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Reduction of Oxygen at the Surface of Copolymer Modified Glassy Carbon Electrode with 1,8-Dihydroxy Anthra-9,10-Quinone

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Abstract

1,8-Dihydroxy anthra-9,10-quinone combined with the copolymer poly(2-octylthiophene-co-3,4- ethylenedioxythiophene) was used to study the oxygen reduction reaction. The electrochemical characterisation of poly(2-octylthiophene-co-3,4-ethylenedioxythiophene) modified glassy carbon electrode with 1,8-Dihydroxy anthra-9,10-quinone were investigated. The stability of the poly(2-octylthiophene-co-3,4-ethylenedioxythiophene) was studied. The diffusion coefficient values of anthraquinone at the copolymer modified electrode, influence of pH on the electrochemical behaviour and the number of electrons involved in anthraquinone reduction were evaluated by chronoamperometric and chronocoulometric techniques. 1,8-Dihydroxy anthra-9,10-quinone combined with the conducting copolymer poly(2-octylthiophene-co-3,4-ethylenedioxythiophene) showed excellent electrocatalytic ability for the reduction of oxygen. Scanning electron microscopy images were included to show the excellent modification of the modified electrodes.

Keywords: Copolymer, modified electrode, 1,8-Dihydroxy anthra-9,10-quinone, Oxygen reduction.

Introduction:

Various researches were carried out on the modified electrodes. The modified electrodes play an important role in the fuel cells and sensors. For the electrochemical devices, oxygen reduction is an important reaction. Anthraquinones are the important compounds in industry and medicines [1-3]. A large variety of compounds such as quinones [4-10] manganese oxide [11], copper [12], ruthenium-iron cluster [13], nano tube [14], metal pthalocyanine [15], metal macrocyclic complexes [16] , titanium silicates [17], Au nanoparticle [18], pyrimidine bases [19], napthoquinone [20], anthraquinone derivatives [21-23] carbon paste electrodes [24], clay modified glassy carbon electrode [25] and polypyrrole [26] have been reported as electrocatalyst for the reduction of oxygen. In the present investigation, the electrochemical behaviour of 1,8-Dihydroxy anthra-9,10-quinone at poly(2- octylthiophene-co-3,4-ethylenedioxythiophene) modified glassy carbon electrode, the stability and efficiency of such combination for the electro catalysis of oxygen reduction were examined by cyclic voltammetry, chronoamperometry and chronocoulometric techniques.

Experimental

The chemicals such as 1,8-Dihydroxy anthra-9,10-quinone (DHAQ), 3,4-Ethylenedioxythiophene (EDOT) and 2-Octylthiophene (OCT) were purchased from Sigma-Aldrich. HPLC grade Acetonitrile

from Lobochem was used as solvent. The various buffer solutions from 1 to 13 were prepared. Hanna pH meter was used to measure pH of the solution. 50% aqueous acetonitrile pH solutions were used as electrolyte along with DHAQ. During the experiments, Nitrogen and Oxygen gases with 99.99% purity were used. A three electrode cell consisting of glassy carbon as working electrode, a platinum wire as counter electrode and silver electrode as reference electrode was kept in the solution containing DHAQ.
The copolymer modified glassy carbon electrode was prepared by electrodeposition. Various techniques such as Cyclic Voltammetry, Chronoamperometry and Chronocoulometry were employed using CH Instrument Electrochemical workstation.

Results and Discussion

Glassy carbon electrode was modified with the copolymer by means of electrodeposition and the voltammetric studies of DHAQ at the modified electrode was performed under deaerated and oxygen saturated conditions in the pH range 1.0 - 13.0.

Electrochemical Behaviours of DHAQ at OCT/EDOT/GCE

For the copolymer modified electrode, cyclic Voltammograms of DHAQ display a single redox couple in the deaerated condition. These voltammograms at various scan rates were recorded to determine the influence of scan rate with cathodic peak current. The cyclic voltammetric response of DHAQ at the modified electrode OCT/EDOT/GCE in pH 7 at scan rates 10, 20, 50, 100, 200, 300, 400, 500, 600 and 700 mVs^{-1} was represented in the Figure 1 and the inset shows the log I_{pc} versus log υ. The plot of cathodic peak current (I_{pc}) versus the square root of scan rate (√υ) is a straight line. Also, the plot of log I_{pc} versus log υ is a straight line with a slope less than 0.5 which predicts the diffusion controlled process.

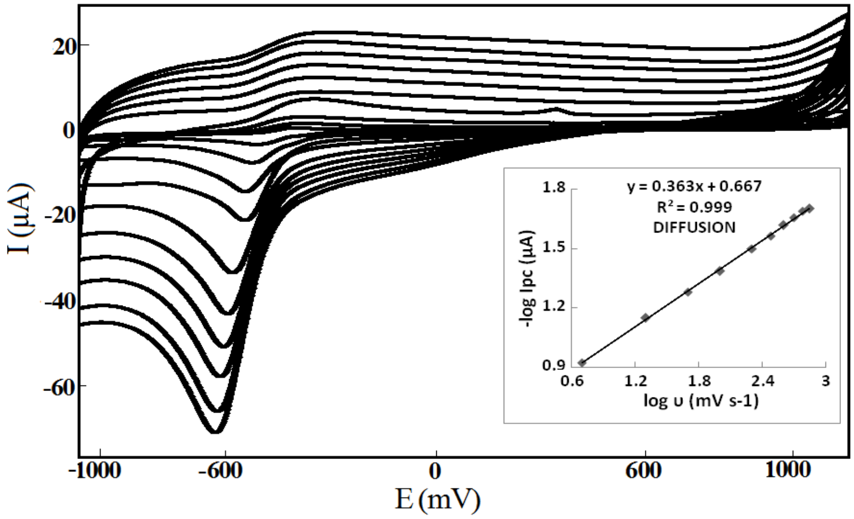

Fig.1 Cyclic voltammograms of DHAQ at OCT/EDOT/GCE (pH 7) under de-aeration at scan rates 10, 20, 50, 100, 200, 300, 400, 500, 600 and 700 mVs^{-1} and the inset shows the log I_{pc} versus log υ

Effect of pH under deaeration

Three distinct linear portions with different slope values were observed indicating the different forms of anthraquinone. The pH-potential diagram for DHAQ at OCT/EDOT/GCE was given in the figure 2 At low pH values, the reaction is a two electron, three proton process involving the formation of protonated hydroquinones. In the intermediate pH range, the anthraquinone derivatives undergo a two-electron, two proton process, producing the corresponding hydroquinones. At pH above 10, the electrode surface reaction is a two electron one proton process, which leads to the formation of a semi-hhydroquinone anion.

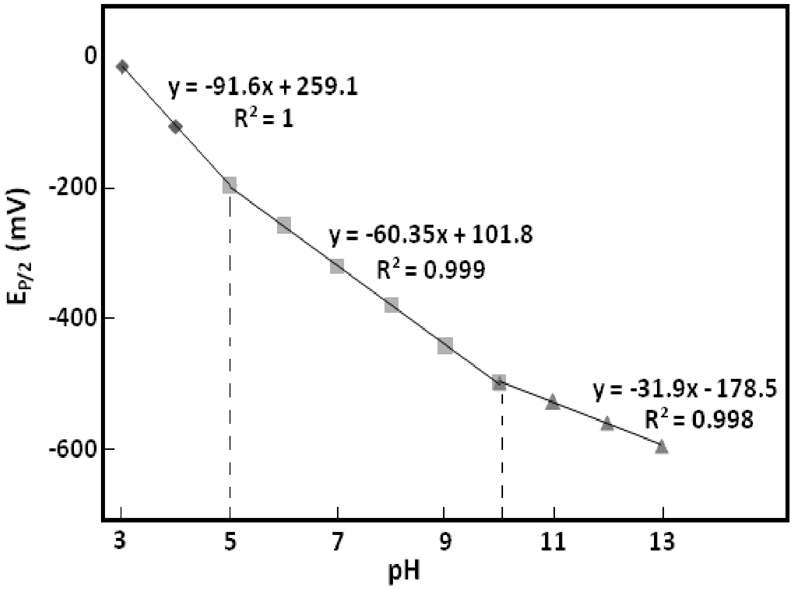

Fig. 2 pH-potential diagram for DHAQ at OCT/EDOT/GCE

Stability of the modified electrodes

The glassy carbon electrode modified with copolymer was examined for its stability. The stability of the copolymer modified electrode and the reproducibility of its electrochemical behaviour was determined using cyclic voltammetry. The modified electrodes were immersed in acidic medium with DHAQ for 40 h and in neutral medium containing DHAQ for 30 h. After such scanning, the voltammograms were also recorded under deaerated conditions. The results show no changes in the peak current or separation of the peak which confirms the stability of the copolymer modified electrode.

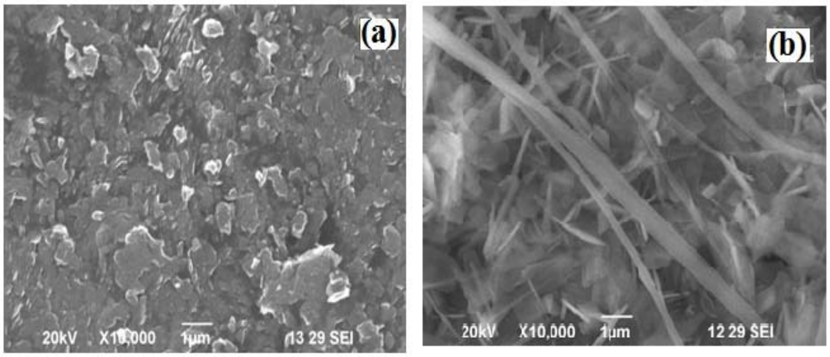

Fig. 3 SEM photographs of (a) OCT/EDOT/GCE (b) OCT/EDOT/GCE with DHAQ

Surface coverage of the modified electrode

The surface coverage of the copolymer modified electrode along with the catalyst was evaluated 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 C mol^{-1}) the Faraday constant and A is the geometric area of (0.0314 cm^2) glassy carbon electrode. The surface coverage value of DHAQ at copolymer modified electrode was 0.46 x 10^{-8} mol cm^{-2}. Also, the adsorption of DHAQ at the surface of conducting polymer modified electrode was also confirmed by SEM studies. Figure 3 shows the scanning electron microscopy images of OCT/EDOT/GCE (a) and OCT/EDOT/GCE with DHAQ (b).

Catalytic reduction of oxygen at OCT/EDOT/GCE

Effect of pH under aeration

The catalytic effect of DHAQ in different pH media at OCT/EDOT/GCE was studied. Cyclic voltammograms of DHAQ at OCT/EDOT/GCE in the presence and absence of oxygen at pH 7.0 are shown in the Figure 4. Under aeration, the enhancement of cathodic current followed by the disappearance of anodic peak prove the irreversible electrocatalytic oxygen reduction process at the copolymer modified electrode were investigated.

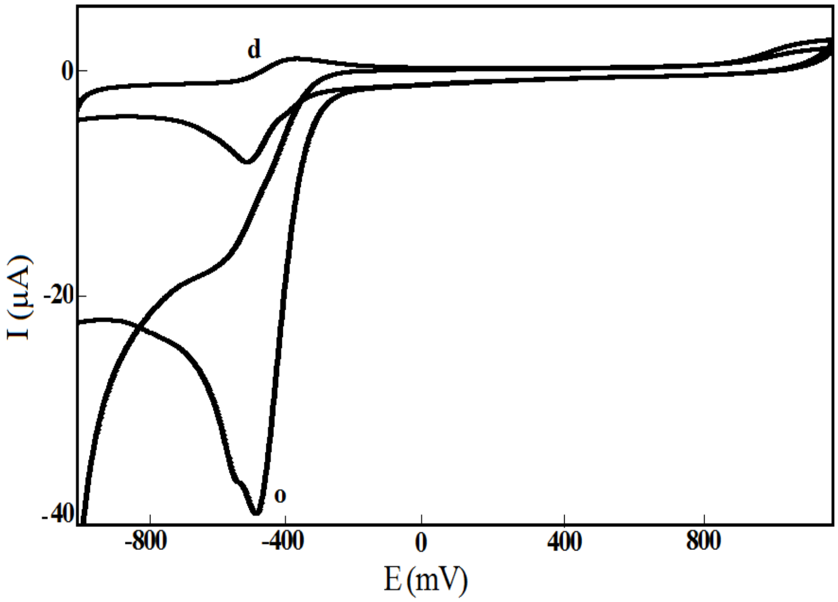

Fig. 4 Cyclic voltammograms of DHAQ at OCT/EDOT/GCE in the presence (o) and absence (d) of oxygen at pH 7.

As the pH increases, the cathodic peak current increases up to pH 7. Figure 5 shows the variation of cathodic peak current versus pH for OCT/EDOT/GCE with DHAQ under aeration. Since oxygen reduces at –1027.5mV on a plain GCE, the reduction occurred at -501.9 mV on OCT/EDOT/GCE in presence of DHAQ. Thus, the modified electrode with DHAQ causes the shift in oxygen reduction potential (ΔE) of about 525.6 mV in pH 7.

Effect of scan rate under aeration

Under aeration, the reduction of oxygen is a diffusion controlled process. The linear variation of cathodic peak current (I_{pc}) with square root of scan rate ($\upsilon^{1/2}$) was obtained for the copolymer modified electrode in presence of DHAQ as shown in Figure 7A which clearly confirms the diffusion controlled process for oxygen reduction. Figure 6 shows the variation of shift in oxygen reduction potential with pH for OCT/EDOT/GCE in presence of DHAQ.

Also, Figure 7B shows the plot of logarithmic cathodic peak current versus logarithm of scan rate for oxygen reduction at OCT/EDOT/GCE in presence of DHAQ at pH 7 with slope less than 0.5 confirms the diffusion controlled oxygen reduction process.

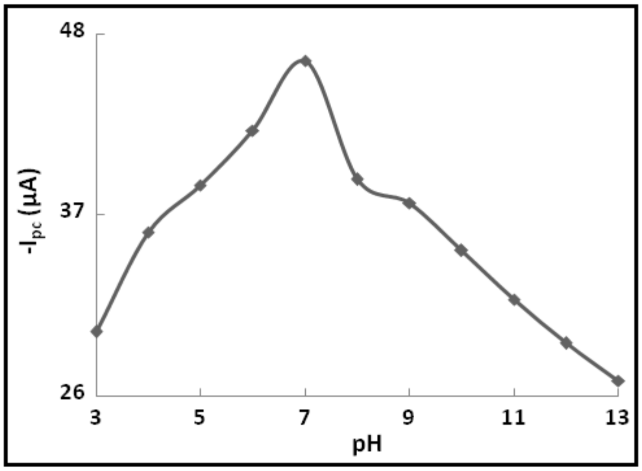

Fig. 5 Plot of pH versus cathodic peak current (I_{PC}) for DHAQ at OCT/EDOT/GCE under aeration

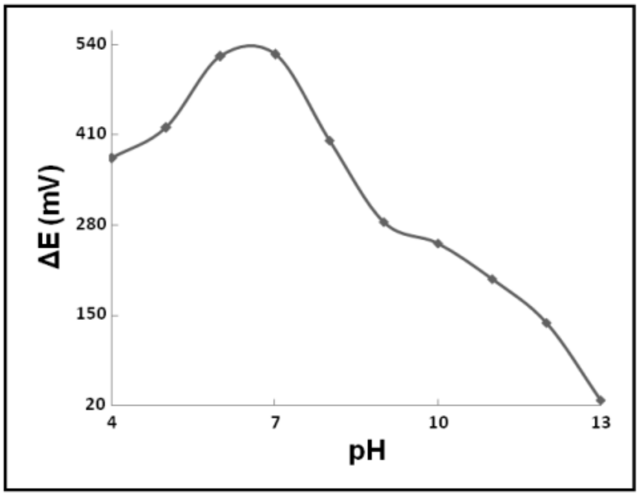

Fig. 6 Plot of pH versus shift in oxygen reduction potential at OCT/EDOT/GCE with DHAQ

Chronoamperometric studies

The chronoamperometric response of copolymer modified GCE (OCT/EDOT/GCE) in DHAQ was studied in the presence and absence of oxygen, by applying double potential step at an initial and final potential of -400 and -1000 mV.

As an example, chronoamperogram of OCT/EDOT/GCE in DHAQ at pH 7 under aerated and de-aerated conditions were reported in figure 8. The net electrolysis current I_{net} was determined by point to point subtraction of the background current in the presence and absence of oxygen. Under de-aerated condition a plot of net current against $t^{-1/2}$ shows a straight line which extrapolates close to origin. From the slope of I Vs $t^{-1/2}$ under de-aerated condition, the diffusion coefficient values of anthraquinones were determined using the Cottrell equation

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

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

Where C_{aq} is the concentration of DHAQ, D is the diffusion co-efficient of DHAQ and A is the geometric area of (0.0314 cm^2) the glassy carbon electrode. The calculated Diffusion coefficient (D_{Aq}) value of DHAQ was 9.37 x 10^{-9} cm^2 sec^{-1}.

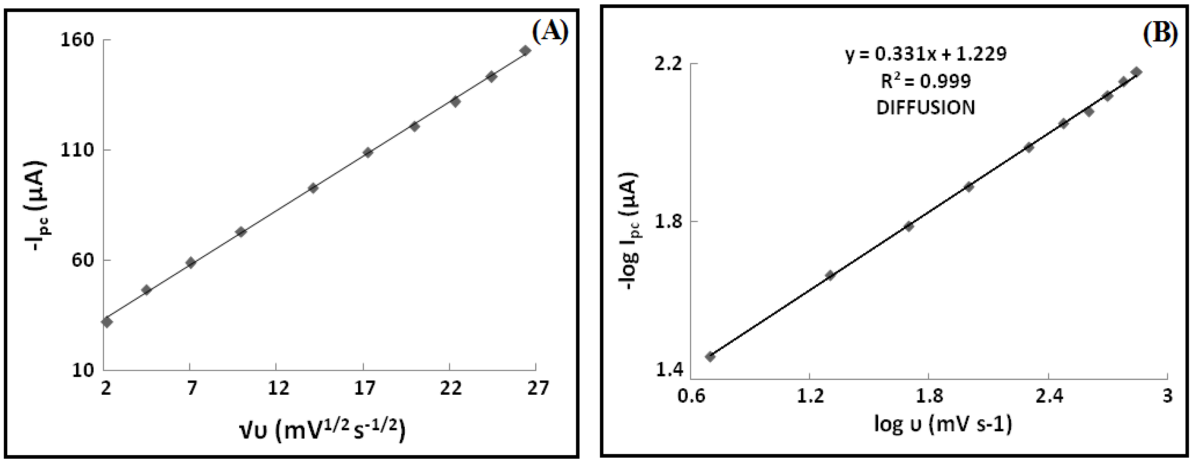

Fig.7 Plots (A) I_{pc} versus √υ (B) log I_{pc} versus log υ for DHAQ at OCT/EDOT/GCE in pH 7.0

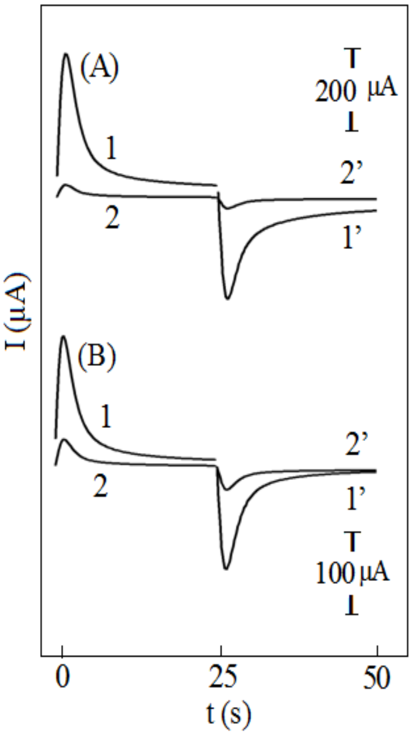

Fig. 8 Chronoamperograms for DHAQ at OCT/EDOT/GCE in pH 7 by double potential step technique at an initial potential of -400mV and final potential of -1000mV vs silver electrode. (A) 1,1' for OCT/EDOT/GCE in presence of DHAQ under aeration, 2,2' for plain GCE in the absence of DHAQ. (B) 1,1' for OCT/EDOT/GCE in presence of DHAQ under deaeration, 2,2' for plain GCE in the absence of DHAQ.

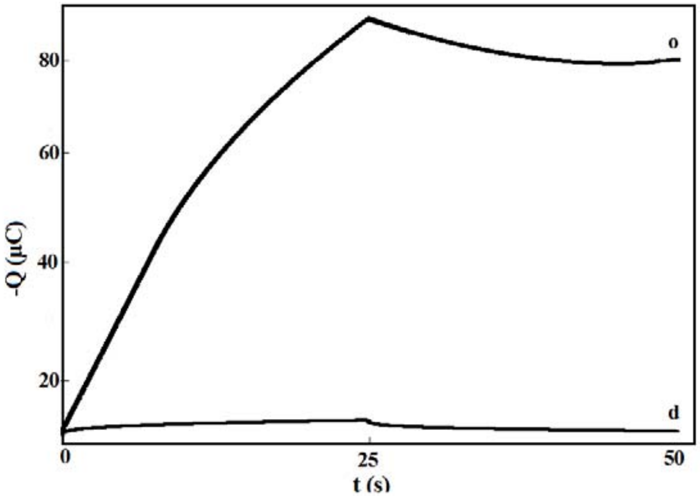

Fig. 9 Chronocoulometric curves of DHAQ at OCT/EDOT/GCE
in the presence (o) and absence (d) of oxygen.

Chronocoulometry

Chronocoulometric studies were performed with anthraquinones at copolymer modified electrode OCT/EDOT/GCE in the presence and absence of oxygen with an initial and final potential of about -400 and -1000mV versus silver electrode, respectively. An example of chronocoulomogram for DHAQ at OCT/EDOT/GCE in the presence and absence of oxygen at pH 7 is represented in the figure 9.

Under deaerated condition, reversible curve was observed when the potential was reversed. But under aeration, a large enhancement in the charge and nearly flat on reversal of potential prove the irreversible electrocatalytic reduction of oxygen. The number of electrons (n_{O2}) involved in the reduction of anthraquinones 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 chronoamperometic data's.

The number of electrons involved in the oxygen reduction was also calculated from the slope of Q vs $t^{1/2}$ under aerated condition.when C = 1.25 mM, A = 0.0314 cm^2 and D = 1.57×10^{-5} cm^2s^{-1}. The number of electrons involved in the reduction of DHAQ (n_{Aq}) and number of electrons involved in oxygen reduction (n_{O2}) were 2.05 and 2.14 respectively

Conclusion

Modified electrodes show excellent results for the oxygen reduction process. Various techniques such as Cyclic voltammetry, chronocoulometry and chronoamperometry were employed to investigate the electrochemical and catalytic behaviour of the copolymer modified electrode in the presence of 1,8-Dihydroxy anthra-9,10-quinone at the optimum pH 7.0. The scanning electron microscopy images show the good adsorption of 1,8-Dihydroxy anthra-9,10-quinone at the surface of conducting polymer modified electrode.The diffusion coefficient values, surface coverage and the number of electrons were investigated. The results of the modified electrode clearly suggests this electrode can be used for sensors.

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