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Substituent effects on the electrocatalytic reduction of oxygen on quinone-modified glassy carbon electrodes

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Received 9th December 2003, Accepted 30th January 2004
First published as an Advance Article on the web 23rd February 2004

The reduction of oxygen catalysed by two sulfur-containing derivatives of anthraquinone has been investigated. The quinones were chemically grafted to a glassy carbon electrode surface and the oxygen reduction reaction in alkaline solution followed a two-electron pathway yielding hydrogen peroxide. The mechanism proposed corresponds to an electrochemical–chemical (EC) reaction where the semiquinone radical anion electrochemically formed reacts chemically with oxygen. The influence on reactivity of electron withdrawing groups present in the quinone molecules has been studied and it is shown that there is an unexpected small dependence between reactivity and standard potential of the grafted quinones. It is shown that steric effects appear important in determining their electrocatalytic properties.

1 Introduction

The reduction of oxygen on quinone modified carbon surfaces has been extensively investigated. These studies include 1,4-naphthoquinone, 9,10-anthraquinone-2-sulfonate[1,2] and 9,10-phenanthrenequinone[3] adsorbed on highly oriented pyrolytic graphite (HOPG), and anthraquinone derivatives adsorbed on glassy carbon (GC);[4–7] 1,4-naphthoquinone and its derivatives;[8,9] anthraquinone (AQ) and its derivatives[3,8–12] and phenanthrenequinone (PQ) covalently attached to GC.[13] Carbon paste electrodes modified with 1,4-naphthoquinone derivatives have also been employed for this purpose.[14] A large increase in the electrocatalytic effect of AQ modified GC on the rate of oxygen reduction by employing ultrasonic waves has recently been observed.[15] It has also been shown that the O_2 reduction behaviour is significantly altered when the anodically pre-treated GC electrode is modified with AQ.[16]

Quinone grafting by the electrochemical reduction of diazonium salts of anthraquinone[10,12] and phenanthrenequinone[13] on glassy carbon leads to a considerable improvement of the rate of oxygen reduction to hydrogen peroxide. The reduction rate is proportional to the surface concentration of the semiquinone radical formed by the electrochemical reduction of the quinone groups.[10,12,13] The radical reacts with molecular oxygen to yield superoxide ($O_2^{\bullet-}$) which either disproportionates or is further reduced to form the hydroperoxide anion in alkaline solution. The reaction follows an EC mechanism:

$$Q + e^- \rightarrow Q^{\bullet-} \qquad (I)$$

$$Q^{\bullet-} + O_2 \xrightarrow{k_c} O_2^{\bullet-} + Q \qquad (II)$$

$$O_2^{\bullet-} \xrightarrow{e^-, H_2O} HO_2^- \qquad (III)$$

where Q is the surface quinone. Reaction (II) is assumed to be the rate-determining step. Thus, carbon surfaces modified with AQ derivatives are good electrocatalytic candidates for the production of hydrogen peroxide. Different quinones have been employed for the modification of carbon electrodes, but the influence of the attached chemical functionalities on the rate of oxygen reduction is still not understood. The presence of electron-withdrawing groups (*e.g.* –CN, $–SO_2$, $–NO_2$) would be expected to shift the half wave potential to more positive values, but their influence on the rate of reaction of the semiquinone intermediate with molecular oxygen is still not known.

The purpose of the present work was to compare the kinetics of oxygen reduction on glassy carbon (GC) electrodes modified with thiophenyl and benzenesulfonyl derivatives, with that for the unsubstituted anthraquinone. The influence of the chemical functionalities on their electrochemical properties was also studied. These compounds were chosen for two reasons, to include groups close to both carbonyl functions and to provide substituents with widely different electron withdrawing properties. The concentration of KOH was chosen the same as in previous studies to allow a comparison of the kinetic parameters calculated.[10,12,13]

Grafting of the quinones was carried out by the electrochemical reduction of the corresponding diazonium salts according to:[17]

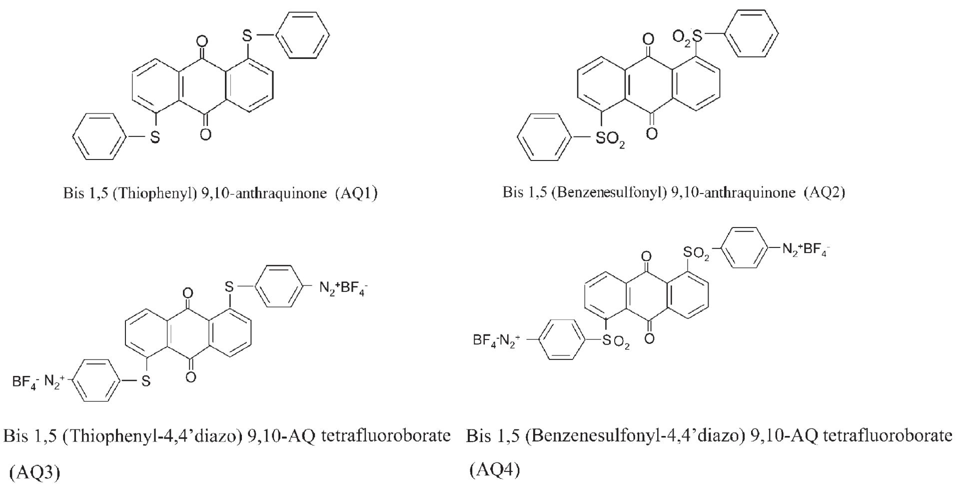
$$RN_2^+ + e^- \rightarrow R^\bullet + N_2 \qquad (IV)$$

$$R^\bullet + C \rightarrow R–C \qquad (V)$$

C represents here the carbon surface. This method was previously employed for the attachment of AQ and PQ to a GC electrode[10,13] and to carbon powder.[18]

Thiophenyl and benzenesulfonyl derivatives of AQ (compounds AQ1 and AQ2, Scheme 1) were synthesized and used for the electrochemical investigations in organic media (Scheme 1). Diazonium tetrafluoroborate salts of the above compounds (compounds AQ3 and AQ4) were synthesized for the modification of GC surfaces. Compounds AQ3 and AQ4 had two points of attachment to the carbon surface. The structure of the derivatives employed was dictated by synthetic requirements, which made difficult the preparation of a mono-derivative. Although this may give rise to some heterogeneity in the organisation of the grafted quinones, the substrate itself is so highly heterogeneous that the possibility of multiple orientations of the quinone is not important. For quinone molecules attached by one end only, the $–N_2^+$ residue will decompose to yield a –H termination. The electrochemical parameters obtained for the kinetics of oxygen reduction on

DOI: 10.1039/b315963a


Bis 1,5 (Thiophenyl) 9,10-anthraquinone (AQ1)

Bis 1,5 (Benzenesulfonyl) 9,10-anthraquinone (AQ2)

Bis 1,5 (Thiophenyl-4,4'diazo) 9,10-AQ tetrafluoroborate (AQ3)

Bis 1,5 (Benzenesulfonyl-4,4'diazo) 9,10-AQ tetrafluoroborate (AQ4)

Scheme 1 Chemical structures of the quinone compounds used.

these electrodes were compared with previous measurements with unsubstituted AQ.[10,12]

2 Experimental

Compounds AQ1 and AQ2 were synthesised in the same way as AQ3 and AQ4 (see below) except that the starting material was thiophenol instead of *p*-aminothiophenol.

Compound AQ3 was synthesized from bis-1,5(4,4′-aminothiophenylanthraquinone). The latter was prepared with 90% yield from the reaction of 20 mmol of 1,5-dichloro-AQ and 40 mmol of *p*-aminothiophenol in dimethylformamide (DMF) in the presence of potassium carbonate at 110–130 °C and the product recrystallised from DMF. Elemental analysis gave C: calc. 69.00%, found 68.48%, H: calc. 3.56%, found 3.69%, N calc. 6.19%, found 5.90%, S calc. 14.17%, found 14.32%. This diamino compound was diazotised in acetic acid containing fluoroboric acid by the addition of sodium nitrite at 10 °C. For the synthesis of AQ4, the amino groups were protected by acetylation in acetic acid and acetic anhydride before diazotation. The thioether groups were then oxidised in excess of 30% hydrogen peroxide in boiling acetic acid and recrystallised from acetic acid. Elemental analysis for the product, bis-1,5(4,4′-*N*-acetylamino)benzenesulfonyl-anthraquinone was as follows: C: calc 59.79% found 58.22%, H: calc 3.67, found 3.84, N: calc. 4.64% found 4.45%. The acetylated compound was then hydrolysed to the amine by reacting with KOH and diazotised into diazonium fluoroborate. Dication main peaks for AQ3 and AQ4 were observed at 239 and 271 Da, respectively, with electrospray mass spectrometry in accordance with their molecular weights. All the chemicals were used with the highest purity available.

A commercial GC disk–Au ring electrode (Pine Instrument Company, USA) with a disk geometrical area of 0.164 cm^2 was employed for the rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) measurements. The electrode collection efficiency (N) was determined with ferrocene in DMF as 0.22. An AFMSRX rotator and MSRX speed controller (Pine Instrument Company, USA) were employed. The potential was controlled with a PGSTAT20 (Eco-Chemie B.V., The Netherlands) potentiostat/galvanostat running under the General Purpose Electrochemical System (GPES) software.

The electrochemical properties of compounds AQ1 and AQ2 were studied in 0.5–5 mM solutions in DMF containing 0.1 M tetrabutylammonium tetrafluoroborate (TBABF$_4$) as base electrolyte. TBABF$_4$ (99.9%, Aldrich) was vacuum dried and DMF (Aldrich, anhydrous 99.8%) was dehydrated over molecular sieves before use. Compounds AQ3 and AQ4 were grafted on GC from a 10 mM solution in DMF containing 0.1 M TBABF$_4$. The electrode was polished with 1 and 0.3 μm alumina and the subsequent grafting procedure was similar to that previously described.[10] This involved cycling the potential four times between +0.75 and −0.45 V *vs.* SCE at 0.1 V s^{-1} and finally keeping the electrode at −0.2 V in the same solution for 2 min to ensure completion of the reaction. The modified electrodes were rinsed with DMF, acetone and water to remove physically adsorbed compounds and then voltammograms were recorded in 0.1 M KOH to check the surface coverage obtained. Electrode modification with physically adsorbed compounds was performed by placing a drop of 1 mM solution of the corresponding compound in acetonitrile on the electrode surface and leaving it to evaporate in air. A saturated calomel electrode (SCE) was used as the reference and all potentials are referred to this electrode. For comparison with other reference electrodes, the half wave potential of the ferrocene/ferrocenium couple (Fc/Fc$^+$) was measured and a value of 0.415 V with respect to the SCE used was found. All experiments were carried out in a three-compartment glass cell at room temperature. The solutions were deoxygenated with pure argon. Both argon and high purity oxygen were supplied by BOC gases, UK.

Non-linear regression analysis (NLR) fits were performed using Origin® software (version 6, Microcal Inc.).

3 Results and discussion

3.1 Compounds AQ1 and AQ2 in DMF

Fig. 1 shows voltammograms of AQ1 at different sweep rates. A large peak separation (*ca.* 100 mV) that increases with sweep rate is observed. These results show only a one-electron transfer reaction with an average half-wave potential extrapolated to zero sweep rate of −0.778 ± 0.005 V. A second reduction wave could only be observed at potentials more negative than −1.4 V. The current function $I_c^p/\nu^{1/2}$ and the ratio of anodic to cathodic currents (I_p^c/I_p^a) were independent of sweep rate. I_p^c and I_p^a are the cathodic and anodic peak currents and ν is the sweep rate. Water has a strong influence on the electrochemistry of quinones and for this reason, voltammograms were also recorded for quinone solutions to which activated alumina (heated to 230 °C overnight) had been added to eliminate residual water. No difference in the current and potential of the first wave was observed. Voltammograms were also recorded with the addition of 10% H$_2$O to the DMF. Although a positive shift (*ca.* +200 mV) was observed for the second peak, the quinone/semiquinone reduction wave was

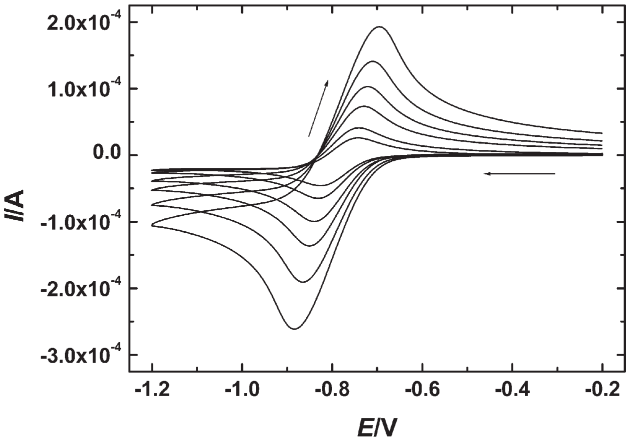


Fig. 1 Cyclic voltammograms of compound AQ1 in Ar-saturated DMF containing 0.1 M TBABF$_4$ and 5 mM AQ1 at different sweep rates: 20, 40, 80, 150, 250, 400 mV s^{-1}.

unaffected confirming that water does not influence the electrochemical behaviour studied.

Fig. 2 shows rotating ring-disk polarisation curves for AQ1 in DMF and some of the corresponding Koutecky–Levich (K.–L.) plots at different potentials are shown in Fig. 3 showing a characteristic quasi-reversible behaviour. The diffusion coefficient was calculated from the limiting slopes, assuming a one-electron reaction (Table 1).

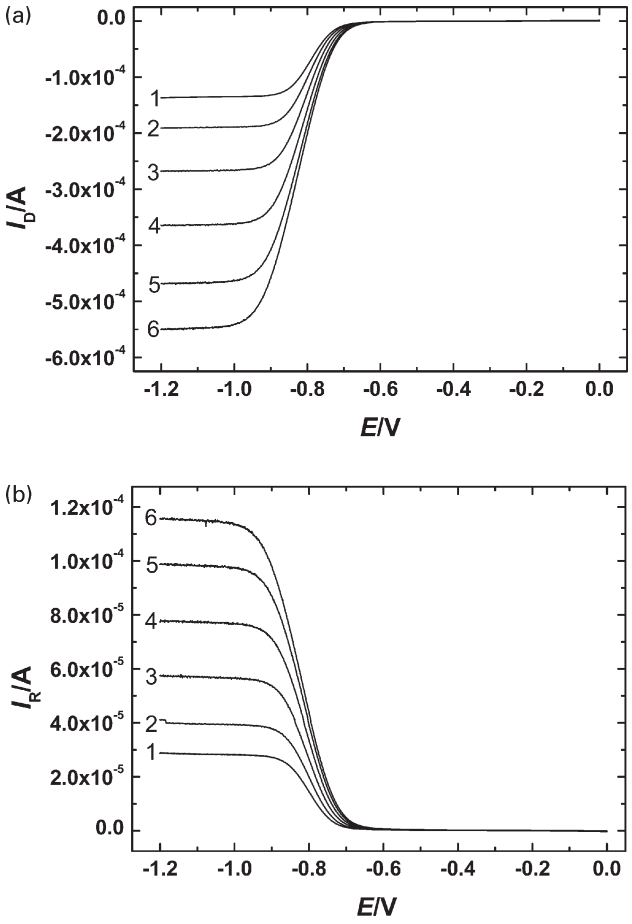


Fig. 2 RRDE current–potential curves for compound AQ1 in Ar-saturated DMF containing 0.1 M TBABF$_4$ and 5 mM AQ1. Rotation rates: (1) 200, (2) 400, (3) 800, (4) 1500, (5) 2500 and (6) 3500 rpm; (a) disk, (b) ring. Sweep rate = 10 mV s^{-1}.

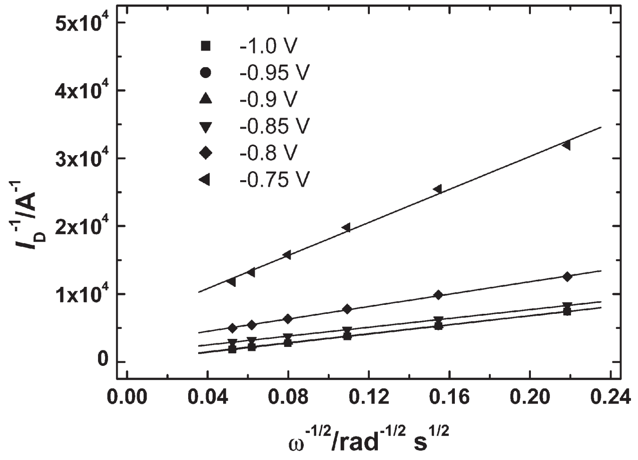


Fig. 3 Koutecky–Levich plots of compound AQ1 in DMF at different potentials (data from Fig. 2(a)).

Fig. 4 shows a cyclic voltammogram of compound AQ2 in DMF. In this case, two well-separated reduction peaks are observed at −0.55 and −0.85 V. A further reduction process is also observed for potentials more negative than −1.2 V, probably due to the reduction of the benzenesulfonyl groups.[19] The first peak corresponds to a reversible one-electron transfer process (Fig. 5) to yield the corresponding semiquinone. The radical formed is stable in the time scale of the voltammetric experiments, as indicated by a current ratio I_p^a/I_p^c close to unity and independent of sweep rate. The current efficiency for the ring is close to 100% and independent of rotation rate, confirming that the reduction to the semiquinone is a simple reversible one electron-transfer reaction. Fig. 6 shows RRDE polarisation curves for this compound and the corresponding Koutecky–Levich plots are presented in Fig. 7. From these results and the sweep rate dependence of the cathodic peak potentials (plot not shown), values of n and D were calculated as 0.98 and 6.1×10^{-6} cm^2 s^{-1}, respectively.

The kinetics parameters were calculated using a non-linear regression analysis (NLR)[10] by fitting the experimental data to the equation for a quasi-reversible reaction:[20]

$$\frac{1}{j} = -\frac{1}{FC^{*}k^{0}\mathrm{e}^{-\alpha f(E-E^{0})}} + \frac{1+b^{-1}\mathrm{e}^{f(E-E^{0})}}{j_{\mathrm{D}}} \qquad (1)$$

where $b = (D_R/D_{Ox})^{2/3}$ and $f = F/RT$ and the other terms have their usual meaning. The diffusion coefficient for the reduced and oxidised species was considered to be equal. Averages of the results obtained from different rotation rates are given in Table 1. In order to ascertain the validity of the parameters obtained from NLR, polarisation curves for ferrocene in DMF as a standard reversible redox compound were also measured on the same electrode. This is particularly important since the behaviour of GC surfaces is strongly affected by its variable chemical composition determined by the experimental conditions and/or the method of surface preparation, as already described by Kneten and McCreery.[21] The electrochemical standard rate constant however, could not be determined by the NLR method employed since no difference in the calculated fit and measured current could be found for

Table 1 Reduction parameters obtained from NLR analysis of the quinones studied in DMF solution

Compound	$E_{1/2}$/V	D/ cm^2 s^{-1}	α	n	$10^3 k^0$/ cm s^{-1}
AQ1	-0.778 ± 0.005	4.6×10^{-6}	0.66 ± 0.08	1	1.0 ± 0.3
AQ2	-0.511 ± 0.001	6.1×10^{-6}	0.55 ± 0.02	1	16 ± 1
AQ	-0.825 ± 0.006	8.9×10^{-6}	0.47 ± 0.03	1	6.7 ± 0.9

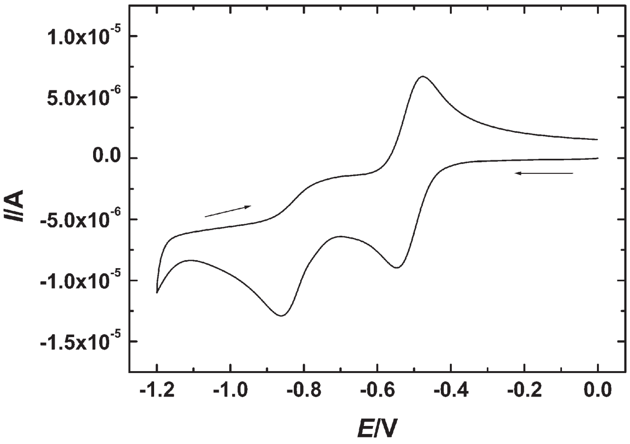


Fig. 4 Cyclic voltammogram of compound AQ2 in Ar-saturated DMF containing 0.1 M TBABF$_4$ and 0.58 mM AQ2; sweep rate = 20 mV s^{-1}.

$k^0 > 0.1$. Thus, the rate constants measured in DMF are not dependent on the electrode surface treatment observed by McCreery and co-workers for aqueous redox couples.[21,22]

For comparison purposes, the same measurements were carried out with unsubstituted anthraquinone (Table 1). The rate of the electron transfer reaction for AQ1 is lower than AQ2 and AQ. The addition of thioether functionalities to AQ shifts the potential 47 mV to a more positive value. This shift is much larger (*i.e.* 314 mV) for the benzenesulfonyl derivative (AQ2) due to the stronger electron withdrawing properties of this group, which results in the stabilisation of the radical intermediate.

3.2 Compounds AQ3 and AQ4 grafted to GC

Fig. 8 shows the first and second sweeps for the electrochemical surface grafting of the quinones by reduction of the corresponding diazonium salt. A large cathodic wave is observed for the first sweep, but this is absent in the second sweep, clearly indicating an almost complete blocking of the surface by the grafted quinone.

The cyclic voltammograms of the quinone-modified GC electrodes in Ar-saturated 0.1 M KOH (Fig. 9) present a large peak-to-peak separation for AQ3. The peak currents show a linear relationship with sweep rate, a clear indication of a surface process (results not shown). The charge densities of the cathodic peaks correspond to surface coverages of 4.0×10^{-10} and 4.3×10^{-10} mol cm^{-2} for AQ3 and AQ4, respectively. These values can be compared with that for 9,10-anthraquinone-2-monosulfonate, 1.4×10^{-10} mol cm^{-2}, obtained on the basal plane of pyrolytic graphite.[23] The difference between these surfaces is due to the surface roughness of GC and the orientation of the grafted molecules. It can be concluded that the surface coverages obtained with GC were close to a monolayer.

The large peak-to-peak separation obtained is unexpected for compounds attached to a surface and indicates that the surface reactions proceed by different routes for reduction

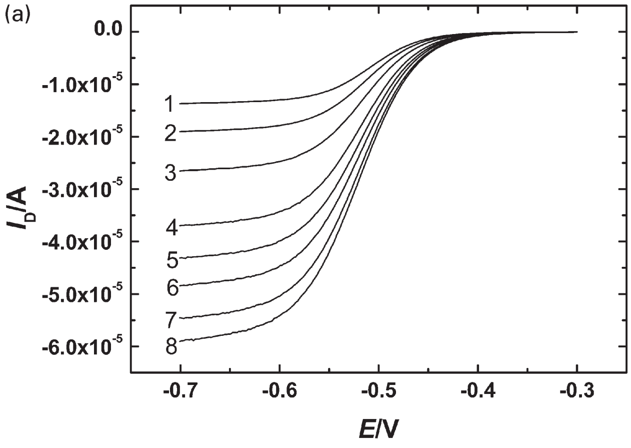


Fig. 6 RRDE current–potential curves for AQ2 in Ar-saturated DMF containing 0.1 M TBABF$_4$ and 0.58 mM AQ2; rotation rate = (1) 100, (2) 200, (3) 400, (4) 800, (5) 1100, (6) 1400, (7) 1800 and (8) 2100 rpm; (a) disk, (b) ring currents, sweep rate = 10 mV s^{-1}.

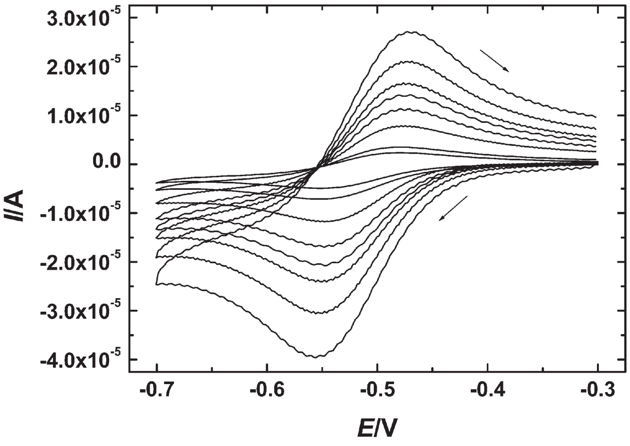


Fig. 5 Cyclic voltammograms of compound AQ2 in Ar-saturated DMF containing 0.1 M TBABF$_4$ and 0.58 mM AQ2: sweep rate = 10, 20, 40, 80, 120, 160, 250, 400 mV s^{-1}.

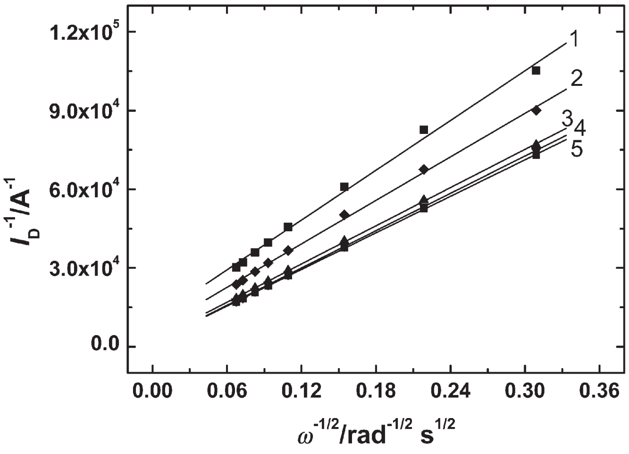


Fig. 7 Koutecky–Levich plot obtained from the results shown in Fig. 6. Potential: (1) −0.53, (2) −0.55, (3) −0.6, (4) −0.65 and (5) −0.7 V.

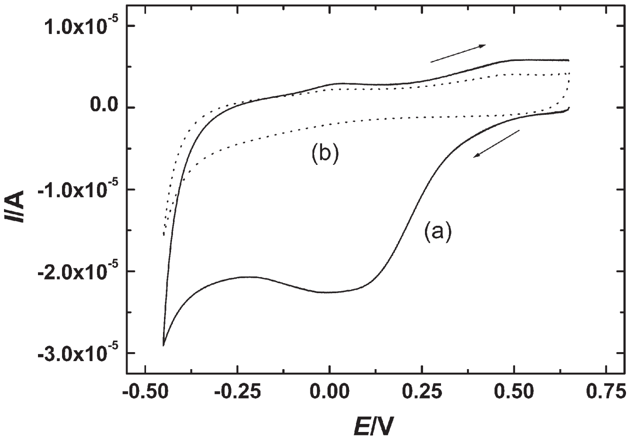


Fig. 8 First (a) and second (b) sweeps for the grafting of compound AQ3 on GC in Ar-saturated DMF containing 0.1 M TBABF$_4$ and 10 mM AQ3; sweep rate = 100 mV s^{-1}.

and oxidation, as previously observed for other quinones. These reactions follow electron and proton transfer steps. In the present case, it is proposed that the reduction sequence follows electron transfer to yield the corresponding semiquinone:[24]

$$AQ + e^- \rightarrow AQ^{\bullet -} \tag{VI}$$

followed by either

$$AQ^{\bullet -} + e^- \rightarrow AQ^{2-} + H^+ \rightarrow HAQ^- \tag{VII}$$

or

$$AQ^{\bullet -} + H^+ \rightarrow HAQ^{\bullet} + e^- \rightarrow HAQ^- \tag{VIII}$$

This mechanism involves two consecutive reductions. Either of the reactions leads to the formation of the corresponding quinol anion according to the overall reaction:

$$AQ + H^+ + 2e^- \rightarrow HAQ^- \tag{IX}$$

The average value of the half-wave potential for AQ3 was -0.873 ± 0.005 V, which is 28 mV more negative than that of grafted anthraquinone (Table 2).[10] The value of $E_{1/2}$ for the attached benzenesulfonyl derivative (AQ4) is 151 mV more positive than that of anthraquinone. A similar large positive shift is also observed for AQ2 physically adsorbed on GC (Table 2). The effect of electron-withdrawing groups on the Hammett substituent parameters (σ) and thus on the oxidation potential, has already been described.[25] It is known that CF_3SO_2 and $C_6H_5SO_2$ groups have the largest electron-withdrawing property on the ionisation of benzoic acid with σ values of 0.93 and 0.7, respectively. The value of σ for CF_3S, however, is only 0.5 indicating a small electron affinity of thioether groups. A correlation between Hammett substituent parameters and the shift of the reduction potentials of benzoquinone (BQ) has been demonstrated.[25] It was shown that by increasing the σ value of the substituent the positive shift of the BQ reduction potential is increased. Therefore, it can be concluded that the thioether substituent in AQ1 does not have a large effect on the reduction potential due to the weak electron-withdrawing ability of the –SAr group. In contrast, the compound containing –SO_2Ar groups (AQ2) shows a large positive shift with respect to AQ both in DMF and in alkaline solution when chemically attached to GC (Tables 1 and 2).

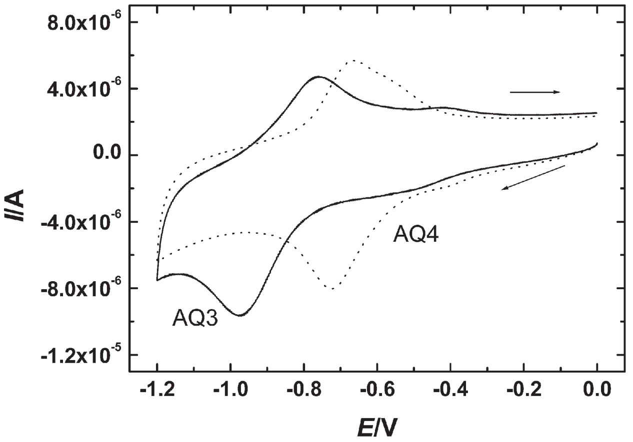


Fig. 9 Cyclic voltammograms of GC grafted with AQ3 and AQ4 in Ar-saturated 0.1 M KOH solution; sweep rate = 100 mV s^{-1}.

Table 2 Half-wave potentials of AQ derivatives attached to a GC electrode in 0.1 M KOH, sweep rate = 40 mV s^{-1}.

Electrode	$E_{1/2}$/V (*vs.* SCE)
GC/AQ[10]	−0.845[10]
GC/AQ3	-0.873 ± 0.005
GC/AQ4	-0.694 ± 0.001
AQ2 physically adsorbed on GC	-0.699 ± 0.005

3.3 Electrocatalysis of O_2 reduction by grafted quinones

Fig. 10 shows RDE results for O_2 reduction on a GC/AQ3 electrode at different rotation rates; the corresponding K.–L. plots are given in Fig. 11. As can be seen, the attached quinone considerably enhances the rate of O_2 reduction in comparison to a bare GC electrode. The value of *n* calculated from these results using the K.–L. plots in Fig. 11 is 1.95 ± 0.05 showing that the O_2 reduction sequence stops at the peroxide stage.

Fig. 12 compares O_2 reduction results for GC/AQ4 and for bare GC electrodes. In contrast to previous work[10] for GC/AQ, the effect of the native quinone groups of GC is not apparent at low rotation rates. This reflects the closeness of the values of the redox potentials of the native and attached quinone groups (see later). Fig. 13 shows K–L plots of these results at different potentials. The number of electrons involved in the reduction is almost independent of potential and is close to two (Fig. 13), *i.e.*, oxygen reduction also stops at the peroxide stage for this compound. The percentage of

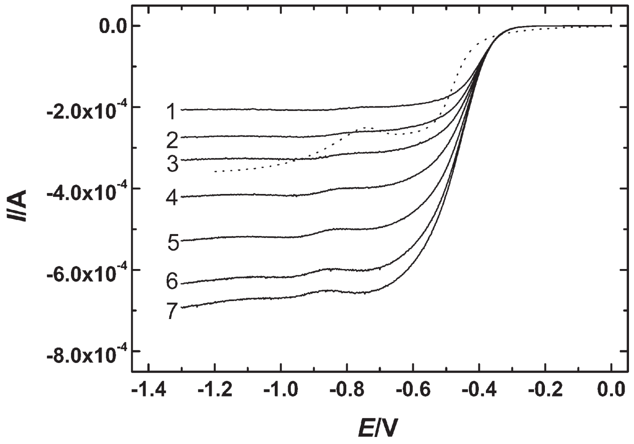


Fig. 10 RDE polarisation curves for oxygen reduction on a GC/AQ3 electrode in O_2-saturated 0.1 M KOH. Rotation rates = (1) 360, (2) 610, (3) 900, (4) 1500, (5) 2500, (6) 3800 and (7) 4600 rpm. For comparison (dashed line), the polarisation curve for a bare GC electrode in the same solution at 960 rpm is shown.

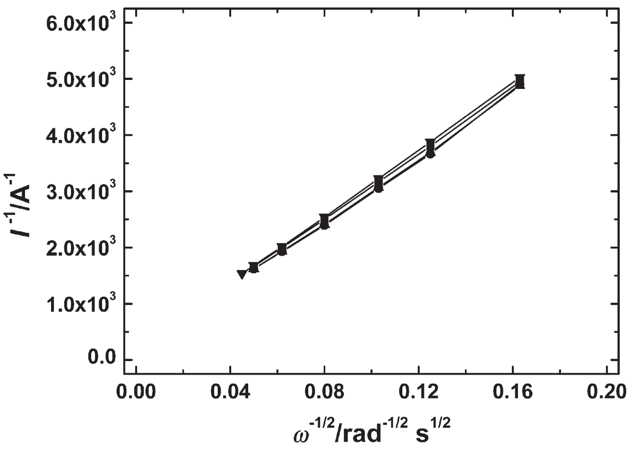


Fig. 11 Koutecky–Levich plot for GC/AQ3 in O_2-saturated KOH at potentials: −0.7, −0.8, −1 and −1.1 V (from top to bottom).

peroxide formation (Φ) was calculated using eqn. (2) as previously proposed:[26]

$$\Phi = \frac{200 \times I_R/N}{I_D + I_R/N} \tag{2}$$

where I_D and I_R are disk and ring currents and N is the electrode collection efficiency. An average of peroxide production yield of 89 ± 2% and 97 ± 2% was calculated for the electrode modified with compounds AQ3 and AQ4, respectively.

Attempts were made to use the electrodes modified with physically adsorbed AQ1 and AQ2 for comparing their kinetics parameters with those of quinones chemically attached to the electrode surface. However, the physisorbed compounds were rapidly desorbed from the surface on cycling in alkaline solution. Similar behaviour was previously observed with unsubstituted AQ physically adsorbed on GC.[10]

The kinetics parameters for oxygen reduction were calculated from the RDE measurements using the non-linear regression analysis previously described.[12,13] The symbols employed are the same as those in previous publications.[10,12,13] Briefly, both the native GC quinone groups and the grafted quinones are considered in the analysis (subscripts 1 and 2, respectively). E_i^0 is the standard potential of quinone i, k^0 is the electrochemical rate constant for oxygen reduction on the free glassy carbon surface, α is the transfer coefficient, ΔE_i is the difference between the standard potentials of the $Q^{\bullet -}/Q^{2-}$ and $Q/Q^{\bullet -}$ couples for the different surface quinone species, k_i is the rate constant for the chemical reaction of O_2 with the semiquinone radical (reaction (II)) for the surface quinone groups and Γ_i is the quinone surface concentration. Table 3 compares the kinetics parameters of oxygen reduction electrocatalysed by the different grafted quinones.

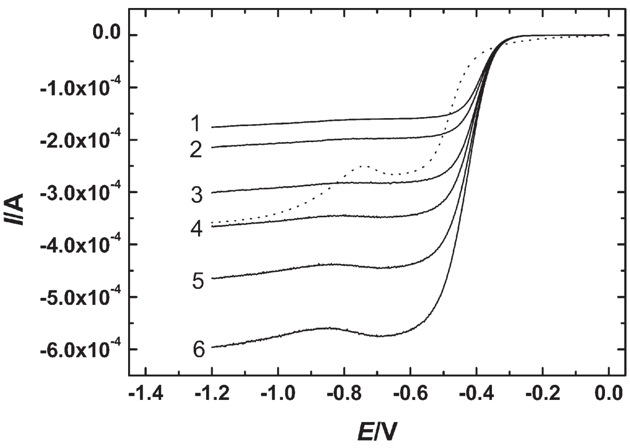


Fig. 12 RDE polarisation curves for oxygen reduction on a GC/AQ4 electrode in O_2-saturated 0.1 M KOH; rotation rates = (1) 200, (2) 300, (3) 600, (4) 900, (5) 1500 and (6) 2500 rpm. For comparison (dashed line), the polarisation curve for a bare GC electrode in the same solution at 960 rpm is shown.

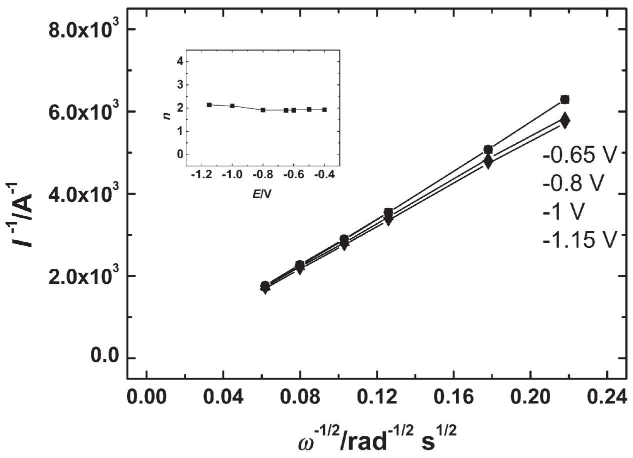


Fig. 13 Koutecky–Levich plot of GC/AQ4 in O_2-saturated 0.1 M KOH at different potentials: −0.65, −0.8, −1.0 and −1.15 V, respectively. The inset shows the dependence of the number of electrons transferred on potential.

The standard potential of the native GC quinone groups, E_1^0, falls within ±50 mV for the different quinones studied. This quantity is not easy to measure, in particular for AQ4, due to the potential overlap of the reduction range for both native and grafted quinones. In spite of this problem, the standard potential of the native quinones is not strongly affected by the grafted material. The effect of attachment appears to be more noticeable for k^0. This quantity refers to unit geometric area and the trend observed, AQ > AQ3 > AQ4, probably reflects the greater coverage of active free carbon surface by the grafted quinones. The component $k_1\Gamma_1$ does not change much for the different quinones studied. This term corresponds to the reactivity of the semiquinone formed by reduction of the native quinone groups with oxygen. Since the thermodynamic driving force for the radical–molecular oxygen reaction is not very strongly dependent on the grafted quinone (see entries in column 1 of Table 3), it is not surprising that $k_1\Gamma_1$ is unaffected by the properties of the attached quinones.

Perhaps the most interesting observation is the comparison of the chemical rate constant for reaction (II) for the different quinones. The values of k_2 calculated were 1.2×10^9, 3×10^8 and 1.6×10^8 $cm^3\ mol^{-1}\ s^{-1}$ for AQ, AQ3 and AQ4, respectively. The last column in Table 3 reveals that there is a systematic *decrease* in its value as the standard potential of the quinone is made more positive and the thermodynamic driving force for electron transfer is increased, *i.e.* for more negative values of the Gibbs free energy of reaction. This effect, however, is relatively small. The trend is what would be expected for a simple activated chemical reaction, with an increase in the activation energy as the different substituents *increase* the thermodynamic stability of the intermediate radical. It is somewhat surprising though, that such small variations in k_2 are observed considering that the change in standard potential going from AQ to AQ4 is 151 mV. This indicates that other parameters must be considered to rationalise the values of the chemical rate constant measured, such as surface orientation of the electrocatalytic species and consequent steric effects of the intermediates of the reaction between the semiquinone radical and oxygen.

In relation to the above, it is interesting to note that the rate constants for the reduction of the quinones in solution do not follow the expected Marcus *normal* behaviour.[20] This would require the values of k^0 to follow the order AQ < AQ1 < AQ2,

Table 3 Summary of non-linear regression parameters for oxygen reduction on GC electrodes grafted with AQ derivatives

Electrode	E_1^0/V	E_2^0/V	10^4k^0/cm s^{-1}	α	ΔE_1/V	ΔE_2/V	$k_1\Gamma_1$/cm s^{-1}	$k_2\Gamma_2$/cm s^{-1}
GC/AQ[10]	-0.56 ± 0.01	-0.9 ± 0.02	3.2 ± 1.5	0.23 ± 0.01	-0.25 ± 0.02	-0.3 ± 0.1	0.019 ± 0.002	0.3 ± 0.15
GC/AQ3	-0.50 ± 0.02	-0.76 ± 0.03	2.5 ± 1	0.36 ± 0.03	-0.10 ± 0.01	-0.22 ± 0.01	0.017 ± 0.005	0.12 ± 0.06
GC/AQ4	-0.64 ± 0.03	-0.67 ± 0.01	0.6 ± 0.1	0.30 ± 0.04	-0.39 ± 0.08	-0.50 ± 0.03	0.026 ± 0.002	0.07 ± 0.04

which is not the order observed. The likely reason for this is the nature of the substituents that determines the degree of proximity of the redox centre to the surface. This seems to be the overriding effect, determining the value of the electrochemical rate constant.

4 Conclusions

A large positive shift of the redox potential of compound AQ2 in DMF solution compared to AQ1 and AQ was observed. The rate constants for the one-electron reduction of AQ1 and AQ2 to the corresponding semiquinone radical in DMF were determined using RDE data and non-linear regression analysis. The electron transfer reaction for AQ2 is 16 times faster than for AQ1 in DMF. This could be due to the delocalisation of electrons caused by the sulfone groups, thus stabilising the radical formed. A positive potential shift for covalently attached AQ4 compared with grafted AQ is also observed in alkaline solution, which is in agreement with that expected from inductive effects of the benzenesulfonyl group on radical formation as also observed in DMF. Therefore, reaction (I) is thermodynamically more feasible when electron-withdrawing functionalities are incorporated in the AQ molecule. However, the chemical rate parameter ($k_2\Gamma_2$) of oxygen reduction for the surface bound molecules is lower for compounds AQ3 and AQ4 in comparison with that of AQ. It is proposed that these functionalities reduce the rate of the reaction (II) due to both the stabilisation of the semiquinone radical and by steric hindrance by these groups. Since the rate determining step is reaction (II), a suitable functionality to improve reaction (I) does not necessarily enhance the rate of the chemical reaction between the semiquinone radical anion and molecular oxygen. This is an indication of kinetic control of reaction (II), which is not influenced by the thermodynamic feasibility of the electrochemical step. The number of electrons transferred per O_2 molecule for all cases was close to two indicating that the reduction of oxygen stops at the peroxide stage.

Acknowledgements

Support from the European Union Framework V Growth programme, CLETEPEG project Contract No. G5RD-CT-2001-00463, is gratefully acknowledged. This work was partly supported by the Estonian Science Foundation. F. M. is grateful to Kashan University, Iran for the award of a study leave at Liverpool University.

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