-Co oxides in reactions such as ethanol oxidation [9], urea oxidation [10] and glucose oxidation [11] show that Ni-Co oxides are promising materials.

Also, recently, we have demonstrated that the poly (*o*-amino phenol)(SDS)/Ni modified carbon paste

*Corresponding author. Tel: +(98) 241 4155048; Fax: +(98) 241 4155050; E-mail: norouz2020@yahoo.com

electrodes can successfully catalyze the oxidation of methanol and EG in alkaline medium [12].

In this study, the electrocatalytic activity and stability of CPE/PDMAN-SDS containing Ni and Co oxides with different percentages in alkaline medium was investigated. In addition, we have examined the influence of the concentrations of EG and supporting electrolytes on the reaction.

Results and discussion

Electrochemical behavior of polymeric film

Previously PDMAN film was studied at the surface of CPE [13]. In this work, electropolymerization at the surface of CPE using consecutive cyclic voltammetry (for 10 cycles) between 0 and 1.1 V at 50 mV s^{-1} was performed in sulfuric acid solution containing 5 mM DMAN and 5 mM SDS (Figure 1). As can be seen, at the first cycle and in the forward scan, oxidation of monomer occurs about 0.82 and 1.0 V (a, b) and in the reverse scan two reduction peaks appear at the potentials about 0.5 and 0.3 V (c', d') related to the polymer formed, respectively. At the second cycle, also two new oxidation peaks (c, d) related to the polymer can be observed. In the higher cycles, the peaks height of polymer growth increasingly, but the peak height related to the monomer oxidation decreases.

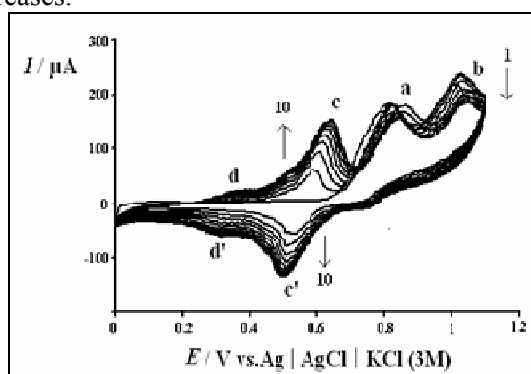


Figure 1: Cyclic voltammograms during consecutive potential cycles between 0 and 1.1 V in a 0.1 M H_2SO_4 solution containing 5 mM DMAN and 5 mM SDS at a carbon paste electrode, $v=50 \text{ mV s}^{-1}$.

The redox behavior of the polymeric film was strongly dependent on the pH of the electrolyte solution. As can be seen in Figure 2 (a), obtained polymer shows a well defined redox behavior in acidic supporting electrolyte solution. The response obtained in an alkaline solution (pH = 10) showed a complete loss of electrode activity in the potential range from -0.2 to 1.1 V (Figure 2(b)).

Incorporation of Ni(II) and Co(II) ions into PDMAN-SDS film and cyclic polarization behavior

In order to incorporate Ni(II) and Co(II) ions into the PDMAN-SDS film, the freshly electropolymerized CPE was placed at open circuit in a well stirred aqueous solutions of 1.0 M NiCl_2 , 0.8 M NiCl_2 and 0.2 M CoCl_2 (80:20), 0.5 M NiCl_2 and 0.5 M CoCl_2 (50:50) and 1.0 M CoCl_2 . Accumulation of nickel and cobalt ions were carried out by complex formation between Ni(II) and Co(II) with amine sites in the polymer backbone, for a given period of time.

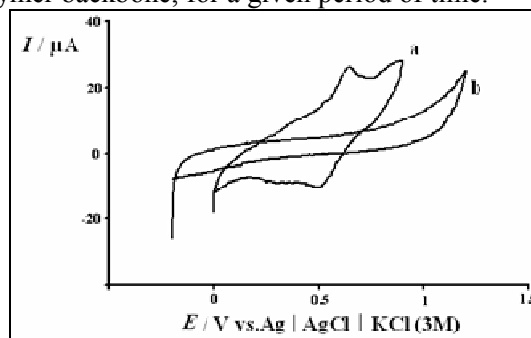


Figure 2: Electrochemical responses of CPE/PDMAN-SDS: (a) in 1 M H_2SO_4 solution; (b) in alkaline solution (pH=10), $v=50 \text{ mV s}^{-1}$.

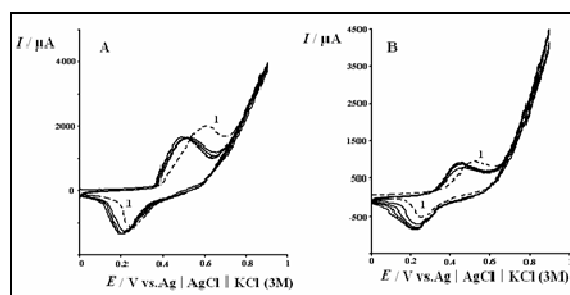


Figure 3: Cyclic polarization behavior of (A) CPE/PDMAN-SDS/Ni and (B) CPE/PDMAN-SDS/ $\text{Ni}_{80}\text{Co}_{20}$ in 1 M NaOH solution at anodic potentials, $v=50 \text{ mV s}^{-1}$.

Cyclic voltammograms of CPE/PDMAN-SDS/Ni and CPE/PDMAN-SDS/ $\text{Ni}_{80}\text{Co}_{20}$ at anodic potentials in the potential range of 0-0.9 V in 1 M NaOH with a potential sweep rate of 50 mV s^{-1} are presented in Figure 3. The observed peaks are related to $\text{Ni}(\text{OH})_2/\text{NiOOH}$ and $\text{Ni}_{80}\text{Co}_{20}(\text{OH})_2/\text{Ni}_{80}\text{Co}_{20}\text{OOH}$ in the surfaces.

Also, anodic and cathodic peak currents are linearly proportional to the potential sweep rate at low values from 10 to 100 mV s^{-1} (not shown) for these modified electrodes. These can be attributed to an electrochemical activity of an immobilized redox couple at the surface. The surface coverages of the immobilized active substance in the films of about 4×10^{-11} and $7 \times 10^{-11} \text{ mol cm}^{-2}$ were derived, respectively.

Electrochemical behavior of modified electrodes in the presence of EG

In this work the oxidation of EG was studied at the surface of modified electrodes by cyclic voltammetric experiments in 1 M NaOH solution.

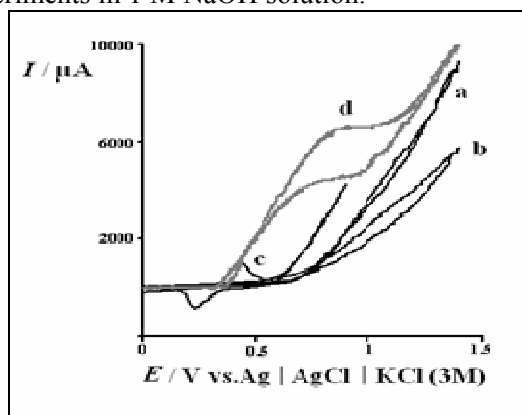


Figure 4: Cyclic voltammograms of CPE/PDMS-SDS in 1 M NaOH solution with $v = 20 \text{ mV s}^{-1}$ to: (a) 0, (b) 0.1 M EG and CPE/PDMS-SDS/Ni to: (c) 0, (d) 0.1 M EG.

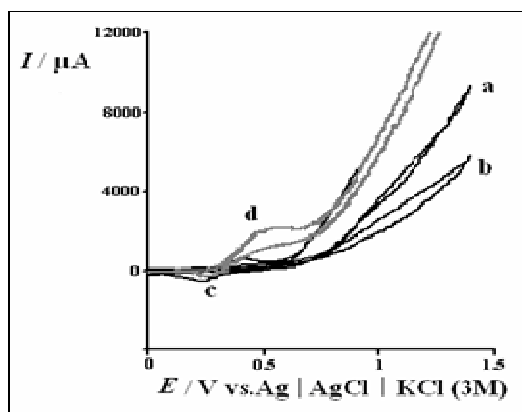


Figure 5: Cyclic voltammograms of CPE/PDMS-SDS in 1 M NaOH solution with $v = 20 \text{ mV s}^{-1}$ to: (a) 0, (b) 0.1 M EG and CPE/PDMS-SDS/Ni₈₀Co₂₀ to: (c) 0, (d) 0.1 M EG.

The obtained results are shown in Figure 4, Figure 5 and Figure 6. All of the modifier layers at the surface of electrodes act as catalysts for the oxidation of EG in 1 M NaOH solution. EG oxidation appears an increase in anodic peak current by a decrease in cathodic peak current in the negative sweep (an EC' mechanism). The results exhibit that CPE modified with PDMS-SDS/Ni has more current in the presence of EG and oxidation of EG occurs at more positive potential. The responses of CPEs modified with PDMS-SDS/Ni₈₀Co₂₀ and PDMS-SDS/Ni₅₀Co₅₀ are shown less currents with less positive potential for oxidation of EG.

A set of experiments was carried out to study the effect of EG concentration. Cyclic voltammetric curves at a scan rate of 20 mV s^{-1} for EG concentrations ranging from 0 to 0.2 M in 1 M NaOH were recorded in Figure

7. Peak heights increase with the increase of EG concentrations up to 0.1 M. Also Figure 8 represents the CVs of the CPE/PDMS-SDS/Ni₈₀Co₂₀ in the range of 0–1 V at the scan rate of 20 mV s^{-1} . The concentration of EG in 1 M NaOH solution is changed from 0 M to 0.5 M. It is observed from Figure 8 that when EG concentration increases, the current density of the anodic peak increases significantly while the cathodic peak current decreases and even disappears when the concentration of EG become more than 0.35 M. This indicates an electrocatalytic oxidation of EG. The EG oxidation current increased steadily up to a concentration of 0.5 M of EG after which it remained almost constant. It appears that the reaction sites get saturated at this concentration.

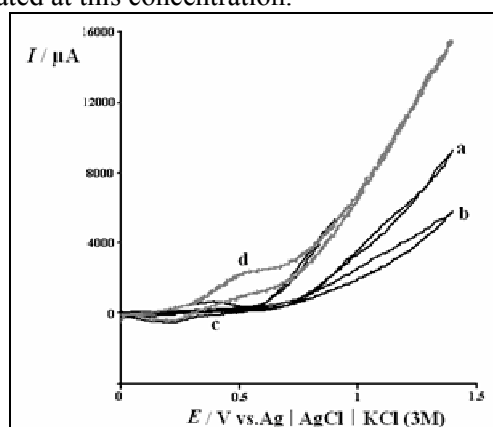


Figure 6: Cyclic voltammograms of CPE/PDMS-SDS in 1 M NaOH solution with $v = 20 \text{ mV s}^{-1}$ to: (a) 0, (b) 0.1 M EG and CPE/PDMS-SDS/Ni₅₀Co₅₀ to: (c) 0, (d) 0.1 M EG.

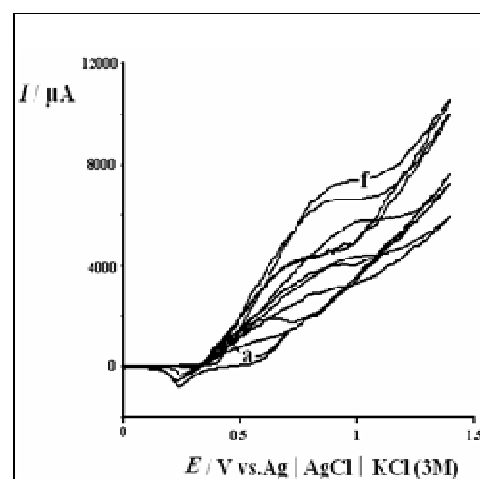


Figure 7: Cyclic voltammograms of the CPE/PDMS-SDS/Ni in 1 M NaOH solution with different concentrations of EG (a) 0, (b) 0.02, (c) 0.05, (d) 0.08, (e) 0.1 and (f) 0.2 M, respectively.

Values of CV parameters for EG oxidation reaction on different electrodes in 1 M NaOH are shown in Table

1. Table 1 shows the small addition of Co to Ni shifts the anodic peak potential (E_{pa}) in the negative direction, the magnitude of the shift, however, being the greatest with 20% Co. Thus, values of the E_{pa} indicate that the modified electrode with PDMAN-SDS/Ni₈₀Co₂₀ would improve the kinetics of EG oxidation reaction. Results demonstrate that among the electrodes investigated CPE/PDMAN-SDS/Ni is the greatest active electrode for the electrooxidation of EG. Based on the apparent oxidation peak current densities, observed during the forward scan, electrocatalysts follow the activity order:

PDMAN-SDS/Ni > PDMAN-SDS/Ni₈₀Co₂₀ > PDMAN-SDS/Ni₅₀Co₅₀

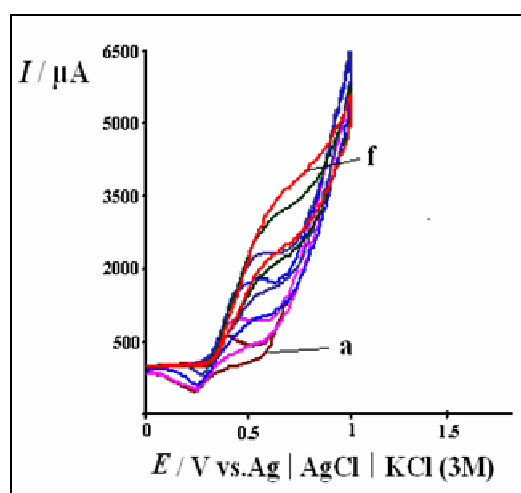


Figure 8: Cyclic voltammograms of the CPE/PINA(SDS)/Ni₈₀Co₂₀ in 1 M NaOH solution with different concentrations of EG (a) 0, (b) 0.02, (c) 0.08, (d) 0.15, (e) 0.35 and (f) 0.5 M, respectively.

Table 1: Cyclic voltammetry parameters for EG oxidation on different electrodes

| Electrode | E_{pa}/V | $J/mA\ cm^{-2}$ |
|---|------------|-----------------|
| CPE/PDMAN-SDS/Ni | 0.8 | 83 |
| CPE/PDMAN-SDS/Ni ₈₀ Co ₂₀ | 0.5 | 39 |
| CPE/PDMAN-SDS/Ni ₅₀ Co ₅₀ | 0.52 | 31 |

Conclusion

Novel electrodes have been described herein, consisting of nickel and cobalt ions loaded into CPE/PDMAN-SDS, by immersion of the polymeric modified electrodes in nickel and cobalt chlorides solution. The CPE/PDMAN-SDS/Ni, CPE/PDMAN-SDS/Ni₈₀Co₂₀ and CPE/PDMAN-SDS/Ni₅₀Co₅₀ can catalyze the oxidation of EG. Among the electrodes

investigated, the CPE/PDMAN-SDS/Ni has shown the greatest current densities and CPE/PDMAN-SDS/Ni₈₀Co₂₀ has the less anodic peak potential compared to other electrodes.

Experimental

Reagents and materials:

The solvent used in this work was twice distilled water. Sulfuric acid from Fluka was used as the supporting electrolyte. DMAN and sodium dodecyl sulfate (SDS) from Fluka were used as received. Sodium hydroxide, nickel chloride, cobalt chloride and EG used in this work were analytical grade of Fluka origin and used without further purification. High viscosity paraffin (density = 0.88 g cm⁻³) from Fluka was used as the pasting liquid for the carbon paste electrode (CPE). Graphite powder (particle diameter = 0.10 mm) from Merck was used as the working electrode (WE) substrate. All other reagents were of analytical grade.

Instrumentation:

The electrochemical experiments were carried out using a potentiostat/galvanostat (BHP 2063-C Electrochemical Analysis system, Behpajoo, Iran) coupled with a Pentium IV personal computer. Voltammetry was conducted using a three-electrode cell. A modified CPE, a platinum electrode, and Ag|AgCl|KCl (3 M) were used as WE, counter electrode and reference electrode, respectively.

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