Journal of Advanced Chemical Sciences 2(3) (2016) 366–368

ISSN: 2394-5311

Contents List available at JACS Directory

Journal of Advanced Chemical Sciences

journal homepage: www.jacsdirectory.com/jacs

Electrochemical Behaviour of 1,4-Diaminoanthra-9,10-quinone at Conducting Polymer Based Modified Electrode

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ARTICLE DETAILS

Article history:
Received 11 August 2016
Accepted 23 August 2016
Available online 31 August 2016

Keywords:
1,4-Diaminoanthra-9,10-quinone
Voltammetry
Conducting Polymer
Modified Electrode

ABSTRACT

Conducting polymer based modified electrode was employed for this investigation. The electrochemical techniques such as cyclic voltammetry, chronoamperometry and chronocoulometry were used to study the behaviour of the electrode under the condition of deaeration in the pH range 1.0 to 13.0. The diffusion coefficient value of anthraquinone and number of electrons involved in the anthraquinone reduction were evaluated from the chronoamperometric and chronocoulometric data's.

1. Introduction

The electrochemical investigation plays an important role in fuel cells and sensors. Various electrochemical investigation of the compounds were reported previously in the literature [1-10]. Anthraquinones are the important compounds for the electroanalytical investigations [11]. Conducting polymer modified electrodes are important due to its attractive properties [12]. The electrochemical behaviour of 1,4-diamino anthra-9,10-quinone was studied at plain glassy carbon electrode (plain GCE) and GCE modified with the copolymer poly(2-hexylthiophene-co-3,4-ethylenedioxythiophene)(HEX/EDOT/GCE) using cyclic voltammetry. Also, the chronoamperometry and chronocoulometric studies were done to determine the diffusion coefficient and the number of electrons involved in the reduction processes.

2. Experimental Methods

The anthraquinone derivative, 1,4-diamino anthra-9,10-quinone (DIAMAQ) and 3,4-ethylenedioxythiophene (EDOT) were purchased from Sigma-Aldrich. Acetonitrile was used as a solvent and it was purchased from Lobochem. For this investigation, 0.01 M solutions of 1,4-diamino anthra-9,10-quinone was used. Buffer solutions were prepared using doubly distilled water. 99.99 % pure nitrogen and oxygen gases were used. A three electrode cell set up was used. Glassy carbon electrode was used to modify the electrode surface with the copolymer by means of electrodeposition using electrochemical workstation.

3. Results and Discussion

At the surface of plain and copolymer modified GCE, the voltammetric behaviour of DIAMAQ under deaerated condition was studied in the pH range 1.0 - 13.0.

3.1 Voltammetric Behaviour of 1,4-Diaminoanthra-9,10-quinone

At various scan rates such as 10, 20, 50, 100, 200, 300, 400, 500, 600 and 700 mVs^{-1} the voltammograms were recorded for 1,4-diaminoanthra-9,10-quinone at HEX/EDOT/GCE. Effect of pH and scan rate was studied at this modified electrode. A single redox couple for 1,4-diaminoanthra-9,10-quinone was obtained in the deaerated condition. At pH 7, the cyclic voltammogram of DIAMAQ at the modified electrode HEX/EDOT/GCE using the scan rate 20 mVs^{-1} is shown in the Fig. 1.

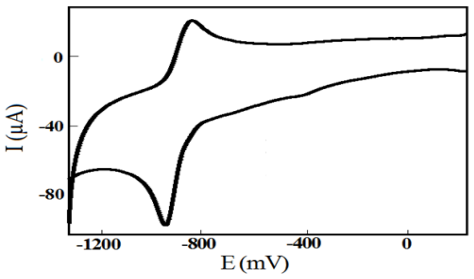

Fig. 1 Cyclic voltammogram of DIAMAQ at HEX/EDOT/GCE in pH 7 under deaeration

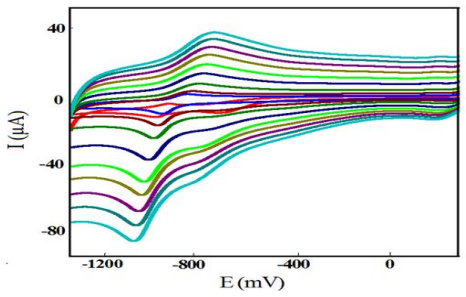

Fig. 2 Cyclic voltammograms of DIAMAQ at HEX/EDOT/GCE (pH 6) under de-aeration at scan rates 10, 20, 50, 100, 200, 300, 400, 500, 600 and 700 mVs^{-1}

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Cite this Article as: G. Amala Jothi Grace, A. Gomathi, C. Vedhi, Electrochemical behaviour of 1,4-diaminoanthra-9,10-quinone at conducting polymer based modified electrode, J. Adv. Chem. Sci. 2(3) (2016) 366–368.

Fig. 2 shows the cyclic voltammograms of DIAMAQ at HEX/EDOT/GCE (pH 6) under deaeration at scan rates from 10 to 700 mVs^{-1}. The voltammograms show an increase in peak separation with increase in scan rate which proves the quasi-reversibility of the electron transfer process. The plot of cathodic peak current (I_{PC}) versus scan rate (υ) is a straight line as illustrated in Fig. 3A and it is non-linear for the plot of cathodic peak current (I_{PC}) versus square root of scan rate ($υ^{1/2}$). Fig. 3B represents the linear changes of logarithm cathodic peak current (log I_{pc}) with logarithm of scan rate (log υ) with slope around 0.6 which confirms the adsorption controlled process.

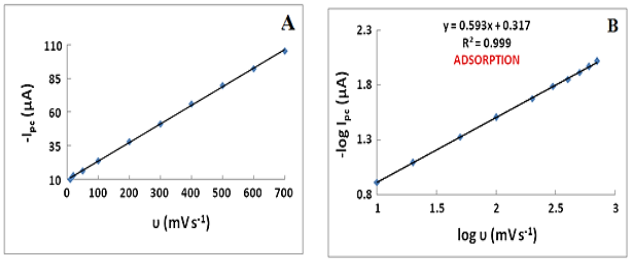

Fig. 3 (A) Plot of I_{pc} versus υ (B) Plot of log I_{pc} versus log υ of DIAMAQ at HEX/EDOT/GCE (pH 6) under de-aeration

The stability of the modified electrode was determined in the presence of DIAMAQ. The voltammograms were recorded for the copolymer modified electrode in the acidic medium and in the neutral medium containing the catalyst. There were no changes in the peak current or separation of the peak in cyclic voltammograms after 100 cycles of repetitive scanning at scan rate 20 mVs^{-1} in pH 7.0 buffer. A slight deviation is only observed for DIAMAQ at HEX/EDOT/GCE. This shows the good stability of the copolymer modified electrode.

The half peak potential versus pH was plotted for DIAMAQ at HEX/EDOT/GCE. The anodic and cathodic peak potentials shift towards more negative values, while increasing the pH of the solution.

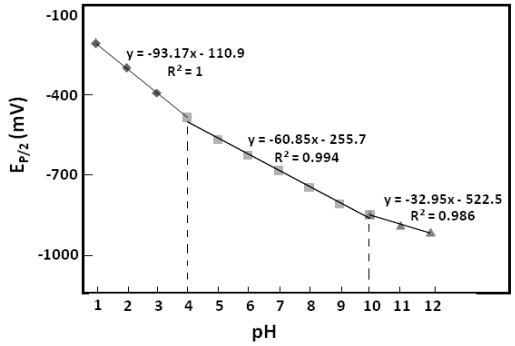

Fig. 4 pH-potential diagram for DIMAQ at HEX/EDOT/GCE

From the Fig. 4, it was clear that the reaction is a two electron, three proton process at low pH values. The anthraquinone derivatives undergo a two-electron, two proton reduction process in the intermediate pH range and at pH above 10, the electrode surface reaction is a two electron, one proton process.

The surface coverage of the DIAMQ were determined from the cyclic voltammograms at 20 mVs^{-1} scan rate using the relation $Γ_{aq}$= Q/nFA, where Q is the charge consumed, n is the number of electrons involved, F (96500 $Cmol^{-1}$) the Faraday constant and A is the geometric area (0.0314 cm^2) of glassy carbon electrode. The calculated values of DIAMAQ at plain GCE and HEX/EDOT/GCE are represented in the Table 1.

Table 1 Surface coverage ($Γ_{aq}$) value, Diffusion coefficient (D_{Aq}) and the number of electrons involved in the reduction of anthraquinone (n_{Aq}) for DIAMAQ at Plain GCE and HEX/EDOT/GCE in pH 7

Electrode	$Γ_{aq}$ mol cm^{-2} (x 10^{-8})	D_{Aq} (cm^2s^{-1}) x 10^{-9}	n_{Aq}
Plain GCE	0.65	7.24	1.70
HEX/EDOT/GCE	0.49	11.40	1.98

The surface coverage of DIAMAQ at HEX/EDOT/GCE is slightly lesser than plain GCE. The adsorption of DIAMAQ at the surface of conducting polymer modified electrode were also confirmed by SEM studies. The SEM photograph of the copolymer modified electrode HEX/EDOT/GCE in the absence of DIAMAQ is presented in the Fig. 5a and SEM image of the modified electrode HEX/EDOT/GCE with DIAMAQ is presented in the Fig. 5b which shows the strong adsorption of the compound on the copolymer modified electrode HEX/EDOT/GCE.

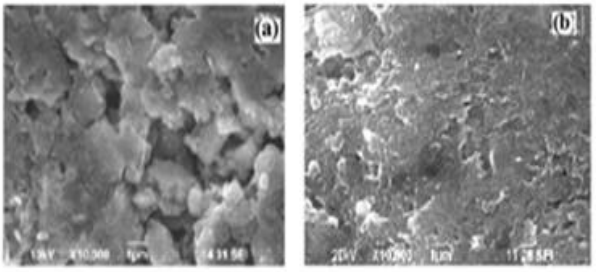

Fig. 5 SEM photographs of (a) HEX/EDOT/GCE (b) HEX/EDOT/GCE with DIAMAQ. GCE with DHAQ in pH 7

3.2 Chronoamperometric Studies of 1,4-Diaminoanthra-9,10-quinone

The chronoamperometric responses of modified GCE with DIAMAQ were examined in absence of oxygen at an initial and final potential of -200 and -900 mV. As an example, chronoamperogram of DIAMAQ at HEX/EDOT/GCE in pH 7 in absence of oxygen is reported in Fig. 6.

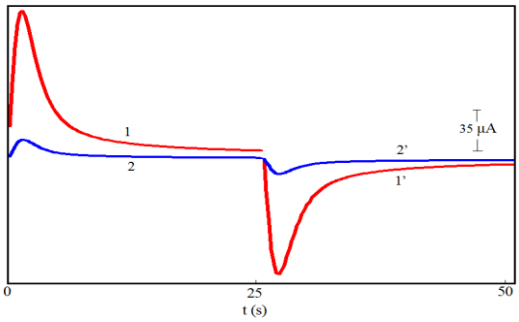

Fig. 6 Chronoamperograms for DIAMAQ at HEX/EDOT/GCE in pH 7 by double potential step technique at an initial potential of -200 mV and final potential of -900 mV vs. silver electrode. 1,1' for HEX/EDOT/GCE in DIAMAQ under deaeration, 2,2' for plain GCE

Under deaerated condition, a plot of net current against $t^{-1/2}$ shows a straight line which extrapolates close to origin. From the slope of I $Vst^{-1/2}$ under deaerated condition, the diffusion coefficient values of DIAMAQ were determined using the Cottrell equation

$$I = nFD^{1/2}AC_{aq}\pi^{-1/2}t^{-1/2}$$
$$Slope = nFD^{1/2}AC_{aq}\pi^{-1/2}$$

where C_{aq} is the concentration of DIAMAQ used, D is the diffusion co-efficient of DIAMAQ (D_{Aq}) and A is the geometric area of (0.0314 cm^2) of glassy carbon electrode. The calculated values of D_{Aq} at plain GCE and the copolymer modified GCE were given in Table 1.

3.3 Chronocoulometry of 1,4-Diaminoanthra-9,10-quinone

Double potential–step chronocoulometric studies was carried out on DIAMAQ at modified electrode in the absence of oxygen with an initial and final potential of about -200 and -900 mV versus silver electrode, respectively. For example, the chronocoulometric response of DIAMAQ at OCT/EDOT/GCE in pH 7 is represented in the Fig. 7.

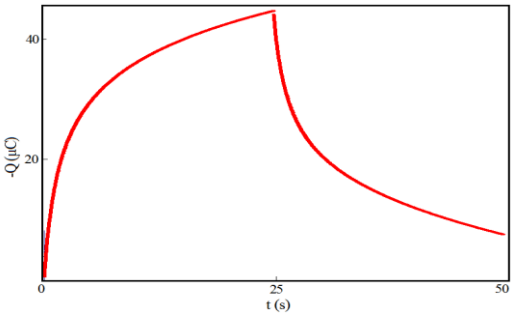

Fig. 7 Chronocoulometric curves of DIAMAQ at HEX/EDOT/GCE in pH 7 under deaeration

Under deaerated condition, the reversible peaks were observed. The number of electrons (n_{Aq}) involved in the reduction of DIAMAQ at the optimum pH was calculated from the slope of Q versus $t^{1/2}$ under deaeration condition using the Cottrell equation,

$$Q = 2n\,FACD^{1/2}\,\pi^{-1/2}\,t^{1/2}$$

By employing the diffusion coefficient values of anthraquinones from chronoamperometric data. When C = 1.25 mM, A = 0.0314 cm^2 and D = 1.57 x 10^{-5} cm^2s^{-1}. The value of n_{Aq} is 1.98.

4. Conclusion

Copolymer modified electrode poly(2-hexylthiophene-co-3,4-ethylenedioxythiophene) have been used in the presence of 1,4-diamino anthra-9,10-quinone to study the electrochemical behaviour. The techniques such as cyclic voltammetry, chronocoulometry and chronoamperometry techniques were employed for this investigation. SEM images show the good adsorption of the modified electrode. The diffusion coefficient, surface coverage and the number of electrons involved were determined for the combination of this copolymer modified electrode with DIAMAQ.

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