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Electrocatalysis of O_2 Reduction at Glassy Carbon Electrodes Modified with Adsorbed 1,4-Dihydroxy-9,10-anthraquinone Derivatives

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The preparation and electrochemical characterization of glassy carbon electrodes modified by four recently synthesized 1,4-dihydroxy-9,10-anthraquinone derivatives are reported. The anthraquinones used were strongly and irreversibly adsorbed on the preanodized glassy carbon electrodes. The electrochemical behavior and stability of the modified electrodes were studied by cyclic voltammetry at different acidic and basic aqueous solutions, and pH of 6—7 was chosen as the optimum working pH. The adsorbed anthraquinone derivatives showed excellent electrocatalytic ability for the reduction of O_2 to H_2O_2 with overpotentials of from 560 to 650 mV lower than that of a plain glassy carbon electrode. The heterogeneous rate constants for the reduction of O_2 at the surface of the modified electrodes were determined by rotating-disk electrode voltammetry using the Koutecky–Levich plots. The apparent diffusion coefficient of O_2 in buffered aqueous O_2-saturated solutions was also estimated.

In recent years, there has been considerable interest in the electrocatalytic reduction of dioxygen under different experimental conditions,[1—14] mainly due to its involvement in energy conversion and storage.[15] A wide variety of compounds have been proposed as electrocatalysts for modifying electrode surfaces with an electron-transfer material for dioxygen reduction. Among these compounds are metalloporphyrin complexes,[1—3] metal phthalocyanines,[4,5] macrocyclic Co^{2+} complexes,[6—8] some complexes of Cu^{2+} [9,10] and Fe^{3+} [11] with chelating ligands, vitamin B_{12},[12] anthraquinone polymers,[13] and 1,4-naphthoquinone derivatives.[14] However, in many cases, the resulting modified electrodes suffer from limited lifetimes and/or difficulties in the modification step. Thus, there is still a great deal of interest in the development of new materials, especially those immobilized on electrodes' surfaces, for the electrocatalytic reduction of dioxygen to water or hydrogen peroxide.

Studies of the electrochemical behavior of different quinone derivatives, especially 9,10-anthraquinones, have received considerable attention during the past decade,[16—21] due to the fundamental importance of these compounds in both industry and in medicine.[22—24] The anthraquinone derivatives have also shown strong adsorption tendencies on various electrode materials, including Pt,[25] Hg,[26] graphite,[27,28] and glassy carbon.[29] It has been shown that the electrochemical oxidation of glassy carbon electrodes in a 1 : 1 concentrated nitric acid–sulfuric acid mixture enhances the quinone–hydroquinone adsorption on the electrode's surface.[30]

In recent years, we conducted studies on some new derivatives of 9,10-anthraquinone and 9-anthrone, including pK_a determinations,[31—33] the solubility in supercritical CO_2,[34] the electrochemical behavior[21] and some of their applications in the preparation of liquid membranes for the extraction and transport of metal ions[35] and in the preparation of ion-selective electrodes.[36,37] In this work, we examined four recently synthesized 1,4-dihydroxy-9,10-anthraquinone derivatives (Fig. 1)[38] for the modification of glassy carbon electrodes. When adsorbed on the surface of preanodized glassy carbon electrodes, the used anthraquinones revealed enhanced catalytic activity for the electroreduction of dioxygen. The electrochemical behavior, efficiency and stability of the resulting modified electrodes were investigated by cyclic voltammetry and rotating-disk electrode voltammetry.

Experimental

Anthraquinone derivatives (1-hydroxy-4-(prop-2′-enyloxy)-9,10-anthraquinone (**A1**), 1-methoxy-4-(prop-2′-enyloxy)-9,10-anthraquinone (**A2**), 1,4-bis(methoxy)-9,10-anthraquinone (**A3**), and 1,4-bis(prop-2′-enyloxy)-9,10-anthraquinone (**A4**)) were synthesized,[38] and after recrystallization from reagent-grade benzene (Merck) and vacuum drying were characterized by IR, NMR, GC-MS, and elemental analysis. HPLC-grade acetonitrile (Fluka) was used as received. Triply distilled deionized water was used throughout. All chemicals used were of the highest purity available, and were used without any further purification, except for vacuum drying over P_2O_5. The buffers having different pH values were 0.1 $mol\,dm^{-3}$ H_2SO_4+NaOH (for pH = 0.5—1.5), 0.1 $mol\,dm^{-3}$ H_3PO_4+NaOH (For pH = 2.0—3.0), 0.1 $mol\,dm^{-3}$ acetate buffer (for pH 3.5—6) and 0.1 $mol\,dm^{-3}$ NaH_2PO_4+NaOH (for pH = 6.5—13.0). N_2 gas with 99.999% purity was used to deaerate the solutions during the experiments.

The glassy carbon electrodes (GC, Metrohm, 0.031 cm^2 area) were polished with alumina (0.05 μm) for 5 min and then washed

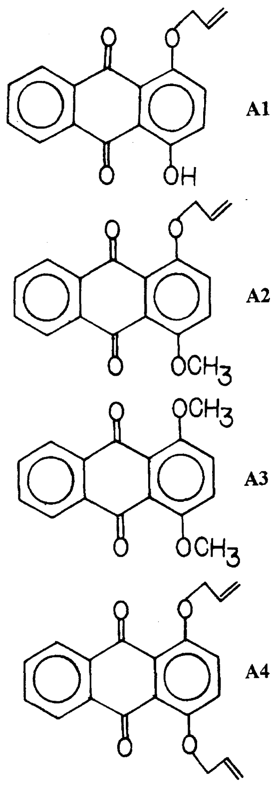

Fig. 1. Structure of the anthraquinone derivatives used.

with water. Preanodization of glassy carbon electrodes was performed by oxidizing the electrodes by potential cycling between 1.8 and −0.5 V at scan rates of 100 mV s^{-1} in solutions containing 0.5 mol dm^{-3} H_2SO_4 for 5 to 20 min, until a constant background was observed. The polarized GC electrodes were then placed in the deposition solutions (1.0×10^{-3} mol dm^{-3} anthraquinone in acetonitrile) at open circuits for varying time periods (2—6 h).[39] The resulting modified electrodes were rinsed thoroughly with water before being subjected to electrochemical measurements.

A three-electrode system with a Pt wire counter electrode, an Ag/AgCl (satd) in a 3 mol dm^{-3} KCl reference electrode and a modified GC working electrode was employed. Electrochemical measurements were carried out at a thermostated temperature of 25.0±0.1°C. All voltammograms were recorded on a Metrohm multipurpose instrument (model 693 VA processor) equipped with a 694 VA stand and a thermal printer. A Metrohm drive shaft for rotating disk electrodes was used. The pH measurements were made with a Metrohm 632 pH meter using a combined glass electrode.

Results and Discussion

Electrochemical Behavior and Stability of the Modified Electrodes. Glassy carbon electrodes modified by adsorptive films of anthraquinones **A1**—**A4** were prepared by the electrochemical oxidation of GC electrodes, followed by their immersion in anthraquinone solutions in acetonitrile. Figure 2 shows cyclic voltammograms of the GC electrode modified by compound **A1** in a 0.5 mol dm^{-3} H_2SO_4 solution at various scan rates. A well-defined redox peak corresponding to the reversible reduction of the anthraquinone was observed. A formal potential of −60 mV vs. Ag/AgCl was obtained by averaging the cathodic and anodic peak potentials. The ratio of the anodic-to-cathodic peak currents obtained at various scan rates was almost unity. The anodic and cathodic currents increased linearly with the scan rate within the studied range, as shown in the inset of Fig. 2. The cyclic voltammograms are almost symmetric at −80 mV, and small separation of peaks were observed at low scan rates (i.e. lower than 20 mV s^{-1}). A similar electrochemical behavior was observed for the case of other anthraquinones (**A2**—**A4**).

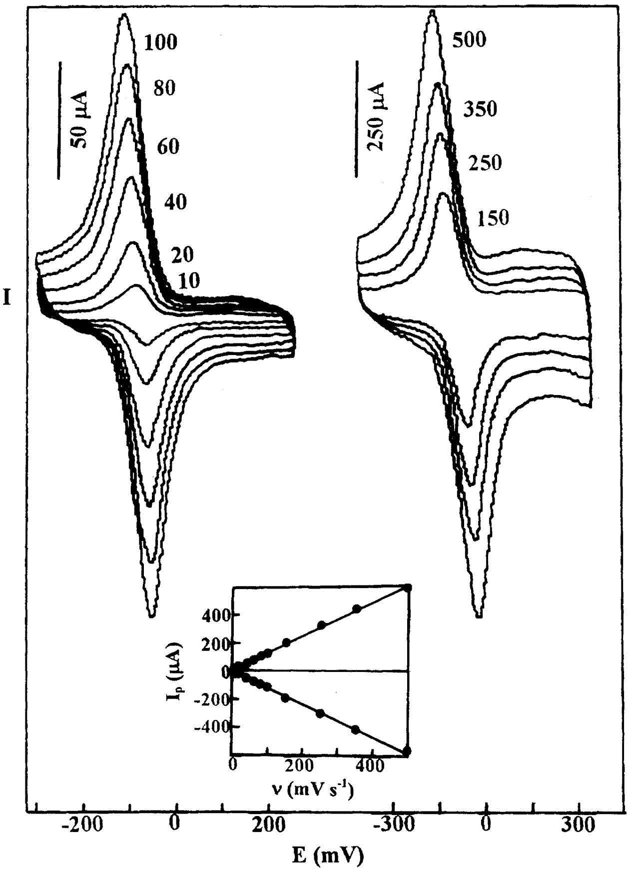

Fig. 2. Cyclic voltammograms for compound **A1** adsorbed on a glassy carbon electrode at various scan rates. The scan rates in mV s^{-1} are shown on the corresponding cyclic voltammograms. The inset shows the plots on the anodic and cathodic currents vs. scan rates.

Actually, it was theoretically established by Laviron[40] that the observed peak separation becomes an index of the electron-transfer rate between the electrode and the adsorbed species. According to this theory, it is possible to evaluate the standard rate constant (k_s) for an electron transfer as well as the transfer coefficient (α) by measuring the variations in the peak potentials (ΔE) with the scan rate (log v). A sample Laviron diagram is shown in Fig. 3, and the resulting k_s and α values for different anthrauqinones used are summarized in Table 1.

The formal potentials evaluated for anthraquinones **A1**—**A4** are listed in Table 2. As can be seen, the formal potentials of all anthraquinone derivatives are closely located around −60 mV. This is most probably because the R-substituents are located far enough from the electroative centers of the mother molecule so that they have no measur-

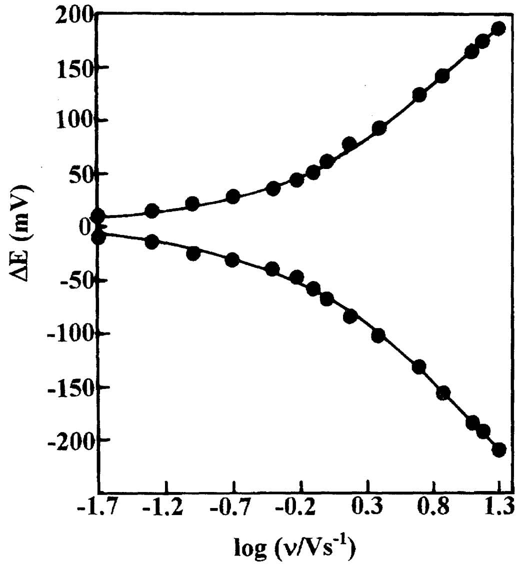

Fig. 3. Laviron plot of ΔE vs. $\log v$ for a GC electrode modified with **A3** in 0.5 M H_2SO_4.

Table 1. The Standard Rate Constants (k_s) and Transfer Coefficients (α) Obtained from Laviron Plots for the GC Electrodes Modified by Anthraquinones **A1**—**A4**

Anthraquinone	k_s/s^{-1}	α
A1	16.5	0.36
A2	14.5	0.39
A3	15.5	0.42
A4	17.6	0.40

Table 2. Formal Potential (E_f), Surface Coverage (Γ), Dioxygen Reduction Peak Shift (ΔE), Heterogeneous Rate Constant (k), and Diffusion Coefficient (D) for the Electrocatalytic Reduction of O_2 at the Surface of GC Electrodes Modified by Anthraquinones **A1**—**A4**

Anthraquinone	E_f	$10^9\,\Gamma$	ΔE	$10^{-3}\,k$	$10^5\,D$
	mV	$mol\,cm^{-3}$	mV	$mol^{-1}\,dm^3$	$cm^2\,s^{-1}$
A1	−58	8.4	560	6.5	1.5
A2	−55	7.8	630	6.1	1.7
A3	−60	3.6	650	6.8	1.6
A4	−62	2.1	570	5.7	2.0

able effect on the formal potentials of different anthraquinone derivatives. The surface coverage (Γ) can be evaluated from the equation

$$\Gamma = Q/nFA,$$

where Q is the charge obtained by integrating the cathodic peak under the background correction (at a low scan rate of 5 $mV\,s^{-1}$); all other symbols have their usual meanings. The calculated Γ values for compounds **A1**—**A4** are also included in Table 2. As can be seen, the surface coverage decreased in the order **A1** > **A2** > **A3** > **A4**. This trend seems to reflect the decreased adsorbing tendency of the anthraquinone derivatives by increasing the bulkiness and the symmetry of substituents on their 1- and 4-hydroxy groups.

The stability of the modified electrodes were tested by their immersing in a 0.5 $mol\,dm^{-3}$ H_2SO_4 solution for varying periods of time, followed by recording the corresponding cyclic voltammograms. It was observed that there was only a slight decrease in the corresponding peak currents (i.e. < 10%) after immersing in acid solutions for 72 h. On the other hand, the loss of the adsorptive anthraquinone species was more pronounced when the electrodes were exposed to basic solutions, since, in this case, the OH of anthraquinone is in its reduced form,[31—33] and dissolves in aqueous solutions. It is interesting to note that, although the adsorptive anthraquinone species were continuously detached from the electrode surface after prolonged soaking in basic solutions, the very last few monolayers of the adsorbed species remained lightly bound to the preanodized GC surfaces. They remained at the electrode surfaces even after brief polishing with alumina on a polishing cloth; sometimes it required extensive polishing with sand paper to remove the residual adsorptive anthraquinones.

The stability of the modified electrodes was also investigated in the presence of dioxygen. The modified electrodes were found to be quite stable against O_2 reduction, under the used experimental conditions. Forty minutes of repetitive scanning between 0 and −800 mV at pH 6, including more than 50 complete cyclic voltammograms, revealed no measurable decrease in the redox peak currents. Moreover, in cases where the modified electrodes were applied as rotating electrodes, the observed decrease in the current was negligible. However, in the presence of dioxygen, the adsorptive anthraquinones began to detach after prolonged soaking in alkaline solutions.

pH Dependence of the Modified Electrodes. Since the electrochemical behavior of most anthraquinone derivatives is pH dependent, due to the occurrence of a two-proton, two-electron reduction in aqueous solution,[18,19] we anticipated that the redox response of the modified electrodes would be pH dependent. In order to ascertain this, the voltammetric responses of the modified electrodes were obtained in aqueous solutions of varying pH from 1.0 to 8.0. Figures 4A and 4B show the cyclic voltammograms of a GC electrode modified with compound **A3** at various pH values. As can be seen, all of the cyclic voltammograms possess a single redox couple whose anodic and cathodic potentials shift toward more negative values upon increasing the pH of the solution.

For all of the anthraquinone derivatives used, the corresponding plots of the formal potential against the pH resulted in a straight line (at pH $\leq$ 8) with a slope of 61—64 mV per pH unit. A sample potential–pH plot is shown in Fig. 4C. The results are indicative of a two-electron two-proton process, resulting in the formation of the corresponding hydroquinone derivative. It is interesting to note that, as is obvious from Figs. 4A and 4B, there is a gradual decrease in the surface coverage of the modified electrode by increasing the pH of the solution. The resulting loss of adsorptive anthraquinone could be due to either displacement of the adsorbed material by anions that are part of the buffer systems or, alternatively, due to hydrolysis of the adsorbed anthraquinones at high pH

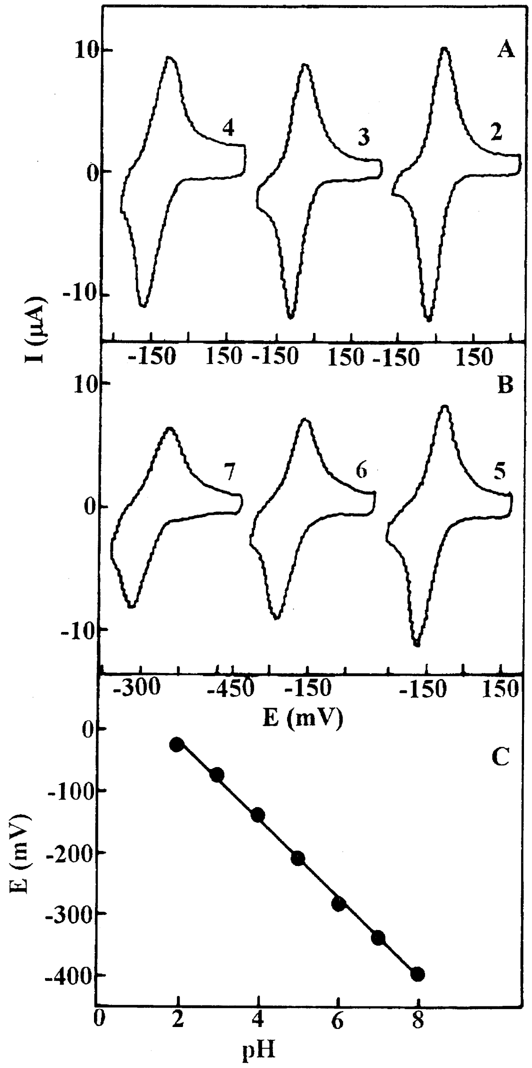

Fig. 4. A, B) cyclic voltammograms for the glassy carbon electrode modified by compound **A3** at a scan rate 20 mV s^{-1} at different pH values. The pH values are indicated on the corresponding cyclic voltammograms. C) pH dependence of the formal potential for compound **A3** adsorbed on a glassy carbon electrode.

values.[31—33] The cyclic voltammograms obtained at pH > 8 showed a rather dramatic loss in surface coverage and poorly defined waves.

Electrocatalysis of Dioxygen Reduction at Modified Electrodes. The anthraquinone polymers[13] and 1,4-naphthoquinone[14] have been shown to act as highly active electron-transfer mediators for the electrocatalytic reduction of dioxygen. In preliminary experiments, we found that the electrocatalytic reduction of dioxygen to hydrogen peroxide can successfully occur at the surface of GC electrodes modified by anthraquinones **A1**—**A4** in acidic media. Although the reduction potentials of both dioxygen and anthraquinones are pH dependent,[41] their displacement may be unequal, because of their different kinetic behavior.[14] Thus, a pH of about 6—7 (depending on the nature of the modifying anthraquinone) was found to be the optimum pH, where the electrode's anodic wave completely disappeared and the cathodic wave reached its maximum value.

As an example, cyclic voltammograms at pH 7.0 of a GC electrode modified by compound **A1** in both the absence and presence of O_2 were compared with the corresponding voltammograms at the surface of a bare GC electrode, as shown in Fig. 5. Figure 5A shows that while the bare GC electrode gives no detectable peak in a deaerated solution, in the presence of dioxygen, O_2 reduction occurs irreversibly with a peak potential located at about -1180 mV. On the other hand, in the presence of dioxygen, these is a rather large enhancement in the cathodic peak current of a GC electrode modified with **A1** (Fig. 5B), while the corresponding anodic peak has disappeared. This is clearly indicative of the electrocatalytic reduction of O_2 at a peak potential of about -550 mV. The observed shifts in the reduction of dioxygen at the surface of the GC electrodes modified by anthraquinones **A1**—**A4** are also included in Table 2. It is noteworthy that the potential shifts (ΔE) observed in this work were larger than those reported for most of the catalytic reductions of O_2 at the surfaces of different modified electrodes.[1—14] Figure 6 shows the influence of the O_2 concentration on the cyclic voltammogram of the GC electrode modified with **A1**. As can be seen, while the cathodic peak current increases with the dioxygen concentration, there is a simultaneous gradual decrease in the anodic peak current, so that the corresponding peak completely disappears at a 1.2×10^{-3} M concentration of dioxygen (1 M = 1 mol dm^{-3}).

A sample scan-rate dependence of cyclic voltammograms for the GC electrode modified by anthraquinone **A3** in a buffer solution of pH 6.0 saturated with O_2 is shown in Fig. 7. It can be seen that the catalytic reduction peak poten-

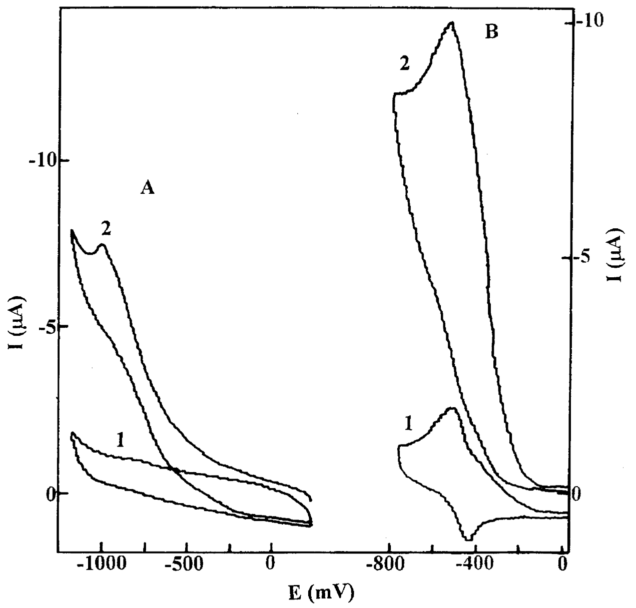

Fig. 5. A) cyclic voltammograms for a bare glassy carbon electrode in a 0.1 mol dm^{-3} phosphate buffer (pH = 7) at a scan rate of 20 mV s^{-1} in the absence (1) and presence (2) of O_2. B) Same as A for a glassy carbon electrode modified with compound **A1**.

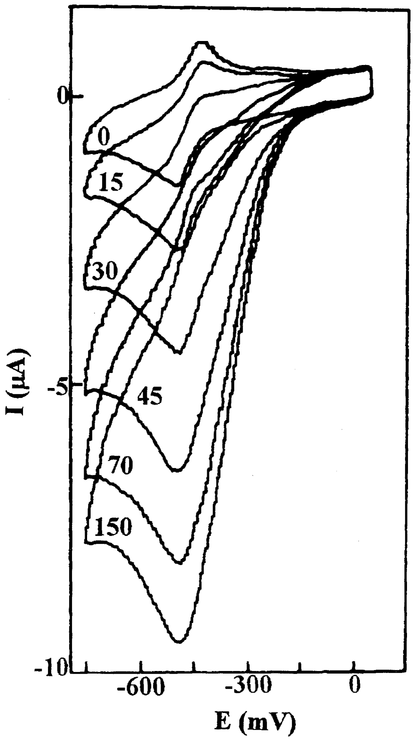

Fig. 6. Voltammetric behavior at 20 mV s^{-1} in a 0.1 mol dm^{-3} phosphate buffer (pH = 7) solution at a glassy electrode modified with compound **A1** in the absence (1) and presence (2—6) of increasing concentration of O_2. The oxygenation time (*s*) is: 1, 0; 2, 15; 3, 30; 4, 45; 5, 70; 6, 120.

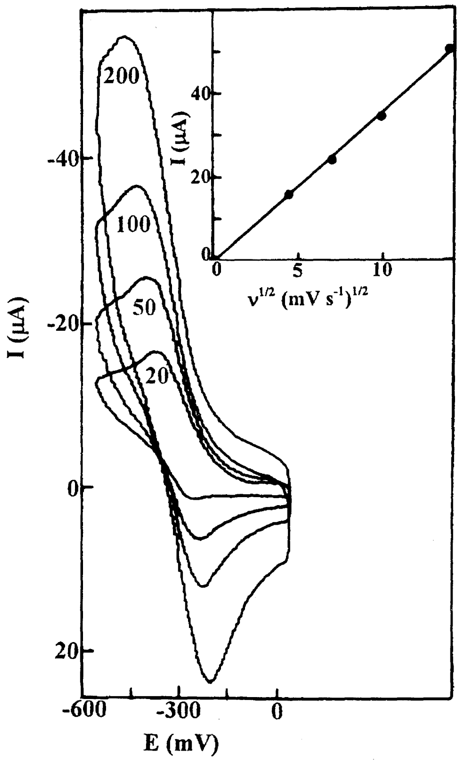

Fig. 7. Cyclic voltammograms of a glassy carbon electrode modified with compound **A3** in a buffered (pH = 6) O_2-saturated aqueous solution at various scan rates. The scan rates in mV s^{-1} are indicated on the corresponding cyclic voltammograms. The inset shows the corresponding plot of I_{PC} vs. $v^{1/2}$.

tial for dioxygen shifts slightly in the negative direction and the anodic peak begins to grow with increasing scan rate. A similar scan-rate dependence was observed for other modified electrodes. Such a behavior is most probably indicative of a kinetic limitation existing in the reaction between the adsorbed anthraquinone and dioxygen. Actually, the reduction current for O_2 increases linearly with the square root of the scant rate (inset of Fig. 7), indicating that at sufficient overpotentials the reaction is transport limited.[42,43] A similar behavior has also been reported for some other modified electrodes.[14,42—44] The obtained results show that the overall electrochemical reduction of dioxygen at the modified electrodes introduced might be controlled by the diffusion of O_2 in solution and by the cross-exchange process between O_2 and the redox sites of the anthraquinone derivatives used.

Reduction of O_2 at a Rotating-Disk Electrode Modified by Anthraquinones A1—A4. The catalysis of dioxygen reduction by adsorbed anthraquinone derivatives was also examined at rotating-disk electrodes. Figure 8A shows a set of current–potential curves recorded in an O_2-saturated solution with a rotating GC disk electrode on which 8.4×10^{-9} mol cm^{-2} of compound **A1** was adsorbed. Curve a is the response of the modified electrode in the absence of O_2. The rotating GC disk electrodes modified by other anthraquinones used show a similar behavior. As can be seen from Fig. 8A, a plateau current can be hardly achieved for the catalyzed reduction of O_2 by the adsorbed anthraquinone, even at a potential of −650 mV; the current still tends to increase with cathodic shifts. A gradual desorption of the anthraquinone from the electrode surface was found to be insignificant during the time required to record the current–potential curves.

In saturated dioxygen solutions, Levich[45] (Fig. 8B) and Koutecky–Levich[46] (Fig. 8C) plots were prepared from the current–potential curves. The Levich plot in Fig. 8B is very close to the calculated line for a two-electron process ($n = 2$), although some negative deviation at higher rotation speeds (ω) is observed. For a catalyzed reduction in which a current-limiting chemical step precedes the electron transfer, such non-linearity is not unexpected.[9] Similar results have also been reported in the literature.[6,11,14] However, the corresponding Koutecky–Levich plot (Fig. 8C) is quite linear, with a slope close to that of the calculated line for the reduction of O_2 via two electrons, indicating that the adsorbed catalyst accomplished the reduction of O_2 to H_2O_2. A similar behavior was observed in the case of other anthraquinones used.

The catalytic reaction rate between the reduced anthraquinone AQH_2 and O_2 ($AQH_2+O_2 \rightarrow AQ+H_2O_2$) can be evaluated from a Koutecky–Levich plot. Accordingly, the limiting current (I_l) corresponding to the mediated reduction is a function of the Levich current (I_{lev}) representing the mass transfer of O_2 in solution and the kinetic current (I_k)

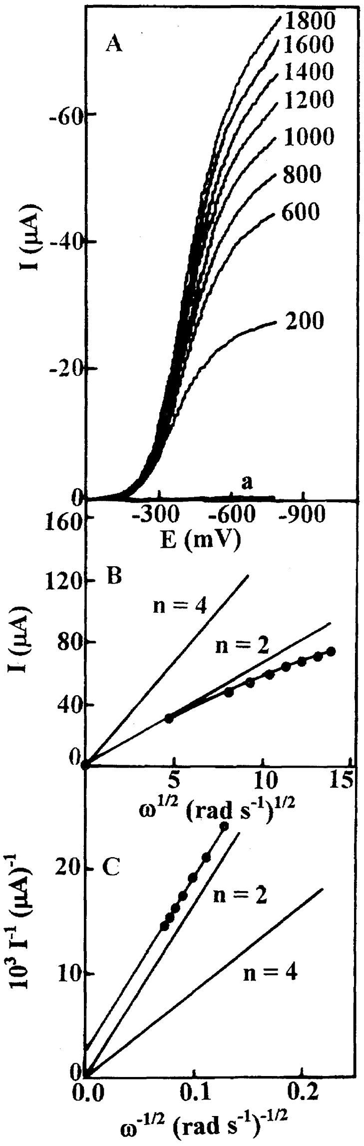

Fig. 8. A) current potential curves for the reduction of O_2 (1.25 mmol dm^{-3}) at a rotating glassy carbon electrode modified with **A1** in a 0.1 mol dm^{-3} phosphate buffer solution (pH = 7) at different rotation rates and a scan rate of 6 mV s^{-1}. The rotation rates (rev min^{-1}) are indicated on the corresponding curves. Curve a corresponds to the modified electrode in the absence of O_2. B) (1) Levich plot of limiting currents at −650 mV; (2) and (3) theoretical Levich plots for two-and four-electron reduction of O_2, respectively. C) (1), (2), and (3) corresponding Koutecky–Levich plots of the data.

corresponding to the electron cross-exchange between O_2 and the anthraquinone, as

$$1/I_l = 1/I_{lev} + 1/I_k, \tag{1}$$

and

$$I_{lev} = 0.62nFAD^{2/3}\nu^{-1/6}C_{O2}\omega^{1/2}, \tag{2}$$

$$I_k = nFAk\Gamma C_{O2}, \tag{3}$$

where C_{O2} is the bulk concentration of O_2, ω is the rotation speed, ν is the hydrodynamic viscosity, Γ is the surface coverage, k is the rate constant, and all other parameters have their usual meaning. The rate constants (k) for the reduction of dioxygen were evaluated from the intercepts of Koutecky–Levich plots for the case of the GC electrodes modified by anthraquinones **A1**–**A4**; the results are also summarized in Table 2. It should be noted that, since no well defined plateau is observed in the current-potential curves (see Fig. 8A), the k values are expected to be a function of the electrode potential. In other words, the electron-transfer rate between the electrode and the adsorbed anthraquinone seems to be related to the reaction rate.

The diffusion coefficient of O_2 in a buffered aqueous O_2-saturated solution (pH = 7) was determined to be $(1.5\pm0.1)\times10^{-5}$ cm^2 s^{-1} using the Levich equation at various rotation speeds of the rotating GC electrodes. The values of the kinematic viscosity of water (ν) and the concentration of O_2 in solution (C_{O2}) used in this calculation were 0.01 cm^2 s^{-1} and 1.25 mM, respectively.[47,48] The value obtained for the diffusion coefficient of O_2 is comparable with the reported values.[14,49]

Conclusion

Four recently synthesized 1,4-dihydroxy-9,10-anthraquinone derivatives were used to modify GC electrodes for the electrocatalytic reduction of O_2. Anthraquinones **A1**–**A4** were strongly and irreversibly adsorbed on preanodized GC electrode surfaces. The formal potential of the modified electrodes were shifted toward more negative values with increasing pH, showing a near Nernstian behavior. The cyclic voltammograms of the resulting modified electrodes revealed the presence of a single couple redox reaction (two-electron, two-proton) with formal potentials of about −60 mV with respect to Ag/AgCl (satd), 3 mol dm^{-3} KCl. The modified GC electrodes exhibited potent electrocatalytic activity towards dioxygen reduction in a phosphate buffer solution of pH 6—7 with an overpotential of about 560—650 mV lower that at a plain GC electrode. The electrocatalytic properties of the electrode were studied by cyclic voltammetry. The electrocatalytic reaction rate constant and the diffusion coefficient of dioxygen were evaluated from rotating-disk voltammetric measurements.

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