



Copolymer Modified Electrode with Hydroxyl and Amino Derivatives of Anthraquinones for Oxygen Reduction

G. Amala Jothi Grace^{1,2*}, A. Gomathi³ and C. Vedhi⁴

¹Manonmaniam Sundranar University, Tirunelveli, India

²Department of Chemistry, Chandy College of Engineering, Thoothukudi, India

³Department of Chemistry, Sri K.G.S Arts and Science College, Srivaikuntam, India

⁴Department of Chemistry, V.O.Chidambaram College, Thoothukudi, India
arsahana2010@gmail.com

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Abstract

The electrochemical characterisation of poly (3-methylthiophene-co-3,4-ethylenedioxythiophene) modified glassy carbon electrode with hydroxyl and amino derivatives of anthraquinones were determined. The consequence of pH on the electrochemical behaviour and stable behaviour towards the modified poly(3-methylthiophene-co-3,4-ethylenedioxythiophene) were investigated. Using chronoamperometric and chronocoulometric techniques, the diffusion coefficient values and the number of electrons were calculated. Excellent electrocatalytic response was given by hydroxyl and amino derivatives of anthraquinones combined with the copolymer poly(3-methylthiophene-co-3,4-ethylenedioxythiophene) for oxygen reduction. The glassy carbon electrode coated with the copolymer was described using Scanning electron microscope.

Keywords: Oxygen reduction, Voltammograms, Copolymer modified electrode, EDOT.

Introduction

Modified electrodes are essential for fuel cells and sensors. In the electrochemical devices, oxygen reduction is an important reaction. A large number of compounds have been reported. The previous reports were made on ruthenium-iron cluster¹, manganese oxide², copper³, titanium silicates⁴, pyrimidine bases⁵, metal phthalocyanine⁶, metal macrocyclic complexes⁷, Au nanoparticle⁸, naphthoquinone^{9,10}, anthraquinone derivatives¹¹⁻¹⁵, clay¹⁶, polypyrrole¹⁷, carbon paste electrodes¹⁸ and metal complexes¹⁹⁻²³. Based on literature, the electrochemical behaviour of 1,8-Dihydroxy anthraquinone and 1-Amino anthraquinone at poly(3-methylthiophene-co-3,4-ethylenedioxythiophene) modified electrode for the electrocatalysis of oxygen reduction were examined by electroanalytical techniques.

Materials and Methods

1,8-Dihydroxyanthraquinone (DHAQ), 1-Aminoanthraquinone (1-AMAQ), 3,4-Ethylenedioxythiophene (EDOT) and 3-Methylthiophene were purchased from Sigma-Aldrich and 0.01M solutions were prepared in acetonitrile. The various ranges of pH solutions were prepared. For the aerated and deaerated conditions, Nitrogen and Oxygen gases were used. A three electrode cell set up was used. It consists of a glassy carbon as working electrode, silver electrode as reference electrode and a platinum wire as counter electrode. This cell setup was kept in the solution containing DHAQ and 1-AMAQ. The copolymer modified electrode was prepared by

electrodeposition. CH Instrument Electrochemical workstation was employed to study the electrochemical, electrocatalytic behaviour, chronoamperometric and chronocoulometric response.

Results and Discussion

By means of electrodeposition, glassy carbon electrode was coated with the copolymer and the voltammetric studies of DHAQ and 1-AMAQ at the modified electrode was performed under de-aerated and aerated conditions in the various pH ranges.

Electrochemical Behaviours of DHAQ and 1-AMAQ at METH/EDOT/GCE: The voltammetry results for the compounds such as DHAQ and 1-AMAQ at various scan rates 5, 20, 50, 100, 200, 300, 400, 500, 600 and 700 mVs⁻¹ were recorded to study the influence of scan rate with cathodic peak current. Figure-1 represents the cyclic voltammogram of DHAQ and 1-AMAQ at METH/EDOT/GCE (pH 7) under de-aeration at scan rate 20 mVs⁻¹.

Figure-2 shows the pH versus cathodic potential under de-aeration in presence of DHAQ and 1-AMAQ at METH/EDOT/GCE. On increasing the pH, reduction peak potentials move in the direction of negative values.

Figure-3 shows the scheme of log I_{pc} versus log ν for DHAQ and 1-AMAQ at METH/EDOT/GCE under de-aeration in pH 7.0. The voltammogram exhibit a straight line for the plot of

cathodic current (I_{pc}) with the scan rate (ν) and a slight deviation was obtained for the plot of I_{pc} with $\sqrt{\nu}$. The scheme of logarithm of cathodic peak current vs. logarithm of scan rate shows perfectly a linear, which indicates the adsorption controlled process for DHAQ.

The voltammogram of 1-AMAQ shows a straight line for I_{pc} with $\nu^{1/2}$ and a slight deviation was obtained for the plot of I_{pc} with ν . The scheme of logarithm of cathodic peak current vs. logarithm of scan rate is a straight line indicating the process as a diffusion controlled for 1-AMAQ.

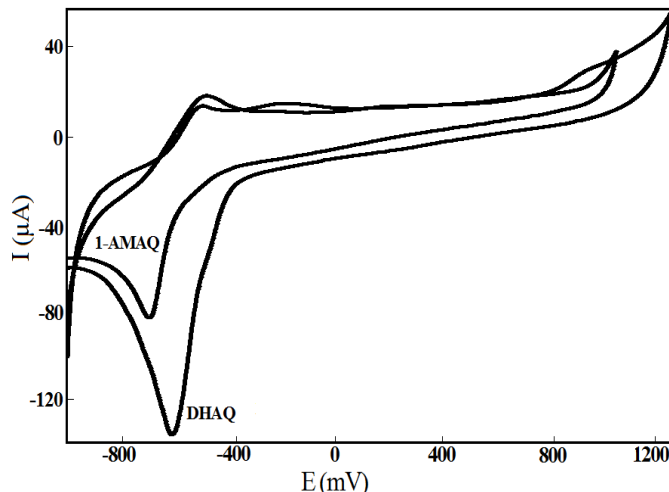


Figure-1

Cyclic voltammogram of DHAQ and 1-AMAQ at METH/EDOT/GCE (pH 7) under de-aeration at scan rate 20 mVs⁻¹

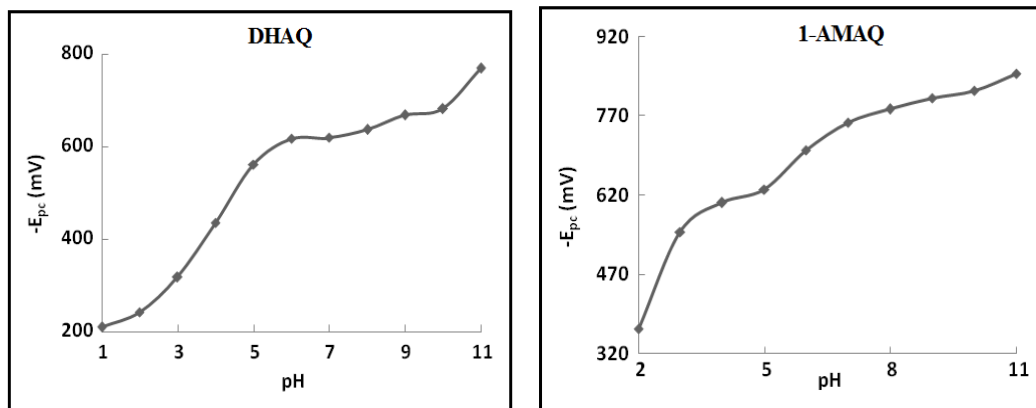


Figure-2

Plot of E_{pc} versus pH for DHAQ and 1-AMAQ at METH/EDOT/GCE under de-aeration at SR 20 mVs⁻¹

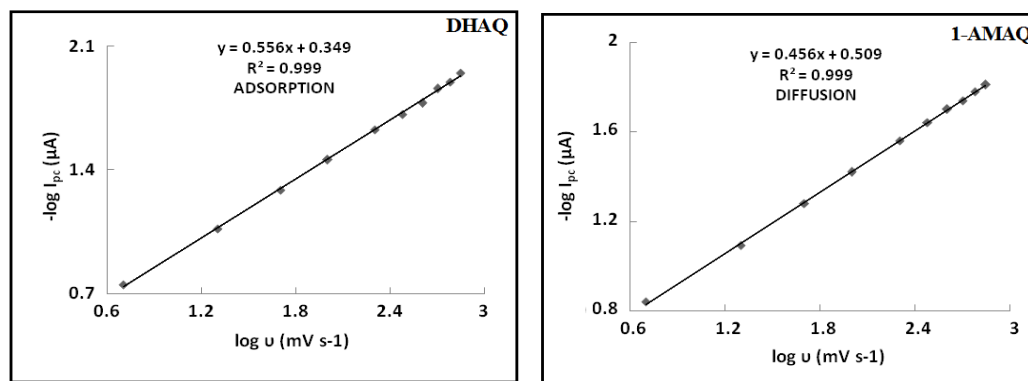


Figure-3

Scheme of $\log I_{pc}$ versus $\log \nu$ for DHAQ and 1-AMAQ at METH/EDOT/GCE under de-aeration in pH 7.0

The plot shows three distinct linear portions with different slope values which indicate the different forms of anthraquinone. The pH-potential diagram for DHAQ and 1-AMAQ at METH/EDOT/GCE was given in the Figure-4. At low pH values 1 to 3, DHAQ and 1-AMAQ undergoes two-electron three-proton reduction process. At the pH range 4 to 10, the compound undergoes two-electron, two proton process. At pH above 10, the electrode surface reaction is a two electron, one proton process.

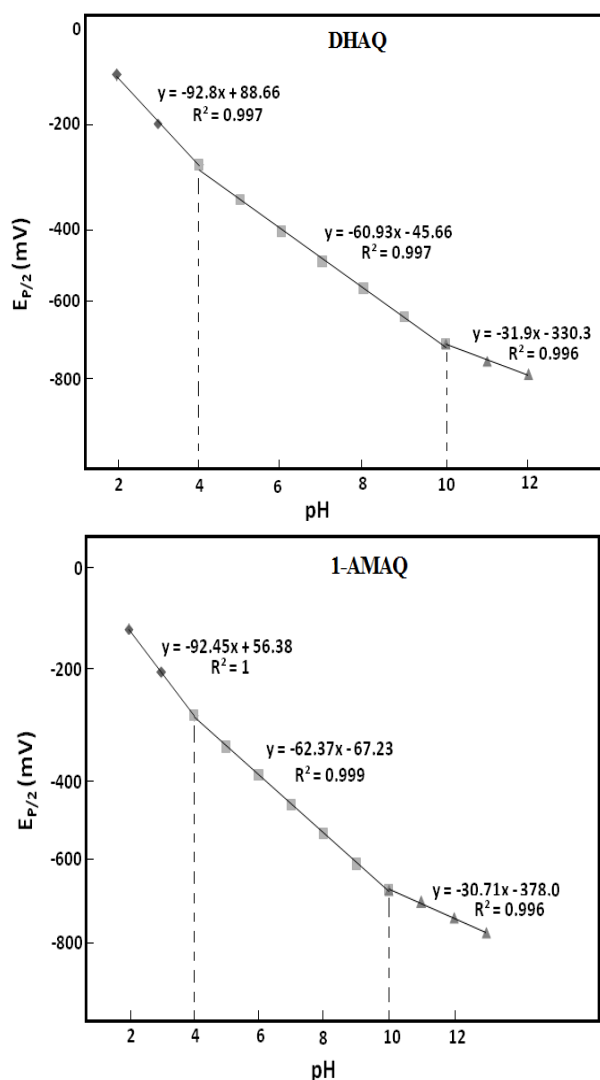


Figure-4
 pH-cathodic potential diagram for DHAQ and 1-AMAQ at METH/EDOT/GCE

The constancy of the copolymer modified electrode and the reproducibility of its electrochemical behaviour was investigated. The copolymer modified electrodes were placed in acidic medium with DHAQ and 1-AMAQ for 40 h and in neutral medium for 30 h. The cyclic voltammetry behaviours were recorded. The voltammograms show only a slight decrease which confirms the stable nature of the modified electrode.

The surface coverage of the copolymer modified electrode was evaluated using the voltammograms recorded at 20 mVs⁻¹ scan rate. Using the relation $\Gamma_{aq} = Q/nFA$ where Q is the charge consumed, n is the number of electrons involved, F (96500 C mol⁻¹) the Faraday constant and A is the area of the (0.0314 cm²) electrode used. The surface coverage value of DHAQ and 1-AMAQ at copolymer modified electrode was represented in Table-1. Also, the adsorption of DHAQ and 1-AMAQ in the presence of conducting polymer modified electrode was also confirmed by SEM studies. Figure-5 shows the scanning electron microscopy images of METH/EDOT/GCE (a), METH/EDOT/GCE with DHAQ (b) and METH/EDOT/GCE with 1-AMAQ.

Table-1
 Half-peak potential ($E_{P/2}$) and Surface coverage (Γ_{aq}) values of DHAQ and 1-AMAQ at METH/EDOT/GCE in pH 7.0

AQNEs	$-E_{P/2}$ (mV)	Γ_{aq} mol cm ⁻² (x 10 ⁻⁸)
DHAQ	479.3	0.90
1-AMAQ	504.5	0.90

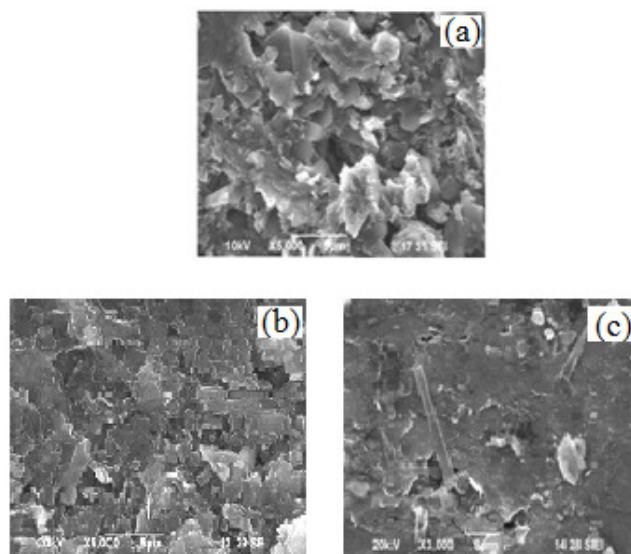


Figure-5
 SEM photographs of (a) METH/EDOT/GCE (b) METH/EDOT/GCE with DHAQ and (c) METH/EDOT/GCE with 1-AMAQ

Catalytic reduction of oxygen at METH/EDOT/GCE for DHAQ and 1-AMAQ: In various pH media at METH/EDOT/GCE, the catalytic effect of DHAQ and 1-AMAQ was studied. The displacement may be unequal [13, 14]. The cathodic peak current increases upto pH 7. Figure-6 explains the variation of oxygen reduction potential shift with pH for METH/EDOT/GCE in presence of DHAQ and 1-AMAQ which clearly indicates that the highest shift is observed at pH 7.

Cyclic voltammograms of DHAQ and 1-AMAQ at METH/EDOT/GCE in pH 7.0 under aeration was represented in the Figure-7. On a plain GCE, oxygen reduces at -1027.5mV . The reduction of oxygen occurred at -603.2 and -722 mV on METH/EDOT/GCE in presence of DHAQ and 1-AMAQ. The oxygen reduction potential shift (ΔE) values are given in Table-2. Figure-7 show that there is a huge increase in the cathodic peak current for DHAQ and 1-AMAQ at the copolymer modified electrode under aeration. Also, the corresponding anodic peak has left as shown in the Figure-7.

Under aerated condition, the reduction process is a diffusion controlled. For the copolymer modified electrode in presence of DHAQ and 1-AMAQ, the variation of cathodic peak current with scan rate was observed. Figure-8 describe the plots of I_{pc} versus \sqrt{v} and $\log I_{pc}$ versus $\log v$ for DHAQ and 1-AMAQ at METH/EDOT/GCE under aeration in pH 7.0. From the plots, the diffusion controlled process for oxygen reduction was observed. Also, the straight line variation of logarithmic cathodic peak with logarithm of scan rate with slope less than 0.5 confirms the process is a diffusion controlled.

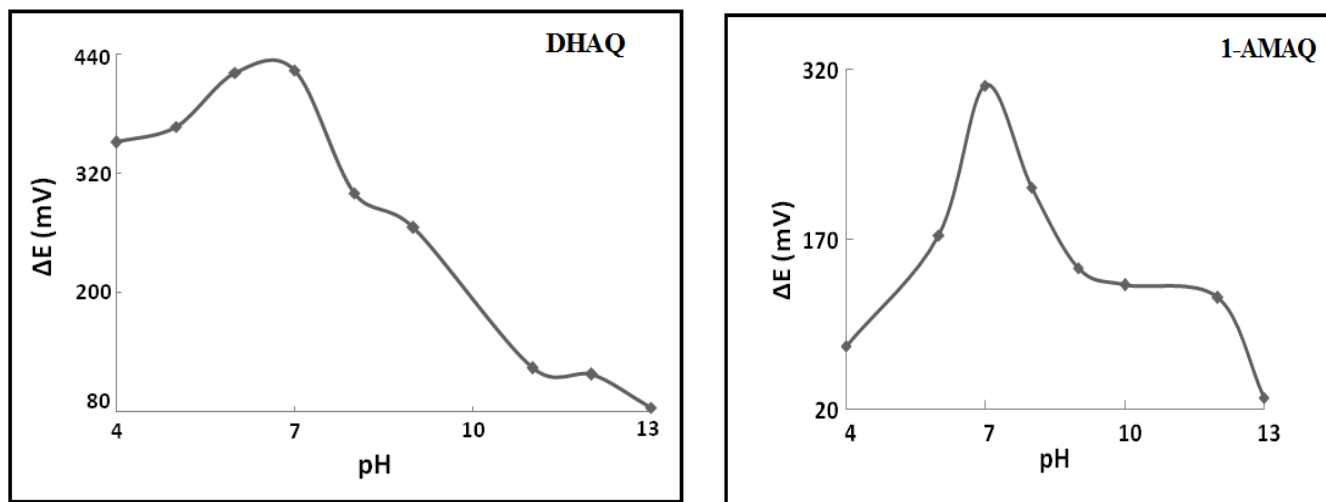


Figure-6
 Plot of pH versus oxygen reduction potential shift at METH/EDOT/GCE with DHAQ and 1-AMAQ

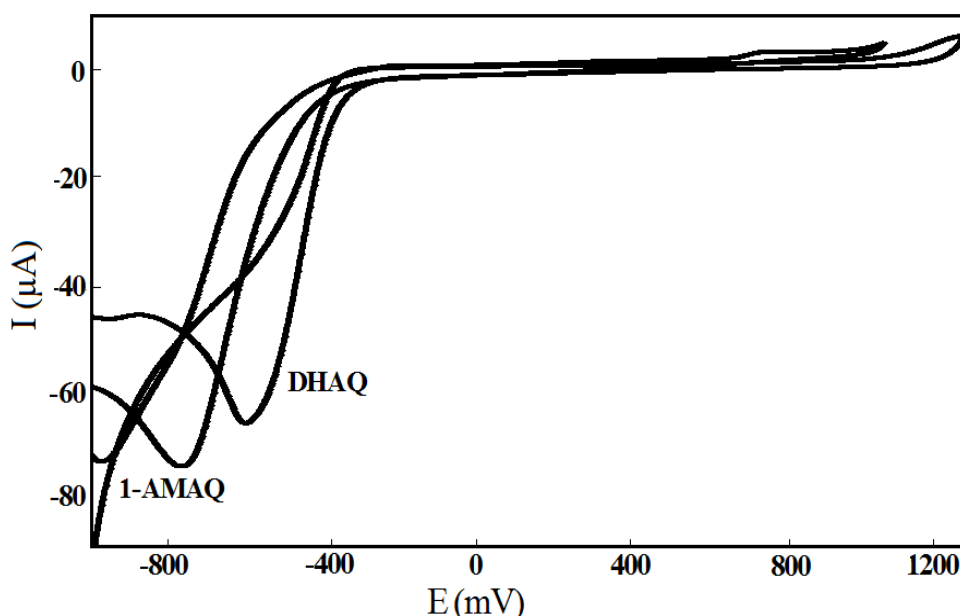


Figure-7
 Cyclic voltammogram of DHAQ and 1-AMAQ at METH/EDOT/GCE (pH 7) during oxygen purging at scan rate 20 mVs^{-1}

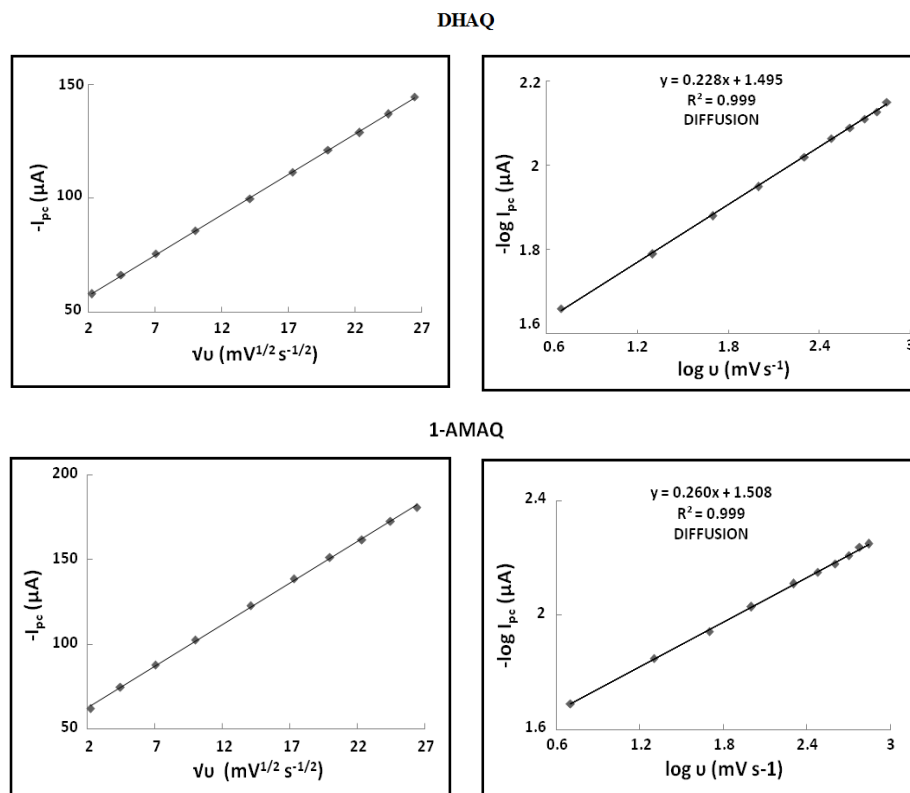


Figure-8

Plots I_{pc} versus $\sqrt{\nu}$ and $\log I_{pc}$ versus $\log \nu$ for DHAQ and 1-AMAQ at METH/EDOT/GCE under aeration in pH 7.0

Chronoamperometry: The chronoamperograms were performed by applying the potentials in the range of -400 and -1000 mV for copolymer modified GCE under aeration and deaeration at the optimum pH 7. Figure-9 shows the chronoamperogram of DHAQ at METH/EDOT/GCE in pH 7 in the presence and absence of oxygen. The net electrolysis current I_{net} was obtained from the background current under aeration and deaeration.

In the de-aerated condition, a plot of net current against $t^{-1/2}$ shows a direct line which extrapolates close to origin. The diffusion coefficient values of anthraquinones were determined.

The Cottrell equation is

$$I = n F D^{1/2} A C_{aq} \pi^{-1/2} t^{-1/2}$$

$$\text{Slope} = n F D^{1/2} A C_{aq} \pi^{-1/2}$$

Where: C_{aq} is the concentration of anthraquinone, D is the diffusion co-efficient of DHAQ and 1-AMAQ and A is the area of (0.0314 cm²) the electrode used.

From the Cottrell equation, the Diffusion coefficient (D_{Aq}) values of DHAQ and 1-AMAQ calculated and the values are reported in Table-2.

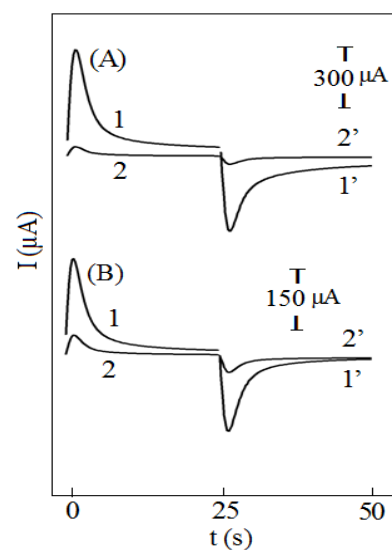


Figure-9

Chronoamperograms of DHAQ at METH/EDOT/GCE in pH 7 at the potential range of -400 mV to -1000 mV vs. silver electrode. (A) 1,1' for METH/EDOT/GCE in presence of DHAQ under aeration; 2,2' for plain GCE in the absence of DHAQ. (B) 1,1' for METH/EDOT/GCE in presence of DHAQ under de-aeration; 2,2' for plain GCE in the absence of DHAQ

Chronocoulometry: The chronocoulometric studies of DHAQ at plain GCE and modified electrode under aerated and deaerated condition was examined in the potential range of about -400 and -1000mV versus silver electrode, respectively. As an illustration, the chronocoulometric response of DHAQ at METH/EDOT/GCE in pH 7 is shown in the Figure-10. Under deaeration, a reversible curve was observed when the potential was reversed. But under aeration, a large enhancement in the charge and a flat line on potential reverse condition prove the irreversible electrocatalytic reduction of oxygen. The number of electrons (n_{Aq}) involved in the reduction of METH/EDOT/GCE with DHAQ at the maximum pH was evaluated.

Using the Cottrell equation,
 $Q = 2n F A C D^{1/2} \pi^{-1/2} t^{1/2}$

and by employing the diffusion coefficient values of anthraquinones from chronoamperometric data's the number of electrons concerned under deaerated condition was determined. The number of electrons (n_{O_2}) concerned in the oxygen reduction was also calculated from the slope of Q versus $t^{1/2}$ under aeration. The values obtained by using the Cottrell equation are given in the Table 2 when $C = 1.25\text{mM}$, $A = 0.0314\text{cm}^2$ and $D = 1.57 \times 10^{-5} \text{cm}^2\text{s}^{-1}$.

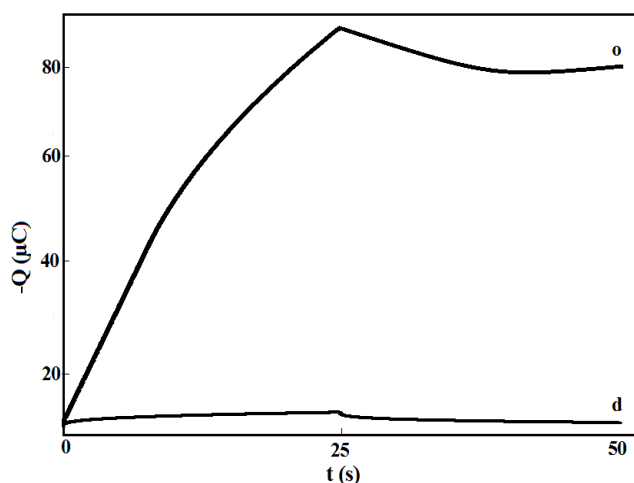


Figure-10

Chronocoulometric curves of DHAQ at METH/EDOT/GCE with (o) and without (d) oxygen

Table-2

Oxygen Reduction Potential Shift (ΔE), Diffusion coefficient (D_{Aq}), Number of electrons concerned in the reduction of anthraquinones (n_{Aq}) and number of electrons concerned in oxygen reduction (n_{O_2}) for DHAQ and 1-AMAQ at METH/EDOT/GCE (pH 7)

AQNEs	ΔE (mV)	$D_{Aq} (\text{cm}^2\text{s}^{-1}) \times 10^{-9}$	n_{Aq}	n_{O_2}
DHAQ	424.3	7.13	2.04	1.95
1-AMAQ	305.5	5.58	1.98	2.00

Conclusion

Cyclic voltammograms, Chronocoulomograms and Chronoamperograms obtained from the electroanalytical techniques were used to investigate the electrochemical and catalytic behaviour of the copolymer modified electrode along with the anthraquinones. The surface morphology of the conducting polymer modified electrode was confirmed by SEM studies. The experimental factors such as diffusion coefficient values, surface coverage and the number of electrons were investigated.

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