Bulletin of Electrochemistry 6 (6) June 1990, pp 630–632

Quinone/hydroquinone modified glassy carbon electrode

T Madan Mohan, H Gomathi and G Prabhakara Rao
Central Electrochemical Research Institute, Karaikudi-623 006, INDIA

Glassy carbon electrode has been modified with quinone/hydroquinone redox species by an electrochemical method. The surface attached species were found to catalytically mediate the electron transfer for the oxidation of ferrocene, ascorbic acid and ferrocyanide. A CE mechanism is suggested.

Key words: Glassy carbon electrode, quinone-hydroquinone electrocatalysis, chemically modified electrodes

INTRODUCTION

There has been growing interest to develop chemically modified electrodes, with desired properties, using fast-outer sphere electron transfer agents, electron transfer mediator catalysts, photosensitizers etc. An exhaustive review on chemically modified electrodes is given by Murray [1]. We reported briefly our observations on the modifications of carbon by quinhydrone and confirmed the same from the voltammetric data [2]. In the present study using such quinone/hydroquinone modified carbon surface, the oxidations of ferrocene, ascorbic acid and ferrocyanide have been investigated with a view to assess the catalytic activity of such modified carbon and the relevance of mediated electron transfer during the above oxidations using the surface bound quinone/hydroquinone.

EXPERIMENTAL

The voltammetric experiments were carried out with Wenking Potentioscan-Generator (POS 73) coupled to X-Y recorder.

The electrolytic cell had provisions for working, counter and reference electrodes and also for deaeration. 3mm dia glassy carbon electrode (Chemtix Inc., USA) mounted in teflon and attached to glass body with suitable ground joint was used as working electrode. A counter electrode of platinum foil and reference electrode of Ag/AgCl were employed.

Working solutions were prepared using pure chemicals, and double distilled water. Ferrocene was dissolved in ethanol and made up in perchloric acid + sodium perchlorate medium. For ascorbic acid glycine buffer (pH 2.5) and for ferrocyanide 0.5 M KCl were employed as background electrolytes.

RESULTS AND DISCUSSION

Modification of the electrode and its characterisation

Glassy carbon electrode polished with emery strips (0 to 4 grade) gives a background response represented in Fig. 1(a) in 0.1M sulphuric acid, when the electrode is cycled in the potential range −0.4V to +1.5V for 30 min. in 0.1M H_2SO_4 containing 1mM hydroquinone, the electrode gets modified. The response of the modified electrode in 0.1M H_2SO_4 is given is Fig. 1(b); well defined peaks are obtained both in the anodic and cathodic directions. The features were permanent after thorough washing and withstood several hundreds of cycling in 0.1M sulphuric acid.

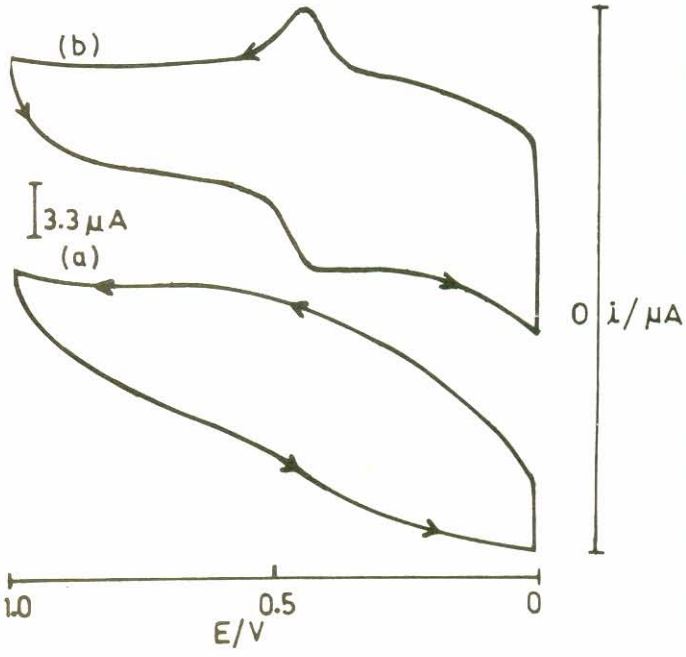


Fig. 1: CV response of (a) untreated GC (b) Q/H₂Q modified GC in 0.5 M H_2SO_4. Scan rate = 20 mV sec $^{-1}$

Influence of pH

The surface attached quinone/hydroquinone shows a marked shift in redox potential with pH as seen from Fig. 2. The shift in peak potential is 60mV for a unit change in pH. It is interesting to note that redox couple is stable on the surface and shows reversible characteristics in the pH range 1 to 10. It is therefore possible to use the modified electrode as pH indicator electrode.

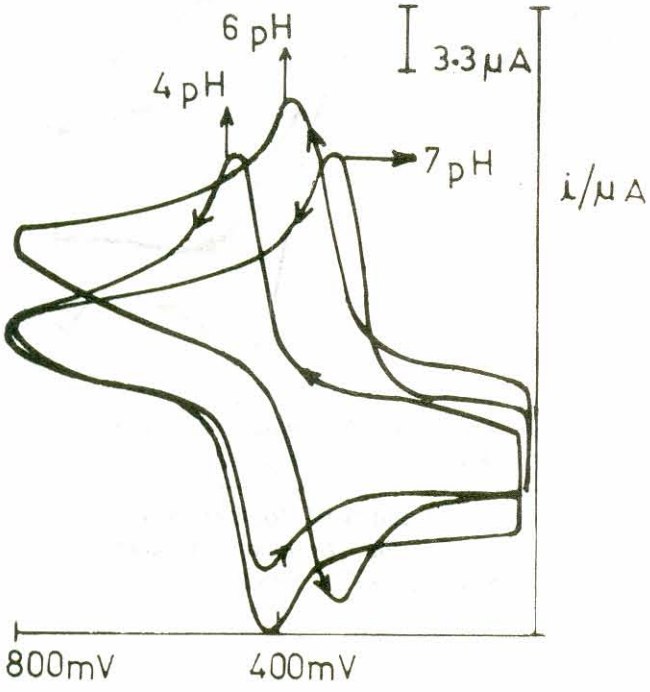


Fig. 2: CVs obtained with Q/H_2Q modified GC in various pH buffers. Scan rate = 5 mV.sec^{-1}

Electrocatalytic activity

Ferrocene oxidation: The modified electrode gives the response represented in Fig. 3(b) for the oxidation of ferrocene in the medium studied. When compared with the response of unmodified electrode (Fig. 3(a)), there is enhancement of current for the oxidation of ferrocene in the medium studied.

On an untreated GC electrode, ferrocene undergoes a direct single electron transfer reaction. Analysis of cyclic voltammograms obtained at different scan rates for ferrocene oxidation shows that the current function ($i_p/\nu^{1/2}$) decreases as the scan rate ν increases with V characterising a preceding chemical reaction [3], suggesting a CE mechanism. On a modified electrode, the electron transfer is mediated by the surface attached quinone/hydroquinone molecule as given by the following reaction scheme.

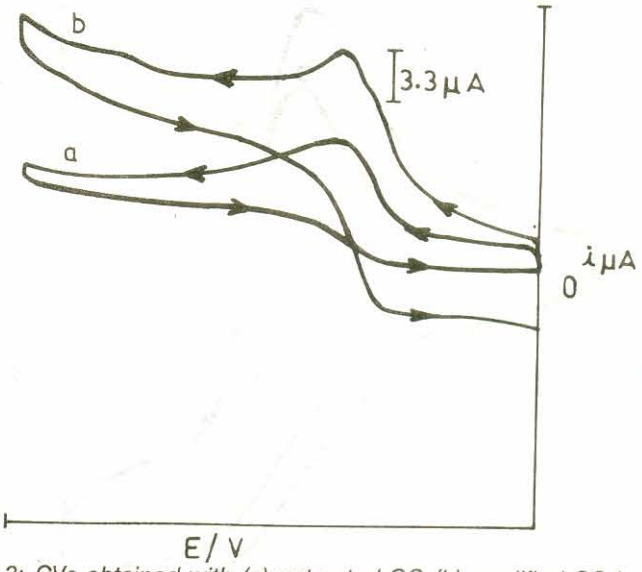
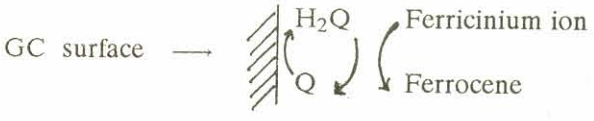


Fig. 3: CVs obtained with (a) untreated GC (b) modified GC in ferrocene + $HClO_4$ + $NaClO_4$ solution
Scan rate = 5 mV.sec^{-1}

$$Z \underset{K_b}{\overset{K_f}{\rightleftharpoons}} O + ne \overset{K}{\rightleftharpoons} R \qquad (1)$$



(2)

Ascorbic acid oxidation

Ascorbic acid oxidation is also catalysed by the Q/H_2Q modified electrode as seen from Fig. 4. In this case, the peak potential shifts anodically with increasing scan rate. Current function decreases as ν increases characterising again a CE mechanism.

Ferrocyanide oxidation

The catalytic effect of the modified electrode on ferrocyanide oxidation is seen from Fig. 5. The details of the model of electron transfer in this case and also the rates of electron transfer reactions are being worked out.

CONCLUSION

Good catalysis on modified glassy carbon with quinone/hydroquinone for the oxidation of ferrocene, ferrocyanide and ascorbic acid has been recorded. These catalytic oxidations have been found to take place through the mediated electron transfer with the agency of quinone/hydroquinone.

REFERENCES

1. R W Murray, *Chemically Modified Electrodes in Electroanalytical Chemistry*, (Ed), A J Bard, Vol. 13,

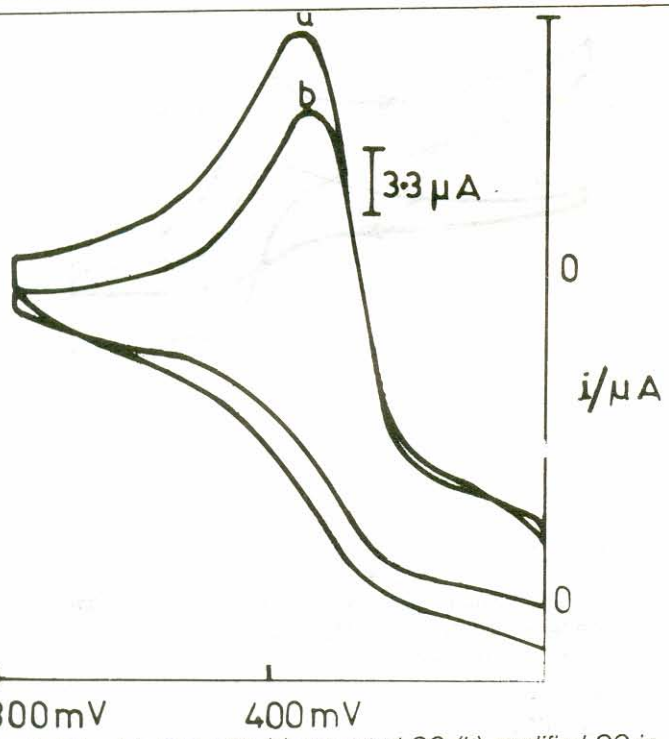


Fig. 4: CVs obtained with (a) untreated GC (b) modified GC in 10 mM ascorbic acid and glycine buffer
Scan Rate = 5 mV.sec^{-1}

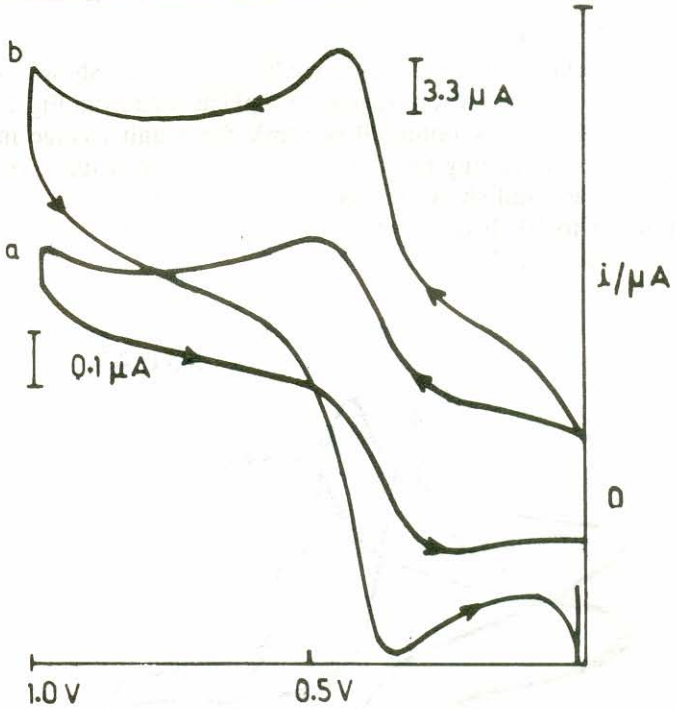


Fig. 5: CVs obtained with (a) untreated GC (b) modified GC 1N 1 mM $K_4Fe(CN)_6$ + 0.5M KCl. Scan rate = 5 mV.sec^{-1}

Marcel Dekker Inc., New York, (1984), p 191

2. H Gomathi and G Prabhakara Rao, *J Electroanal Chem* **190** (1985) 85

3. A Weissberger and B W Rossiter, (Ed) *Physical Methods of Chemistry-Part IIA, Electrochemical Methods*, Wiley, Interscience, (1971) p 482