www.sphinxsai.com

ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9, No.09 pp 405-412, 2016

Analysis of 1-Amino anthra-9,10-quinone with the copolymer poly(2-octylthiophene-co-3,4- ethylenedioxythiophene) for oxygen reduction

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

[1]Department of Chemistry, Chandy College of Engineering, Thoothukudi,
Tamil Nadu, India.
[2]Department of Chemistry, Sri K.G.S Arts College, Srivaikundam,
Tamil Nadu, India.
[3]Department of Chemistry, V.O.Chidambaram college, Thoothukudi, Tamilnadu, India.

Abstract : Polymers play a vital role in every field. 1-Amino anthra-9,10-quinone combined with the copolymer poly(2-octylthiophene-co-3,4- ethylenedioxythiophene) was used to study the oxygen reduction reaction. This investigation reports the electrochemical characterisation of the combination of anthraquinone compound with the copolymer. From the cyclic voltammograms, the stability of the copolymer poly(2-octylthiophene-co-3,4-ethylenedioxy thiophene) was studied. From the chronoamperometric and chronocoulometric data's, 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 determined. 1-Amino 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-Amino anthra-9,10-quinone, Oxygen reduction.

Introduction

Fuel cells[1-7] and sensors are the important research field. The focus of oxygen reduction reaction is very important in electrochemical devices. Various researches were carried out on the modified electrodes to identify a perfect electrode for the electrocatalytic reactions. In the electroanalytical chemistry, various studies have been carried out using metal macrocyclic complexes[8], Au nanoparticle[9], pyrimidine bases[10], anthraquinone derivatives[11,12], copper[13], ruthenium-iron cluster[14] and nano tube[15].

In the present investigation, the electrochemical behaviour of 1-Amino anthra-9,10-quinone at poly(2-octylthiophene-co-3,4- ethylenedioxythiophene) modified glassy carbon electrode for oxygen reduction were examined by cyclic voltammetry, chronoamperometry and chronocoulometric techniques.

Experimental

Anthraquinone derivative namely 1-Amino anthra-9,10-quinone (1-AMAQ), 3,4-Ethylene dioxythiophene (EDOT) and 2-Octylthiophene (OCT) were purchased from Sigma-Aldrich. HPLC grade Acetonitrile from Lobochem was used as solvent. Buffer solutions from 1 to 13 were prepared and it was checked using Hanna pH meter. 1-AMAQ is added to the electrolyte containing 50% aqueous acetonitrile pH solutions. Gases such as nitrogen and oxygen with 99.99% purity were used for the aerated and de-aerated conditions. The solution containing 1-AMAQ was kept for analysis using glassy carbon electrode, a platinum wire and silver electrode. The copolymers were coated by electrodeposition methods. Using CH Instrument Electrochemical workstation, the analysis was carried out using cyclic voltammetry, chronoampermetry and chronocoulometry.

Results and Discussion

Voltammetric studies of 1-AMAQ was performed at OCT/EDOT/GCE in the presence and absence of oxygen at various pH media in the range 1.0 – 13.0.

Cyclic volatammetric behaviour

For the copolymer modified electrode, cyclic voltammograms of 1-AMAQ present a single redox couple in the deaerated condition. At various scan rates, the voltammograms were recorded to determine the influence of scan rate with cathodic peak current. Figure 1 shows the cyclic voltammetric response of copolymer modified electrode OCT/EDOT/GCE with 1-AMAQ in pH 7 at various scan rates.

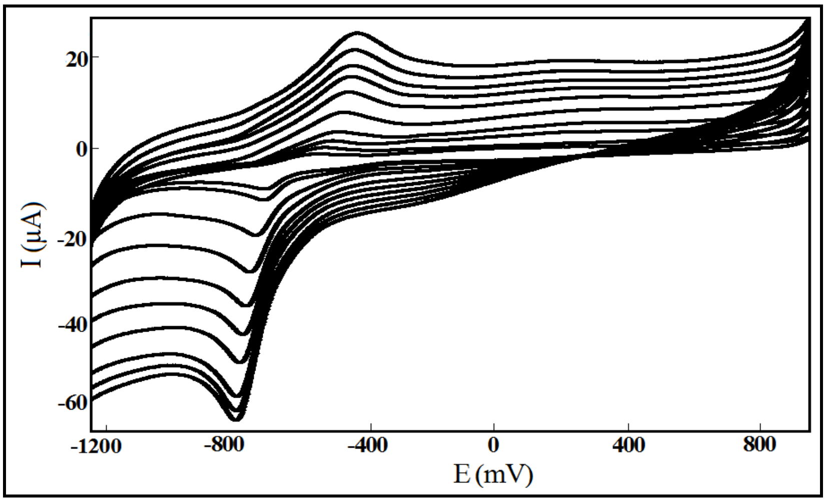

Figure 1. Cyclic voltammograms of 1-AMAQ at OCT/EDOT/GCE (pH 7) under de-aeration at scan rates 10, 20, 50, 100, 200, 300, 400, 500, 600 and 700 mVs^{-1}

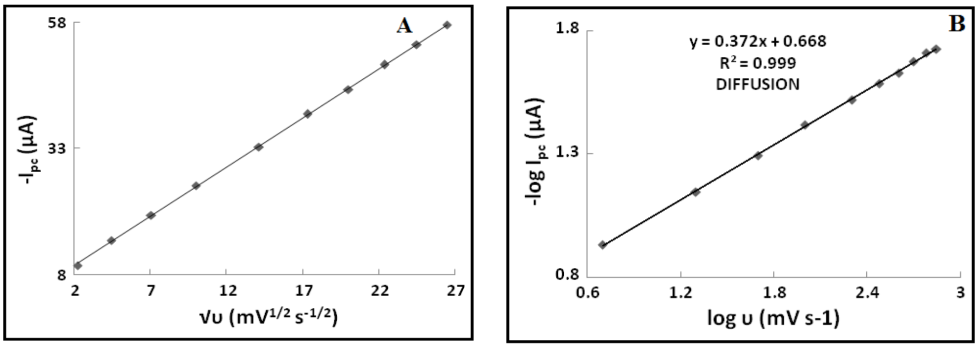

Figure 2. (A) I_{pc} versus √υ (B) log I_{pc} versus log υ for 1-AMAQ at OCT/EDOT/GCE in pH 7.0

By plotting the cathodic peak current (I_{pc}) with square root of scan rate ($\upsilon^{1/2}$), diffusion controlled process for 1-AMAQ [Fig. 2A] at OCT/EDOT/GCE was confirmed by its straight line. Moreover, non-linear variation of I_{pc} with υ is reported and a straight line for the plot of log I_{pc} vs. log υ with slope value 0.4 for 1-AMAQ [Fig. 2B] prove the diffusion controlled anthraquinone reduction process.

pH effect in the presence of nitrogen

From the cyclic voltammograms, it was clear that the cathodic peak current also increases upto pH 7 and then the current value reduced slowly after its optimum level. This results can be clearly viewed in fig 3.

On comparing the current with potential, pH trend was directly proportional to the cathodic peak potential as given in fig 4.

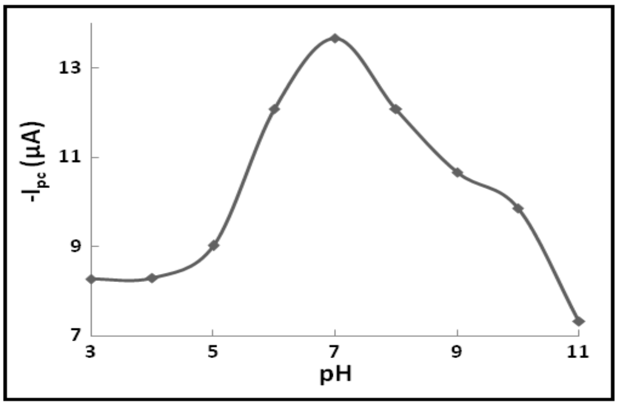

Figure 3. Plot of pH versus cathodic peak current (I_{PC}) for 1-AMAQ at OCT/EDOT/GCE

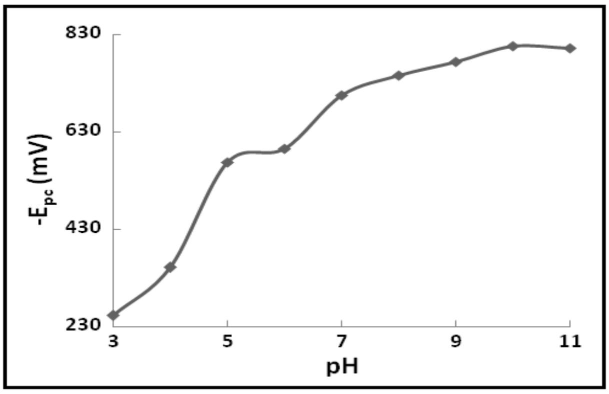

Figure 4. Plot of pH versus cathodic peak potential (E_{PC}) for 1-AMAQ at OCT/EDOT/GCE

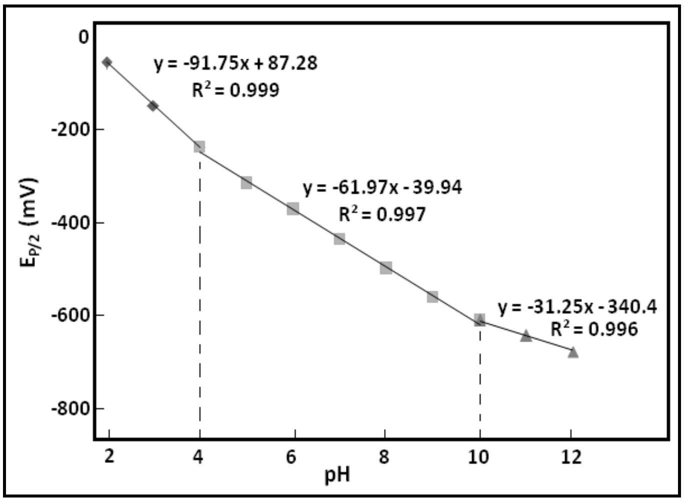

Figure 5. pH-potential diagram for 1-AMAQ at OCT/EDOT/GCE

From the values of half peak potential, the number of electrons involved in the process can be determined. The half peak potential $E_{p/2}$ versus pH consists of three distinct linear segments with slopes 90 mV up to pH 4, 60 mV at intermediate pH and 30 mV at pH above 10 for 1-AMAQ at OCT/EDOT/GCE. The $E_{P/2}$ value for 1-AMAQ at OCT/EDOT/GCE in pH 7 was -477.5 mV. The reaction is a two electron, three proton process at low pH values and two-electron, two proton process in the intermediate pH range. At pH above 10, the electrode surface reaction is a two electron one proton process. This shows the formation of protonated hydroquinones at low pH values, corresponding hydroquinones in the intermediate pH range and a semi-hydroquinone anion at high pH values. The pH-potential diagram for 1-AMAQ at OCT/EDOT/GCE was given in the figure 5.

Stable nature of the modified electrode

The steadiness of OCT/EDOT/GCE modified electrode and reproducibility of their electrochemical behaviour were investigated by immersing them in acidic and neutral buffers. The cyclic voltammograms recorded shows only a less decrease in the corresponding voltammograms. In addition, thirty minutes of repetitive scanning at sweep rate 20 mVs^{-1} between 0 to -1000 mV at pH 7.0 including more than 40 complete cycles, reports no decrease. After such repetitive scanning, the cyclic voltammogram recorded under deaerated and aerated conditions was compared. A considerable decrease in the peak height with no change in the peak separation shows the stability of the copolymer modified electrode.

Surface coverage of the modified electrode

The surface coverage value of 1-AMAQ at copolymer modified electrode was 0.46 x 10^{-8} mol cm^{-2}. This value was determined from the cyclic voltammogram 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.

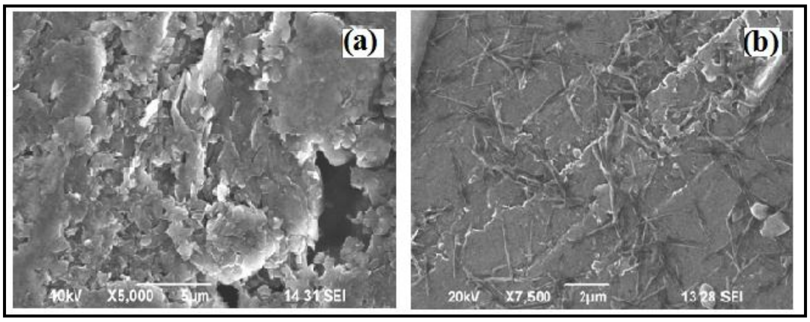

Figure 6. SEM photographs of (a) OCT/EDOT/GCE (b) OCT/EDOT/GCE with 1-AMAQ

Also, the adsorption of 1-AMAQ at the surface of conducting polymer modified electrode was also confirmed by SEM studies. Figure 6 shows the scanning electron microscopy images of OCT/EDOT/GCE (a) and OCT/EDOT/GCE with 1-AMAQ (b).

Catalytic reduction of oxygen at OCT/EDOT/GCE

pH effect in the presence of oxygen

From the cyclic voltammograms obtained under aeration, the cathodic peak current increase up to pH 7 was determined. For instance, Fig. 7 shows the variation of cathodic peak current with pH for oxygen reduction at OCT/EDOT/GCE in presence of 1-AMAQ. The optimum pH for oxygen reduction was found to be 7.0 to study the electrocatalytic reduction of oxygen.

Fig. 8 shows the variation of shift in oxygen reduction potential with pH for 1-AMAQ at OCT/EDOT/GCE. At –1027.5mV, oxygen reduces on a plain GCE. Oxygen reduction occurs at -555.2mV in the presence of 1-AMAQ at OCT/EDOT/GCE. Thus the copolymer modified GCE causes the shift in oxygen reduction potential (ΔE) at 472.3 mV for 1-AMAQ at pH 7.

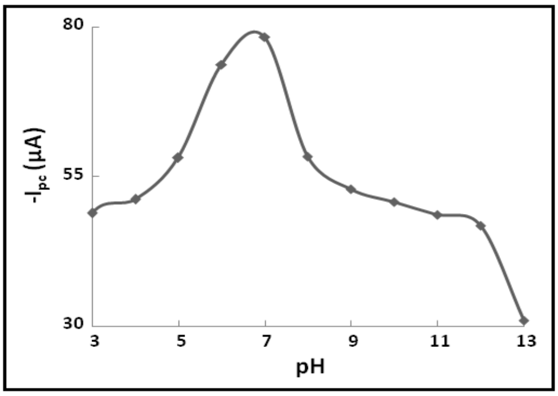

Figure 7. Plot of pH versus cathodic peak current (I_{PC}) for 1-AMAQ at OCT/EDOT/GCE

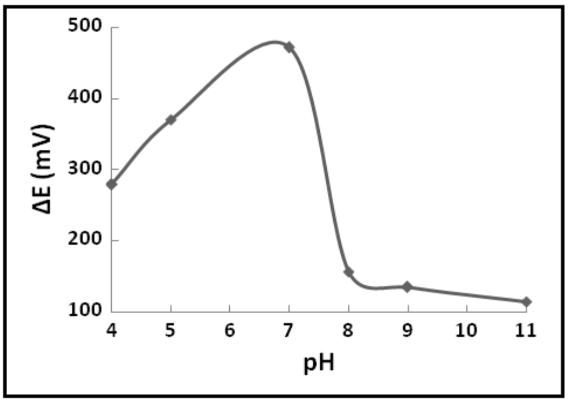

Figure 8. Plot of pH versus shift in oxygen reduction potential at OCT/EDOT/GCE with 1-AMAQ

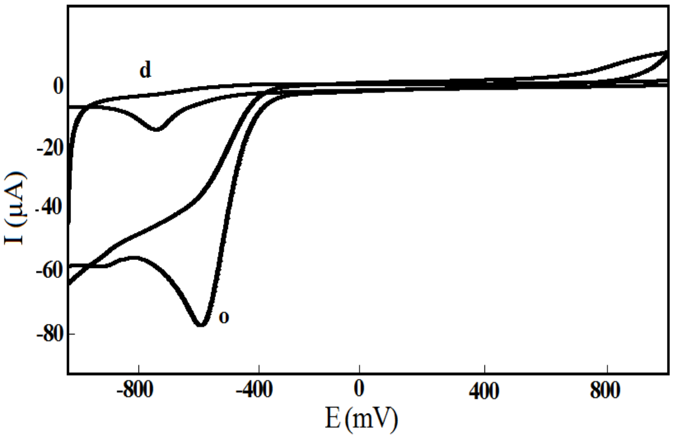

Figure 9. Cyclic voltammograms of 1-AMAQ at OCT/EDOT/GCE in the presence (o) and absence (d) of oxygen at pH 7.

Figure 9 shows the cyclic voltammogram of 1-AMAQ at OCT/EDOT/GCE in the presence and absence of oxygen at pH 7.0. In oxygen saturated solution, the enrichment in cathodic current followed by the loss of anodic peak confirm the irreversible electrocatalytic oxygen reduction at the modified electrode.

Scan rate effect in the presence of oxygen

In the presence of oxygen, a linearity in plot of the cathodic peak current (I_{pc}) with square root of scan rate $\upsilon^{1/2}$ shows the diffusion controlled process for 1-AMAQ [Fig 10A] at OCT/EDOT/GCE. Non-linear variation of I_{pc} with υ and the straight line plots of log I_{pc} versus log υ was observed. Figure 10B shows the plot of logarithmic cathodic peak current versus logarithm of scan rate with slope value 0.2 for 1-AMAQ at OCT/EDOT/GCE confirming diffusion controlled oxygen reduction process.

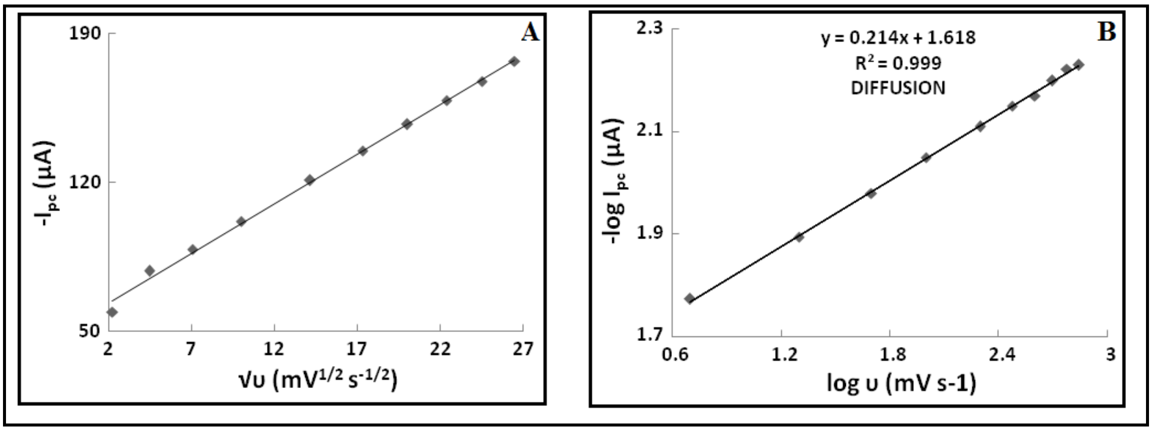

Figure 10. (A) I_{pc} versus $\sqrt{\upsilon}$ (B) log I_{pc} versus log υ for 1-AMAQ at OCT/EDOT/GCE in pH 7.0

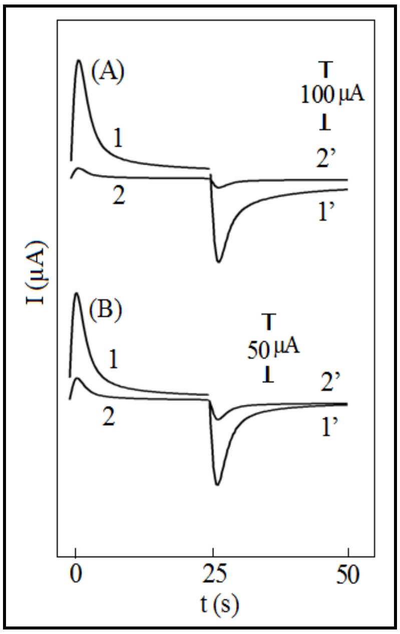

Figure 11. Chronoamperograms for 1-AMAQ at OCT/EDOT/GCE in pH 7 by double potential step technique at an initial potential of -400mV and final potential of -800mV vs silver electrode. (A) 1,1' for OCT/EDOT/GCE in presence of 1-AMAQ under aeration, 2,2' for plain GCE in the absence of 1-AMAQ. (B) 1,1' for OCT/EDOT/GCE in presence of 1-AMAQ under deaeration, 2,2' for plain GCE in the absence of 1-AMAQ.

Chronoamperometric behaviour

Under the condition of aeration and deaeration, the chronoamperometric response of OCT/EDOT/GCE in 1-AMAQ was studied by applying an initial and final potential of -400 and -800 mV. The chronoamperogram of OCT/EDOT/GCE in 1-AMAQ at pH 7 under aerated and de-aerated conditions were reported in figure 11. In the absence of oxygen, 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 1-AMAQ 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 1-AMAQ, D is the diffusion co-efficient of 1-AMAQ and A is the geometric area of (0.0314 cm^2) the glassy carbon electrode. The calculated Diffusion coefficient (D_{Aq}) value of 1-AMAQ was 6.06 x 10^{-9} cm^2 sec^{-1}.

Chronocoulometric behaviour

Chronocoulometric behaviour of OCT/EDOT/GCE was performed with 1-AMAQ in the presence and absence of oxygen by applying an initial and final potential of about -400 and -800mV versus silver electrode. For instance, the chronocoulomogram for 1-AMAQ at OCT/EDOT/GCE in the presence and absence of oxygen at pH 7 is presented in Fig. 12. Under de-aeration, reversible curves were observed. The irreversible electrocatalytic reduction of oxygen was confirmed by a large increasing charge in the forward curve and nearly flat line was obtained when the potential was reversed. The number of electrons (n) involved in the anthraquinone reduction at pH 7 was calculated from the slope of Q versus $t^{1/2}$ under deaeration using the Cottrell equation,

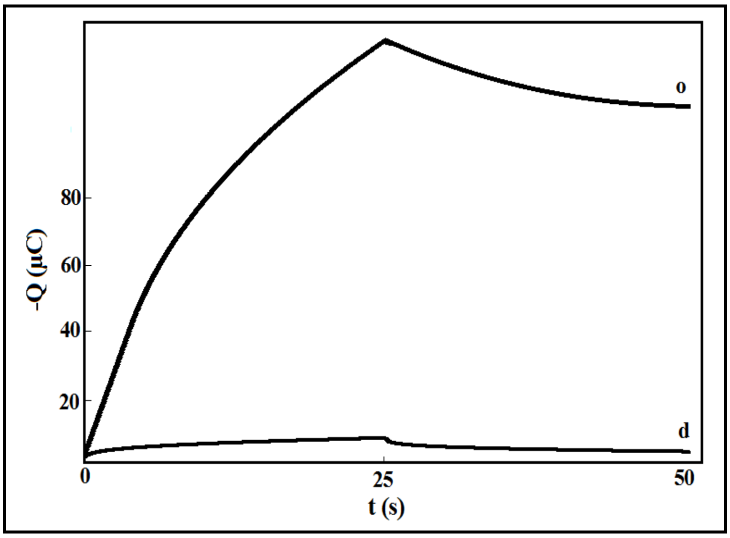

Figure 12. Chronocoulometric curves of 1-AMAQ at OCT/EDOT/GCE in the presence (o) and absence (d) of oxygen.

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

where C= 1.25Mm, A = 0.0314cm^2 and D = 1.57 x 10^{-5} cm^2s^{-1}. The total number of electrons involved in the reduction of oxygen is also determined under aerated condition.

when C = 1.25 mM, A = 0.0314 cm^2 and D = 1.57 x 10^{-5} cm^2s^{-1}. The number of electrons involved in the reduction of 1-AMAQ (n_{Aq}) and number of electrons involved in oxygen reduction (n_{O2}) were 2.1 and 2.0 respectively

Conclusions

The electrocatalytic reduction of oxygen at the copolymer modified electrode was determined. The copolymer modified electrodes showing the good electrocatalytic behaviour was investigated from the results of cyclic voltammetry, chronocoulometry and chronoamperometry techniques. Neutral medium is found to be the best medium to study the oxygen reduction reaction. The combination of anthra-9,10-quinone compound and the conducting polymer modified electrode was identified using the scanning electron microscopy images. The number of electrons involved in the reduction of anthraquinones and the number of electrons involved in oxygen reduction were investigated.

References

1. Gowdhamamoorthi M, Arun A, Kiruthika S, Muthukumaran B., Enhanced Performance Of Membraneless Fuel Cells, International Journal of ChemTech Research, 2013, 5 (3): 1143-1151.
2. Elumalai M , and Muthukumaran B., Performance of sodium borohydride in membraneless fuel cells, International Journal of ChemTech Research, 2015, 7 (7): 3033-3038.
3. Thilagaand S, Muthukumaran B., Electrocatalysis of Oxygen Reduction on Carbon Supported Platinum Catalysts in Membraneless Fuel Cells, International Journal of ChemTech Research, 2015, 7 (7): 3141-3147.
4. Nayeemunisa S.M, Kiruthika S, and Muthukumaran B., Electro-oxidation of Isopropanol in Membraneless Fuel Cells, International Journal of ChemTech Research, 2015, 7 (7): 3057-3062.
5. Vijayaramalingam K, Kiruthika S, Muthukumaran B., Electrochemical Oxidation of Platinum Based Anode Catalysts for Membraneless Fuel Cells, International Journal of ChemTech Research, 2015, 7 (7): 3063-3068.
6. Sunita Sundari G, Vijaya Kumar K, Shahenoor Basha S.K., Structural and Electrical properties of PVDF based Ag^+ ion conducting Polymer Electrolyte for Battery Applications, International Journal of ChemTech Research, 2016, 9 (5): 624-631.
7. Manjunatha J.G., Poly (Nigrosine) Modified Electrochemical Sensor for the Determination of Dopamine and Uric acid: A Cyclic Voltammetric Study, International Journal of ChemTech Research, 2016, 9 (2): 136-146.
8. Lin A.S, Huang J.C., Oxygen reduction on Nafion-bound unpyrolyzed metal macrocyclic complexes, Journal of Electroanalytical Chemistry, 2003, 541: 147-151.
9. Zhang Y, Asahina S, Yoshihara S, Shirakashi T., Oxygen reduction on Au nanoparticle deposited boron-doped diamond films, Electrochimica Acta, 2003, 48 (6): 741-747.
10. Peressini S, Tavagnacco C, Costa G, Amatore C., Electrochemical reduction of dioxygen in the presence of 4,6-dimethyl-2-thiopyrimidine in DMF, Journal of Electroanalytical Chemistry, 2002, 532 (1-2): 295-302.
11. Tammeveski K, Kontturi K, Nichols R.J, Potter R.J, Schiffrin D.J., Surface redox catalysis for O_2 reduction on quinine-modified glassy carbon electrodes, Journal of Electroanalytical Chemistry, 2001, 515 (1-2): 101-112.
12. Manisankar P, Gomathi A, Velayutham D, Oxygen reduction at the surface of glassy carbon electrodes modified with anthraquinone derivatives and dyes, Journal of Solid State Electrochemistry, 2005, 9 (9): 601-608.
13. Vukmirovic M.B, Vasiljevic N, Dimitrov N, Sieradzki K., Diffusion-Limited Current Density of Oxygen Reduction on Copper, Journal of Electrochemical Society, 2003, 150 (1): B10-B-15.
14. Gonzalez-Cruz R, Solorza-Feria O, Oxygen reduction in acid media by a $Ru_xFe_ySe_z(CO)_n$ cluster Catalyst dispersed on a glassy carbon-supported Nafion film, Journal of Solid State Electrochemistry, 2003, 7 (5): 289-295.
15. Qu J, Shen Y, Qu X, Dong S., Preparation of hybrid thin film modified carbon nanotubes on glassy carbon electrode and its electrocatalysis for oxygen reduction, Chemical Communications, 2004, 1, 34-35.

*****