Characterization of a glassy-carbon-electrode surface pretreated with rf-plasma

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forces. However not all conformations relevant to determine the stereochemical outcome of a kinetically controlled may be found and we have to be aware of this. Dreiding models on the other hand may suggest such a flexibility that the chemist is bound not to attempt this type of study. Consequently it was important that the pioneers mentioned in the introduction showed that crystallographic data can be used to initiate this type of investigation.

Characterization of a glassy-carbon-electrode surface pretreated with rf-plasma

J. Schreurs, J. van den Berg, A. Wonders and E. Barendrecht*

Laboratory for Electrochemistry, Department of Chemical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
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Abstract. The composition of oxidic groups at a glassy-carbon surface has been studied using phase-sensitive ac-voltammetry. Two types of quinones have been identified, *i.e.* the 1,2-naphtoquinone- and the 9,10-phenanthrenequinone-like structures. The 1,4-naphtoquinone- and 9,10--anthraquinone-like structures are, most probably, also present at the glassy-carbon surface, although in lower surface concentrations. The *o*-quinones can be converted into the corresponding benzophenazines (by reaction with *o*-phenylenediamine), which are also electroactive. The differences in redox potentials between the quinones and phenazines make detection of intermediate reaction stages possible. The effect of oxygen and argon rf-plasma treatment upon the composition of the quinone-surface groups has also been studied. Pretreatment of the glassy-carbon surface by an oxygen rf-plasma is a very powerful and clean oxidation technique. Argon rf-plasma increases the 9,10-phenanthrenequinone-like structures, while oxygen rf-plasma, with successive cooling in an argon atmosphere, diminishes the surface concentration of quinone structures and increases that of the acidic surface groups, as can be concluded from modification experiments. From phase-sensitive ac-voltammetry measurements, a lower limit of 10^3 s^{-1} was determined for both the quinone and the phenazine surface reaction rate constants (k_s).

Introduction

Surface groups are a prerequisite for the chemical modification (*i.e.* by covalent bonding of electrocatalysts) of a carrier electrode. The nature of surface groups on several types of carbon, such as (pyrolytic) graphite and glassy carbon, has been studied by means of spectroscopic[1,2], chemical[3,4] and electrochemical[5-12] techniques. It is known that a variety of oxygen-containing surface groups, such as carboxyl, hydroxyl, lactone, phenol, quinone, etc., exist. Most of these surface groups have been identified via chemical analysis. Spectroscopic techniques are rather difficult to apply, not only since carbon absorbs most radiation, but also because it is difficult to discriminate between the respective surface groups. Electrochemical techniques can only be successfully applied in the potential region where no oxygen or hydrogen evolution can take place; for this reason, detection of carboxylic and hydroxylic surface groups at a carbon-electrode surface is difficult, if not impossible, in most protic media. The irreversible electrochemical behaviour of many surface groups also makes detection very difficult in aprotic media.

The quinone-like surface groups, however, can be easily detected in protic media, because of their quasi-reversible behaviour in a suitable potential region. The presence of quinone-like surface groups has been previously mentioned in the literature[3,5,8]. A quasi-reversible, pH-dependent redox wave at $+0.6$ V *vs.* NHE is generally observed in cyclic voltammetry measurements at carbon electrodes.

[1] *J. M. Thomas, E. L. Evans, M. Barber* and *P. Swift*, Trans. Faraday Soc. **67**, 1875 (1971).
[2] *V. Mayer, J. Vesely* and *K. Stulik*, J. Electroanal. Chem. **45**, 113 (1973).
[3] *H. P. Boehm, E. Diehl, W. Heck* and *R. Sappok*, Angew. Chem. **3**, 669 (1964).
[4] *M. Fujihira, T. Osa* and *A. Kozawa* et al., eds., "Progress in Batteries & Solar Cells", Vol. 2, J.E.C. Press Inc., Cleveland, 1979.
[5] *K. F. Blurton*, Electrochimica Acta **18**, 869 (1973).
[6] *D. Laser* and *M. Ariel*, J. Electroanal. Chem. **52**, 291 (1974).
[7] *B. D. Epstein, E. Dalle–Moll* and *J. S. Mattson*, Carbon **9**, 609 (1971).
[8] *H. V. Drushel* and *J. v. Hallum*, J. Phys. Chem. **62**, 1502 (1958).
[9] *R. E. Panzek* and *P. J. Elving*, Electrochimica Acta **20**, 635 (1975).
[10] *J. P. Randin*, "Comprehensive Treatise of Electrochemistry", *J. O'M. Bockris* et al., eds., Vol. 4, Chapter 10.
[11] *J. P. Randin* and *E. Yeager*, J. Electroanal. Chem. **58**, 313 (1975).
[12] *J. F. Evans* and *T. Kuwana*, Anal. Chem. **49**, 1632 (1977).

This quinone-like redox couple often interferes with the detection of other redox couples, either immobilized or in solution, at carbon electrodes. In this publication we report on the nature of these quinone-like surface groups at the glassy-carbon-electrode surface. A powerful technique for the detection of surface-immobilized electroactive species is phase-selective ac-voltammetry. Even sub-monolayer surface concentrations can easily be detected. In addition, chemical conversion of a surface group into another electroactive compound can be very helpful for the purposes of identification: for example, o-quinones can be converted into phenazines by reaction with o--phenylenediamine. Carbon surfaces can be oxidized using strong oxidizing chemicals, by reaction with oxygen at high temperatures or by (oxygen) rf-plasma treatment[12,13]. Pretreatment of the carbon surface by argon rf-plasma abrades the surface and thus creates an activated surface, which is not only reactive towards oxygen but also towards vinyl or amino groups[14]. Changes in the experimental conditions of the rf-plasma treatment result in a different composition of surface groups; it is therefore of interest to study the parameters of the rf-plasma treatment.

Experimental

Electrodes

Rod-type glassy carbon (GC-A) was obtained from Tokai Electrode Mfg. Co. Ltd., Tokyo, Japan. Electrodes were made by sealing 5 mm pieces of the glassy-carbon rod ($\varnothing$ 5.6 mm) into pyrex glass tubes ($\varnothing$ 12 mm). The geometrical electrode area is 0.246 cm^2.
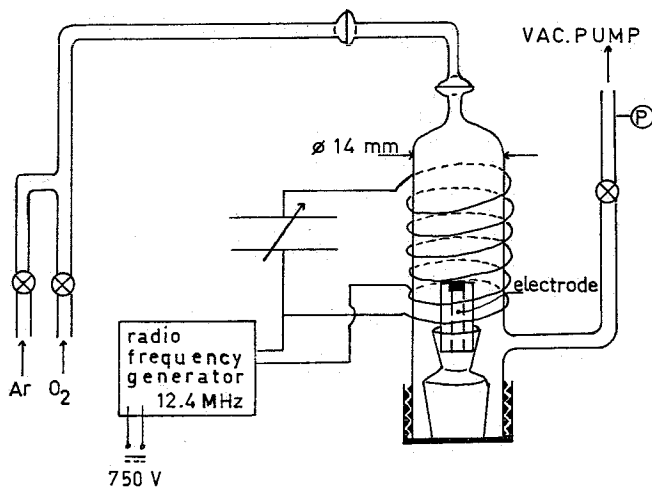

Fig. 1.   Experimental set-up for the rf-plasma treatment of glassy-carbon electrodes.

Surface pretreatment

Prior to the plasma treatment, electrodes were successively polished using 5 μ, 0.3 μ and 0.05 μ alumina on a polishing cloth (Buehler Ltd, Evanston, Illinois, USA), washed copiously with distilled water, treated for 1 h in an ultrasone bath and then degreased in n-pentane. The electrodes were stored in n-pentane. A home-made radio-frequency generator (12.4 MHz, 150 W) was used for plasma treatments (Fig. 1). The glassy-carbon electrodes were exposed to the oxygen rf-plasma (pale blue) at 150 mTorr for only 5 min, since otherwise drastic surface roughening occurs, as can be visually observed. Exposure to the argon rf-plasma (purple-violet) was carried out for 20 min at 300 mTorr. The plasma treatments were started at room temperature. The oxygen, argon and CO_2 gases were used without further purification.

Chemicals

The ampulla of phosphate-buffer solution (pH 7, 25.88 mM KH_2PO_4, 40.82 mM $Na_2HPO_4 \cdot 2H_2O$), obtained from Merck, was replenished with double distilled water. A specific conductivity (κ) of $7.2 \cdot 10^{-3} \, \Omega^{-1} \cdot cm^{-1}$ was measured for the phosphate buffer; this value increased to $13.8 \cdot 10^{-3} \, \Omega^{-1} \cdot cm^{-1}$ on addition of $LiClO_4$ (0.1 M). Perchloric acid (p.a.) was also obtained from Merck and a conductivity (κ) > $0.50 \, \Omega^{-1} \cdot cm^{-1}$ was measured for a 1 M aqueous solution. For measurements of the pH dependency of the different surface groups, the following electrolytes were used: phosphate-buffer solution (Merck) for pH 7, 0.05 M H_2SO_4 (Merck) for pH 1.4, 0.2 M NaH_2PO_4 for pH 4.4 and 0.2 M Na_2HPO_4 for pH 9.6. The quinones and o-phenylenediamine were obtained from Aldrich and used without further purification. The benzophenazines were prepared by reaction of o-phenylenediamine with the corresponding quinones for 45 min in ethanol[15] or in DMF, and recrystallized from acetic acid. Elemental analysis (theoretical values in parenthesis): benzophenazine: N 11.46 (12.17), C 84.18 (83.45), H 4.36 (4.38); dibenzophenazine: N 10.14 (10.0), C 85.25 (85.69), H 4.61 (4.31). 2-Anilino-1,4-naphtoquinone and 4-anilino-1,2-naphtoquinone were prepared by reaction of the corresponding quinones with aniline in DMF at 100°C and recrystallized from a mixture of ethanol/water (1/4). Elemental analysis: 4-anilino-1,2-naphtoquinone: N 5.37 (5.62), C 77.52 (77.09), H 4.33 (4.45); 2-anilino--1,4-naphtoquinone: N 4.61 (5.62), C 78.87 (77.09), H 4.31 (4.45). The phenazines and substituted quinones were also identified by means of IR spectroscopy.

Modification of the glassy-carbon surface

Modification of glassy carbon with o-phenylenediamine was carried out by placing the electrodes in a refluxing solution of 0.005 M o-phenylenediamine in ethanol (or at 100°C in DMF) for 6 h. Ethanol and DMF were dried over 4 Å molecular sieves. The electrodes were thoroughly washed with ethanol or DMF to remove any adsorbed diamine. The reaction of glassy carbon with aniline was performed analogously.

Procedure

Electrochemical measurements were carried out in conventional cells. All solutions were deoxygenated by saturation with argon for 15 min. The reported potentials are relative to the standard calomel electrode (SCE), connected to the electrochemical cell via an agar-agar/KCl bridge. A platinum coil served as counter electrode.
Cyclic voltammetry was carried out using a Wenking Potentioscan POS-73, a Data Precision 2480 digital multimeter and a Philips PM 8041 XY-recorder. For phase-selective ac-voltammetry, a PAR-5204 (or 129A) Lock-In Amplifier, a Philips PM-5167 function generator, a HP-7046A XYY'-recorder and a Fluke 1910A multi-counter completed the experimental set-up. To avoid interference with the applied potential, no correction for the uncompensated solution resistance (R_u) was applied. The ac-voltammetric measurements were corrected vectorially for R_u and the double-layer capacity C_d as described by *Smith*[16]. The measured phase angle (ϕ) is then converted to the faradaic phase angle (ϕ_f). The frequency-dependent phase-angle shifts, caused by the internal circuit of the potentiostan and the external circuit, were corrected by adjusting the detection angle.

Unless otherwise stated, the experimental conditions were: phosphate buffer: pH = 7, $\omega = 60 \, \pi \, s^{-1}$, $\varepsilon = 10$ mV (rms), $v = 20$ mV·s^{-1}.
For immobilized species, a detection angle (λ) of 90° was used, but for redox systems in solution, $\lambda = 45°$.
Impedance measurements were carried out using a Solartron/ Schlumberger 1250 Frequency Response Analyser and a 186 Electrochemical Interface, connected to a HP 9825A microcomputer set-up.

[13]   *J. F. Evans* and *T. Kuwana*, Anal. Chem. **51**, 358 (1979).
[14]   *R. Nowak, F. A. Schultz, M. Umaña, H. Abruña* and *R. W. Murray*, J. Electroanal. Chem. **94**, 219 (1978).
[15]   *A. I. Vogel*, "A Textbook of Practical Organic Chemistry", p. 749.
[16]   *D. E. Smith* in "Electroanalytical Chemistry", *A. J. Bard*, ed., Vol. 1, p. 1.
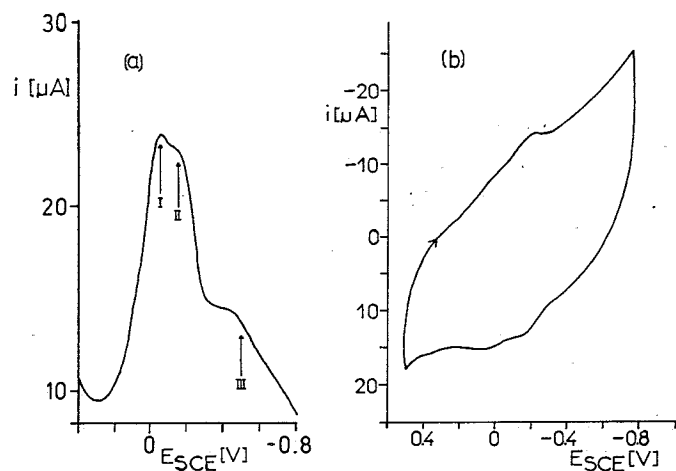
Fig. 2. ac-Voltammogram (a) and cyclic voltammogram (b) of a glassy-carbon electrode after an oxygen rf-plasma treatment. (λ 90°, respectively v 0.5 V·s⁻¹).

Characterization of the surface groups

The oxidized glassy-carbon electrode

The ac- and cyclic-voltammograms of a glassy-carbon electrode, after exposure to an oxygen rf-plasma, are shown in Fig. 2a,b. In the cyclic voltammogram (b), the redox peaks are poorly developed, while pronounced peaks are observed in the phase-selective ac-voltammogram (a). Three reduction peaks are observed, i.e. at -0.05 V (I), -0.16 V (II) and at -0.5 V (III) vs. SCE (pH 7). The relative intensity of the first two peaks is reproducible but the absolute peak heights are strongly dependent upon the experimental conditions, in particular upon the pretreatment procedure. Peak III is very broad and is sometimes no longer distinguishable from the background current. The observed redox peaks possess properties very similar to those of proton-involved immobilized redox species, such as quinones[17] (Q):

$$Q + 2 H^+ + 2 e^- \rightleftarrows QH_2$$
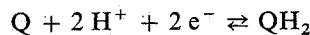
Firstly, there is no influence of convection: rotating the electrode or stirring the solution has no marked influence on the peak height (i.e. peak current, i_p). This also indicates that the protonation of the quinones is not the rate-determining step. Secondly, i_p increases linearly with the frequency (ω). This linear dependence of i_p vs. ω is characteristic of immobilized redox couples, in contrast to the $\sqrt{\omega}$ dependence observed for redox couples in solution. Thirdly, the pH dependence of the peak potentials (E_p) is -62 mV/pH for peak I and -64 mV/pH for peak II (Fig. 3). This is close to the theoretical value of -59 mV/pH at 25°C for a $2e^-/2H^+$ redox couple. As previously mentioned, peak III is often barely distinguishable from the background current, so the pH dependence, although present, cannot be precisely determined.

Parameters of the plasma treatment

For oxidation of the glassy-carbon-electrode surface we used oxygen, argon and CO_2 rf-plasma treatment. Oxidation of the carbon by O_2-plasma treatment proved to be the most effective. The shiny carbon surface becomes lustreless after only a few minutes (surface roughening). Both O_2- and CO_2-plasma treatment show this drastic effect. Rf-plasma treatment with argon, however, leaves the electrode surface shiny, even after an exposure of 15 min; furthermore, the redox peak III is far less pronounced. CO_2-plasma treatment gives a slightly better resolution of the first two redox peaks (I and II) but their
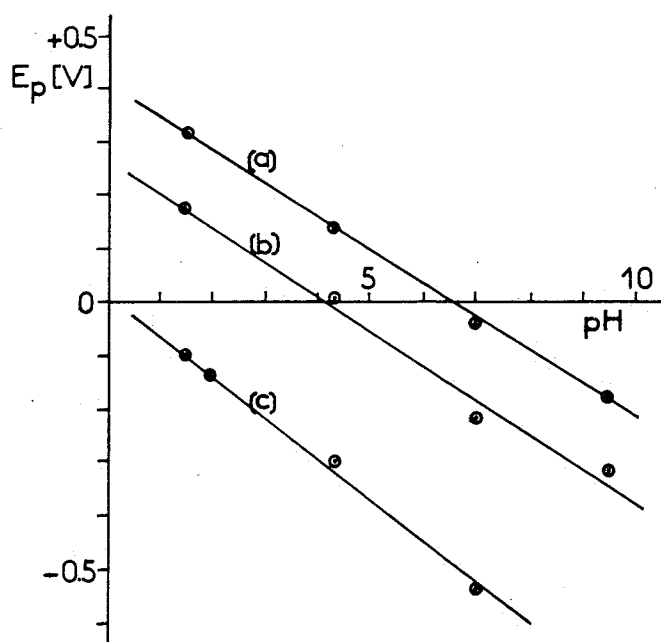

Fig. 3. pH dependence of the peak potential of the surface quinone and phenazine peak. (a) quinone peak I; (b) quinone peak II; (c) phenazine peak.

relative intensity is the same as after an O_2-plasma treatment (Fig. 2a). Only the Ar-plasma shows a marked difference with respect to the O_2-plasma treatment. The peak height at -0.16 V (peak II) is increased after the Ar-plasma treatment. The efficiency of the Ar-plasma treatment increases when the argon pressure is increased to 2 Torr (increase of plasma density[18]), and finally results in a very pronounced peak in the ac-voltammogram (Fig. 4). After the O_2-plasma treatment, an increase was
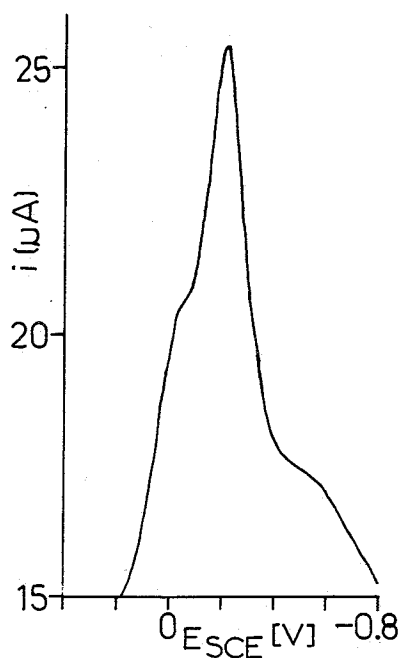

Fig. 4. ac-Voltammogram of a glassy-carbon electrode after argon rf-plasma treatment at 2 Torr for 10 minutes (λ 90°).

[17] J. Q. Chambers in "The electrochemistry of quinonoid compounds", S. Patai, ed., Chapter 14.

[18] G. Kruppa, H. Suhr, G. Janzen and W. Staib, Ber. Bunsenges. Phys. Chem. 85, 1128 (1981).

found for the surface concentration of carboxyl groups, as could be demonstrated by an increased surface concentration of amino-porphyrine, immobilized via amide bonding[18]. An increase in the concentration of carboxyl surface groups was also found when carbon reacts with oxygen at high temperatures[20].

Cyclic- and ac-voltammetry of quinones and phenazines in solution

In order to characterize the different types of quinones, likely to be present at a glassy-carbon surface, half-wave potentials of several quinones in a phosphate buffer (pH 7) solution were measured at a glassy-carbon electrode by means of cyclic voltammetry (Table 1). These redox potentials agree very well with those reported in the literature, which were measured at a platinum electrode in HCl, LiCl, ethanol, water solutions[21].

The quinone concentration in the solution is kept very low in order to minimize adsorption phenomena. Before addition to the phosphate solution, the quinones are dissolved in a very small amount of acetone to accelerate the dissolution process. The effect which quinone addition has upon the ac-voltammogram of a glassy-carbon electrode is shown in Fig. 5 for the following types of quinones: *(a)* 1,2-naphtoquinone, *(b)* 1,4-naphtoquinone, *(c)* 9,10--anthraquinone and *(d)* 9,10-phenanthrenequinone.
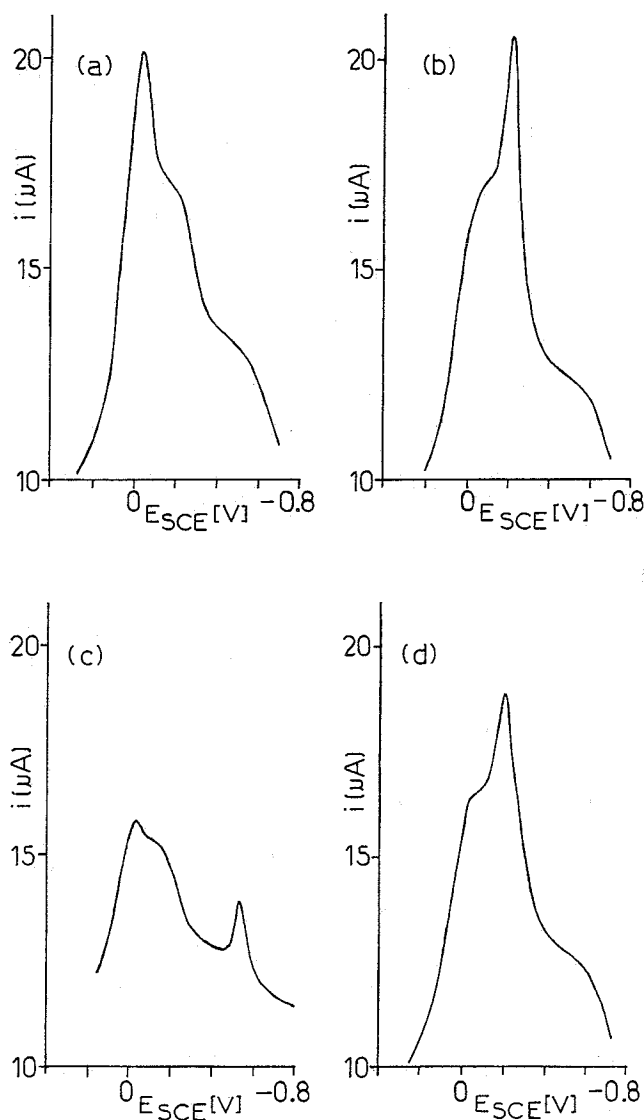

Fig. 5. Effect of quinone addition to the solution on the ac-voltammogram of an oxidized glassy-carbon electrode (λ 45°). (a) 1,2-naphtoquinone; (b) 1,4-naphtoquinone; (c) 9,10-anthraquinone; (d) 9,10-phenanthrenequinone.

To explain several phenomena observed during modification of glassy carbon with *o*-phenylenediamine, we also studied several substituted quinones in solution. Substituted quinones such as 2-anilino-1,4-naphtoquinone and 4-anilino-1,2-naphtoquinone show a remarkable behaviour at low pH. At pH 7, the half-wave potentials ($E_{\frac{1}{2}}$) of these quinones are well separated (100 mV, see Table I), while in strongly acidic media (1 M HClO$_4$), the potentials coincide at the $E_{\frac{1}{2}}$ of the *p*-quinone. The substituted *o*-quinone is obviously converted into the *p*-quinone, as described in the literature[22]. This conversion appears to proceed rather slowly, since it was possible to detect intermediate stages. The redox behaviour of the quinones, in the pH 7 region, is described by a 2H$^+$/2e$^-$ mechanism; this can be concluded from the peak width at mid-height ($W_{\frac{1}{2}} < 70$ mV) of the ac-voltammogram and from the peak potential separation ($\Delta E_p \approx 34$ mV) in the cyclic voltammogram. The redox behaviour of the phenazines is more complicated. At pH 7, only one reduction peak is observed since the phenazines are not protonated (pK ≈ 4), and a two-electron reduction to the dianion, followed by protonation, is the most likely mechanism ($W_{\frac{1}{2}} \approx 60$ mV), although a one-electron reduction to the semi-quinone cannot be ruled out. However, in strongly acidic media (1 M HClO$_4$), one of the two nitrogens of the phenazine is protonated so two one-electron reductions are observed (Fig. 6). For the benzophenazines, the mechanism is probably even more complex, since the two peak heights are no longer equal and have a small separation. For the midpoint potential (E_m), a pH dependence of -63 mV/pH is calculated for dibenzophenazine, -55 mV/pH for benzophenazine and -51 mV/pH for phenazine.

Modification of glassy carbon with o-phenylenediamine

The result of the *o*-phenylenediamine reaction with the glassy-carbon surface is shown in the ac-voltammogram of Fig. 7. Only one new peak appears at -0.54 V *vs.* SCE, while the quinone peaks decrease and finally disappear, except for one small peak at -0.22 V (Fig. 7c). The peak at -0.54 V is larger than the original quinone peaks and a pH dependence of -75 mV/pH is found (Fig. 3c). Comparison of the peak potential (-0.54 V) with the half--wave potentials (-0.52 V and -0.54 V) of the two benzophenazines in solution (Table I) leads to the conclusion that the surface quinones are converted to the corresponding phenazines. The remaining peak at -0.22 V must then be ascribed to the 1,4-naphtaquinone structure, since this *para*-configuration cannot be converted into a phenazine. Moreover, its peak potential is equal to the $E_{\frac{1}{2}}$ (Table I), measured for the *p*-quinone in solution. Considering these results, the redox peaks I and II (Fig. 2) can be ascribed to the *o*-naphtoquinone (peak I) and to the 9,10-phenanthrenequinone and *p*-naphtoquinone (peak II) structures. For the pH dependence of the surface phenazines, a similar behaviour is observed as for the phenazines in solution. In phosphate pH 7 buffer solution, only one peak is observed, while in strongly acidic media (1 M HClO$_4$), two peaks (although scarcely separated) are present in the ac-voltammogram (Fig. 8). It was observed that, if the surface reaction is not fully completed, the peak potentials
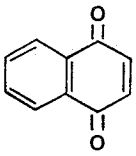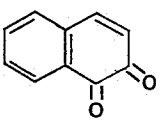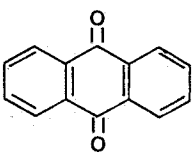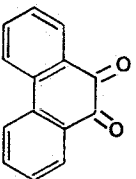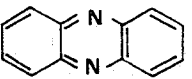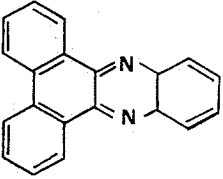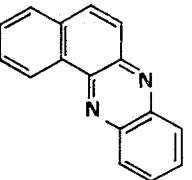
[19] J. Schreurs, Thesis, University of Technology, Eindhoven, The Netherlands, October 1983.

[20] H. P. Boehm and M. Voll, Carbon 8, 227, 741 (1970).

[21] W. M. Clark, "Oxidation – Reduction potentials of Organic Systems", The Williams & Wilkens Company, Baltimore, 1960.

[22] "Methoden der Organischen Chemie" (Houben-Weyl), Chinone Teil II, p. 290.

Table I   Half-wave potentials of quinones and phenazines.

	Compound	$E_{\frac{1}{2}}^a$ (V)		$E_{\frac{1}{2}}^b$ (V)
		Phosphate pH 7	1 M HClO$_4$	
	1,4-naphtoquinone	−0.22	0.20	−0.189
	2-anilino-naphtoquinone	−0.39	0.00	−0.372
	1,2-naphtoquinone	−0.10	0.32	−0.112
	4-anilino-naphtoquinone	−0.29	0.09/ 0.00	−
	9,10-anthraquinone	−0.53	−0.14	−0.504
	9,10-phenanthrenequinone	−0.22	0.20	−0.188
	phenazine	−0.39	0.12/−0.18	−0.36
	dibenzophenazine	−0.54	−0.08/−0.28	−
	benzophenazine	−0.52	0.00/−0.28	−

[a] Glassy carbon working electrode, Pt-coil counter electrode, phosphate (pH 7) buffer solution, respectively, 1 M HClO$_4$ solution.
[b] Platinum working electrode, platinum counter electrode, HCl, LiCl, ethanol, water solution (see ref. 18 for exact composition). The $E_{\frac{1}{2}}$ potentials, referred to the SCE at 25°C, are calculated from published E^o values using −59.1 mV/pH and E^o–E(SCE) = −0.245 V.

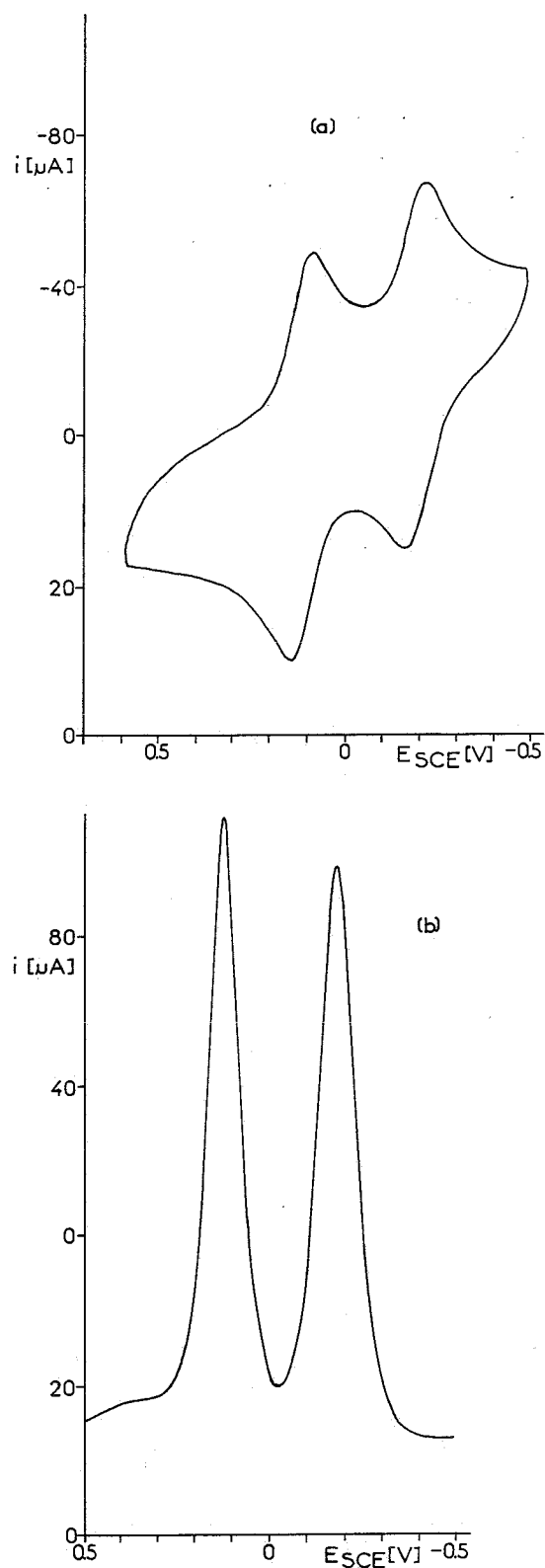Fig. 6.   Cyclic voltammogram (v 0.4 V · s⁻¹)
          (a) and ac-voltammogram (λ 45°)
          (b) of phenazine in 1 M HClO₄, at an oxidized
          glassy-carbon electrode.

Fig. 7.   ac-Voltammogram (λ 90°) of a glassy-carbon
electrode after: (a) argon rf-plasma; (b) partial reaction
with o-phenylenediamine; (c) completed reaction with
o-phenylenediamine.
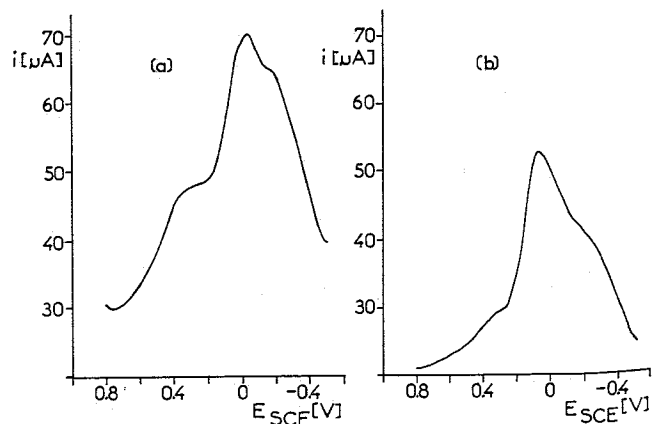
Fig. 8.   ac-Voltammogram (λ 90°) of an oxidized glassy-
-carbon electrode after reaction with o-phenylenediamine
(measured in 1 M HClO₄). (a) reaction not completed, inter-
mediate detectable; (b) reaction completed.

(Fig. 8a) agree reasonably well with the half-wave poten-
tials of benzo- and dibenzo-phenazine in solution (Table I).
However, if the reaction is completed, then the peak
potentials are shifted towards more anodic values (Fig. 8b),
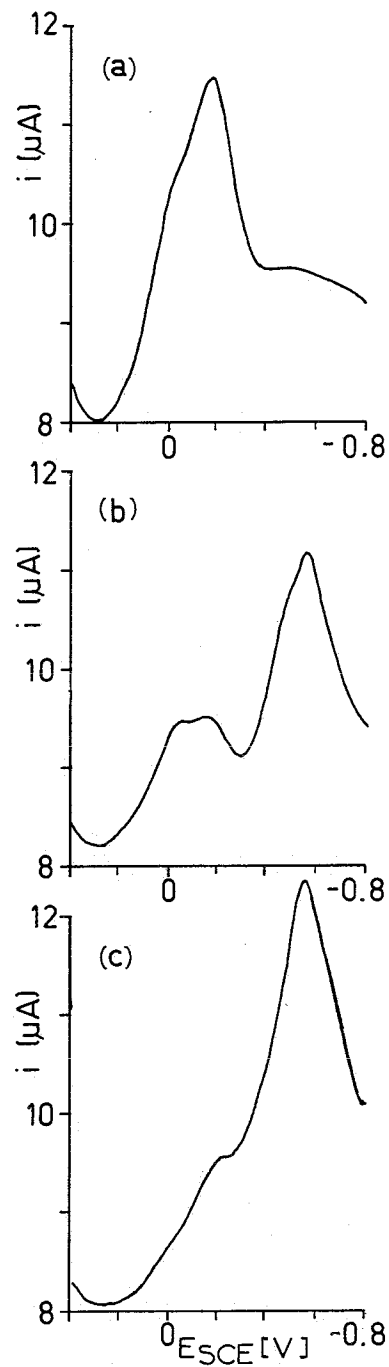corresponding to the half-wave potentials of phenazine.

Sometimes, an extra peak at −0.37 is observed in the ac-voltammogram. A possible side-reaction during this surface synthesis is the reaction of the amino group with the quinonoid ring instead of the carbonyl group, which results in substituted *ortho-* and *para*-quinones. This substitution reaction was also observed during the synthesis of benzophenazine, but not during that of dibenzophenazine. [For this reason, the half-wave potentials of the two possible products, *i.e.* 2-anilino-1,4-naphtoquinone and 4-anilino-1,2-naphtoquinone, were measured (Table I)]. The half-wave potential of the substituted *p*-quinone (−0.39 V) agrees very well with the potential of the extra peak (−0.37 V). In order to obtain further proof for this substitution reaction, the glassy-carbon surface was modified with aniline. A decrease in both quinone peaks I and II (Fig. 2a) is observed and only one new peak (at −0.38 V) appears in the ac-voltammogram (Fig. 9). Quinone peak II (−0.16 V) only slightly decreases and shifts towards −0.20 V. Obviously, the *p*-quinone is substituted but not the phenanthrenequinone, as was observed during the synthesis of dibenzophenazine. From the decrease in peak I it can be concluded that the *o*-naphtoquinone is also substituted. However, as stated earlier, only one new peak appeared (*i.e.* at −0.38 V), and no peak was observed at −0.29 V (*i.e.* the $E_{\frac{1}{2}}$ value of 4-anilino-1,2-naphtoquinone). The substituted *o*-quinone structure at the surface is probably converted into the *p*-quinone, as was observed for substituted *o*-quinones in acidic solutions.
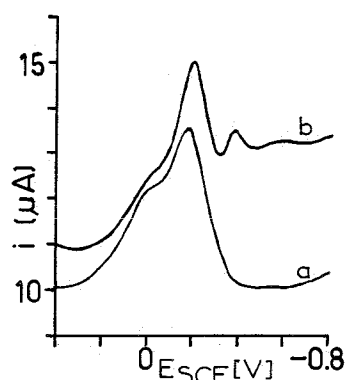

Fig. 9. ac-Voltammogram of an oxidized glassy-carbon electrode before (a) and after (b) reaction with aniline (λ 90°).

Table II   Percentage of the different quinone surface groups at a glassy-carbon electrode, referred to the total quinone surface group concentration (Γ_T).

Γ_T *was calculated, from the ac-voltammogram, to be $2 \cdot 10^{-11}$ mol·cm^{-2} after argon plasma treatment, and $3 \cdot 10^{-11}$ mol·cm^{-1} after oxygen-plasma treatment (corrected for surface roughening).*

Surface structure	% after O₂-plasma	% after Ar-plasma
1,2-naphtoquinone	50	20
1,4-naphtoquinone	10	<10
9,10-phenanthrenequinone	30	70
9,10-anthraquinone	10	nil.

The relative composition of the quinone surface groups, listed in Table II, is calculated from the peak area in the phase-selective (λ = 90°) ac-voltammograms using the geometrical electrode area (A 0.246 cm²). The total quinone surface concentration (Γ_T) is calculated to be $2 \cdot 10^{-11}$ mol cm^{-2} after an Ar-plasma treatment and $3 \cdot 10^{-11}$ mol·cm^{-2} after an O₂-plasma treatment (Table II). In the latter case, Γ_T is corrected for surface rough-

ening by comparing the double-layer capacity of the glassy-carbon electrodes after Ar- and O₂-plasma treatment. This difference in Γ_T is obviously caused by the lack of *o*-naphtoquinones after an Ar-plasma treatment. A theoretical surface coverage of $8 \cdot 10^{-10}$ mol·cm^{-2} is calculated, taking the area occupied by the quinone molecule to be 7 × 3.5 Å². [The 7 Å is estimated from the diameter of a *para*-quinone and the 3.5 Å is the distance between the aromatic planes of the graphite structure]. However, glassy carbon is an isotropic material and the graphite planes are randomly orientated, so probably only 75% of the theoretical value can be obtained, *i.e.* $6 \cdot 10^{-10}$ mol·cm^{-2}. From comparison with the experimental value (about $2.5 \cdot 10^{-11}$ mol·cm^{-2}), it can be concluded that at most 5% of a monolayer is present.

Kinetics of the surface redox reactions

Information about the kinetics of the surface reactions is derived from impedance or phase-selective ac-voltammetric measurements. In Fig. 10, a plot of the total impedance in the complex plane is shown for the quinone surface reaction (at −0.16 V) in phosphate (pH 7) buffer solution. From this lustreless curve, it is impossible to derive a reliable value for the surface-reaction-rate constant (k_s). A similar behaviour is observed for impedance measurements of the quinone-surface reaction in 0.05 M H₂SO₄, and also for the phenazine surface reaction in both the media mentioned above. From measurements using phase-selective ac-voltammetry, a plot of cotg ϕ_f *vs.* ω (Fig. 11) is determined for the quinone surface reaction at −0.16 V in phosphate (pH 7) buffer solution (ϕ_f: faradaic phase-angle, see Experimental). From the slope of this plot, a reaction rate constant (k_s) of $6.1 \cdot 10^3$ s^{-1} is calculated for the quinone surface reaction. Similar values are thus obtained for the quinone as well as for the phenazine surface reaction. The plot of cotg ϕ_f *vs.* ω does not show the expected zero intercept and deviates from
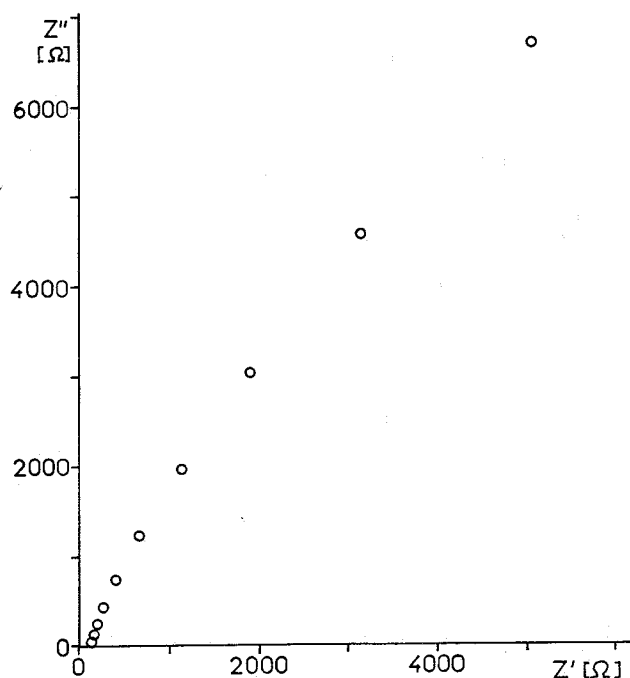

Fig. 10.   Impedance plot of an oxidized glassy-carbon electrode measured in phosphate pH 7 buffer.

the linear behaviour observed at low frequencies. This discrepancy with theory can be ascribed to a contribution by an extra resistive component in series with the faradaic
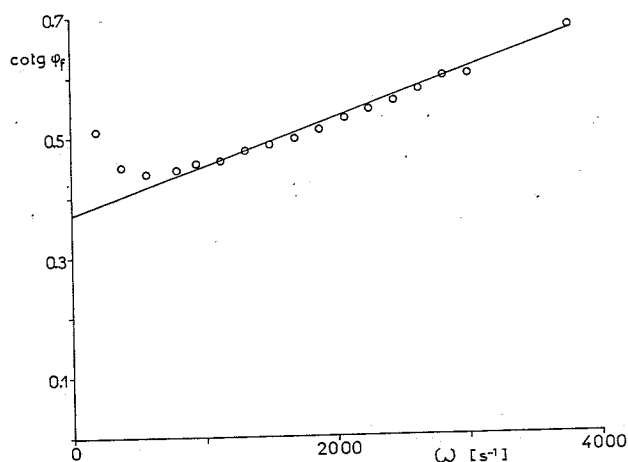
Fig. 11. Plot of cotg ϕ_f vs. ω, calculated from the ac--voltammograms of a glassy-carbon electrode (after Ar--plasma treatment), measured in phosphate (pH 7) buffer solution.
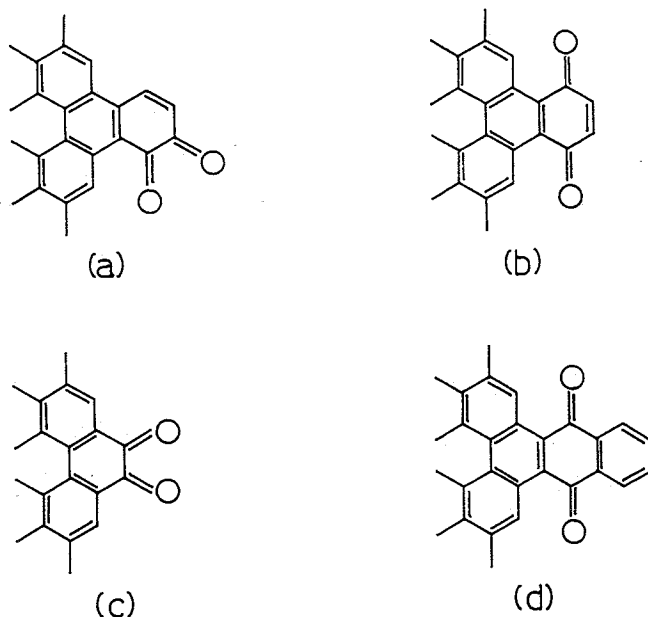

Fig. 12. Quinone structures at an oxidized glassy-carbon surface: (a) 1,2-naphtoquinone; (b) 1,4-naphtoquinone; (c) 9,10-phenanthrenequinone; (d) 9,10-anthraquinone.
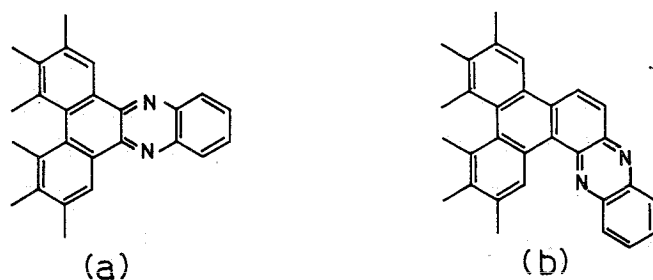

Fig. 13. Phenazine structures at an oxidized glassy-carbon electrode surface after reaction with o-phenylenediamine: (a) dibenzophenazine; (b) benzophenazine.

capacity. This implies that the surface reaction must be even faster than the measured rate constants. For this reason, it would be more appropriate to ascribe a lower limit of about 10^3 s^{-1} to the reaction rate constant of both the quinone and the phenazine surface reactions.

The peaks in the cyclic- and ac-voltammograms of immobilized redox species are usually broadened because of, for example, mutual destabilizing interaction of the molecules, as described by Anson[23] and Murray[24]. If non-ideal behaviour is taken into account, then an interaction parameter (r) of $-1.0 \cdot 10^{12}$ cm$^2 \cdot$ mol^{-1} is determined from the quinone redox peak in the ac-voltammogram (λ 90°). The theoretical peak width at mid-height, $W_{\frac{1}{2}}$ 267 mV, agrees very well with the experimental value of 230 mV. For the phenazine redox peak, an r value of $-2.7 \cdot 10^{11}$ cm$^2 \cdot$ mol^{-1} is determined, while a peak width at mid--height of 290 mV is calculated, i.e. 320 mV experimentally.

Discussion and additional remarks

In summary, the results show that quinone structures such as ortho/para-naphtoquinone and 9,10-phenanthrenequinone exist at the glassy-carbon surface (Fig. 12). The o--quinone structures can be converted into the corresponding phenazines by reaction with o-phenylenediamine (Fig. 13). In the ac-voltammogram, a very broad peak (III) is observed at -0.5 V (Fig. 2a), which can not only be ascribed to a 9,10-anthraquinone-like structure, but also to a set of ring-substituted naphto- and phenanthrene--quinones, since substitution of the quinonoid rings, with one or two groups such as $-CH_3$, $-OH$ or $-OCH_3$, causes peak potential shifts up to -250 mV[21,25]. The reaction of aniline with the surface quinones is only partially effective. The redox peaks of the surface quinones only partially decrease and a small peak at -0.38 V appears (Fig. 9). Obviously part of the surface quinones are already substituted.

The phenazine structures at the modified carbon electrode are stable in neutral and acidic media, but electrochemical reduction at pH > 10 destroys these structures. Neither quinone nor phenazine redox peaks are subsequently observed in the ac-voltammogram at pH 7, and the background current remains constant to within 10%, in the potential region +0.5 to -0.7 V. The same result is observed after treatment of the carbon electrode at strongly reducing potentials (-2.0 V, pH 7). All oxidic surface groups are then irreversibly reduced. The peaks in the cyclic- and ac-voltammograms of immobilized redox species are generally broadened with respect to the theoretical value for the peak width at mid-height, i.e. $W_{\frac{1}{2}}$ 90.6/n mV. For this peak broadening, several explanations are possible. Firstly, destabilizing interactions[23,24] between the immobilized molecules may account for the broadened quinone and phenazine peaks. The values calculated for the $W_{\frac{1}{2}}$ agree very well with those determined from the ac-voltammograms. Secondly, quasi-reversible behaviour also causes frequency-dependent peak broadening. Thirdly, mono-substitution of the quinonoid ring, or of the neighbouring aromatic rings (with groups such as $-CH_3$, $-C_6H_5$, etc.), causes peak potential shifts of maximum -40 mV[21,25]. Substitutions of this kind therefore result in broadened peaks in the voltammograms.

The oxidic surface structures show a remarkably positive effect on the electrochemical response of quinones and phenazines measured in solution. If the surface is not oxidized, then a very poor response is obtained for the qui-

23 A. P. Brown and F. C. Anson, Anal. Chem. 49, 1589 (1977).
24 D. F. Smith, K. Willman, K. Kuo and R. W. Murray, J. Electroanal. Chem. 95, 217 (1979).
25 "Encyclopedia of Electrochemistry of the Elements", Organic Section, Edts. A. J. Bard and H. Lund, Volume XII, Chapter 1.

nones and phenazines in solution. If, on the other hand, the electrode surface is first oxidized, for example by O_2--plasma treatment, then the response is enhanced by several orders of magnitude.

The reaction of the carbon with molecular oxygen, after the Ar-plasma treatment, probably proceeds analogously to the reaction of ethylene compounds with the activated surface[14,26], resulting mainly in o-quinone structures. However, only 9,10-phenanthrenequinone-like structures are created and no o-naphtoquinone-like structures. A study[3] of the oxidation of single crystals of graphite showed that oxidation in the presence of water results in a "zig-zag" boundary, while oxidation with dry oxygen results in an "arm-chair" boundary. If the Ar-plasma treatment selectively creates an "arm-chair" boundary, then indeed 9,10-phenanthrenequinone-like structures will be preponderant after reaction of oxygen with the activated carbon surface. Surface roughening could then explain the appearance of both boundaries after an O_2-plasma treatment.

The reaction of molecular oxygen with the activated carbon surface, created by Ar-plasma treatment, is not likely to yield any carboxylic surface groups. This is con firmed by the negative result of porphyrine modification via amide bonding. During the O_2-plasma treatment, species such as oxygen, atoms, ions, etc. also react with the carbon surface and a variety of oxidic surface groups are created, among them carboxyl groups. The O_2-plasma treatment is obviously similar to reaction of carbon with oxygen at high temperatures, which increases the surface concentration of the carboxyl groups[20], with the surface thus becoming more acidic.

In contrast to the irreversible behaviour of the carboxylic surface groups, and to that of most other oxidic surface groups (e.g. aldehyde, phenol, etc.), the quinone-surface groups show an extremely fast and reversible electrochemical behaviour. A lower limit of 10^3 s^{-1} was determined for the rate constant (k_s) of the quinone and of the phenazine surface reaction. [The rate constants cannot be determined accurately, since they are close to the detection limit of ac-voltammetric measurements.] The rate constants for both surface reactions are much higher than those reported in the literature for adsorbed phenazine (380 s^{-1})[27] and adsorbed 9,10-phenanthrenequinone (320 s^{-1})[28]. The quinone and phenazine surface structures obviously show a less inhibitive effect on electron transfer, probably because they are incorporated in the aromatic planes of the graphite structures at the glassy-carbon surface, so electron transfer will occur through the conjugated π-bondings.

For comparison of the surface reaction with the solution reaction, one can use the relationship $k_s = 6 \cdot 10^8 \cdot k^{0'}$, as derived by Anson[28], where $k^{0'}$ is the standard heterogeneous rate constant. From this equation, a lower limit of $1.7 \cdot 10^{-6}$ cm$\cdot$s^{-1} is calculated for $k^{0'}$. However, heterogeneous rate constants of the order of 10^{-3} cm$\cdot$s^{-1} were measured for several quinones in solution[29], suggesting that the surface reaction rate constant (k_s) must be at least two orders of magnitude greater than the lower limit of 10^3 s^{-1} which we determined. It would be very interesting if the actual value for the surface-reaction-rate constant could be determined, in order to allow a comparison between theory and experiment.

Conclusions

The poorly developed redox waves, which are generally encountered in the cyclic voltammogram of an oxidized carbon electrode and which can be ascribed to a quinone--like surface reaction, turn into pronounced redox peaks when detected by phase-selective ac-voltammetry. At a glassy-carbon electrode, oxidized by rf-plasma treatment, the quinone-like surface structures, o/p-naphtoquinone and 9,10-phenanthrenequinone, are identified by electrochemical analysis in combination with chemical modification (e.g. conversion into a phenazine). The 9,10-anthraquinone-like structure is also thought to be present at the glassy-carbon surface. These quinone surface groups may also be present at similar types of carbon, e.g. pyrolytic graphite. The quinone, as well as the phenazine surface reaction, is shown to be very fast and a lower limit of 10^3 s^{-1} is determined for the surface reaction rate constant (k_s).

Surface pretreatment by rf-plasmas of oxygen or argon proved to be a rapid, reproducible and contaminant-free method for the introduction and enhancement of oxidic surface groups. The carboxylic surface group concentration can be enhanced by oxygen rf-plasma treatment. The oxidic surface groups are very important for obtaining an effective electron transfer to species in solution, as was concluded from measurements involving quinones and phenazines in solution.

Phase-selective ac-voltammetry has proved to be a very powerful technique for the analysis of surface groups which show a (quasi-)reversible electrochemical behaviour.

[26] S. Mazur, T. Matusinovic and K. Cammann, J. Am. Chem. Soc. 99, 3888 (1977).

[27] E. Laviron, J. Electroanal. Chem. 97, 135 (1979).

[28] A. P. Brown and F. C. Anson, J. Electroanal. Chem. 92, 133 (1978).

[29] J. M. Hale and R. Parsons, Trans. Farad. Soc. 59, 1429 (1963).