

Carbon Paste as a Candidated Electrode Substrate for Electrochemical Polymerization of 2,5-Dimethylaniline

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A novel method of generating a rapidly reproducible poly(2,5-dimethylaniline)-coated electrode surface is represented. This involves electropolymerization at monomer-modified carbon paste electrode (MCPE). The electropolymerization was accomplished by three methods: potentiodynamic, potentiostatic and galvanostatic methods. The electrochemical behaviour of polymer was studied at different rates of potential scanning at different pH. The electrochemical behaviour indicates that the poly(2,5-dimethylaniline)/MCPE is stable and electroactive. Present investigations show that I_p for polymer prepared by potentiodynamic method is significantly higher than I_p for the polymers prepared by other methods. It is also found out that the electrochemical response of poly(2,5-dimethylaniline) prepared at the surface of carbon paste electrode is better than its response at the surface of glassy carbon electrode with equal geometric area. The electrocatalytic ability of this polymer containing Ni for electro-oxidation of methanol was demonstrated.

Key Words: Electropolymerization, 2,5- Dimethylaniline, Carbon paste electrode, Cyclic voltammetry.

INTRODUCTION

Traditionally polymers act as insulators and any electrical conduction in polymers were generally regarded as an undesirable phenomenon. In the last decades an opposite trend has started in as much as examination directed to utilization of conducting polymers.

Conducting polymers (CPs) are novel organic semi conducting materials with great promise because of their wide range of potential technological applications. These include their applications in storage batteries^{1,2}, electrochemical devices^{3,4}, light emitting diodes⁵, corrosion inhibitor^{6,7} and a variety of sensors⁸⁻¹⁰. The understanding of the nature of these polymers is of utmost importance for developing electrochemical devices. Among conducting polymers, polyaniline and its derivatives has been studied extensively due to the commercial availability of the monomer, its easy synthesis, well-behaved electrochemistry, high environmental stability and high conductivity.

The electrochemistry of polyaniline is generally more complex with respect to other conducting polymers. This fact is due to their dependence on the both pH values and oxidation states, described by three different forms known as leucoemeraldine base (LB) (fully reduced form), emeraldine base (EB) (50 % oxidized form) and pernigraniline base (PB) (fully oxidized form). The most important one is the emeraldine base form and its protonation by means of H⁺ ions generated from protic acid gives the emeraldine salt form (ES), responsible of the strong increment of conducting properties¹¹. This process is reversible and its possible for the presence of imine groups basic sites located along the conducting polymer backbone^{12,13}.

The disubstituted derivatives of conjugated polymers are also potential candidates in many technological applications. 2,5-Dimethylaniline (2,5-DMA) is a disubstituted derivative of aniline with methyl (-CH₃) groups substituted at *o*- and *m*-positions. Study of the electropolymerization of substituted anilines is of some interest because we can expect several advantages from a proper choice of the substituents, such as, a lower toxicity of byproducts, a better conductivity and stability of material.

It should be noticed that the nature of working electrode (WE) substrate in preparation of poly 2,5-dimethylaniline (P-2,5-DMA) is important, because properties of P-2,5-DMA film depends on the working electrode materials. It was shown that solid electrodes such as Pt, low carbon steel (LCS), Langmuir-Schaefer (LS) films on ITO glass plate have been used as electrode substrate in preparation of (P-2,5-DMA) modified electrode¹⁴⁻¹⁶.

The ease and fast preparation and obtaining new reproducible surface, the low residual current, porous surface and low cost of carbon paste are some advantages over all other solid electrodes^{17,18}. Therefore, carbon paste electrode can be candidate as suitable electrode substrate for preparation of polymeric films.

Previously, we have investigated the preparation of poly 1-naphthylamine and polypyrrole/ferrocyanide at the surface of carbon paste electrode^{19,20}. There is no available report in literature on the study of electrochemical behaviour of P-2,5-DMA film modified carbon paste electrode. Therefore, we motivated to prepare the P-2,5-DMA film modified carbon paste electrode (P-2,5-DMA/MCPE) by potentiodynamically electropolymerization of 2,5-DMA existing in an aqueous solution of H₂SO₄.

EXPERIMENTAL

The solvent used in this work was double distilled water. Sulfuric acid (from Fluka) was used as supporting electrolyte. The 2,5-dimethylaniline (from Fluka) was used as a monomer. Buffer solutions were prepared from *ortho* phosphoric acid and its salts in the pH ranges of 1-13. Graphite powder (particle size: 0.1 mm) (from Merck) was used as a working electrode substrate. High viscosity paraffin (density: 0.88 g cm⁻³) (from Fluka) was used as pasting liquid for carbon paste electrode. A 1:1 (w/w) mixture of graphite powder and paraffin was blended by

hand mixing with a mortar and pestle for preparation of carbon paste. The resulting paste was then inserted in the bottom of glass tube. The internal radius of glass tube for preparation of P-2,5-DMA/CPE was 1.7 mm. The electrical connection was implemented by copper wire lead fitted into the glass tube. The electrochemical experiments were carried out using potentiostat/galvanostat (BHP 2063-C electrochemical analysis system, Behpajoo, Iran) coupled with a Pentium IV personal computer. A platinum wire was used as an auxiliary electrode. The carbon paste electrode and a double junction Ag|AgCl|KCl (3 M) (Azar electrode, Iran) were used as working and reference electrodes, respectively. A pH meter (Ion Analyzer 250, Corning) was used to read pH of the buffered solutions.

RESULTS AND DISCUSSION

Electropolymerization of 2,5-dimethylaniline: Poly 2,5-dimethylaniline (P-2,5-DMA) was prepared at the surface of carbon paste electrode from aqueous solution of 2,5-dimethylaniline (20 mM) in the presence of H₂SO₄ (0.5 M) by using various electrochemical techniques. The electrochemical properties of P-2,5-DMA formed at the surface of working electrode were investigated by cyclic voltammetry in the solution of H₂SO₄ (0.5 M).

In the potentiodynamic method, on the first positive potential sweep, 2,5-DMA is oxidized, with an irreversible peak current at about 0.9 V (Fig. 1A). On the negative sweep, this wave does not show a complementary peak (indicating the existence of very fast follow-up chemical reaction) but appears a new redox peak at about 0.4 V related to the polymer formed on the electrode. By continuous cycling, the current of this system of peaks increase, showing the characteristic behaviour of a deposited electroactive film of the polymer grown on the surface of working electrode (till tenth sweeping potential) (Fig. 1A). This is confirmed when electrode is cycled in supporting electrolyte solution. Fig. 1B shows the CVs of a freshly prepared P-2,5-DMA/MCPE from 0.1-0.8 V at potential sweep rates of 5-1000 mV s⁻¹ in 0.5 M H₂SO₄ solution.

The anodic and cathodic peak currents are proportional to the sweep rate at low values (5-100 mV s⁻¹, Fig. 1C). This points out an electrochemical activity of the surface redox transition. The peak current and scan rate are related as:

$$I_p = n^2 F^2 \Gamma A v / 4RT$$

were Γ , v , A and I_p represent the surface coverage, scan rate, electrode area and peak current, respectively. The above result indicated that the redox process was confined to the surface of the poly (2,5-DMA)/MCPE, confirming the immobilized state of poly (2,5-DMA). At higher scan rates (200-1000 mV s⁻¹), the anodic peak potentials shift to more positive and cathodic peak potentials shift to more negative directions. Fig. 1D shows the plot of the oxidation peak current I_p vs. $v^{1/2}$, which is a straight line indicating that electrode reaction is diffusion controlled.

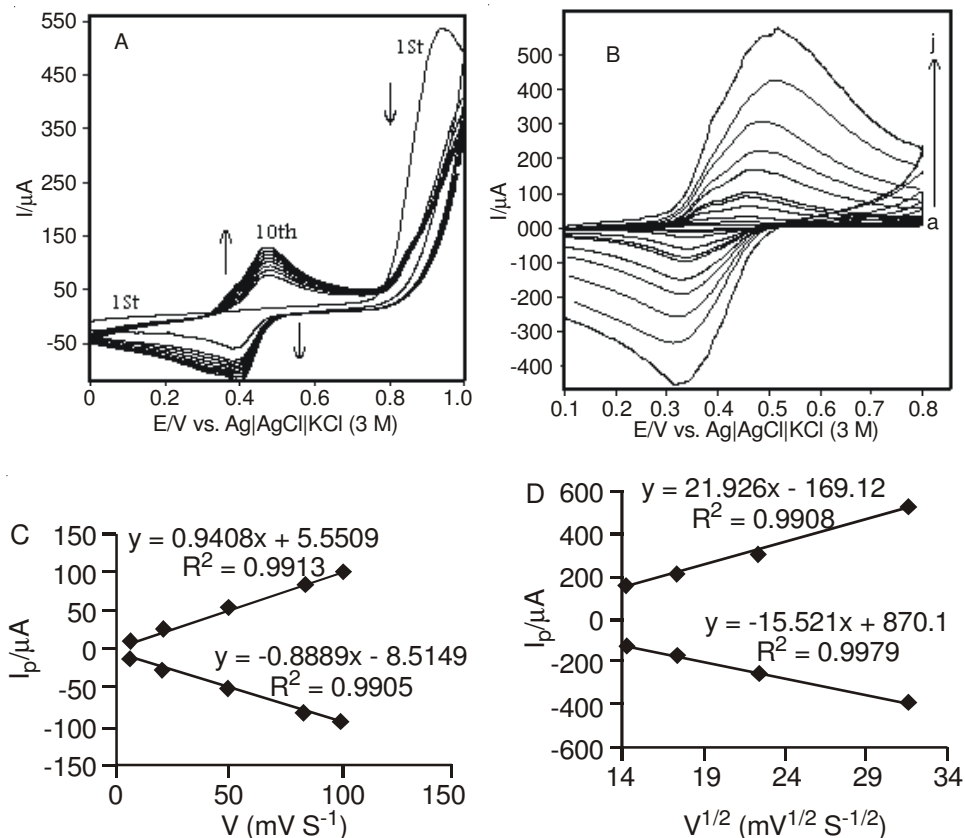


Fig. 1. (A) Cyclic voltammograms of 20 mM of 2,5-DMA in a 0.5 M H₂SO₄ solution at the surface of CPE (E = 0-1.0 V), v = 50 mV s⁻¹. (B) Cyclic voltammograms of P-2,5-DMA/MCPE in 0.5 M H₂SO₄ solution, v : a) 5, b) 10, c) 20, d) 50, e) 83, f) 100, g) 200, h) 300, i) 500, j) 1000 mV s⁻¹. (C) Plot of I_p vs. v at low scan rates (5-100 mV s⁻¹). (D) Plot of I_p vs. v^{1/2} at high scan rates (200-1000 mV s⁻¹)

Electropolymerization by potentiostatic method: Electropolymerization was also investigated by applying a fixed potential of 0.9 V to the electrode for a period of 56 s (Fig. 2A). By applying a fixed potential in this method, the 2,5-dimethylaniline monomer is oxidized and film of polymer grows on the surface of working electrode. This is confirmed by voltammetric studies of polymeric electrode in supporting electrolyte solution (Fig. 2B). Fig. 2C shows the plot of anodic and cathodic peak currents which are proportional to the sweep rates at low values. These results indicate that redox process was surface controlled. At higher scan rates oxidation peak current I_p varies linearly with v^{1/2} indicating diffusion controlled process (Fig. 2D).

Electropolymerization by galvanostatic method: Also electropolymerization was investigated by applying a fixed current of 512 μA (according to the oxidation current of monomer in cyclic voltammetry) to electrode for a period of 18 s

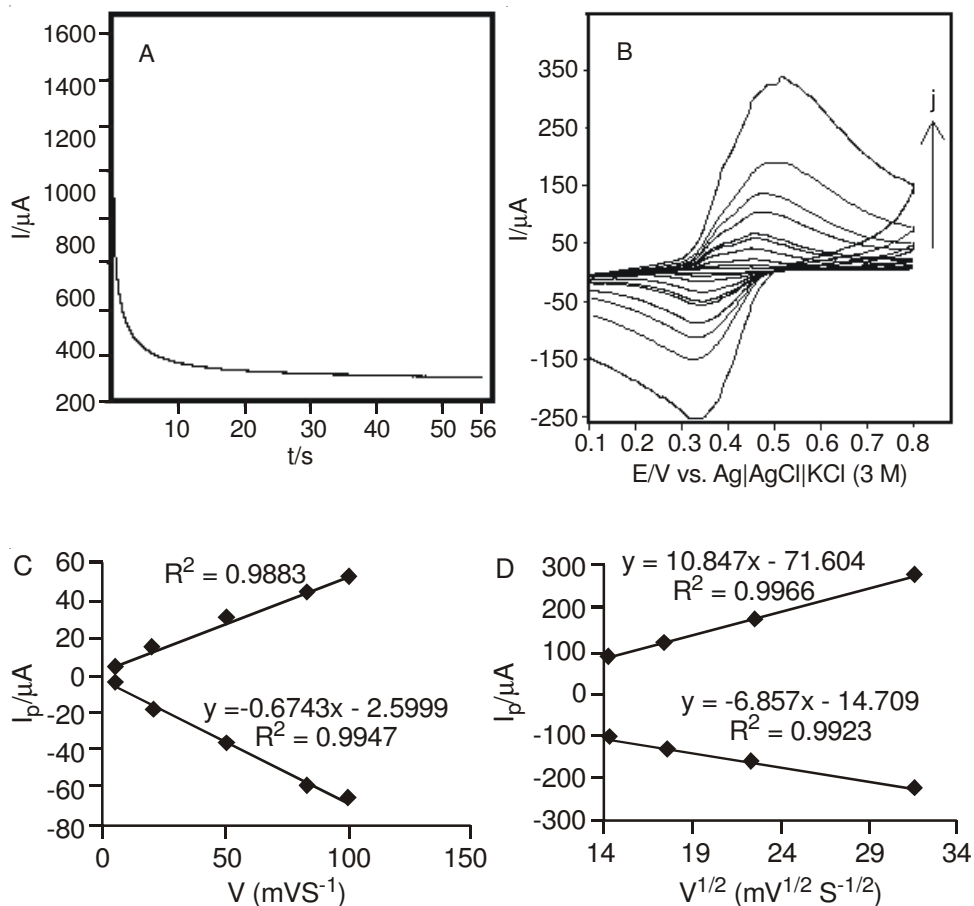


Fig. 2. (A) Chronoamperograms of 2,5-DMA in 0.5 M H_2SO_4 and 20 mM 2,5-DMA solution at CPE ($E = 0.9$ V, $t = 56$ s). (B) Cyclic voltammograms of P-2,5-DMA/MCPE in 0.5 M H_2SO_4 solution, v : a) 5, b) 10, c) 20, d) 50, e) 83, f) 100, g) 200, h) 300, i) 500, j) 1000 mV s^{-1} . (C) plot of I_p vs. v at low scan rates (5-100 mV s^{-1}). (D) Plot of I_p vs. $v^{1/2}$ at high scan rates (200-1000 mV s^{-1})

(Fig. 3A). In the galvanostatic method, film of polymer grows on the surface of carbon paste electrode. This is confirmed by voltammetric studies of the polymeric electrode in supporting electrolyte solution (Fig. 3B).

Fig. 3C,D shows plots of anodic and cathodic peak currents at various scan rates. The results are similar to those of voltammetric studies with the polymer prepared by potentiodynamic method.

A summary of electrochemical data for the polymers obtained at the surface of carbon paste electrodes with equal geometric area and identical conditions using different methods of electropolymerization is presented in Table-1. These results show that voltammetric data for P-2,5-DMA obtained at the surface of CPE by potentiodynamic, potentiostatic and galvanostatic methods with equal charge of

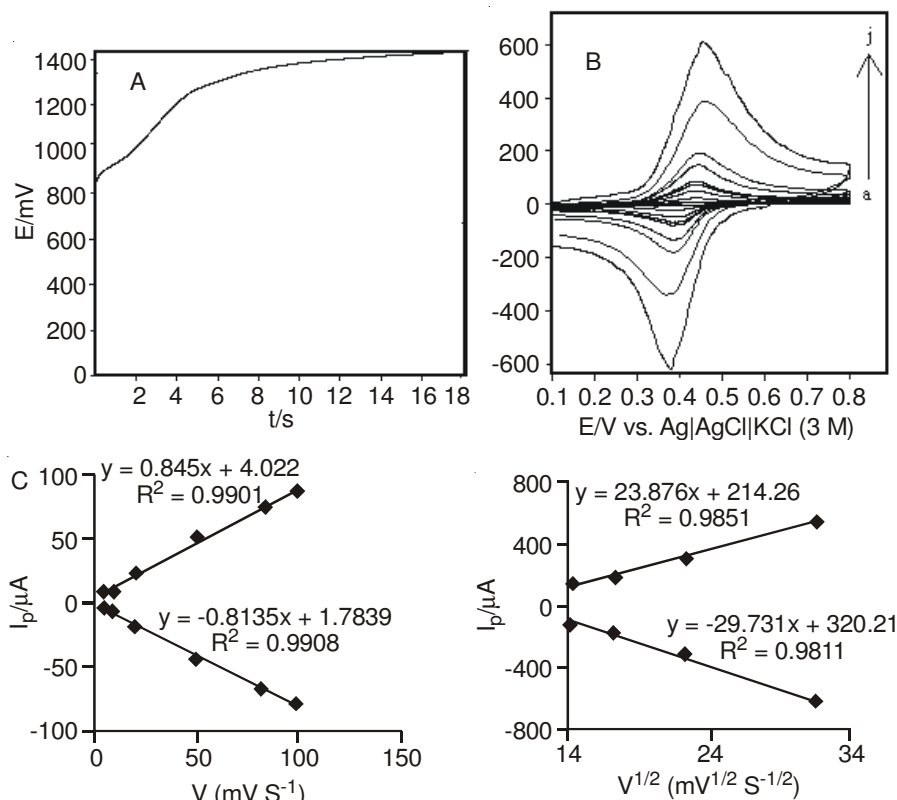


Fig. 3. (A) Chronopotentiograms of 2,5-DMA in 0.5 M H₂SO₄ and 20 mM 2,5-DMA solution at CPE ($I = 512 \mu\text{A}$, $t = 18 \text{ s}$). (B) Cyclic voltammograms of P-2,5-DMA/MCPE in 0.5 M H₂SO₄ solution, v : a) 5, b) 10, c) 20, d) 50, e) 83, f) 100, g) 200, h) 300, i) 500, j) 1000 mV s⁻¹. (C) Plot of I_p vs. v at low scan rates (5-100 mV s⁻¹). (D) Plot of I_p vs. $v^{1/2}$ at high scan rates (200-1000 mV s⁻¹)

TABLE-1
VOLTAMMETRIC DATA FOR *p*-2,5-DMA OBTAINED AT THE SURFACE OF CPE BY DIFFERENT ELECTROCHEMICAL METHODS, $v = 10 \text{ mV s}^{-1}$

Method of electropolymerization	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	ΔE_p (V)	I_{pa} (μA)	I_{pc} (μA)
Potentiodynamic	0.450	0.350	0.400	0.100	13.26	-15.50
Potentiostatic	0.440	0.330	0.385	0.110	6.72	-8.94
Galvanostatic	0.460	0.345	0.402	0.115	8.20	-6.59

9940 μC are almost near and with little differences in ΔE_p . However, I_p for polymer prepared by potentiodynamic method is significantly higher than I_p for polymers prepared by the other methods. Thus, potentiodynamic method was selected as a best method. According to present experiments, it seems that carbon paste electrode can be a better electrode substrate in comparison with other solid electrodes such as glassy carbon not only for its renewability and low cost but also for its higher current probably due to its porosity (Fig. 4).

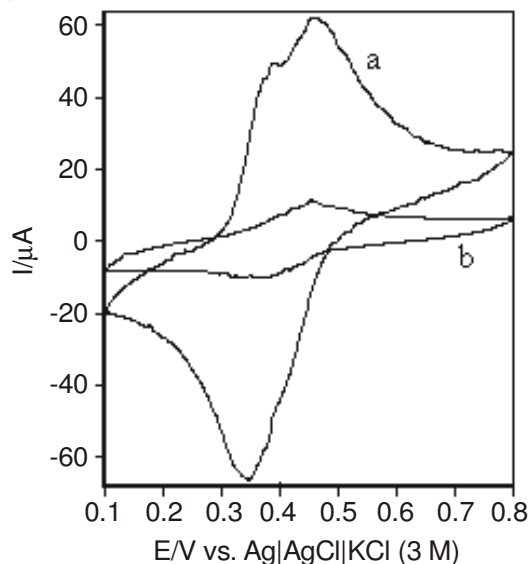


Fig. 4. Electrochemical response of P-2,5-DMA in 0.5 M H_2SO_4 (a) at the surface of carbon paste electrode (b) at the surface of glassy carbon electrode with equal geometric area, $\nu = 50 \text{ mV s}^{-1}$

Influence of pH: It is well known that electrochemical reactions on polyaniline-type polymers need the exchange of electrons and protons²¹. It was of interest to know how important it is in the case of 2,5-dimethylaniline. Thus, we investigated the influence of pH on the behaviour of polymer. Fig. 5 shows the cyclic voltammograms of P-2,5-DMA in different buffered aqueous solutions. If the acidity of medium is not enough, only one electrochemical pair of peak appears and if acidity increases, two electrochemical systems become better and better defined. It has been observed that in basic medium 2,5-dimethylaniline becomes electroinactive because it forms an insulating deposit. However, in strong acidic medium the P-2,5-DMA films degrade quickly by hydrolysis.

Electrocatalytic ability of Ni/P-2,5-DMA/MCPE: Recent research has demonstrated that coating of the electrode surface with polymeric films is an attractive approach for enhancing the power and scope of electrochemically modified electrodes²²⁻²⁴. Fig. 6 shows the electrochemical response of P-2,5-DMA/MMCPE and Ni/P-2,5-DMA/MCPE in 1.0 M NaOH solution. It can be seen from this Figure whereas neither oxidation nor reduction takes place on the P-2,5-DMA/MCPE when the potential is cycled between 0.2 and 0.8 V (Fig. 6a). A well-developed stable redox wave appears with Ni/P-2,5-DMA/MCPE when the potential is cycled between 0.2-0.8 V. This wave is related to the oxidation of Ni(II) to Ni(III) with a peak potential of 0.49 V and reduction of Ni(III) to Ni(II) with a peak potential of 0.35 V (Fig. 6b) and oxygen evolution reaction at about 0.8 V. One of very important usages of nickel as a catalyst is for the oxidation of alcohols^{25,26}. Fig. 7 shows the

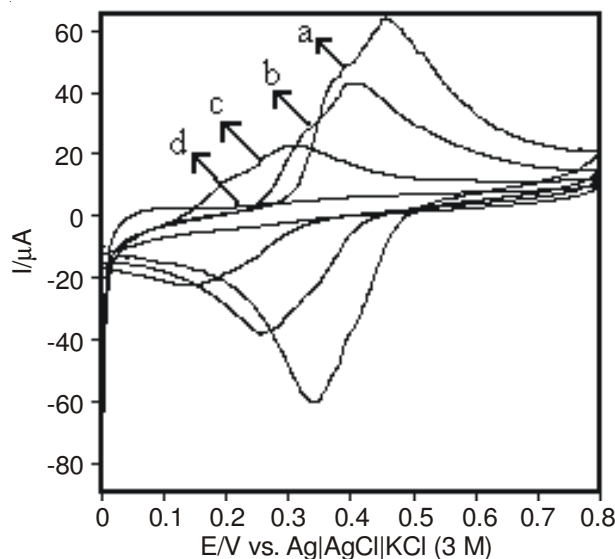


Fig. 5. Electrochemical response of P-2,5-DMA/MCPE (a) in 0.5 M H_2SO_4 , (b) pH = 2, (c) pH = 5, (d) pH = 9, $v = 50 \text{ mV s}^{-1}$

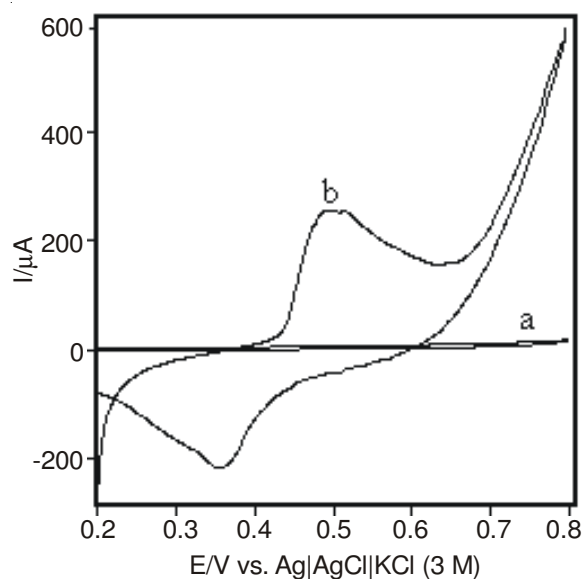


Fig. 6. Electrochemical response of electrodes: (a) P-2,5-DMA/MCPE and (b) Ni/P-2,5-DMA/MCPE after anodic polarization, in 1.0 M NaOH solution, $v = 50 \text{ mV s}^{-1}$

electrocatalytic oxidation of methanol by Ni/P-2,5-DMA/MCPE. As can be seen, the electrochemical response of P-2,5-DMA/MCPE in the absence of methanol is shown in Fig. 7a; the addition of 0.2 M methanol to the alkaline solution causes no

effect on the electrochemical response of the P-2,5-DMA/MCPE (Fig. 7b). The electrochemical response of the Ni/P-2,5-DMA/MCPE in alkaline solution exhibits well defined anodic and cathodic peaks (Fig. 7c) associated with the Ni(II)/Ni(III) redox couple. Fig. 7d shows the behaviour of this modified electrode in the presence of 0.2 M methanol at the scan rate of 20 mV s^{-1} . An increment in the anodic peak current for peak (P_{a1}) followed by the appearance of a new peak (P_{aII}) at more positive potential and a decrease of the cathodic peak current (P_{cII}) during the reverse scan are the main effects observed upon the addition 0.2 M of methanol to the electrolyte. This behaviour is typical of that expected for catalytic oxidation of methanol.

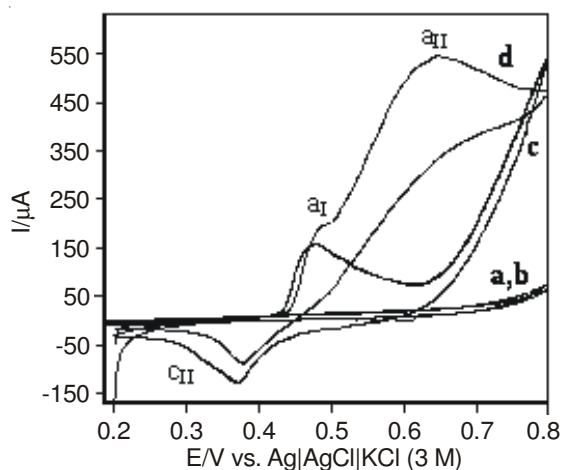


Fig. 7. Electrochemical responses of P-2,5-DMA/MCPE in 1.0 M NaOH solution with $v = 20 \text{ mV s}^{-1}$ to: (a) 0.0 M, (b) 0.2 M methanol and Ni/P-2,5-DMA/MCPE to: (c) 0.0 M, (d) 0.2 M methanol

Conclusion

It is shown that a poly-2,5-dimethylaniline film can be formed at the surface of carbon paste electrode as a low cost substrate. Additionally, the polymer coated surface at the DMA/MCPE is renewed easily and more important, polymer behaviour is reproducible and stable under the conditions of present study. During this investigation we find out that, I_p for the polymer prepared by potentiodynamic method is significantly higher than the I_p for the polymers prepared by other methods. Thus, potentiodynamic method is the best method for electropolymerization of 2,5-DMA at the surface of carbon paste electrode. The electrochemical response of P-2,5-DMA prepared at the surface of carbon paste electrode is better than its response at the surface of glassy carbon electrode with equal geometric area. Finally, the suitability of this polymer-modified carbon paste electrode as a complexing agent for Ni(II) (as a transition metal cation) for electrocatalytic oxidation of methanol was demonstrated.

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