

Studies on the Electrocatalytic Oxidation of Hydroquinone at Poly 1,8 - Diaminonaphthalene Derivatives Modified Electrodes

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Poly thiophenlidine -8-naphthylamine modified platinum electrode (PTPNA/Pt) and poly 1-methyl thiophenlidine -8-naphthylamine modified platinum electrode (PMTNA/Pt) were prepared by electrochemical oxidation and polymerization of their respective monomers. Both the modified electrodes improve the electrocatalytic properties of the substrates, decrease the overpotential, decrease the potential difference (ΔE), increase the reaction rate and improve the stability of the electrode response, the performance of the modified electrode was found depends on its structure. The nature of the electrode process was studied, it was found that the anodic and cathodic peak current (I_{pa} , I_{pc}) increased with film thickness(in range 5-25 cycles),after that there is a leveling off, also $I_{pc} / I_{pa} < 1$, which indicates that the adsorption of the reactant takes place . In general, the redox reaction is explained by the specific adsorption of analyte hydroquinone molecules (H_2Q) onto the emeraldine (EM^{2+}) centers in the polymer film.

Keywords: Quinone/hydroquinone; Electrocatalysis; Modified electrode; Adsorption; Steric hindrance.

1. INTRODUCTION

Modified electrodes have been the focus of various researchers in the past three decades .The underlying motivations for electrode surface modifications stem from the desire for improved electrocatalysis and freedom the surface fouling effects. Alternatively, electrodes can be modified to prevent undesirable reactions from competing kinetically with the desired electrode process [1, 2]

Polymer films modified electrodes have wide applications in the fields of electrocatalysis, chemical sensors and biosensors [3]. One of the most striking properties of conducting polymers (modified electrodes) is the ability to catalyze some electrode reactions, such modified electrodes can significantly improve the electrocatalytic properties of the substrates, decrease the overpotential ,decrease the potential difference (ΔE), increase the reaction rate and improve the stability of the electrode response [4-6] . These electrocatalytic processes, proceeding at modified electrodes, present

a fast growing area of investigation, which yield many unexpected applications in various fields of applied electrochemistry. Electropolymerization is a convenient method for immobilizing polymers on various conductive substrates because the deposition can be controlled by adjusting the electrochemical parameters and the process is located at the electrode surfaces. Thus, thickness, permeation and charge transport characteristics of the modified polymeric films can be well defined [7].

Hydroquinons are a class of polluting chemicals which when absorbed through the skin and mucous membranes can cause damage to the lungs, liver, kidney and genitor urinary tract in the animals and human [7,8]. Electrolytic oxidation is an effective method to remove organic pollutants, but usually it is a high energy cost technique, due to high oxidation potential and low reduction potential for redox of pollutants [9]. Therefore, the key task for electrolytic oxidation is to lower the oxidization potential or increase the reduction potential, so that reduce the energy cost. Due to the importance of this compounds, this paper discuss the influence of the structure of the polymer in its performance, stability in the electrocatalytic oxidation of H_2Q and the nature of this process.

2. EXPERIMENTAL PART

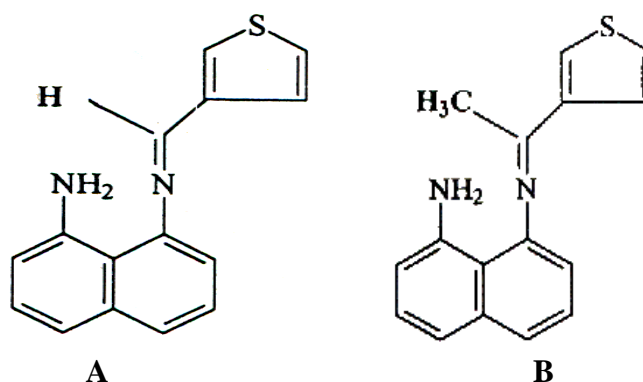


Figure 1. A) Thiophenylidene-8-naphthylamine(TPNA), B) 1-methyl thiophenylidene -8-naphthylamine (MTNA)

The chemicals, 1,8-diaminonaphthalene, 3-thiophenealdehyde, 3-acetylthiophene ,dimethylformamide(DMF), ethanol, sulfuric acid, hydroquinone, tetrabutyl ammonium tetraflurobobate (TBAFB), Lithium perchlorate($LiClO_4$), acetonitrile, were analytical grade chemicals (Aldrich) and used without further purification. Aqueous solutions were prepared from bidistilled water.

Electrochemistry experiments were performed using the EG&G PAR computer measuring system model 250 and a Hewlett-Packard X-Y recorder model 7440. Cyclic voltammetry (CV) was conducted using a three-electrode electrolytic cell (Bioanalytical system, model C-1A) in which a platinum disc electrode (Pt) (3.0 mm diam.), was used as working electrode, a platinum sheet (area $2cm^2$) as counter electrode and Ag/AgCl as reference electrode. All experiments were done at room temperature. TPNA and MTNA Schiff bases were previously prepared and characterized [10,11] and their structure are shown in Fig. 1. For PTPNA the film formed at Pt electrode from the

nonaqueous acetonitrile solution containing 10^{-3} M of TPNA monomer ,and 0.1M TBAFB by repetitive cyclic voltammetry in potential range between 0.0 and 1.1V for 25 repetitive scans at 0.05V/s [10, 11], and for PMTNA the film formed at platinum electrode also from nonaqueous DMF /acetonitrile solution containing 0.1M LiClO_4 and 10^{-3} M of MTNA by repetitive cyclic voltammetry in potential range between -0.5 and 1.4V for 25 repetitive scans at 0.1 V/s. The resulting polymer films of TPNA are active in both aqueous and nonaqueous solution ,but for PMTNA the film was inactive [11], this can be overcome by the loading of Ni^{2+} at the polymer film, this is illustrate the influence of the structure of the polymer towards the activity.

3. RESULTS AND DISCUSSION

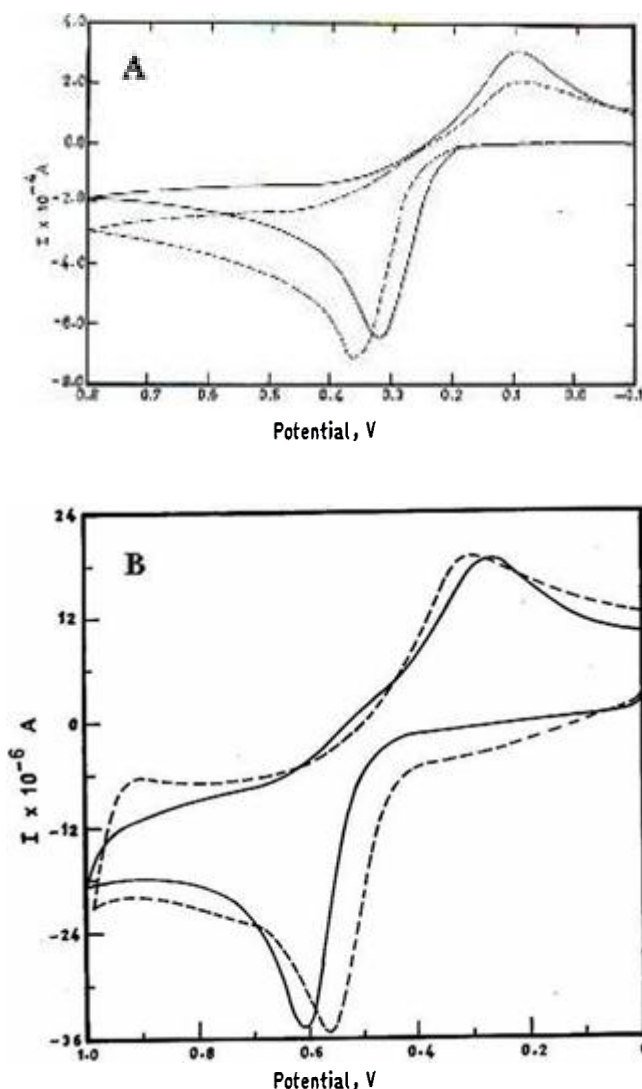


Figure 2.A) Cyclic voltammograms of bare Pt electrode (---),and PTPNA/Pt modified electrode (—). B) Cyclic voltammograms of bare Pt electrode (—) ,and PMTNA /Pt modified electrode (---) , all the voltammograms were carried out in 0.1 M H_2SO_4 containing 10mM H_2Q . The modified electrodes were prepared as mentioned in the text.

Quinone / hydroquinone redox couple implies the transfer of two electrons and two protons ,at least in acidic aqueous solution .The rate of this process is determined by many factors. Among these ,electric conductivity of the polymer layer. Fig.2.illustrates the cyclicvoltammograms obtained for the electrooxidation of 10 mM of hydroquinone in 0.1M H₂SO₄ at PTPNA/Pt and PMTNA/Pt modified electrodes and the naked Pt electrode in the corresponding electrolytes, this Fig. illustrates that the oxidation potential at the naked electrodes are larger than that at the modified electrodes ,also naked Pt electrodes has a large potential gaps (ΔE) than that in case of modified electrodes, and $\Delta E = 0.2V$ and $0.27V$ for PTPNA and PMTNA respectively.

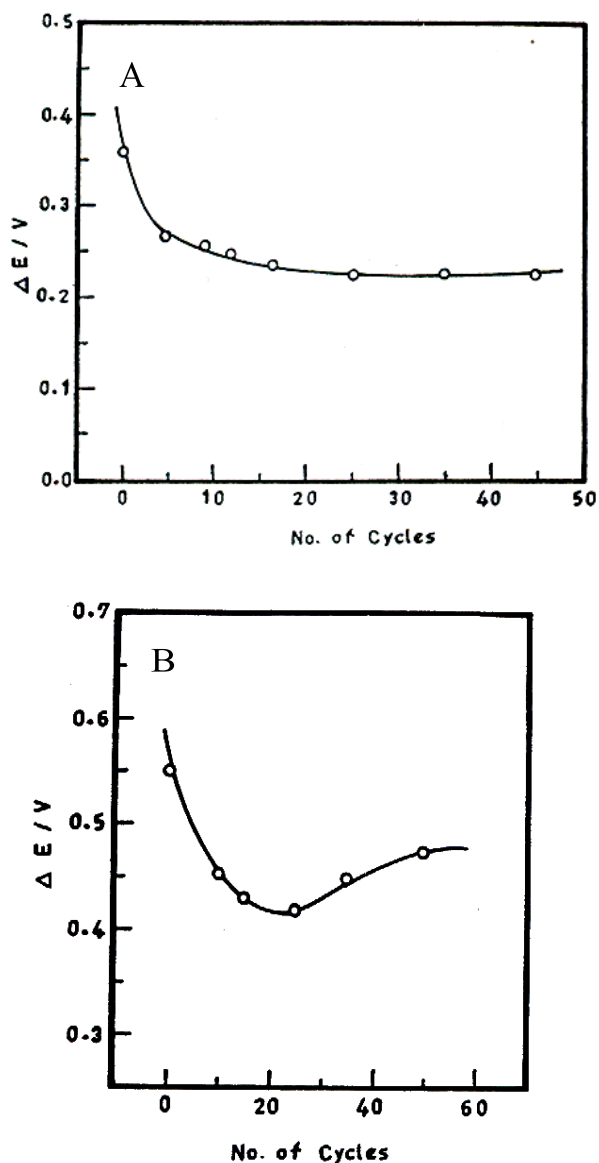


Figure 3.A) Peak separation ΔE against number of cycles of films PTPNA/Pt formed modified electrodes, scan rate = 100mVs^{-1} . B) Peak separation ΔE against number of cycles of films PMTNA/Pt formed modified electrodes, scan rate = 100mVs^{-1} .

No significant increase of the peak current was found in both cases. The redox potential of the quinone /hydroquinone couple is situated in a potential range where in polymer films are in the highly

conducting state, the polymer itself stays in an intermediate state, when reduction occurs, i.e. its degree of doping/degree of oxidation is somewhere between the fully reduced (Lecuoemeraldine (LE)) and the fully oxidized state (emeraldine(EM^{2+})) [12,13]. The catalytic effect visible as a shift of the oxidation potentials to less positive values in case of two electrodes and in case of PTPNA the potential shift to more less value than that in case of PMTNA, Fig.3.illustrates ΔE dependence versus the thickness of PTPNA and PMTNA films, showing that the main decrease in ΔE values takes place already at the lowest film thickness, and there is no significant change with the increase of film thickness in case of PTPNA, this is in contrast to PMTNA, so there is an increase of ΔE again with film thickness [14,15], the improvement of the performance of PTPNA/Pt modified electrode was shown, so it has a lower ΔE than PMTNA/Pt modified electrode, this means that PTPNA/Pt modified electrode more conductive and catalyze the H_2Q oxidation reaction more than PMTNA/Pt modified electrode.

Further more the stability of both films were carried out by obtaining a cyclic voltammogram of H_2Q just after polymer deposition, then the electrode stirred in (methanol + water) mixture, or by exposed to air for about 48 h and then the CVs of H_2Q repeated again, there was no appreciable change in ΔE or in oxidation peak current in case of PTPNA, but in case of PMTNA there is a decrease in oxidation peak current by 5.4% after 24h only [10,11].

The above reported results illustrate that there is a variation of the behavior between PTPNA/Pt and PMTNA/Pt modified electrodes in the electrocatalytic reaction of H_2Q , this is due to the bulky $-CH_3$ group in PMTNA which induce steric hindrance, deformation and decreases the degree of conjugation [16-18] and hence decrease the conductivity of the deposited film and make this polymer less active, less stable than PTPNA, this illustrate the influence of the structure of polymer film for electrocatalytic process.

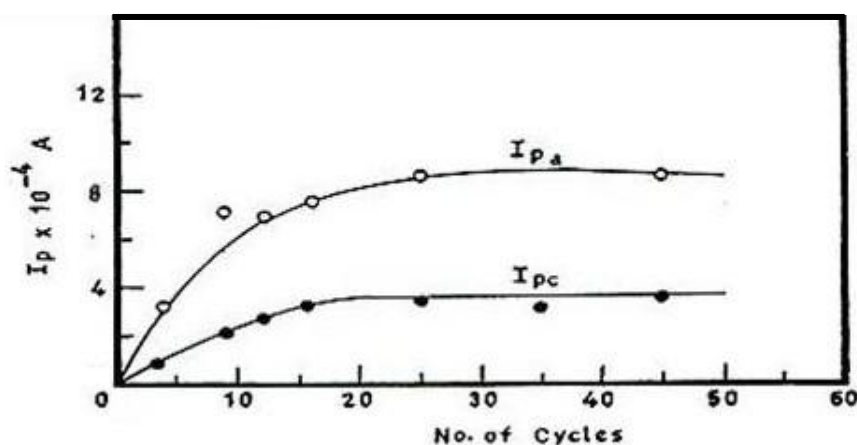


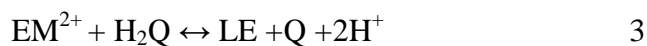
Figure 4. Peak currents I_{pa} , I_{pc} for oxidation and reduction of hydroquinone at PTPNA/Pt modified electrode as a function of the number of cycles.

Fig. 4. shows the relation between the I_{pa} , I_{pc} and the number of cycles of film (film thickness), the Fig illustrates that there is an increase in the peak current with thickness of the film between 5 - 25 cycles after that there is a leveling off, furthermore $I_{pc} / I_{pa} < 1$, this explained by the

adsorption of the reacting species on the polymer film [19], Duić and Grigić[20] found that, although linear, the increase of I_p value is higher than square roots of scan rate dependence requires, suggesting that adsorption of the reacting H_2Q species. This is supported by the fact that $I_{pc} / I_{pa} < 1$, which indicates that the adsorption of the reactant takes place, the depression of the I_p increases at high scan rate values and at high concentrations of H_2Q , also suggest that H_2Q oxidation is not only under diffusion control, but that adsorption and some slow kinetic process are included, several study report that the adsorption is a prerequisite step in the electrochemical oxidation of H_2Q on polymer film [19- 21], the H_2Q oxidation reaction takes place in the EM^{2+} potential region, and one can assume that the following reaction take place:



and



From the above reaction, one EM^{2+} unit can exchange only two electrons to give the reduced form LE, and one H_2Q molecule is required for reaction 3 to proceed, this mean that at potential of H_2Q oxidation there must be a fraction of LE form present although the potential value corresponds to EM^{2+} form. Holze et al [21] proved the existence of LE form at the EM^{2+} potential region by insitu spectro electrochemical measurements of H_2Q oxidation on PANI electrodes.

This is in agreement with the work of Matveeva [22,23], Who found that the redox reactions of H_2Q take place on PANI polymer film practically without overpotential assuming the possibility that two electron charge transfer processes are realized in the system. However, reaction currents depend on the thickness of polymer layer deposited on Pt electrode. It is proposed that a molecular complex is formed and that, due to electronic exchange between polymer layer and H_2Q/Q molecules, electronic conjugation of the adsorbed molecules with polymer results, also the reactions are taking place at polymer/solution interface within the polymer layer. Malinauskas and Holze [21,24,25] established the reduction of EM^{2+} form by H_2Q after positive potential switch, resulting in a diminished fraction of EM^{2+} form to LE. They found that the amount of LE in PANI layer increase with the increase in H_2Q concentration, i.e. the catalytic effect is terminated when all the available EM^{2+} centers are covered by H_2Q molecules, and the oxidation reaction proceeds at higher potentials.

4. CONCLUSION

The study confirms the catalytic effect of PTPNA/Pt and PMTNA/Pt films on Q / H_2Q electrode reaction. The decrease of the H_2Q oxidation potential is achieved in both films. However there is an improvement in the performance of PTPNA/Pt modified electrode compared to PMTNA/Pt

modified electrode, in catalytic oxidation reaction, conductivity, stability and durability, this is due to the presence of bulky $-\text{CH}_3$ group in PMTNA, which cause steric hindrance making the polymer suffer from decrease in activity, conductivity and stability. To study the nature of this electro catalytic reactions, the relation between the I_{pa} , I_{pc} and film thickness was investigated, and the ratio of I_{pc} / I_{pa} was found less than unity, which support the adsorption process, the obtained results confirmed with that reported in the literature, so the oxidation reaction is under prevailing adsorption control, and H_2Q adsorbed at EM^{2+} centers in the polymer film which reduced to LE. However the catalytic effect is terminated when all the available EM^{2+} centers are covered by H_2Q molecules.

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