

Oxygen Reduction at Conducting Polymer Modified Electrode with 1,4-Diaminoanthraquinone

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ABSTRACT: The electrocatalytic behaviour of 1,4-Diaminoanthraquinone at the conducting polymer modified electrode was investigated. The behaviour was studied both in acidic and neutral media. Under the condition of aeration, the optimum working pH was found to be 7. 1,4-Diaminoanthraquinone at the conducting polymer modified electrode shows the excellent electrocatalytic ability for the reduction of oxygen.

KEYWORDS: Copolymer, Modified electrode, Voltammograms, Reduction.

I. INTRODUCTION

The oxygen reduction is an important electrocatalytic reaction. The electroreduction of oxygen proceeds either by two electron or four electron pathway [1,2]. Modifying the electrode surface has attracted the researchers towards the oxygen reduction reaction. A number of catalysts have been used for the modification of the electrodes [3-11]. Conducting polymers have attracted very much due to its extensive applications [12,13]. Literature shows that many mediators have been reported as catalyst [14- 24]. The oxygen reduction reaction involving two electrons or four electrons shows a notable attention in batteries, corrosion, electrocatalysis and industrial process.

In the present investigation, the electrocatalytic behaviour of 1,4-Diaminoanthraquinone was employed. Conducting polymers was deposited by means of electrodeposition. The efficiency of the electrode in the electrocatalysis of oxygen was examined by cyclic voltammetry techniques.

II. RELATED WORK

Energy conversion is the necessary need for the future world.. The reduction of oxygen under different experimental conditions plays an important role in the energy conversion. Salimi et al [10, 23] reported the electrocatalytic ability of the adsorbed 1,4-dihydroxy anthraquinone derivatives and anthraquinone podands on glassy carbon electrodes towards the oxygen reduction. The electrocatalytic reduction of oxygen on redox polymer coated electrodes has been the object of active investigation over the past two decades. Electrochemical reduction of oxygen on quinone modified electrodes were of greater importance. Various modified electrodes were developed by Manisankar et al [24] to study the oxygen reduction reaction. By this study, new modified electrodes using polymers were synthesized which will play important role in the fuel cells and sensors.

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III. MATERIALS AND METHODS

1,4-Diaminoanthraquinone was purchased from Sigma- Aldrich. The copolymer poly(2-hexylthiophene-co-3,4-ethylenedioxythiophene) coated glassy carbon electrode (HEX/EDOT/GCE) was prepared by immersing the GCE in the cell solution containing 2-hexylthiophene and 3,4-ethylenedioxythiophene, tetrabutylammonium perchlorate and acetonitrile. The copolymer was deposited on the glassy carbon electrode by means of electrodeposition. The modified electrode was consequently rinsed with water and then transferred to the electrochemical cell for experiments. Doubly distilled water was used to prepare the buffer solutions. The copolymer modified electrode was placed in 50% aqueous-acetonitrile buffer and 1,4-Diaminoanthraquinone solution to carry out further electrochemical experiments.

IV. EXPERIMENTAL RESULTS

The electrocatalytic reduction of oxygen at the copolymer modified and plain GCE with DIAMAQ was examined in different pH media from pH 1 to 13. The optimum pH was found to be 7 for DIAMAQ used at the copolymer modified electrode. Figure. 1 shows Cyclic voltammogram of DIAMAQ at HEX/EDOT/GCE in pH 7 under aeration which reveals that there is a large enhancement in the cathodic peak current at the copolymer modified GCE in the presence of oxygen, while the corresponding anodic peak has disappeared indicating the electrocatalytic reduction of oxygen that occurs. Table 1 shows the catalytic behaviour of DIAMAQ at HEX/EDOT/GCE in oxygen reduction.

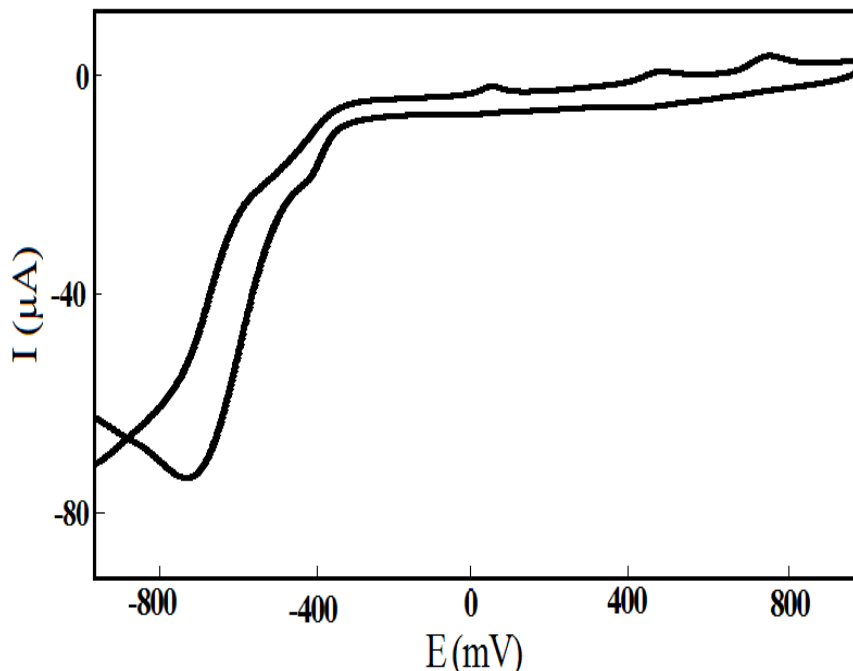


Figure 1. Cyclic voltammogram of DIAMAQ at HEX/EDOT/GCE in pH 7 under aeration.

As the pH increases, the shift in oxygen reduction potential increases up to pH 7. Figure 2 shows the variation of shift in oxygen reduction potential with pH for DIAMAQ at HEX/EDOT/GCE which clearly indicates that the maximum shift is observed at pH 7. The oxygen reduction potential at HEX/EDOT/GCE was -717.3 mV with DIAMAQ while the

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oxygen reduced at -1027.5 mV on plain GCE at pH 7. Thus, the copolymer with DIAMAQ causes the shift in oxygen reduction potential (ΔE) by about 310.2 mV in pH 7. Table 1 shows the catalytic behaviour of DIAMAQ at HEX/EDOT/GCE in oxygen reduction.

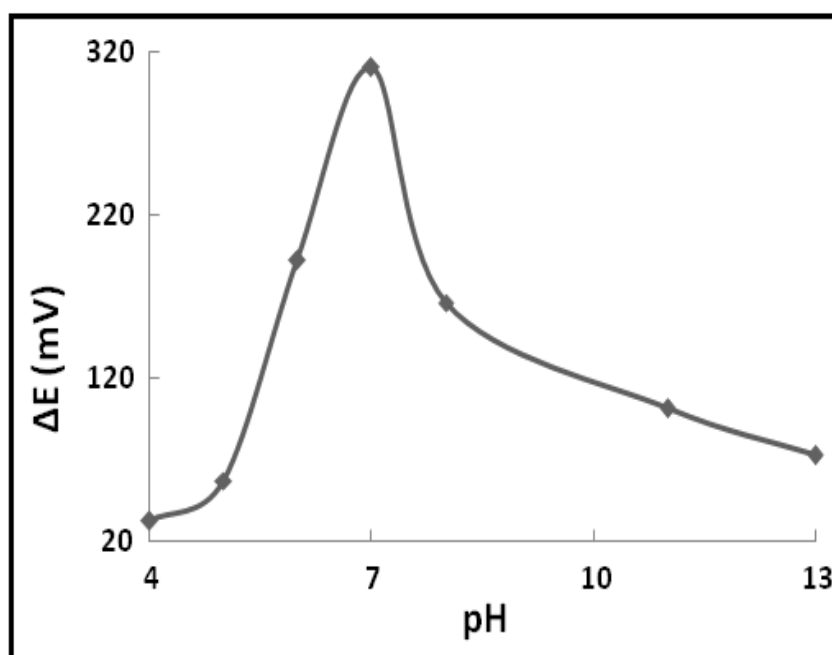


Figure 2. Plot of pH versus shift in O₂ reduction potential for DIAMAQ at HEX/EDOT/GCE.

Table I. Catalytic behaviour of DIAMAQ at HEX/EDOT/GCE in oxygen reduction

pH	Aeration at Scan Rate 20 mVs ⁻¹		Shift in Oxygen Reduction Potential ΔE (mV)
	DIAMAQ at HEX-EDOT/GCE		
	$-E_{pc}$ (mV)	$-I_{pc}$ (μA)	
4	888.3	54.74	32.3
5	898.7	58.27	57.1
6	817.7	59.13	191.9
7	717.3	68.74	310.2
8	712.8	54.89	166.2
9	608.3	54.02	217.9
10	739.5	46.92	2.3
11	631.8	40.78	101.3
12	667.2	39.55	57.0
13	523.7	30.85	72.6

Under aeration, the variation of cathodic peak current with scan rate was studied for DIAMAQ used. The cathodic peak current is linearly proportional to square root of scan rate $v^{1/2}$ which clearly confirms the diffusion controlled process for oxygen reduction in presence of DIAMAQ used at copolymer modified GCE. Further, the linear variation of logarithmic cathodic peak with logarithm of scan rate with slope value 0.3 confirmed the diffusion controlled oxygen reduction processes. As an illustration, figure. 3 shows the plot of cathodic peak current (I_{pc}) versus scan rate (v) and logarithmic cathodic peak current ($\log I_{pc}$) versus logarithm of scan rate ($\log v$) at HEX/EDOT/GCE for oxygen reduction in presence of DIAMAQ in pH 7.

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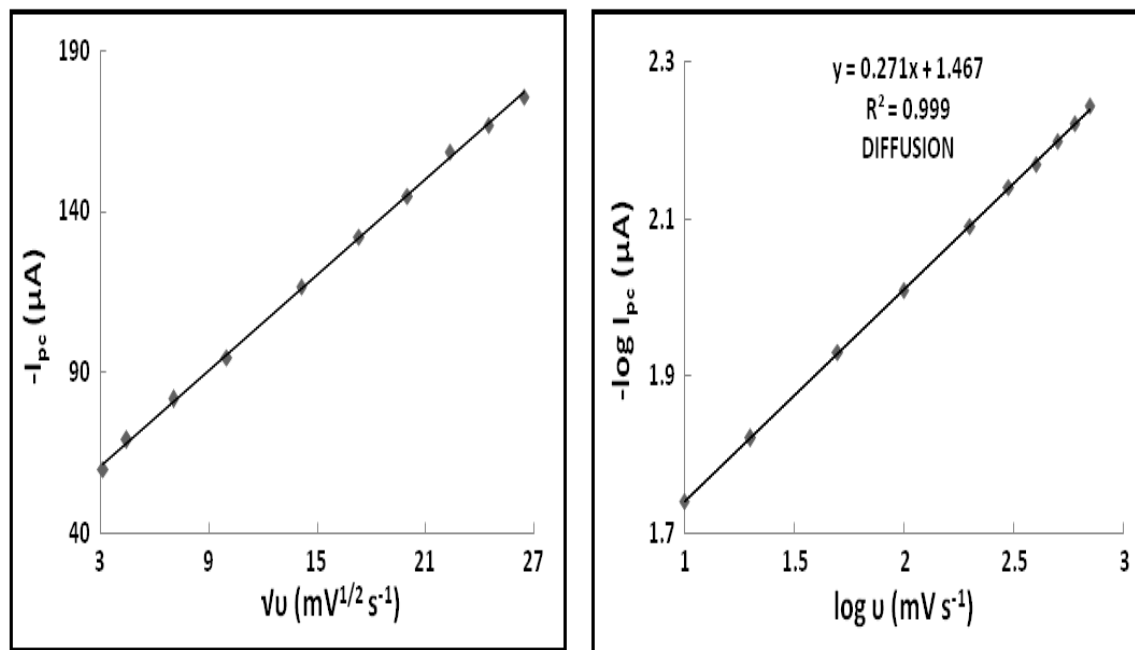


Figure 3. The plot of I_{pc} versus v and $\log I_{pc}$ versus $\log v$ at HEX/EDOT/GCE with DHAQ in pH7.

IV. CONCLUSION

This work describes the catalytic reduction of oxygen at the surface of copolymer modified electrode. Cyclic voltammetry was employed to investigate the catalytic behaviour of the conducting polymer based modified electrode in combination with DIAMAQ. A larger potential shift was observed for the copolymer poly (2-hexylthiophene-co-3,4-ethylenedioxythiophene) modified electrode than the plain glassy carbon electrode at pH7.

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