



RESEARCH ARTICLE

OXYGEN REDUCTION AT THE SURFACE OF POLY (3-METHYLTHIOPHENE-CO-3,4-ETHYLENEDIOXYTHIOPHENE) MODIFIED GLASSY CARBON ELECTRODE WITH 2-AMINO ANTHRA-9,10-QUINONE

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ABSTRACT

The preparation and electrochemical characterisation of poly (3-methylthiophene-co-3,4-ethylenedioxythiophene) modified glassy carbon electrode with 2-Amino anthra-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 chronoamperometric and chronocoulometric techniques. 2-Amino anthra-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.

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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), naphthoquinone (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 anthra-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, chronoamperometry and chronocoulometric techniques.

Experimental

2- Amino anthra-9, 10-quinone (2-AMAQ), 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-AMAQ. During the experiments, Nitrogen and

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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 electrodeposition. 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 electrodeposition 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.

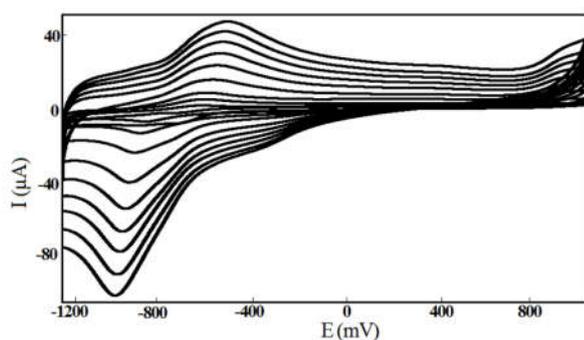


Fig. 1. Cyclic voltammograms of 2-AMAQ at METH/EDOT/GCE (pH 7) under de-aeration at scan rates 10, 20, 50, 100, 200, 300, 400, 500, 600 and 700 mVs^{-1}

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 (I_{pc}) with scan rate (ν). The plot of $\log I_{pc}$ versus $\log \nu$ 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.

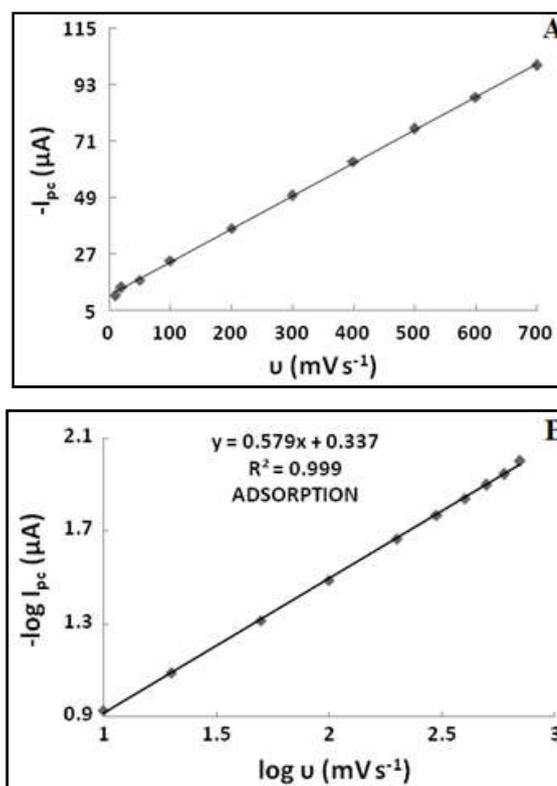


Fig. 2. (A) Plot of cathodic peak current (I_{pc}) vs scan rate (ν) (B) Plot of logarithmic cathodic peak current ($\log I_{pc}$) vs logarithmic scan rate ($\log \nu$) for 2-AMAQ at METH/EDOT/GCE in pH 7 under deaeration

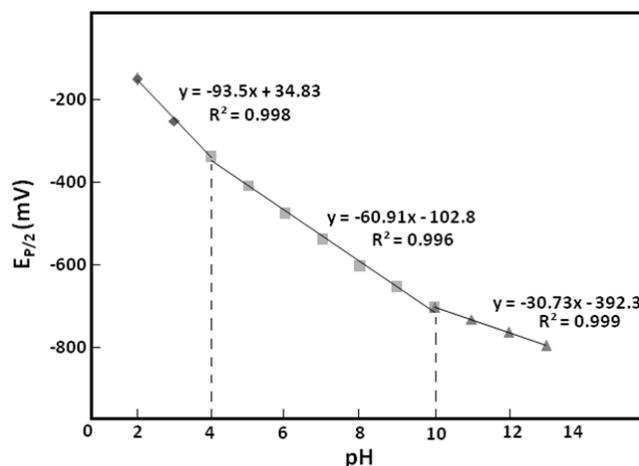


Fig. 3. pH-potential diagram for 2-AMAQ at METH/EDOT/GCE

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 $\Gamma_{aq} = Q/nFA$ 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 geometric area of (0.0314 cm^2) glassy carbon

electrode. The surface coverage value of 2-AMQA at copolymer modified electrode was $0.73 \times 10^{-8} \text{ mol cm}^{-2}$. 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).

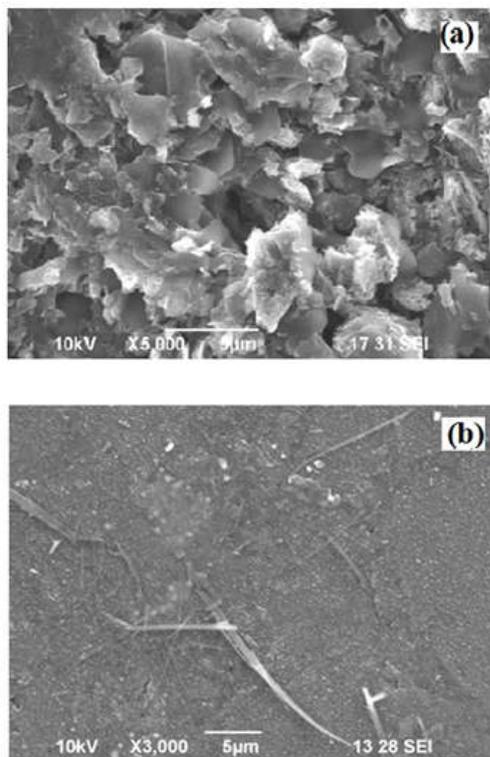


Fig. 4. SEM photographs of (a) METH/EDOT/GCE (b) METH/EDOT/GCE with 2-AMQA

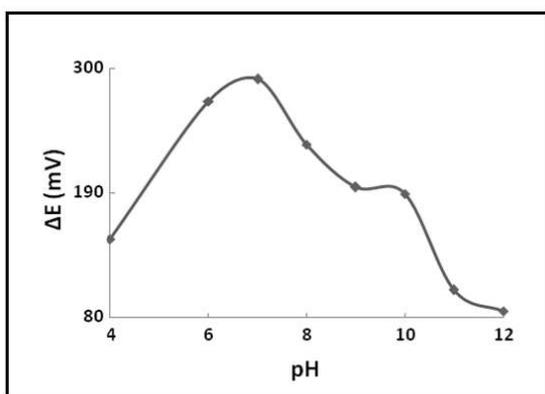


Fig. 5. Plot of pH versus shift in oxygen reduction potential at METH/EDOT/GCE with 2-AMQA

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 upto 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 -1027.5 mV . 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 290.1 mV 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.

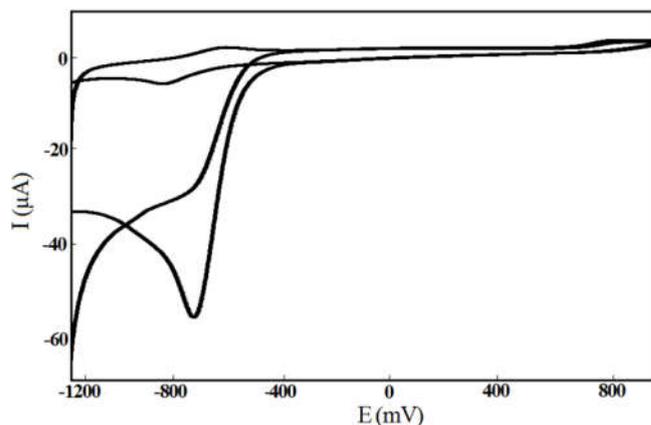


Fig. 6. Cyclic voltammograms of 2-AMQA at METH/EDOT/GCE in the presence (o) and absence (d) of oxygen at pH 7

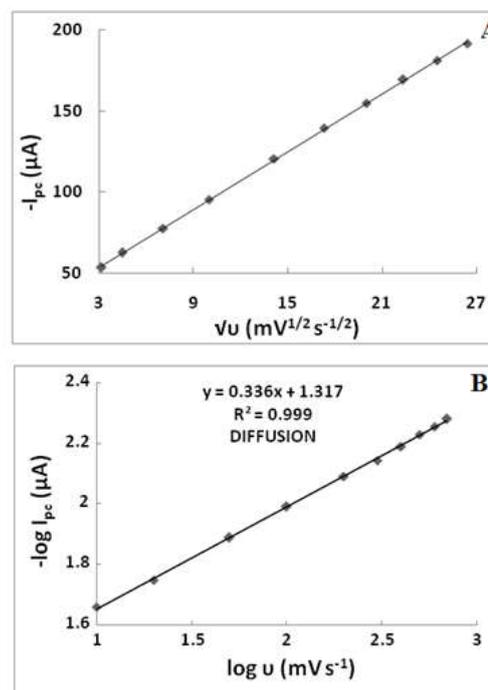


Fig.7. Plots (A) I_{pc} versus \sqrt{v} (B) $\log I_{pc}$ versus $\log v$ for 2-AMQA at METH/EDOT/GCE under aeration in pH 7.0

Scan rate – Effect under aeration

Under aeration, the reduction of oxygen is a diffusion controlled process. The linear variation of cathodic peak

current (I_{pc}) with square root of scan rate ($v^{1/2}$) obtained for the copolymer modified electrode in presence of 2-AMQA as shown in Figure 7A which clearly confirms the diffusion controlled process for oxygen reduction. Also, Figure 7B shows the plot of logarithmic cathodic peak current versus logarithm of scan rate for oxygen reduction at METH/EDOT/GCE in presence of 2-AMQA at pH 7 with slope less than 0.5 confirms the diffusion controlled oxygen reduction process.

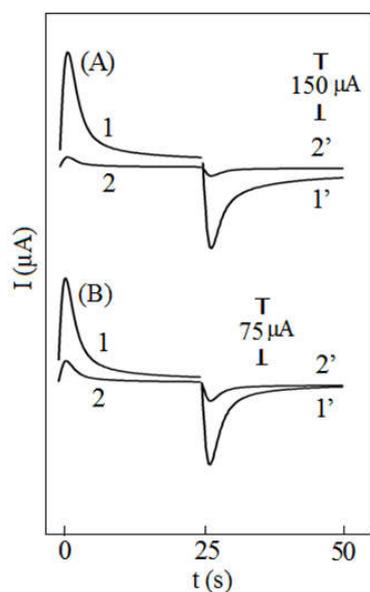


Fig. 8. Chronoamperograms for 2-AMQA at METH/EDOT/GCE in pH 7 by double potential step technique at an initial potential of -400mV and final potential of -1000mV vs silver electrode. (A) 1,1' for METH/EDOT/GCE in presence of 2-AMQA under aeration, 2,2' for plain GCE in the absence of 2-AMQA. (B) 1,1'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

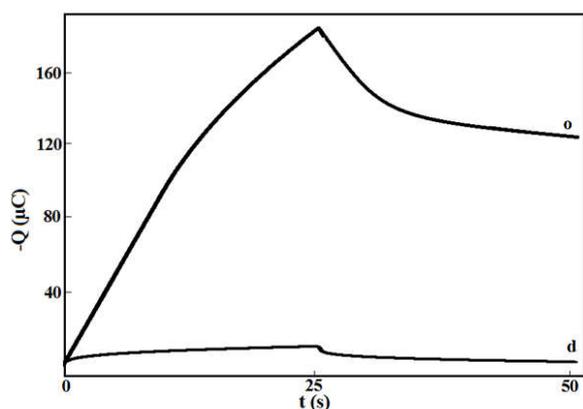


Fig. 9. Chronocoulometric curves of 2-AMQA at METH/EDOT/GCE in pH 7 under deaeration (d) and aeration (o)

Chronoamperometric studies

The chronoamperograms were performed at an initial and final potential of -400 and -1000 mV to study the chronoamperometric responses of plain GCE and copolymer modified GCE in the presence and absence of oxygen at optimum pH 7. Figure 8 shows the chronoamperogram of 2-

AMQA at plain GCE and METH/EDOT/GCE in 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 anthraquinone was 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 2-AMQA, D is the diffusion co-efficient of 2-AMQA and A is the working electrode area (0.0314 cm^2). The calculated Diffusion coefficient (D_{Aq}) value of 2-AMQA was $8.43 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$.

Chronocoulometry

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

$$Q = 2n F A C D^{1/2} \pi^{-1/2} t^{1/2}$$

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

The number of electrons involved in the reduction of 2-AMQA (n_{Aq}) and number of electrons involved in oxygen reduction (n_{O_2}) were 1.97 and 2.03 respectively.

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 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-AMQA at the surface of conducting polymer modified electrode was also confirmed by SEM studies.

REFERENCES

- Chitra, R. and Renuka, R. 2003. *J. Appl. Electrochem.*, 33, 443.
- Golabi, S., Raof, J.B., J. *Electroanal.Chem.* 1996. 416, 75.
- Gonzalez-Cruz, R., Solorza-Feria, O., J. 2003. *Solid State Electrochem*, 7, 289.
- Lin, A.S., Huang, J.C., J. *Electroanal. Chem.* 2003, 541, 147.
- Manisankar, P., and Gomathi, A. 2005. *Bull. Chem. Soc. Jpn.* 78, 1783- 1790.
- Manisankar, P., and Gomathi, A. 2005. *Electroanalysis*, 17, 1051-1057.
- Manisankar, P., and Gomathi, A. 2005. *Journal of Molecular Catalysis*. 232, 45-52.

- Manisankar, P., Gomathi, A., Velayutham, D. 2005. *J. Solid State Electrochem.* 9, 601-608.
- Manisankar, P., Mercy Pushpalatha, A., Vasanthakumar, S., Gomathi, A., Viswanathan, S. 2004. *J. Electroanal. Chem.* 571, 43.
- Mao, L., Zhang, D., Sotomura, T., Nakatsu, K., Koshiha, N., Ohsaka, T., *Electrochim. Acta.* 2003, 48, 1015.
- Peressini, S., Tavagnacco, C., Costa, G., Amatore, C. 2002. *J. Electroanal. Chem.* 532, 295.
- Ramirez, G., Trollund, E., Isaacs, M., Armijo, F., Zagal, J., Costamagana, J., Aguirre, M.J., *Electroanalysis.* 2002, 540.
- Salimi, A., Eshghi, H., Sharghi, H., Golabi, S.M., Shamsipur, M. 1999. *Electroanalysis*, 11, 114.
- Salimi, A., Mousavi, M.F., Sharghi, H., Shamsipur, M. 1999. *Bull. Chem. Soc. Jpn*, 72:2121
- Sarapu, A., Vaik, K., Schiffrin, D.J., Tammeveski, K. 2003. *J. Electroanal. Chem.*, 541, 23.
- Tammeveski, K., Kontturi, K., Nichols, R.J., Potter, R.J., Schiffrin, D.J. 2001. *J. Electroanal. Chem.* 515, 101.
- Vukmirovic, M.B., Vasiljevic, N., Dimitrov, N., Sieradzki, K. 2003. *J. Electrochem. Soc.*, 150, B10.
- Zhang, Y., Asahina, S., Yoshihara, S., Shirakashi, T. 2003. *Electrochim. Acta.*, 48 741.
