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Catalytic Oxygen Reduction at Poly(3-Methylthiophene-Co-3,4-Ethylenedioxythiophene) Modified Electrode with 1,4-Diamino Anthra-9,10-Quinone

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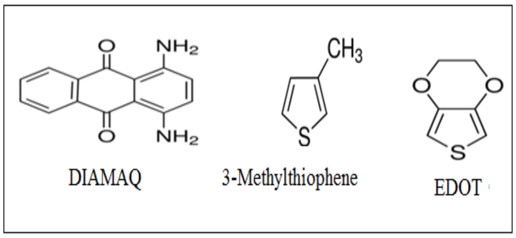
ABSTRACT

The electrocatalytic behaviour of 1,4-Diamino anthra-9,10-quinone at poly(3-methylthiophene-co-3,4-ethylenedioxythiophene) towards oxygen reduction were investigated in the pH range 1.0 – 13.0 using cyclic voltammetric, chronoamperometric and chrononcoulometric techniques. The stability and electrochemical behaviour of the copolymer modified electrode was studied and pH 7.0 was chosen as the optimum working pH by comparing the shift in oxygen reduction potential. The surface morphology of the modified electrode was also characterized by scanning electron microscope. The diffusion coefficient, surface coverage values and the number of electrons involved were determined.

1. Introduction

Fuel cells will play a major role in the future energy system. Dioxygen reduction in energy conversion system is a key component for fuel cells and sensors. The development of these technologies has been a considerable interest and it led to find new catalysts and modified electrodes [1-7]. For the reduction of dioxygen, electrocatalysts such as copper [8], manganese oxide [9], ruthenium-iron cluster [10], titanium silicates [11], Au nanoparticle [12], metal complexes [13-17], metal pthalocyanine [18], cobalt porphyrin [19], metal macrocyclic complexes [20], pyrimidine base [21], napthoquinone [22,23] clay-modified electrodes [24], riboflavin modified electrodes [25], polypyrrole modified electrodes [26] and anthraquinone [27-29] derivatives have been reported earlier.

In this article, we discuss the electrochemical behaviour, efficiency and stability of poly(3-methylthiophene-co-3,4-ethylenedioxythiophene) modified electrode with 1,4-Diamino anthra-9,10-quinone towards oxygen reduction using cyclic voltammetry, chronoamperometry and chronocoulometric techniques.



Scheme 1 Structure of DIAMAQ and the monomers used

2. Experimental Methods

1,4-Diamino anthra-9,10-quinone (DIAMAQ), 3,4-Ethylenedioxythiophene (EDOT) and 3-Methylthiophene (METH) were purchased from Sigma-Aldrich. HPLC grade Acetonitrile from Lobochem was used and doubly distilled water was used throughout the experiments. The different range of pH (1.0–13.0) solutions were prepared and it was checked using a Hanna pH- meter. 0.01 M solution of 1,4-Diamino anthra-9,10-quinone was prepared in acetonitrile. Nitrogen and oxygen gases with 99.99% purity were used during the experiments. A three electrode cell consisting of modified glassy carbon as working electrode (GCE), a platinum wire as counter electrode and silver electrode as reference electrode was used for this investigation. The modified glassy carbon electrode poly(3-methylthiophene-co-3,4-ethylenedioxy thiophene) [METH/EDOT/GCE] was prepared by electrodeposition.

Cyclic voltammetry, chronoamperometry and chronocoulometry were carried out at room temperature on a CH Instrument Electrochemical workstation. The experiments were carried out on a cell containing 20 mL aqueous pH solution and 0.5 mL of 0.01 M DIAMAQ solution. The solution was deaerated by purging N_2 gas for 20 minutes. The same experiments were repeated by purging O_2 gas for 10 minutes.

3. Results and Discussion

Glassy carbon electrode was modified with the copolymer and the voltammetric studies of DIAMAQ at the modified electrode was performed under deaerated and oxygen saturated conditions at various pH medium in the range 1.0 - 13.0.

3.1 Electrochemical Behaviours of DIAMAQ at METH/EDOT/GCE

Voltammograms of DIAMAQ at the glassy carbon electrode modified with copolymer exhibited a single redox couple in the deaerated condition. These voltammograms 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. The cyclic voltammetric response of DIAMAQ at the modified electrode METH/EDOT/GCE in pH 6 was presented in the Fig. 1.

Fig. 2 shows the linear variation of cathodic peak current (I_{pc}) with scan rate (υ). The plot of log I_{pc} versus log υ is a straight line with slope value > 0.5 which predicts the adsorption controlled process as shown in the Fig. 3.

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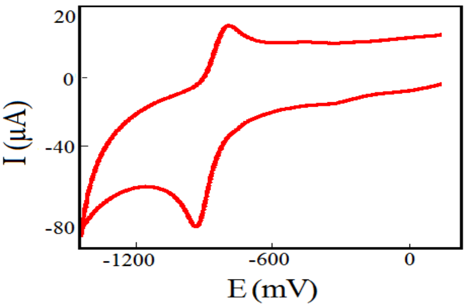

Fig. 1 Cyclic voltammogram of DIAMAQ at METH/EDOT/GCE in pH 6 under deaeration

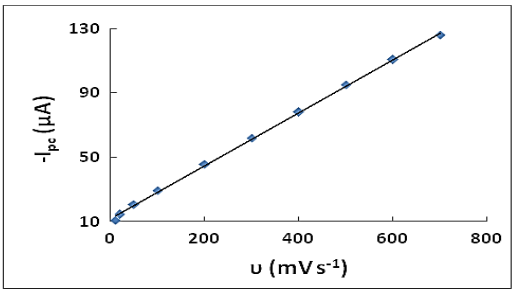

Fig. 2 Plot of cathodic peak current (I_{pc}) vs scan rate (υ) for DIAMAQ at METH/EDOT/GCE in pH 6 under deaeration

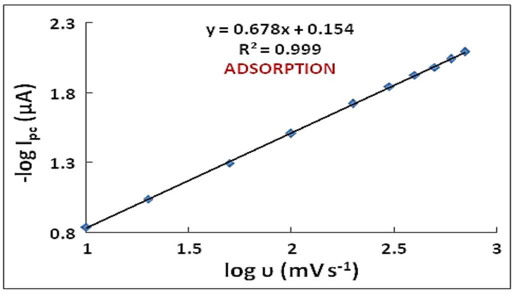

Fig. 3 Plot of logarithmic cathodic peak current (log I_{pc}) vs logarithmic scan rate (log υ) for DIAMAQ at METH/EDOT/GCE in pH 6 under deaeration

3.1.1 Effect of pH

The reduction peak potentials shift cathodically toward more negative values with increase in pH of the solution. Three distinct linear portions with different slope values were observed. For example, pH-potential diagram for DIAMAQ at METH/EDOT/GCE was given in the Fig. 4.

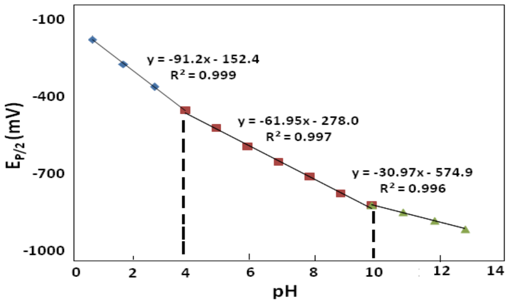

Fig. 4 pH-potential diagram for DIAMAQ at METH/EDOT/GCE

DIAMAQ undergoes two-electron three-proton reduction process involving the formation of protonated hydroquinones at low pH (1 to 4) values. In the intermediate pH range, the compound undergoes two-electron, two proton process to produce the hydroquinone. At pH above 10, the electrode surface reaction is a two electron, one proton process which leads to the formation of a hydroquinone anion.

3.1.2 Stability of the Modified Electrodes

The stability of the modified electrode and the reproducibility of its electrochemical behaviour were investigated by immersing it in acidic medium (pH 1.0) with DIAMAQ for 40 h and in neutral medium (pH 7.0) containing DIAMAQ for 30 h and then cyclic voltammograms were recorded. In both media, there was a slight decrease in the corresponding voltammograms (<4%). In addition, 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.

3.1.3 Surface Coverage

The surface coverage of DIAMAQ was 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 of (0.0314 cm^2) glassy carbon electrode. The surface coverage value of DIAMAQ at copolymer modified electrode was 2.1 x 10^{-9} molcm^{-2}. Also, the adsorption of DIAMAQ at the surface of conducting polymer modified electrode was also confirmed by SEM studies. Fig. 5 shows the scanning electron microscopy images of METH/EDOT/GCE (a) and METH/EDOT/GCE with DIAMAQ (b).

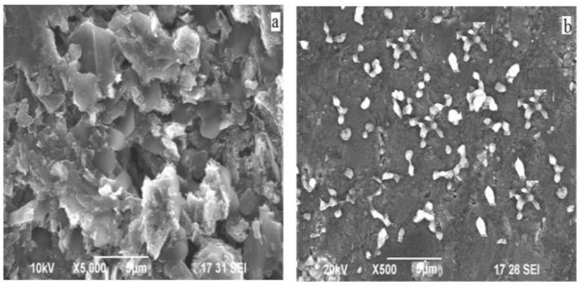

Fig. 5 SEM photographs of (a) METH/EDOT/GCE (b) METH/EDOT/GCE with DIAMAQ

3.2 Catalytic Reduction of Oxygen at METH/EDOT/GCE

3.2.1 Effect of pH

Oxygen reduction was studied at METH/EDOT/GCE with DIAMAQ in different pH media from pH 1 to 13. Due to their different kinetic behaviour, the displacement may be unequal. The optimum pH was found to be 7 where the electrode's anodic wave completely disappeared and cathodic wave reached its maximum current with the maximum shift in oxygen reduction potential (ΔE). Fig. 6 shows the variation of shift in oxygen reduction potential with pH for METH/EDOT/GCE in presence of DIAMAQ which clearly indicates that the maximum shift is observed at pH 7.

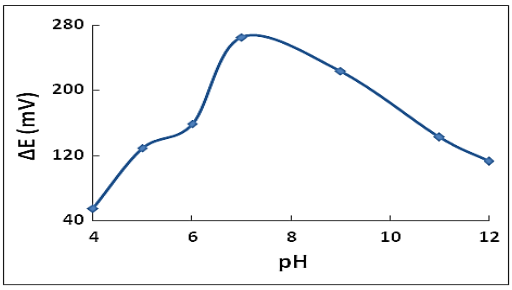

Fig. 6 Plot of pH versus shift in O_2 reduction potential at METH/EDOT/GCE with DIAMAQ

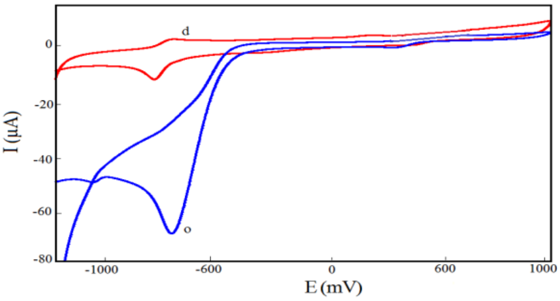

Fig. 7 Cyclic voltammograms of DIAMAQ at METH/EDOT/GCE in the presence (o) and absence (d) of oxygen at pH 7

Cyclic voltammograms of DIAMAQ at METH/EDOT/GCE in the presence and absence of oxygen at pH 7.0 are shown in the Fig. 7. Oxygen reduction at plain GCE occurs irreversibly with a peak potential of about –1027.5 mV at pH 7. Fig. 7 shows that there is a large enhancement in the cathodic peak current for DIAMAQ at the copolymer modified electrode in the presence of O_2, while the corresponding anodic peak has disappeared suggesting the electrocatalytic reduction of oxygen. The reduction of oxygen occurred at

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-761.9 mV on METH/EDOT/GCE in presence of DIAMAQ. Thus, the modified electrode with DIAMAQ causes the shift in oxygen reduction potential (ΔE) 265.6 mV in pH 7.

3.2.2 Effect of Scan Rate

Under oxygen-saturated conditions, the variation of cathodic peak current with scan rate was examined for the copolymer modified electrode in presence of DIAMAQ. The cathodic peak current (I_{pc}) is linearly proportional to square root of scan rate $\upsilon^{1/2}$ which clearly confirms the diffusion controlled process for oxygen reduction. Further, the linear variation of logarithmic cathodic peak with logarithm of scan rate with slope less value 0.3 confirms the diffusion controlled oxygen reduction process. Fig. 8 shows the plot of logarithmic cathodic peak current versus logarithm of scan rate for oxygen reduction at METH/EDOT/GCE in presence of DIAMAQ at pH 7.

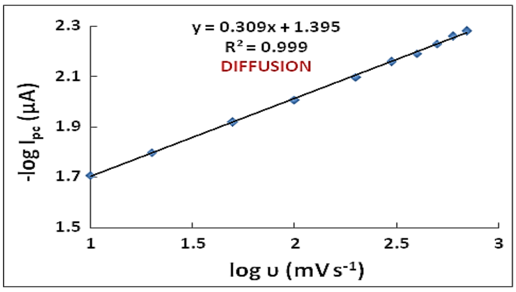

Fig. 8 The plot of logarithmic cathodic peak current versus logarithm of scan rate for oxygen reduction at METH/EDOT/GCE in presence of DIAMAQ at pH 7

3.3 Chronoamperometric Studies

By applying double potential step at an initial and final potential of -400 and -1000 mV, the chronoamperograms were performed to study the chronoamperometric responses of plain GCE and copolymer modified GCE in the presence and absence of O_2 at the optimum pH 7. For instance, chronoamperogram of DIAMAQ at plain GCE and METH/EDOT/GCE in pH 7 in the presence and absence of oxygen was shown in Fig. 9. The net electrolysis current I_{net} was obtained by point to point subtraction of the background current in the presence and absence of oxygen. Under deaeration, 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 deaeration, the diffusion coefficient values of anthraquinones used 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 DIAMAQ, D is the diffusion co-efficient of DIAMAQ and A is the geometric area of (0.0314 cm^2) the glassy carbon electrode. The calculated Diffusion coefficient (D_{Aq}) value of DIAMAQ was 4.08 x 10^{-8} cm^{2}sec^{-1}.

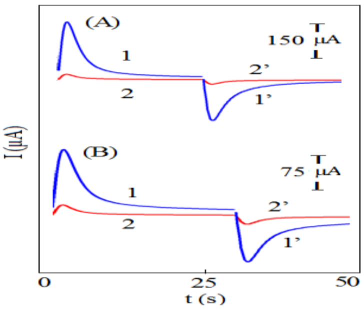

Fig. 9 Chronoamperograms for DIAMAQ at METH/EDOT/GCE in pH 7 by double potential step technique at an initial potential of -400 mV and final potential of -1000 mV vs silver electrode. (A) 1,1' for METH/EDOT/GCE with DIAMAQ under aeration, 2,2' for plain GCE. (B) 1,1' for METH/EDOT/GCE with DIAMAQ under deaeration, 2,2' for plain GCE

3.4 Chronocoulometry

Double potential-step chronocoulometric studies were performed with DIAMAQ at plain GCE and modified electrode in the presence and absence of oxygen. The behaviour was observed with an initial and final potential of about -400 and -1000 mV versus silver electrode, respectively. An example, the chronocoulometric response of DIAMAQ at METH/EDOT/GCE in pH 7 is represented in the Fig. 10. Under deaerated condition, the reversible peaks were observed. Under oxygen saturated conditions, a large enhancement in the charge of forward peak and nearly a flat line observed when the potential is reversed prove the irreversible electrocatalytic reduction of oxygen. The number of electrons (n) 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 value of DIAMAQ obtained from chronoamperometric results. The number of electrons involved in the oxygen reduction at the modified electrode was calculated when C = 1.25 mM, A = 0.0314 cm^2 and D =1.57 x 10^{-5} cm^{2}s^{-1}. The number of electrons involved in the reduction of DIAMAQ (n_{Aq}) and number of electrons involved in oxygen reduction (n_{O2}) were 1.88 and 2.0 respectively.

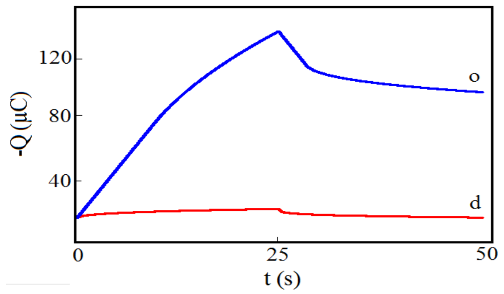

Fig. 10 Chronocoulometric curves of DIAMAQ at METH/EDOT/GCE in pH 7 under deaeration (d) and aeration (o)

4. Conclusion

Cyclic voltammetry, chronocoulometry and chronoamperometry techniques were employed to investigate the electrochemical and catalytic behaviour of the copolymer modified electrode in the presence of 1,4-Diamino anthra-9,10-quinone at the optimum pH 7.0. The diffusion coefficient values, surface coverage and the number of electrons involved were investigated. The adsorption of DIAMAQ at the surface of conducting polymer modified electrode was also confirmed by SEM studies.

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