LIST OF PUBLICATIONS

JOURNALS: Articles published- 2


- Electrochemical Behaviour of 1,4-Diaminoanthra-9,10-quinone at Conducting Polymer Based Modified Electrode, *Journal of Advanced Chemical Sciences*, 2 (3) (2016) 366 – 368, ISSN:2394-5311.

Articles accepted-3

- Catalytic Oxygen Reduction at poly(3-methylthiophene-co-3,4-ethylenedioxythiophene) modified electrode with 1,4-Diamino anthra-9,10-quinone in *Journal of Nano Science and Technology*.


Conferences presented -5

Electrocatalysis of oxygen reduction at poly(aniline-co-3,4-ethylene dioxythiophene) modified electrode in anthraquinone solutions, Alagappa University, March 2015.

Electrocatalytic oxygen reduction at poly (3,4-ethylenedioxythiophene) modified Glassy carbon electrode with 9,10-Anthraquinones, Sara Tucker College, Tirunelveli, 5th January 2016.

Catalytic Oxygen Reduction at poly (3-methylthiophene-co-3,4-ethylenedioxythiophene) modified electrode with 1,4-Diamino anthra-9,10-quinone, V.O. Chidambaram college, 21st & 22nd January 2016.

Electrocatalytic Reduction of Oxygen at the surface of poly (3-methylthiophene-co-3,4-ethylenedioxythiophene) modified electrode with 1,8-Dihydroxy anthra-9,10-quinone, Alagappa University, 21st to 23rd March 2016.
OXYGEN REDUCTION AT THE SURFACE OF POLY (3-METHYLTHIOPHENE-CO-3,4-ETHYLENEDIOXYTHIOPHENE) MODIFIED GLASSY CARBON ELECTRODE WITH 2-AMINO ANTHRA-9,10-QUINONE

*1,2Amala Jothi Grace, G., 3Gomathi, A. and 4Vedhi, C.

1Department of Chemistry, Chandy College of Engineering, Thoothukudi
2Research Scholar, Manonmaniam Sundaranar University, Tirunelveli
3Department of Chemistry, Sri K.G.S Arts and Science College, Srivaikuntam
4Department of Chemistry, V.O.Chidambaram College, Thoothukudi

INTRODUCTION

Oxygen reduction is an important reaction in the electrochemical devices. The modified electrodes play an important role in the fuel cells and sensors. A large range of compounds such as manganese oxide (Mao, 2003), copper (Vukmirovic et al., 2003), ruthenium-iron cluster (Gonzalez-Cruz, 2003), metal phthalocyanine (Ramirez, 2002), metal macrocyclic complexes (Lin, 2003), titanium silicates (Chitra, 2003), Au nanoparticle (Zhang, 2003) pyrimidine bases (Peressini, 2002), napthoquinone (Manisankar, 2004 and Golabi, 1996) anthraquinone derivatives (Sarapuu et al., 2003; Tammeveski, 2001 Salimi et al, 1999; Salimi, 1999 and Manisankar, 2005), carbon paste electrodes (Manisankar, 2005), clay modified glassy carbon electrode (Manisankar, 2005) and polypyrrole (Manisankar, 2005) have been reported as electrocatalyst for the reduction of dioxygen. In the present investigation, the electrochemical behaviour of 2-Amino antra-9, 10-quinone at poly (3-methylthiophene-co-3, 4-ethylenedioxythiophene) modified glassy carbon electrode, the nature of electrode stability and electrode efficiency of such combination for the electrocatalysis of oxygen reduction were examined by cyclic voltammetry, chronocoulometry and chronocoulometric techniques.

Experimental

2- Amino antra-9, 10-quinone (2-AMAO), 3,4-Ethylenedioxythiophene (EDOT) and 3-Methylthiophene were purchased from Sigma-Aldrich. HPLC grade Acetonitrile from Lobochem was used. pH solutions from 1 to 13 were prepared using the chemicals of highest purity from Merck. The pH of the solution was measured using a Hanna pH- meter. 50% aqueous acetonitrile pH solutions were used as electrolyte along with 2-AMAO. During the experiments, Nitrogen and

---

*Corresponding author: 1,2Amala Jothi Grace, G.

1Department of Chemistry, Chandy College of Engineering, Thootukudi
2Research Scholar, Manonmaniam Sundaranar University, Tirunelveli

The preparation and electrochemical characterisation of poly (3-methylthiophene-co-3,4-ethylenedioxythiophene) modified glassy carbon electrode with 2-Amino antra-9,10-quinone were investigated. The influence of pH on the electrochemical behaviour and stability of the poly(3-methylthiophene-co-3,4-ethylenedioxythiophene) was studied. The diffusion coefficient values of anthraquinones at the copolymer modified electrode and the number of electrons involved in anthraquinone reduction were evaluated by chronocoulometric and chronocoulometric techniques. 2-Amino antra-9, 10-quinone combined with the copolymer poly (3-methylthiophene-co-3,4-ethylenedioxythiophene) showed excellent electrocatalytic ability for the reduction of oxygen. Scanning electron microscopy images proved the excellent modification of the modified electrodes.

Copyright©2016, Amala Jothi Grace et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Citation: Amala Jothi Grace, G., Gomathi, A. and Vedhi, C. 2016. “Oxygen reduction at the surface of poly (3-methylthiophene-co-3,4-ethylenedioxythiophene) Modified glassy carbon electrode with 2-amino antra-9,10-quinone”, International Journal of Current Research, 8, (08), 35997-36001
Oxygen gases with 99.99% purity were used. 2-AMAQ was placed in a cell containing three electrodes such as working electrode (glassy carbon electrode), counter electrode (platinum wire) and reference electrode (silver electrode). The copolymer modified glassy carbon electrode was prepared by electropolymerization. Cyclic Voltammetry, Chronoamperometry and Chronocoulometry techniques were studied from CH Instrument Electrochemical workstation.

RESULTS AND DISCUSSION

Glassy carbon electrode was modified with the copolymer by means of electropolymerization and the voltammetric studies of 2-AMAQ at the modified electrode was performed under deaerated and oxygen saturated conditions in the pH range 1.0 - 13.0.

![Graph](image)

**Fig. 1.** Cyclic voltammograms of 2-AMAQ at METH/EDOT/GCE (pH 7) under de-aeration at scan rates 10, 20, 50, 100, 200, 300, 400, 500, 600 and 700 mVs⁻¹

**Electrochemical Behaviours of 2-AMAQ at METH/EDOT/GCE**

For the copolymer modified electrode, cyclic Voltammograms of 2-AMAQ 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 2-AMAQ at the modified electrode METH/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. Figure 2(A) shows the linear variation of cathodic peak current (Ipc) with scan rate (v). The plot of log Ipc versus log v is a straight line with slope value greater than 0.5 which proves the adsorption controlled process as shown in the Figure 2(B).

**pH – Effect under deaeration**

Three distinct linear portions with different slope values were observed indicating the different forms of anthraquinone. The pH-potential diagram for 2-AMAQ at METH/EDOT/GCE was given in the figure 3. At low pH (1 to 4) values, 2-AMAQ involves two-electron three-proton reduction process. In the intermediate pH range, the compound undergoes two-electron, two proton process At pH above 10, the electrode surface reaction is a two electron, one proton process.

**Stability of the modified electrode**

The stability of the copolymer modified electrode and the reproducibility of its electrochemical behaviour was examined. The modified electrodes were immersed in acidic medium with 2-AMAQ for 40 h and in neutral medium containing 2-AMAQ for 30 h. A slight decrease with no changes in the peak current or separation of the peak was obtained.

![Graph](image)

**Fig. 2.** (A) Plot of cathodic peak current (Ipc) vs scan rate (v) (B) Plot of logarithmic cathodic peak current (log Ipc) vs logarithmic scan rate (log v) for 2-AMAQ at METH/EDOT/GCE in pH 7 under deaeration

![Graph](image)

**Fig. 3.** pH-potential diagram for 2-AMAQ at METH/EDOT/GCE

**Surface coverage**

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 = Q/nF/A 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 cm²) glassy carbon
electrode. The surface coverage value of 2-AMQA at copolymer modified electrode was 0.73 x 10⁹ mol cm⁻². Also, the adsorption of 2-AMQA at the surface of conducting polymer modified electrode was also confirmed by SEM studies. Figure 4 shows the scanning electron microscopy images of METH/EDOT/GCE (a) and METH/EDOT/GCE with 2-AMQA (b).

![SEM photographs of (a) METH/EDOT/GCE (b) METH/EDOT/GCE with 2-AMQA](image)

**Fig. 4.** SEM photographs of (a) METH/EDOT/GCE (b) METH/EDOT/GCE with 2-AMQA

![Plot of pH versus shift in oxygen reduction potential at METH/EDOT/GCE with 2-AMQA](image)

**Fig. 5.** Plot of pH versus shift in oxygen reduction potential at METH/EDOT/GCE with 2-AMQA

Catalytic reduction of oxygen at METH/EDOT/GCE

pH – Effect under aeration

The catalytic effect of 2-AMQA in different pH media at METH/EDOT/GCE was studied. As the pH increases, the cathodic peak current increases up to pH 7. Figure 5 shows the variation of shift in oxygen reduction potential with pH for METH/EDOT/GCE in presence of 2-AMQA. Cyclic voltammograms of 2-AMQA at METH/EDOT/GCE in the presence and absence of oxygen at pH 7.0 are shown in the Figure 6. For a plain GCE, oxygen reduces at -1027.5mV. For METH/EDOT/GCE in presence of 2-AMQA, the reduction occurred at -737.4 mV. Thus, the modified electrode with 2-AMQA causes the shift in oxygen reduction potential (ΔE) of about 290.1mV in pH 7. The cathodic peak current for 2-AMQA at the copolymer modified electrode in the presence of oxygen was increased and the anodic peak has left which confirms the electrocatalytic reduction of oxygen.

![Cyclic voltammograms of 2-AMQA at METH/EDOT/GCE in the presence (o) and absence (d) of oxygen at pH 7](image)

**Fig. 6.** Cyclic voltammograms of 2-AMQA at METH/EDOT/GCE in the presence (o) and absence (d) of oxygen at pH 7

![Plots (A) I_p versus √ν (B) log I_p versus log ν for 2-AMQA at METH/EDOT/GCE under aeration in pH 7.0](image)

**Fig. 7.** Plots (A) Iₚ versus √ν (B) log Iₚ versus log ν for 2-AMQA at METH/EDOT/GCE under aeration in pH 7.0

Scan rate – Effect under aeration

Under aeration, the reduction of oxygen is a diffusion controlled process. The linear variation of cathodic peak
current ($I_{p}$) with square root of scan rate ($u^{1/2}$) obtained for the copolymer modified electrode in presence of 2-AMAO at pH 7 in the presence and absence of oxygen. The net electrolysis current $I_{net}$ was determined. From the slope of $I$ vs $t^{1/2}$ under deaeration, the diffusion coefficient values of antraquinone was determined using the Cottrell equation

\[
I = nF D^{1/2} A C_{aq} \pi^{1/2} \tau^{1/2}
\]

Slope = $nF D^{1/2} A C_{aq} \pi^{1/2}$

Where $C_{aq}$ is the concentration of 2-AMAO, $D$ is the diffusion co-efficient of 2-AMAO and $A$ is the working electrode area (0.0314 cm$^2$). The calculated Diffusion coefficient ($D_{o2}$) value of 2-AMAO was $8.43 \times 10^{-5}$ cm$^2$ s$^{-1}$.

**Chronocoulometry**

At the copolymer modified electrode in the presence and absence of oxygen the chronocoulometric response of 2-AMAO was examined with an initial and final potential of about -400 and -1000mV versus silver electrode, respectively. For example, the chronocoulometric response of 2-AMAO at METH/EDOT/GCE in pH 7 is shown in figure 9. The number of electrons ($n$) involved in the reduction of METH/EDOT/GCE with 2-AMAO at the optimum pH was evaluated from the slope of $Q$ versus $t^{1/2}$ under deaeration condition using the Cottrell equation,

\[
Q = 2nFACD^{1/2} \pi^{1/2} \tau^{1/2}
\]

where $C$ = 1.25mM, $A = 0.0314$cm$^2$ and $D=1.57 \times 10^{-5}$ cm$^2$ s$^{-1}$.

The number of electrons involved in the reduction of 2-AMAO ($n_{o2}$) and number of electrons involved in oxygen reduction ($n_{O2}$) were 1.97 and 2.03 respectively.

**Conclusion**

Cyclic voltammetry, chronocoulometry and chronoaamperometry techniques were employed to investigate the electrochemical and catalytic behaviour of the copolymer modified electrode in the presence of 2-Amino anthra-9,10-quinone at the optimum pH 7.0. The diffusion coefficient values, surface coverage and the number of electrons were investigated. The adsorption of 2-AMAO at the surface of conducting polymer modified electrode was also confirmed by SEM studies.

**REFERENCES**


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

G. Amala Jothi Grace¹*, A. Gomathi², C. Vedhi³

¹Department of Chemistry, Chandy College of Engineering, Thoothukudi – 628 005, Tamil Nadu, India.
²Department of Chemistry, Sri K.G.S Arts College, Srivakundam – 628 619, Tamil Nadu, India.
³Department of Chemistry, V. O. Chidambaram College, Thoothukudi – 628 008, Tamil Nadu, India.

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 deaeration at scan rates 10, 20, 50, 100, 200, 300, 400, 500, 600 and 700 mVs⁻¹
Fig. 2 shows the cyclic voltammograms of DIAMAQ at HEX/EDOT/GCE (pH 6) under de-aeration 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 (Ipc) versus scan rate (v) is a straight line as illustrated in Fig. 3A and it is non-linear for the plot of cathodic peak current (Ipc) versus square root of scan rate (v¹/²). Fig. 3B represents the linear changes of logarithm cathodic peak current (log Ip) with logarithm of scan rate (log v) with slope around 0.6 which confirms the adsorption controlled process.

Fig. 3 (A) Plot of Ipc versus v (B) Plot of log Ip versus log v 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 peaks 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 DIAMAQ 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 DIAMAQ were determined from the cyclic voltammograms at 20 mVs⁻¹ scan rate using the relation Γaq = Q/nFA, where Q is the charge consumed, n is the number of electrons involved, F (96500 Cmol⁻¹) is the Faraday constant and A is the geometric area (0.0314 cm²) 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 (Γaq) value, Diffusion coefficient (Daq) and the number of electrons involved in the reduction of anthraquinone (naq) for DIAMAQ at Plain GCE and HEX/EDOT/GCE in pH 7

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Γaq mol cm⁻² x 10⁻⁹</th>
<th>Daq (cm²s⁻¹) x 10⁻⁸</th>
<th>naq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain GCE</td>
<td>0.65</td>
<td>7.24</td>
<td>1.70</td>
</tr>
<tr>
<td>HEX/EDOT/GCE</td>
<td>0.49</td>
<td>11.40</td>
<td>1.98</td>
</tr>
</tbody>
</table>

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.

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 Vs t⁻¹/² under deaerated condition, the diffusion coefficient values of DIAMAQ were determined using the Cottrell equation

\[ I = \frac{nFD^{1/2}A}{\pi^{1/2}} t^{-1/2} \]

where C₀ is the concentration of DIAMAQ used, D is the diffusion coefficient of DIAMAQ (D₀) and A is the geometric area of (0.0314 cm²) of glassy carbon electrode. The calculated values of D₀ 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 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 Vs t⁻¹/² under deaerated condition, the diffusion coefficient values of DIAMAQ were determined using the Cottrell equation

\[ I = \frac{nFD^{1/2}A}{\pi^{1/2}} t^{-1/2} \]

where C₀ is the concentration of DIAMAQ used, D is the diffusion coefficient of DIAMAQ (D₀) and A is the geometric area of (0.0314 cm²) of glassy carbon electrode. The calculated values of D₀ at plain GCE and the copolymer modified GCE were given in Table 1.
Under deaerated condition, the reversible peaks were observed. The number of electrons ($n_{\text{aq}}$) 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,

$$Q = 2n_{\text{aq}} F C D^{1/2} \pi^{-1/2} t^{1/2}$$

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

References


