J. Antony Rajam et al. International Journal of Recent Research Aspects ISSN: 2349-7688, Special Issue: Conscientious Computing Technologies, April 2018, pp. 972-976

Electrochemical reduction of Oxygen on Copper Nanoparticle Deposited Glassy Carbon Electrode with 1, 4 Naphthoquinone and its derivatives

J. Antony Rajam[1], A. Gomathi[2], C. Vedha[3]
[1,2,3] Department of Chemistry
[1]St. Mary's College, (Autonomous), Thoothukudi, [2]Sri K.G.S Arts College, Srivaikuntam.
[3]V.O.Chidambaram College, Thoothukudi.

Abstract: - The electrochemical reduction of oxygen has been studied on copper nanoparticle modified glassy carbon electrode (CuNP/GCE) with 1,4-naphthoquinones (NQ) in various buffer solutions of pH 1 to 13 employing cyclic voltammetry, chronoamperometry and chronocoulometric techniques. The stability of the modified electrodes was ascertained in acidic and neutral media. The modified electrode was prepared by solvent evaporation of copper nanoparticle on the surface of GCE. The surface morphology of CuNP/GCE was examined by atomic force microscopy (AFM). The influence of pH and scan rate on the electrochemical and electrocatalytic behavior of the modified electrode was studied and pH 7.0 or 8.0 was chosen as the optimum working pH by comparing the shift in oxygen reduction potential. The oxygen reduction behaviour of CuNP/GCE was compared with that of a bare GCE. Electrochemical studies reveal that CuNP/GCE shows a high electrocatalytic activity towards O_2 reduction. The oxygen reduction proceeds by a two-electron pathway.

Keywords: Copper nanoparticle modified glassy carbon electrode, 1,4-Naphthoquinone, Oxygen reduction.

1. INTRODUCTION

Oxygen reduction in energy conversion system is an important reaction for the electrochemical devices. Modifying the surface of electrode has been one of the most interesting areas of research in electrochemistry [1]. In this way, a variety of compounds such as copper [2], vanadium [3], phenanthrenequinone [4], anthraquinone [5], naphthoquinone [6, 7], Au nanoparticle [8], silver nanoparticle [9] have been employed as electrocatalysts for the oxygen reduction. However, naphthoquinone/copper nanoparticle modified glassy carbon electrode has not been used so far for the study of reduction of oxygen.

In our present investigation, electrochemical behaviour of 1,4-naphthoquinone and its derivatives at copper nanoparticle deposited glassy carbon electrode (CuNP/GCE), efficiency and the stability of the modified electrodes in the electrocatalytic oxygen reduction have been studied by cyclic voltammetry, chronoamperometry and chronocoulometry. The nature of the electrode process and diffusional parameters were also determined.

2. EXPERIMENTAL

1,4-Naphthoquinone NQ), 2-Hydroxy-1,4-naphthoquinone (2-HyNQ), 5-Hydroxy-1,4-naphthoquinone (5-HyNQ) and 2-Amino-3-chloro-1,4-naphthoquinone (2-Am-3-ClNQ) and all other chemicals were purchased from Sigma-Aldrich. 1.25 mM solutions of NQs were prepared in ethanol. The buffer solutions of pH 1 to 13 were prepared using the chemicals of highest purity and doubly distilled water. The pH of the solution was measured using a Hanna pH-meter. 50% aqueous ethanol pH solutions were used as electrolyte along with the NQ compounds. 99.99% pure nitrogen and oxygen gases were used during the experiments.

A three electrode cell consisting of glassy carbon as working electrode, a platinum wire as counter electrode and silver electrode as reference electrode was used for this investigation. The copper nanoparticle modified electrode was fabricated by the evaporation of copper nanoparticle over the surface of glassy carbon electrode and used as working electrode. The copper nanoparticle coated GCE (CuNP/GCE) was immersed in the cell solution containing 50% aqueous – ethanol buffer and NQ solutions to carry out the electrochemical studies using CH Instrument Electrochemical workstation.

3. RESULTS AND DISCUSSION

3.1 Electrochemical Behaviour of NQs at CuNP/GCE

The cyclic voltammetric studies of 1,4-naphthoquinones were performed on the surface of CuNP/GCE under deoxygenated and oxygen saturated buffers of pH 1.0 – 13.0.

3.1.1 Voltammetric Behaviour of NQs

Voltammograms of 1,4-naphthoquinones at the copper nanoparticle modified glassy carbon electrode (CuNP/GCE) under deaeration were obtained at different scan rates to study the influence of scan rate on peak current. The peak separation increases with an increase in scan rate which proves the quasi-reversibility of the electron transfer process at CuNP/GCE.

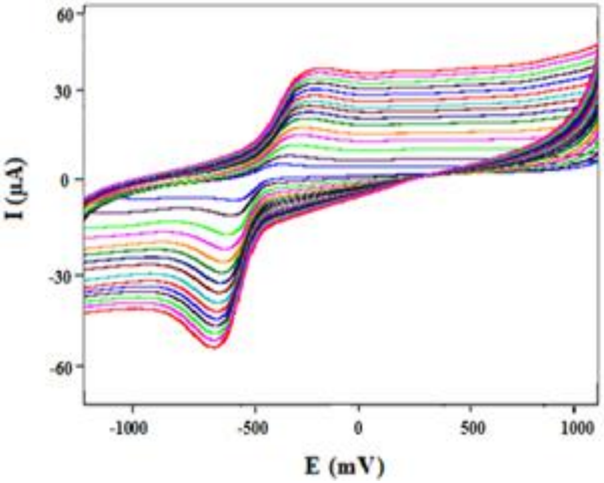


Figure 1 Cyclic voltammograms of 2-Am-3-ClNQ at CuNP/GCE in deoxygenated buffer of pH 6.0 at scan rates 20, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650 and 700 mVs^{-1}

For instance, figure 1 represents the cyclic voltammetric response of 2-Am-3-ClNQ on CuNP/GCE at different scan rates. The plot of cathodic peak current (I_{pc}) versus square root of scan rate ($\upsilon^{1/2}$) is a straight line. Moreover, the linear variation of logarithmic value of cathodic peak current (log I_{pc}) with logarithmic value of scan rate (log υ) with slope values less than 0.5 (0.401, 0.397 and 0.453) suggests that for the reduction of NQ, 2-HyNQ and 2-Am-3-ClNQ, the process is mass transfer as diffusion controlled process [10, 11].Also, for 5-HyNQ the plot of cathodic peak current (I_{pc}) versus scan rate (υ) is linear. And there is a linear variation of log I_{pc} with log υ with slope value greater than 0.5 (0.595) which indicates the adsorption controlled process for 5-HyNQ reduction.

3.1.2 Influence of pH

From our investigation, the voltammetric peak potentials are pH dependent. By increasing the pH of the cell solution, the cathodic peaks shift towards the more negative potentials. The plots of half peak potential (EP/2) versus pH have three distinct linear portions with different slope values of around 90 – 93 mV at low pH values 1.0 – 4.0, around 61 – 62 mV at intermediate pH values and around 31 – 33 mV at high pH values above 10 for all naphthoquinones used. Figure 2 exhibits the half - peak potential versus pH diagram of 2-HyNQ at CuNP/GCE.

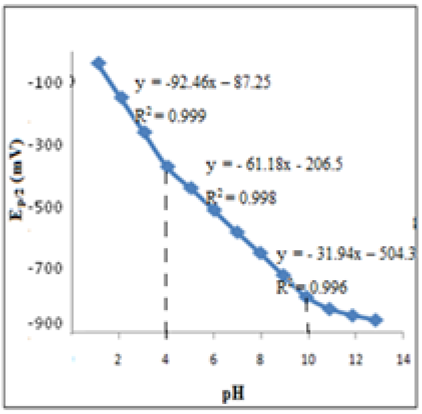


Figure 2 pH – potential diagram for 2-HyNQ

Table: Optimum pH, Maximum shift in oxygen reduction potential (ΔE), surface coverage (Γ_{nq}) values and Diffusion co-efficient of NQs (D_{nq}) at the surface of CuNP/GCE.

NQs	Opt. pH	ΔE (mV)	Γ_{nq} x 10^{-8} Mol cm^{-2}	D_{nq} x 10^{-9} (cm^{2}s^{-1})
NQ	8	427.3	0.91	8.37
2-HyNQ	7	386.7	0.78	9.05
5-HyNQ	7	400.6	0.34	11.73
2-Am-3-ClNQ	7	418.0	0.63	35.85

At low pH values, the electrochemical reaction is a two-electron, three-proton process involving the formation of protonated hydroquinones. However in the intermediate pH range from 4.0 to 10.0, the naphthoquinone derivatives produce the corresponding hydroquinones through a two-electron, two proton process. At higher pH above 10.0, the electrode surface reaction is a two-electron, one-proton process, which leads to the formation of semi-hydroquinone anion.

3.1.3 Stability of the modified electrodes

In order to examine the stability of the modified electrode in the presence of catalyst and the reproducibility of its electrochemical behaviour, the copper nanoparticle modified electrodes was immersed in acidic medium (pH 1.0) containing the catalyst for 20 hours and in neutral medium (pH 7.0) containing NQs for 30 hours and then cyclic voltammograms were recorded. In both acidic and neutral media, there was a slight decrease in the corresponding voltammograms (< 4%). In addition, 30 minutes of repetitive scanning at sweep rate 50 mVs−1 between 0 to -1000 mV at optimum pH including more than 50 complete cycles, revealed no measurable decrease in the peak height or separation of peaks. The reproducibility of the electrocatalytic effect of the modified electrode was ascertained from the unaltered peak potentials and current observed in the cyclic voltammograms of 50 minutes of repetitive cycling at a scan rate of 50 mVs−1 under oxygenated condition at optimum pH. After the repetitive scanning, the cyclic voltammogram was recorded under deaerated condition.

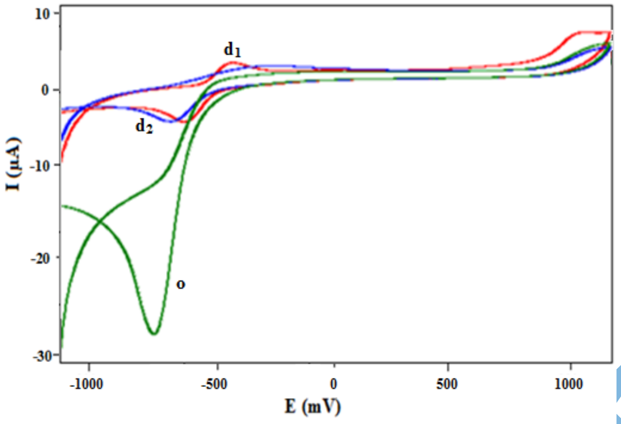
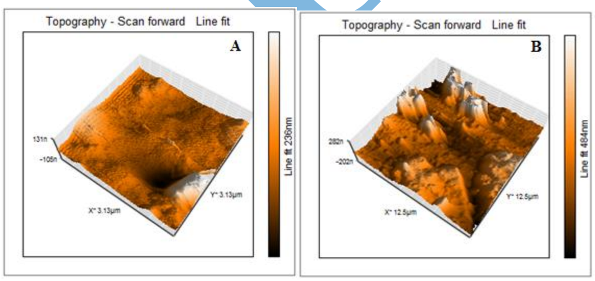


Figure 3 Cyclic voltammograms of 2-Am-3-ClNQ at CuNP/GCE in deoxygenated buffer of pH 8.0 at the beginning (d1), oxygen saturated (o) and again deoxygenated (d2) buffers. Scan rate 20 mVs^{-1}.

A 5% decrease in the peak height with a slight change in the peak separation was observed. As an illustration, the cyclic voltammograms obtained under deoxygenated, oxygen saturated and again deoxygenated conditions are presented in figure 3 for the compound 2-Am-3-ClNQ at CuNP/GCE in pH 8.0 buffer. Thus the stability of the modified electrode against electrocatalytic studies was established.

3.1.4 Surface Coverage

The values of surface coverage of NQs at CuNP/GCE in the optimum pH were calculated from cyclic voltammograms at scan rate 20 mVs^{-1} using the formula $\Gamma_{nq} = Q / nFA$, where Q is the charge consumed, n is the number of electrons involved, F is the Faraday constant (96,500 C mol^{-1}) and A is the geometric area of glassy carbon electrode (0.0314 cm^2). The calculated surface coverage values are tabulated.



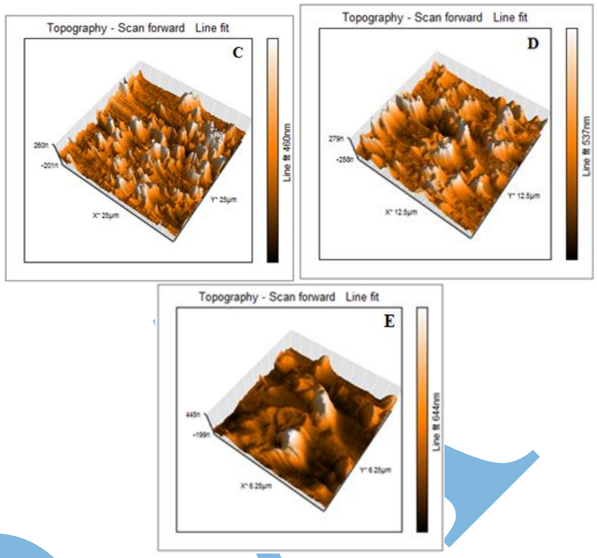


Figure 4 AFM images of (A) CuNP/GCE (B) CuNP/GCE with NQ (C) CuNP/GCE with 2-HyNQ (D) CuNP/GCE with 5-HyNQ and (E) CuNP/GCE with 2-Am-3-ClNQ.

The AFM image of CuNP/GCE without NQs is represented in the Figure 4A and the modified electrodes CuNP/GCE with NQ, 2-HyNQ, 5-HyNQ and 2-Am-3-ClNQ are presented in the figures 4B, 4C, 4D and 4E respectively. These AFM images exhibit the strong adsorption of naphthoquinones on the surface of CuNP/GCE.

3.2 Catalytic oxygen reduction at CuNP/GCE

3.2.1 Influence of pH

The electrocatalytic reduction of oxygen at CuNP/GCE in the presence of naphthoquinones was studied in different buffer solutions of pH1.0 to 13.0. The displacement in the reduction potential of both oxygen and naphthoquinones may be unequal due to their different kinetic behaviour, though the reduction potentials of both are pH dependent [7, 10]. For example, figure 5 exhibits the cyclic voltammograms of naphthoquinone in deoxygenated and oxygenated buffer solutions at CuNP/GCE. Under deoxygenated condition, a single redox couple is observed, but in oxygenated buffer solution the anodic wave vanished and the cathodic peak reached to maximum current. This confirms that the electrocatalytic reduction of oxygen is irreversible at the CuNP/GCE.

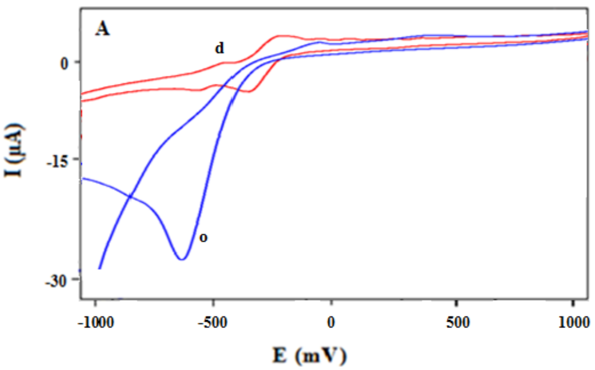


Figure 5 Cyclic voltammograms of NQ at CuNP/GCE in deoxygenated (d) and oxygenated (o) buffers of pH 8.0. Scan rate 20 mVs^{-1}.

The maximum cathodic peak current enhancement and maximum shift in the oxygen reduction potentials at the modified electrode lead to the selection of optimum pH. By this way, pH 8.0 is an optimum pH to examine the electrocatalytic reduction of oxygen in presence of 1,4-naphthoquinone. Raoof and Golabi also reported pH 8.0 for the reduction of oxygen using carbon paste electrode modified by1,4-naphthoquinone [7]. But the optimum pH for other NQ derivatives is 7.0.

The oxygen reduction occurs irreversibly at bare GCE with a peak potential at about -1147.5 mV in the buffer of pH 7.0 and -977.3 in pH 8.0 buffer. The CuNP/GCE with NQ reduces oxygen at potential -550.0 mV and the maximum shift in oxygen reduction potential (ΔE) was observed by about 427.3 mV in the buffer solution of pH 8.0. Similarly the CuNP/GCE induces the reduction of oxygen at potentials -760.8, -746.9 and -729.5 mV in 2-HyNQ, 5-HyNQ and 2-Am-3-ClNQ solutions respectively. Thus the ΔE values were observed by about 386.7, 400.6 and 418.0 mV in 2-HyNQ, 5-HyNQ and 2-Am-3-ClNQ solutions respectively in the buffer of pH 7.0. The optimum pH and the shifts in oxygen reduction potential for all NQs at CuNP/GCE are given in the table.

3.2.2 Influence of Scan rate

The influence of scan rate on cathodic peak current was also investigated for oxygen reduction at the copper modified electrode CuNP/GCE in NQ solutions. Here, the linear variation of cathodic peak current (I_{pc}) with square root of scan rate ($\upsilon^{1/2}$) and the non-linear variation of cathodic peak current (I_{pc}) with scan rate (υ) clearly confirm the diffusion controlled process [10, 11] for oxygen reduction with all NQs used. The straight line plots of log I_{pc} versus log υ with slope values around 0.2 - 0.4 for all NQs used at CuNP/GCE in the optimum pH, also prove the diffusion controlled process of oxygen reduction.

3.3 Chronoamperometric studies

By applying the double potential step technique at an initial and final potentials of -100 and -800 mV respectively, the chronoamperograms were carried out for all NQs at CuNP/GCE in deoxygenated and oxygenated buffer solutions. As an example, chronoamperograms of 2-Am-3-ClNQ at CuNP/GCE in deoxygenated and oxygenated buffer solutions of pH 7.0 are given in Figure 6. The net electrolysis current (I_{net}) was determined by point to point subtraction of the background current in the presence and absence of oxygen. Under deoxygenated condition, a plot of net current against $t^{-1/2}$ shows a straight line which extrapolates close to origin. From the slope of I versus $t^{-1/2}$ under deoxygenated condition, the diffusion coefficient values of naphthoquinones were calculated using the Cottrell equation.

$$I = n F D^{1/2} A C_{nq} \pi^{-1/2} t^{-1/2.}$$

$$\text{Slope} = n F D^{1/2} A C_{nq} \pi^{-1/2}$$

Where C_{nq} is the concentration of NQs used, D is the diffusion co-efficient of NQs and A is the geometric area of glassy carbon electrode (0.0314 cm^2). The calculated D_{nq} values are reported in the table.

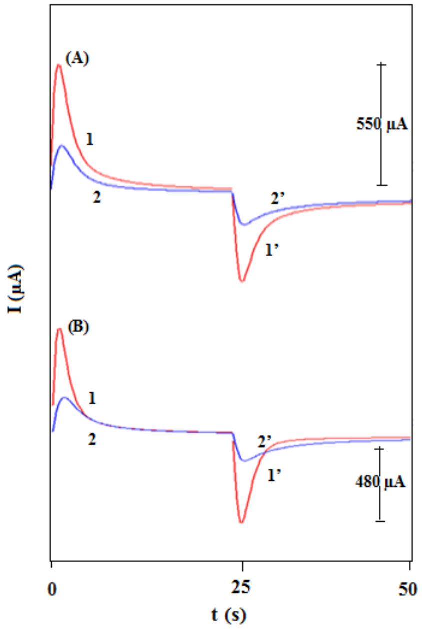


Figure 6 Chronoamperograms obtained in pH 7.0 by the double potential-step technique at an initial potential of –100 mV and final potential of –800 mV versus silver electrode. (A) 1,1' for CuNP/GCE in presence of 2-Am-3-ClNQ in oxygenated buffer, 2,2' as 1,1' for the bare GCE in the absence of 2-Am-3-ClNQ. (B) 1,1'for CuNP/GCE in presence of 2-Am-3-ClNQ in deoxygenated buffer, 2,2' as 1,1' for the bare GCE in the absence of 2-Am-3-ClNQ.

3.4 Chronocoulometric studies

Chronocoulometric studies were carried out by double potential – step technique at an initial and final potential of about -100 and -800mV respectively for all NQs at CuNP/GCE in deoxygenated and oxygenated buffer solutions. An example of chronocoulomogram for 5-HyNQ at CuNP/GCE in the buffer solution of pH 7.0 is represented in the figure 7. Under deoxygenated condition, reversible curve was observed. But under oxygenated condition, a large enhancement in the charge of forward curve and a nearly flat line when the potential was reversed prove the irreversible electrocatalytic reduction of oxygen.

The number of electrons involved in the reduction of naphthoquinones (n_{nq}) at the optimum pH was calculated from the slope of Q versus $t^{1/2}$ plot under deoxygenated condition using the Cottrell equation.

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

By applying the diffusion coefficient values of NQs from chronoamperometric data, n_{nq} was found to be 2.0. The number of electrons involved in the oxygen reduction (n_{O_2}) was also calculated from the slope of Q versus $t^{1/2}$ plot under oxygenated condition and found to be 2.0 when C =1.25 mM, A = 0.0314 cm^2 and D = 1.57 $x10^{-5}$ cm^2 s^{-1}.

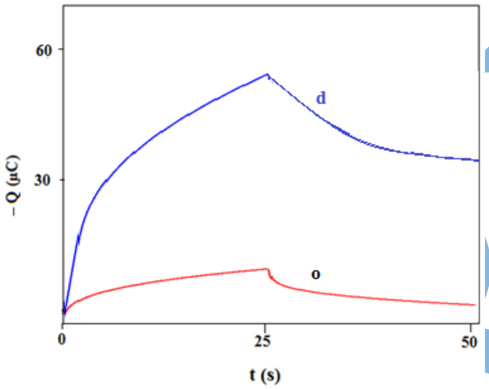


Figure 7 Chronocoulometric curves of 5-HyNQ at CuNP/GCE in deoxygenated (d) and oxygenated (o) buffers of pH 7.0.

4. CONCLUSION

1,4-Naphthoquinone and some of its derivatives have been used as electrocatalysts for the reduction of oxygen at bare and copper nanoparticle modified glassy carbon electrode. Cyclic voltammetric, chronoampero- metric and chronocoulometric techniques were employed to study the electrochemical and catalytic behaviour of CuNP/GCE in combination with NQ. CuNP/GCE combined with naphthquinones exhibited the electro- catalytic ability with overpotentials of about 386 - 427 mV lower than at a bare GCE. Thus, the CuNP/GCE with NQ can be used as oxygen sensors. The diffusion coefficient, surface coverage and the number of electrons involved in reduction processes were determined. Also, the surface of the modified electrode was characterised using AFM images.

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