Journal of the Iranian Chemical Society, Vol. 2, No. 1, March 2005, pp. 1-25.

JOURNAL OF THE
Iranian
Chemical Society

An Overview of the Electrochemical Reduction of Oxygen at Carbon-Based Modified Electrodes

B. Šljukić, C.E. Banks and R.G. Compton*
Physical and Theoretical Chemistry Laboratory,
Oxford University, South Parks Road,
Oxford OX1 3QZ, United Kingdom

(Received, 23 November 2004, Accepted 14 December 2004)

We present an overview of the electrochemical reduction of oxygen in water, focussing on carbon-based and modified carbon electrodes. This process is of importance for gas sensing, in fuel cells and in the electrosynthesis of hydrogen peroxide.

Keywords: Electrochemical reduction, Oxygen, Carbon-based modified electrodes

INTRODUCTION

The electrochemical reduction of oxygen plays significant role in fuel cells, gas sensors and in the electrosynthesis of hydrogen peroxide. The oxygen reduction reaction proceeds either as a direct four-electron process or a two-electron process [1,2]. Production of water by a four-electron oxygen reduction is used both in fuel cells and gas sensors, while hydrogen peroxide is produced by a two-electron reduction of oxygen.

The importance of the reduction of oxygen to water in fuel cells and metal/air batteries is well-known. Platinum electrodes were the first choice for use in fuel cells, but their high cost has lead to researches for modified electrodes that decrease the oxygen reduction overpotential. Supported metal catalysts are often used to accelerate electrochemical processes. Particular demand arose recently for the best catalysts for low-temperature fuel cells, and in this sense platinum group metals dispersed on fine carbon particles displayed satisfactory characteristics [3]. The use of high surface area carbon materials as platinum catalyst supports in fuel cells electrodes [4,5] has attracted attention since carbon electrodes modified by a metal macrocycle can reduce oxygen to water in alkaline solutions [6-8]. There are a variety of different carbon materials [9] such as carbon powder, carbon felt or glassy carbon which may be used as a support of metal catalyst.

Chemists are seeking the “greener” synthesis of organic materials. Recently Usui *et al.* have reported the green synthesis of the catalytic dihydroxylation of olefins with hydrogen peroxide avoiding the use of any organic solvents or metal catalysts. They report high yield and selectivity noting that hydrogen peroxide is an ideal oxidant, because the atom efficiency is excellent and water is theoretically the sole by-product.

Hydrogen peroxide is made commercially *via* the anthraquinone-mediated reduction of oxygen known as the ‘AO-process’. This involves the hydrogenation, for example, of 2-alkyl-9,10-anthraquinone (with a catalyst such as nickel or palladium), forming the corresponding hydroquinone, and oxidation with oxygen (usually air) to yield hydrogen peroxide and reforming the starting anthraquinone. Commonly the anthraquinone is dissolved in a solvent or solvent mixture for

---

* Corresponding author. E-mail: Richard. Compton@ chemistry.ox.ac.uk

hydrogenation, oxidation and extraction. Due to the differing solubility of the quinone and hydroquinone species, solvent mixtures are commonly employed.

An alternative method is the electrochemical reduction of oxygen, which generates hydrogen peroxide. The focus of electrode substrates is on carbon based materials since the oxygen reduction on these surfaces forms hydrogen peroxide as an end product. Their low cost also makes them suitable for commercial applications where electrodes of high surface, such as reticulated carbon, are required.

The reduction of oxygen is also used in Clark cells, electrochemical detectors specific for molecular oxygen. Oxygen is reduced to hydroxide releasing four electrons for each molecule of oxygen with the current linearly proportional to the amount of oxygen present. The most common cathode electrode materials are noble metals like gold or silver or noble-metal-plated materials [10]. For detection of oxygen in liquid samples, Clark cells with a massive cathode surface are usually applied [11]. However, it was noted that, under certain conditions, hydrogen peroxide is generated at this electrodes [12]. For more sensitive values, especially for detection of oxygen in gaseous samples, net or grid electrodes are preferred.

It is established that the rate of electrochemical process is extensively influenced by the catalytic activity of the electrode surface, both the catalyst and the supporting material are significant factors. In this article we review the present literature and report the advances made using modified carbon based electrode substrates.

MECHANISM OF THE OXYGEN REDUCTION REACTION

The oxygen reduction reaction (ORR) has been investigated on various electrode substrates such as platinum, mercury, silver, gold, and carbon-based materials. It has been established [7] that the electrochemical reduction of oxygen is influenced by the nature of the electrode material and by the solution medium. The effect of electrode materials and various solvents on the electrochemical reduction of oxygen through their influence on the reduction potentials and currents has been extensively studied and highlighted in the literature [7]. However, the detailed mechanism of the electroreduction of oxygen is still unclear. It is generally believed, however debatable, that the reduction of oxygen proceeds by either a direct four-electron pathway or a two-electron pathway [1,2]:

1. Direct four- electron pathway

In alkaline solutions

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-; E^0 = 0.401V \qquad (1)$$

In acid solutions

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O; E^0 = 1.229V \qquad (2)$$

2. Peroxide Pathway

In alkaline solutions

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-; E^0 = -0.065V \qquad (3)$$

is followed either by the further reduction

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-; E^0 = +0.867V \qquad (4)$$

or by decomposition under a disproportionation reaction

$$2HO_2^- \rightarrow 2OH^- + O_2 \qquad (5)$$

In acid solutions

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2; E^0 = 0.67V \qquad (6)$$

is followed either by

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O; E^0 = 1.77V \qquad (7)$$

or by disproportionation

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (8)$$

where E° is the standard electrode potential and all potentials refer to the standard state values *vs*. the normal hydrogen electrode at 25 ºC [4].

Oxygen reduction at ‘active’ metal electrodes in aqueous solutions is catalysed and produces water at a reduction potential characteristic for the particular metal [13]. On the contrary, at ‘passivated’ metal electrodes, the ORR yields hydrogen peroxide *via* a one-electron mechanism with facile disproportionation of the O_2^- intermediate [14].

Carbon electrodes are of interest for electrochemical reduction of oxygen since high surface area carbon materials were used as platinum catalyst supports in fuel cell electrodes [4,5]. However, oxygen reduction reaction on carbon electrodes proceeds predominantly as a two-electron process producing hydrogen peroxide which is unwanted side product in fuel cells as it reduces the power efficiency [15-18]. Therefore carbon is an electrode material suitable for the electrochemical synthesis of hydrogen peroxide. Many different types of carbon have been studied for the oxygen reduction reaction: highly oriented pyrolytic graphite (HOPG) [6], pyrolytic graphite (PG) [6,19], graphite powder, porous graphite, natural graphite, glassy carbon (GC) [20-26], pyrolytic carbon, active carbon, carbon black [27] and carbon single crystals.

To date, there is no agreement on the mechanism, rate-determining step RDS, or adsorbed intermediates of the electrochemical reduction of oxygen on carbon surfaces. Most researchers agree that the adsorption of oxygen or superoxide is involved, but variations in surface conditions and pre-treatment result in different electrode behaviour. Next we summarise suggested mechanisms.

It has been reported that the mechanism of ORR on basal plane of ordinary pyrolytic graphite, OPG, and on glassy carbon, GC, electrodes is dissimilar [4]. The oxygen reduction is first order in O_2 and zero order in OH^- on both surfaces. The Tafel slopes in alkaline solution were found to be -0.12 V per decade on OPG [15], but -0.060 V per decade on GC surface [25]. Several authors proposed different possible mechanisms for ORR on GC surfaces. Taylor and Humffray [26] suggested the scheme where surface migration of adsorbed O_2^- to the active sites, reaction [10], is the RDS:

$$O_2 + e^- \rightleftharpoons O_2^{\cdot -}{}_{ads,\ before\ migration} \tag{9}$$

$$O_2^{\cdot -}{}_{ads,\ before\ migration} \rightleftharpoons O_2^{\cdot -}{}_{ads,\ after\ migration} \tag{10}$$

$$2O_{2\ ads}^{\bullet -} + H_2O \rightarrow O_2 + HO_2^- + OH^- \tag{11}$$

According to Zhang *et al*. [14], two different forms of the superoxide, $[O_2^-{}_{ads}]$ and $\{O_2^-{}_{ads}\}$, are present on the GC surface [28]. The proposed mechanism is consistent with the experimental data if reaction (14) is rate controlling step the reduction reaction:

$$O_{2\ ads} + e^- \rightarrow \left[O_{2\ ads}^-\right] \tag{12}$$

$$\left[O_{2\ ads}^-\right] \rightarrow \left\{O_{2\ ads}^-\right\} \tag{13}$$

$$\left\{O_{2\ ads}^-\right\} + HOH \rightarrow HO_{2\ ads} + OH^- \tag{14}$$

$$HO_{2\ ads} + e^- \rightarrow HO_{2\ ads}^- \tag{15}$$

$$HO_{2\ ads}^- \rightarrow HO_2^- \tag{16}$$

For graphite electrodes Morcos and Yeager [15] suggested the following mechanism:

$$O_2 \rightarrow O_{2\ ads} \tag{17}$$

$$O_{2\ ads} + e^- + H_2O \rightarrow HO_{2\ ads} + OH^- \tag{18}$$

$$2HO_{2\ ads} + OH^- \rightleftharpoons HO_2^- + H_2O + O_2 \tag{19}$$

with the reaction (18) determining reaction rate in the Tafel linear region and reaction (19) involving several steps. Earlier ^{18}O labelling experiments have shown that the oxygen reduction into HO_2^- proceeds as a unit without bond rupture [18].

Appleby and Marie [18] suggested a mechanism for ORR on carbon black electrodes in alkaline solutions which involves a second electron transfer:

$$O_2 + e^- \rightarrow O_{2\ ads}^- \tag{20}$$

$$O_{2\ ads}^- + H_2O + e^- \rightarrow HO_2^- + OH^- \tag{21}$$

or

$$O_2 + H_2O + e^- \rightarrow HO_{2\ ads} + OH^- \tag{22}$$

$$HO_{2\ ads} + e^- \rightarrow HO_2^- \tag{23}$$

where reaction (21) or reaction (23) is the RDS.

Xu *et al.* [29] have proposed a mechanism for several different carbon materials such as electrochemically pretreated GC, laser-treated GC, fractured GC, low defect HOPG basal plane surfaces, and modified GC:

$$O_2 + e^- \Leftrightarrow O_{2\ ads}^{\bullet -} \tag{24}$$

$$O_{2\ ads}^{\bullet -} + H_2O \Leftrightarrow HO_{2\ ads}^{\bullet} + OH^- \tag{25}$$

$$HO_2^{\bullet} + O_2^{\bullet -} \Leftrightarrow HO_2^- + O_2 \tag{26}$$

or

$$HO_{2\ \mathrm{ads}}^{\bullet} + e^- \rightarrow HO_{2\ aq}^- \tag{27}$$

They established that adsorption of O_2^- is crucial to enhancing the oxygen reduction rate by acceleration of the protonation of O_2^-, reaction (25). If O_2^- becomes more basic upon adsorption, protonation and subsequent disproportionation or reduction of HO_2^- are accelerated. Although the proposed mechanisms for oxygen reduction on different carbon electrodes [15,25-27,29] are consistent with the experimental data and seem to be logical, they are still not proved.

The electroreduction of oxygen on carbon surfaces is much slower than that on 'active' metals such as platinum or gold. This observation has initiated a search for catalysts for electrochemical reduction of oxygen on carbon electrodes under different experimental conditions. Modification of electrode substrates with electrocatalytic materials is a promising and nowadays quite common approach for the improvement of oxygen reduction [30] by reducing the typically large over-potentials required [31,32]. Several techniques have been proposed for electrode surface modification. The usual approach is through the immobilisation of catalytic materials onto the electrode surface *via* physical adsorption; an alternative is through attachment of catalytic compounds by the electrochemical reduction of the appropriate salt of these compounds [22-24]. A variety of catalysts have been used for modification of carbon electrodes in order to increase the rate of the ORR on such electrodes. These include both metal-containing catalysts like Co(II)-macrocycle complexes [33], manganese dioxide [34], copper-nickel alloys [35], cobaloxime complexes [30], transition metal phthalocyanines [36], gold nanoparticles [37] and non-metal ones like carbon nanotubes [38] or quinones [20,23,31,32,39-41].

EFFECT OF ELECTRODE SUBSTRATE ON OXYGEN REDUCTION REACTION AT CARBON ELECTRODES

The reactivity of carbon electrodes is, to a great extent, determined by the microstructure of the carbon material [42-45], the cleanliness of the electrode surface [46-48] and the functional groups present on the surface [49-54]. Therefore, study of oxygen reduction on carbon electrodes inevitably rises questions about active sites [5,6,55,56] and the role of functional groups present at the carbon surface. The main difference in the microstructure of carbon materials is in size of the crystallites, forming the solid material. Still, what constitutes an active site remains undefined. Active sites may be surface radicals or oxides, which participate in the reaction. However, it is unlikely that specific oxides could catalyse proton transfer in alkaline solutions, since they would be deprotonated in solutions of high pH values. It is proposed that oxides may enhance adsorption of O_2^- by withdrawing electrons from the surface. It was observed that polarisation curves of glassy carbon and polished pyrolytic carbon show two peaks in oxygen-saturated alkaline solutions [26,57,58] corresponding to the oxygen reduction on two different surface sites. The current of the first peak does not reach the diffusional value and is limited by number of the most active surface catalytic sites. The polarisation curve of the basal plane of pyrolytic graphite shows only one reduction wave that can be assigned to a first electron transfer step as all carbon atom valences are satisfied [15].

The oxygen reduction on polished GC surface was compared to the one on the basal plane of HOPG [29]. The peak potential for the oxygen reduction is much more positive for GC than for HOPG electrode, between 850 mV in case of the low defect basal surface and 350 mV for more defective basal plane. For the low defect basal plane surface a significant reduction current is observed at potentials more negative than -0.80 V. At a more defective basal surface peak current was observed at more positive potentials but still more negative than that observed at GC electrodes. McIntyre *et al.* [59] made this conclusion by comparing OPG with HOPG, with the more ordered surface showing a more negative oxygen reduction peak potential and less electrocatalytic activity for the ORR. Furthermore, the graphite edges are much more reactive than the graphite basal plane toward electron transfer and adsorption [60,61]. Hossain *et al.* [6] examined the effect of the electronic and surface properties of graphite on the kinetics of oxygen reduction to O_2^- in acetonitrile. OPG electrode proved to be electrocatalytically active for oxygen reduction to HO_2^- in alkaline solution, while the basal plane of HOPG electrode was found to suppress the reaction significantly [15]. The current densities for the reduction of oxygen to O_2^- and HO_2^- are established to be far lower on the basal plane of graphite than those found for oxygen reduction on ordinary pyrolytic graphite and glassy carbon in alkaline solutions [4]. The low reactivity of the graphite basal plane is a result of its low density of electronic states and the lack of functional groups and adsorption sites [6, 19,55,59,62]. The basal plane of HOPG is unusual in that all the valencies are satisfied in the plane of surface [63,64]. In addition, while active surface functional groups are present on OPG electrode, they were not found on HOPG one. A strong interaction of oxygen with functional groups on the surface usually takes part during the oxygen reduction on carbon and graphite.

Various surface functional groups, such as carboxyl, phenolic hydroxyl, quinine-type carbonyl and normal lactones, are present on carbon surfaces. The question is which types of functional groups are responsible for electrocatalysis of oxygen reduction. Evans and Kuwana suggested that oxygen-containing groups might serve as mediators between the electrode and the electroactive species [65]. Garten and Weiss [16,17] proposed that surface quinones are involved in the reduction of oxygen to peroxide. There are indications that surface oxidative treatments, which tend to increase the coverage of quinonoid type functional groups, make the surface more active for oxygen reduction in alkaline solution [8]. Zhang *et al.* [25] and Hossain *et al.* [6] attempted to establish the type and role of surface functional groups responsible for oxygen reduction to HO_2^- in alkaline aqueous solutions by adsorptive and covalent attachment of the functional groups on the graphite surfaces. They have adsorptively attached various quinones: 1,4-naphthoquinone, anthraquinone-2-sulfonate, phenanthraquinone, all to the basal plane of HOPG to verify the assumption of surface quinone groups electrocatalytic activity toward the oxygen reduction. Fagan *et al.* [47] and Zhang *et al.* [8] concluded that o-quinones are possible candidates for the catalysis of the reduction of oxygen.

Nagaoka *et al.* [66] argued that the quinone groups present at the surface could be active as mediators for oxygen reduction reaction. They compared the electrochemical behaviour and electrocatalytic activity toward the ORR of an anodically pretreated glassy carbon (AP-GC) electrode and a glassy carbon electrode modified with one of several different quinones, Q-GC, 9,10-phenanthraquinone, PAQ, naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) and juglone (5-hydroxy-1,4-naphthoquinone). The oxygen reduction peak potential was shifted positively on both electrode systems, AP- and Q-GC electrodes, relatively to the bare and untreated GC surface. However, significant differences between the oxygen reduction reaction on the AP-GC and Q-GC electrodes were noticed. First, an increase in the surface-quinone concentrations resulted in shift of the oxygen reduction peak potential at AP-GC electrode in a positive direction, while the peak potential of oxygen reduction at Q-GC electrode remained the same, though the peak current increased. Second, the peak current of AP-GC was almost unaffected in the pH range investigated. The oxygen reduction peak current at Q-GC electrodes was constant in neutral and weakly acid solutions but rapidly reduced in acidic solutions. Third, the potentials of oxygen reduction at AP-GC electrode were practically unchanged with varying pH value, while those for Q-GC electrodes moved by about 60 mV/pH unit. Based on these results, Nagaoka *et al.* [66] have concluded that enhanced activity of anodically pre-treated GC electrode for oxygen reduction cannot be attributed to the mediation by surface-confined quinone groups. The improved electrocatalytic activity could be a result of change in adsorption sites.

The effect of different electrolyte cations on the oxygen reduction reaction was also investigated by different researchers [7,29] and it was found that the reduction peak potential moves to more positive values in solutions containing cations following the order $Li^+ \sim Na^+ > K^+ > TEA^+$

(tetraethylammonium cation from the supporting electrolyte, $TEA^+ClO_4^-$). The effect of cation species on the peak potential can be explained either by the cation influence on the electron transfer step *via* an ion pair or double layer interaction, or by the alteration of chemical steps following O_2^- formation by cation. Sawyer *et al.* [7] noted that metal ions enhanced disproportionation of O_2^- in dimethylformamide, DMF, to the point that the oxygen reduction became irreversible if cations like Zn^{2+}, Cd^{2+}, Fe^{2+}, Mn^{2+} and Co^{2+} present in electrolyte. The results indicate involvement of proton transfer in the RDS of oxygen reduction and a strong dependence of O_2/O_2^- electron transfer rate on the carbon surface conditions. The results support a oxygen reduction mechanism involving adsorption of O_2^- and associated enhancement of proton transfer from water to O_2^-.

EFFECT OF PRE-TREATMENT ON THE OXYGEN REDUCTION REACTION AT CARBON ELECTRODES

The surface of glassy carbon is deactivated gradually by exposure to the atmosphere or to a working solution [67,68]. Thus, it is necessary to renew and activate the surface periodically during use. The electrochemical behaviour and electrocatalytic activity of carbon materials depends strongly on the electrode pre-treatment. The most common method for the renewal of glassy carbon is polishing the surface with an abrasive material, such as alumina, silicon oxide or diamond slurry [67,69]. Other surface treatment methods for activation include electrochemical and chemical oxidation [48,51,70-72], exposure to radio frequency plasmas [49,73], heating at low pressures [74,75], *in situ* laser irradiation [76], vacuum heat treatment [47] and dispersion of metal oxides [77,78].

The improvement of electrode activity by pre-treatment is not entirely understood, but it is believed that treatment methods control the surface area, the roughness and the nature and quantity of functional groups. Common for all surface treatments for activation of glassy carbon surface are the removal of any surface impurities and the exposure of ‘fresh’ carbon. Hu [67] has found that there is a close correlation between the purity of the working electrode and the time of deactivation of active glassy carbon. However, it is not clear what sites are ‘blocked’ by impurity adsorption. Activation of the oxygen reduction by surface pre-treatment could be accredited to increased concentration of O_2^-. The aim of pre-treatments is to increase the number of active sites, that is, to increase the site density or the roughness. Furthermore, pre-treatments introduce functional groups containing oxygen on carbon surfaces, which may serve as mediators. The effect of different electrode treatments on the presence of surface hydroxyl and carbonyl groups, and their consequent influence on electron transfer kinetics was also investigated by Chen and McCreery [79]. Using X-ray photoelectron spectroscopy it was found that the typical polished GC surface has a 7-20% O/C ratio, with various functional groups and usually surface impurities. Vacuum heat treatment in various forms has yielded GC surfaces with low, 1-6%, O/C ratio [47,80,81]. Polishing in alumina/cyclohexane slurry reduces the O/C ratio to 4%.

Xu *et al.* [29] have examined the reduction of oxygen in alkaline solution on glassy carbon electrodes, either pre-treated or modified ones. It was noted that all applied pre-treatment procedures-polishing, laser activation, electrochemical oxidation, fracturing and vacuum heat treatment-shifted the O_2/HO_2^- reduction peak positive with the greatest change at electrochemically pre-treated GC electrode. Observed changes in oxygen reduction voltammetry by surface modification can be explained by changes in O_2^- adsorption and rate of O_2^- formation from O_2. Adsorption is essential to increase the rate of oxygen reduction by accelerating protonation of O_2^-. Increase in $O_2^-{}_{ads}$ from surface pre-treatments can be the result either of the formation of new adsorption sites or of the increase in the microscopic surface area. The influence of the adsorption of several covalent and physisorbed organic compounds on the electrochemical reduction of oxygen was also studied [29]. The peak potential at a GC electrode modified with anthraquinone 2,6-disulfonate, AQDS-GC, was shifted positively relative to the unmodified polished surface, as reported for graphite surfaces. This change was attributed to the presence and activity of redox functional groups [6]. Covalent adsorbates such as dinitrophenylhydrazine, DNPH, which reacts with surface carbonyls [82], dinitrobenzoyl chloride, DNBC, which reacts with surface hydroxyls [83] and the nitrophenyl radical, NPR, which is thought to non-selectively chemisorb [84] shifted the oxygen reduction peak potential negatively for both polished and the electrochemically pre-treated surface. Physisorbed materials such as bismethylstyryl benzene, BMB, [85] had a rather small, but negative effect on the peak potential. Since the O_2^- adsorption is crucial to increase the rate of reaction (25) and therefore the production of hydrogen peroxide, adsorbates that partially blocked adsorption, like BMB or DNPH, slow down the reaction and shift the oxygen reduction peak potential toward more negative values.

The effect of oxidative pre-treatment on the electrocatalytic activity of carbon electrode toward oxygen reduction has been reported by several authors [26,29,57,86,87]. Oxidative pre-treatments lead to an increase of the oxygen reduction rate due to electrocatalysis by oxygen containing surface species [26,29,66]. Oxidised carbon surfaces also catalyse the further reduction of hydrogen peroxide in alkaline solutions [29,57]. The enhancement of quinone-hydroquinone adsorption on GC electrodes after oxidising treatment in a 1:1 concentrated nitric acid- sulphuric acid mixture has been reported by Gomathi and Rao [87].

Vaik *et al*. [23] observed noteworthy differences between rotating ring disc electrode data of an oxidised GC and polished GC electrode. Both the pre-wave and the second current wave increased for the oxidised electrode indicated that the surface concentration of the active C-O functionalities is increased by the anodic pre-treatment, resulting, therefore, in an enhancement of the oxygen reduction rate. It was proposed that the pre-wave of the polarisation curves is caused by oxygen reduction on the native and very active sites of glassy carbon. Additionally, anodisation was suggested to introduce other surface sites, which are involved in the further reduction of HO_2^- at more negative potentials. As a result, current significantly exceeds the limiting current of the two-electron process. As expected, the rate parameter of the chemical step of oxygen reduction by quinone groups present on the unmodified glassy carbon surface, $k_1\Gamma_1$, increased by surface oxidation compared with polished glassy carbon. A simple comparison of rate constants, *k*, evaluated from the Koutecky-Levich plots [23] at the potential of the current maximum showed that the value of rate constant for oxygen reduction increased by *ca*. 40-50% for the oxidised glassy carbon electrode. At the present time it is not possible to unquestionably attribute the current increase to an increased coverage of a particular type of oxygen-containing species although quinine-like groups are the most probable surface functionalities responsible for an enhanced oxygen reduction activity at the pre-wave potentials. It is well- established that the surface concentration of active oxygen-containing groups, such as quinones, can be increased by surface oxidation of carbon electrodes leading to the higher rate of the oxygen reduction reaction on oxidised carbon electrodes [15,57,88,89,90]. The chemical nature of C-O functional groups depends on the pre-treatment conditions. For instance, naphthoquinone and phenanthraquinone functionalities were considered the most likely species to be present on the surface of GC [91].

Vaik *et al*. [23] also investigated how oxidation alters the response of anthraquinone-modified surfaces. The cyclic voltammetry and RRDE data for oxidised glassy carbon electrode grafted with anthraquinone were similar to the polished AQ-grafted glassy carbon electrode [22,41,91]. There was no significant change in the values of kinetic parameters for oxygen reduction found for polished and oxidised AQ-modified GC electrodes. According to authors, a smaller chemical rate parameter, $k_2\Gamma_2$, of the oxygen reduction reaction on the oxidised GC electrode bearing attached AQ arises mainly from the higher value of the diffusion-limiting current density used in the analysis. As mentioned above, the reduction current exceeds the level of limiting current of two-electron process at the electrodes of the current plateau and can cause an apparent underestimation in the value of $k_2\Gamma_2$.

OXYGEN REDUCTION USING QUINONE-MODIFIED CARBON ELECTRODES

It is believed that native quinone groups present on the surface of GC are very active for oxygen reduction, as is shown by the reduction pre-wave observed on GC electrodes [22]. However, the surface coverage of quinone groups on freshly polished GC electrodes is probably rather low and no clear reduction waves could be observed even when strong electrocatalysis was manifested. Therefore, modification of carbon surface by quinone is a common method to increase the electrocatalytic activity of carbon electrodes toward oxygen reduction. Quinones and their derivatives have shown strong adsorption tendencies on various electrode materials such as platinum [92], mercury [93], graphite [94], and glassy carbon. A variety of quinones have been employed for the modification of carbon electrodes [4,6,22,32,41,66,95-98].

Different methods have been employed for electrode surface modification by quinones. For example, adsorptive attachment of quinones onto carbon surfaces is an easy procedure for preparation of electrodes for electrocatalysis of oxygen reduction [6,31,32,66,95]. A disadvantage of this technique is that carbon electrodes modified with immobilised quinones are not very stable as quinones tend to desorb from the surface with time, particularly in alkaline solutions [95]. A better method of modification of carbon electrodes is through covalently binding of quinone to the carbon surface [6,22,98], but the procedures of grafting are often not simple. Several authors [6,22-24,41,99] have employed modification of carbon electrodes with quinones by the electrochemical reduction of appropriate diazonium salts of quinones, *i.e.* by cycling potential in a nonaqueous solution of quinone diazonium salt, reactions (28) and (29):

$$RN_2^+ + e^- \rightarrow R^\bullet + N_2 \qquad (28)$$

$$R^\bullet + GC \rightarrow R - GC \qquad (29)$$

The carbon surfaces were modified by the electrochemical reduction of appropriate diazonium salt with different quinones, for instance anthraquinone [22,23,41,99] and phenanthraquinone [6,24]. It was shown that grafting of quinones on glassy carbon leads to a significant improvement of the rate of oxygen reduction to hydrogen peroxide as evidenced by the shift of the reduction peak potential to more positive values and increase of the reduction peak current.

Several attempts have been made to determine the mechanism of oxygen reduction on quinone-modified carbon electrodes. It is believed that the reduction rate is proportional to the surface concentration of the semiquinone radical formed by the electrochemical reduction of quinone groups [6,22,41]. The radical anion reacts with molecular oxygen to yield the superoxide anion, $O_2^{\cdot -}$, which either disproportionates or follows an electrochemical-chemical, EC, mechanism:

$$Q + e^- \rightarrow Q^{\bullet -} \qquad (30)$$

$$Q^{\bullet -} + O_2 \xrightarrow{k_c} O_2^{\bullet -} + Q \qquad (31)$$

$$2O_2^{\bullet -} + H_2O \longrightarrow O_2 + HO_2^- + OH^- \qquad (32)$$

or

$$O_2^{\bullet -} + H_2O + e^- \longrightarrow HO_2^- + OH^- \qquad (33)$$

where Q is surface quinone. Reaction (31) is assumed to be the rate-determining step. Both of the disproportionation (32) or electrochemical-chemical reactions (33), are considered to be fast and lead to the formation of peroxide. The benefit of the quinone-modified electrode is that the reduction of oxygen stops at the peroxide stage and thus carbon electrodes modified with quinones could be used to produce peroxide in practical system.

The reduction of oxygen on quinone-modified carbon surfaces has been extensively investigated. The adsorbates studies include 1,4-naphthoquinone,9,10-anthraquinone–2 sulfonate [4], and 9,10-phenanthraquinone [6] adsorbed on highly oriented pyrolytic graphite (HOPG), anthraquinone derivatives adsorbed on glassy carbon [32,66,95,96], 1,4-naphthoquinone and its derivatives [97,98], anthraquinone and its derivatives [6,22,41,97,98] and phenanthraquinone covalently attached to glassy carbon [24] and other substrates. Carbon paste electrodes modified with 1,4-naphthoquinone have also been explored [31]. The 9,10-anthraquinones are the largest group of naturally occurring quinines [32]. Under dry non-aqueous conditions, these compounds are characterised by two-proton two-electron reduction when a proton donor exists in solution [100-103]. Note in the absence of such a donor, two one-electron reactions constitute the electrode process. In the former case the first reduction step to a semiquinone radical is generally an electrochemically reversible process, while the second step to a dianion is a quasi-reversible, or irreversible process, depending on the experimental conditions employed. However, surface confined anthraquinones undergo a two-proton two-electron reduction to corresponding hydroanthraquinone derivatives in the presence of proton donors, *i.e.* in aqueous solutions [104]:

$$Q(ads) \ + 2e^- + 2H^+(aq) \rightarrow H_2Q(ads) \qquad (34)$$

Further, the oxygen is reduced to hydrogen peroxide in the presence of surface attached hydroanthraquinone species:

$$H_2Q(ads) + O_2(aq) \xrightarrow{k} Q(ads) + H_2O_2(aq) \quad (35)$$

RRDE voltammograms of bare glassy carbon electrode in oxygen-saturated solution show characteristic waves at low potentials, which are assigned to the reduction of oxygen by quinone groups present on the unmodified glassy carbon surface [6,22,41]. This current does not reach a diffusion-limited plateau since it is limited by the number of active surface catalytic sites. It was noted that this current decreases on the anthraquinone-modified glassy carbon electrodes implying that the attached anthraquinone blocks native glassy carbon surface sites and lower the rate of oxygen reduction on them. At the glassy carbon electrodes modified with anthraquinone by reduction of appropriate diazonium salt, a sharp current increase at much more positive potentials is noted [22,41], indicating the strong electrocatalytic effect of anthraquinone on oxygen reduction. The enhancement of reduction current is proportional to the surface coverage of anthraquinone (Table 1), confirming the assumption that, at these potentials, the reduction involves the reaction of oxygen with the anthraquinone semiquinone intermediate. It was found that grafting of glassy carbon with anthraquinone increases the overall rate of oxygen reduction by a factor of 15 [22].

Moreover, it was noted that the reduction of hydrogen peroxide is very slow on the anthraquinone-modified glassy carbon electrode. This is very useful since any electrode employed for hydrogen peroxide electrosynthesis should not catalyse its further reduction. The RRDE results confirmed that electroreduction of oxygen at anthraquinone-modified glassy carbon electrode stops at peroxide stage. Therefore, it was established that grafting of glassy carbon surface with anthraquinone results in electrocatalytic active surface for the reduction of oxygen to hydrogen peroxide [22,23,41,99].

The influence of the functional groups attached to quinones, such as -CN, $-SO_2$, $-NO_2$, on the rate of oxygen reduction is still not understood. Mirkhalaf *et al*. [99] have investigated the influence of substituents on the electrochemical properties of quinone-modified GC electrodes and their electrocatalytic activity for reduction of oxygen. They compared the kinetics of oxygen reduction on GC electrodes modified with thiophenyl, AQ1, and benzenesulfonyl, AQ2, derivatives of anthraquinone, with that

Table 1. Chemical Rate Parameters for Oxygen Reduction on Glassy Carbon Electrodes Modified with Anthraquinone at 25 °C as a Function of the Surface Coverage of Anthraquinone Obtained by non-linear Regression Analysis [41]

Γ (10^{-10} mol cm^{-2})	$k_1 \Gamma_1$ (cm s^{-1})	$k_2 \Gamma_2$ (cm s^{-1})
0	0.025 ± 0.001	-
0.52	0.028 ± 0.002	0.037 ± 0.001
0.73	0.027 ± 0.002	0.040 ± 0.001
1.9	0.011 ± 0.002	0.072 ± 0.004
2.3	0.019 ± 0.002	0.120 ± 0.010
3	0.014 ± 0.002	0.130 ± 0.010
3.7	0.018 ± 0.003	0.140 ± 0.030
4.3	0.018 ± 0.002	0.240 ± 0.020
2.2*	0.008 ± 0.002	0.071 ± 0.003

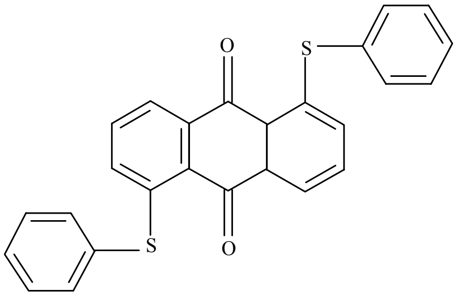
* This AQ-GC electrode was prepared by modification in aqueous solution of Fast Red AL Salt $k_1 \Gamma_1$ - the chemical rate parameter of oxygen reduction by quinone groups present on the unmodified glassy carbon surface $k_2 \Gamma_2$- the chemical rate parameter of oxygen reduction on the anthraquinone-modified glassy carbon surface.

of unsubstitued anthraquinone. Diazonium tetrafluoroborate salts of these compounds, AQ3 and AQ4, scheme 1, were also used for the modification of GC surfaces. The number of electrons transferred per oxygen molecule for all cases was close to two indicating that the reduction of oxygen stops at the peroxide stage, but some significant differences were noted. The redox potentials of substituted anthraquinone in DMF solution were shifted positively compared to that modified with anthraquinone. The change is in particular remarkable for AQ2-modified GC surface, due to the stronger electron withdrawing properties of benzenesulfonyl group, which results in the stabilisation of the radical intermediate.

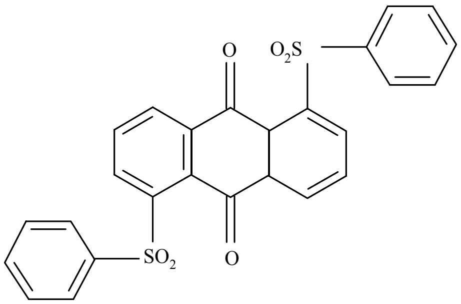
The rate constant of one-electron reduction of substituted anthraquinone to the corresponding semiquinone radical, reaction (30), was found to be 16 times faster than for AQ2 than AQ1 in DMF solution. This was explained by delocalisation of electrons caused by the sulfone groups, which stabilises the radical formed. A positive shift of redox potential was also observed for the AQ4-modified GC electrode in alkaline solution compared to the AQ-grafted one. This is expected from inductive effects of the benzensulfonyl group on radical formation as also observed in DMF. Hence, reaction (30) is thermodynamically more probable when electron-withdrawing function groups are incorporated in the anthraquinone molecule.

On the other hand, the chemical rate parameter, $k_2\Gamma_2$, of oxygen reduction reaction is lower for AQ3 and AQ4 covalently modified GC electrodes than for AQ-modified GC surface, which is summarised in Table 2. It is believed that these functional groups decrease the rate of reaction (31) by both stabilisation of the semiquinone radical and by steric obstruction by these groups [99]. Since the rate-determining step is a chemical reaction (31), functional groups that enhance this reaction (30) do not automatically increase the rate of chemical reaction of semiquinone radical anion and molecular oxygen. This illustrates that the reaction (31) is not effected by the thermodynamics of the electrochemical step of oxygen reduction.

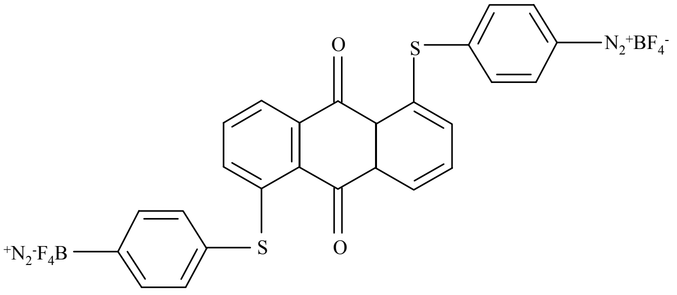
Salimi *et al.* [32] have investigated the electrochemical behaviour, and the electrocatalytic activity towards the oxygen reduction, of different 1-hydroxy-9,10-AQ substituted ‘podands’. GC electrodes modified with adsorptive films of compounds AQ5-AQ10, scheme 2, were prepared by the



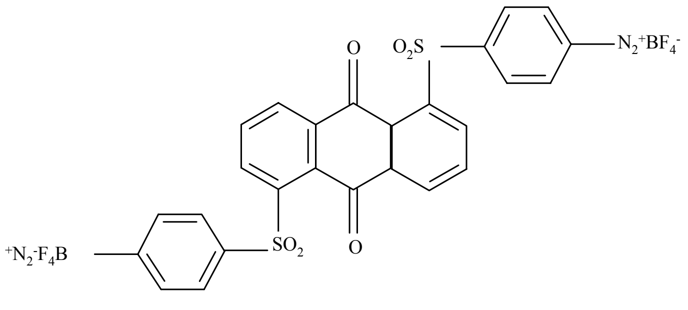
Bis-1,5-(thiophenyl)-9,10-anthraquinone (AQ1)



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. Structure of the anthraquinone derivatives AQ1-AQ4 [99].

Table 2. Comparison of Kinetic Parameters for Oxygen Reduction on Glassy Carbon Electrode Grafted with Different Anthraquinone Derivatives at 25 °C Obtained by Non-linear Regression Analysis [99]

Electrode	$k_1\Gamma_1$ (cm s^{-1})	k_2 (10^5 M^{-1} s^{-1})	Γ_2 (10^{-10} mol cm^{-2})	$k_2\Gamma_2$ (cm s^{-1})
AQ-GC	0.019 ± 0.002	12.0	2.5	0.30 ± 0.15
AQ3-GC	0.017 ± 0.005	3.0	4.0	0.12 ± 0.06
AQ4-GC	0.026 ± 0.002	1.6	4.4	0.07 ± 0.04

$k_1\,\Gamma_1$: the chemical rate parameter of oxygen reduction by quinone groups present on the unmodified glassy carbon surface.

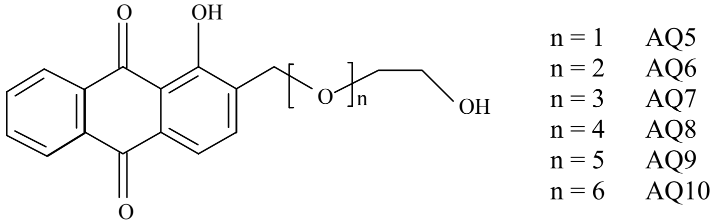
k_2: the rate constant of oxygen reduction reaction on anthraquinone-modified GC electrode

Γ_2: the surface coverage of anthraquinone derivatives on GC electrode.

$k_2\,\Gamma_2$: the chemical rate parameter of oxygen reduction on the anthraquinone-modified glassy carbon surface.

electrochemical oxidation of glassy carbon electrodes followed by immersing the electrodes in AQ solutions in acetonitrile. It was shown that the resulting modified electrodes are stable in acidic solution as after immersing in sulphuric acid for 16 h; only a slight decrease of less than 5% of the corresponding voltammetric peaks was observed in the time. The modified electrodes are less stable in basic solutions with the greater loss of adsorbed species manifested by the decrease of the voltammetric peaks. Species were found to continuously desorb from the GC surface. However, it was demonstrated that the very last few monolayers of the adsorbed species were remained tightly attached to the pre-anodised GC electrodes. These adsorptive species stayed on the electrode even after brief polishing with alumina. Residual adsorbed AQ derivatives could be removed by extensive polishing with ‘sand-paper’ for a longer period. This is probably because the AQ derivatives used were not only simply adsorbed but also possibly trapped inside pores or crevices of the GC electrodes.

The cyclic voltammograms of the GC electrodes modified with the adsorbed anthraquinone derivatives, AQ5-AQ10, evidenced the presence of a single couple, two-electron, two-proton redox reaction, with a formal potential around -200 mV *vs*. Ag/AgCl (saturated 3M KCl) electrode. Glassy carbon electrodes modified with each anthraquinone derivative exhibited the expected Nernstian pH dependence of the peak potentials for two-proton two-electron reduction in aqueous solutions and for pH values under 7.5 the corresponding plots of formal potential against pH resulted in a straight line with a slope between 61 and 64 mV/pH unit. However, in basic solutions of pH greater than 7.5, slope of the E-pH plots is about 31-32 mV per pHunit which is indicative of a two-electron one-proton process resulting in the formation of the corresponding semi hydroquinone derivatives. The modified electrodes exhibited potential electrocatalytic activity towards oxygen reduction at pH 4.5, with an overpotential of about



Scheme 2. Structure of the anthraquinone substituted podands AQ5-AQ10 [32].

400-500 mV lower than at a bare GC electrode. The kinetic parameters obtained for GC electrodes modified with AQ derivatives are shown in Table 3.

OXYGEN REDUCTION USING PHENANTHRAQUINONE MODIFIED CARBON ELECTRODES

The electrochemical reduction of the appropriate diazonium salt was also used for the covalent attachment of phenanthraquinone (PAQ) onto polished glassy carbon electrodes [24]. Analysis of the RRDE data confirmed that the reduction product at modified GC surface is peroxide. Further, the current for peroxide reduction on PAQ-GC electrodes was very small between 0 and -1.0 V giving further evidence that the reduction of oxygen on GC electrode with attached PAQ stops at peroxide stage. The potential of oxygen reduction at PAQ-GC electrode is more positive than at the bare GC electrode evidencing greater electrocatalytic activity of GC surface modified with PAQ.

Comparison of the glassy carbon electrode modified with phenanthraquinone or anthraquinone by grafting under the same conditions shows that a higher surface coverage of PAQ on GC was obtained than in the case of AQ. The difference in surface coverage of PAQ and AQ attached on GC surface could be the result of the chemical reactivity of the aryl radicals formed during surface grafting, leading to multilayer growth of quinone, as previously observed for GC and HOPG, [105,106]. The growth rate depends on the grafting conditions and the nature of the radical attached to the surface.

PAQ-modified glassy carbon electrodes show a larger increase in electrocatalytic activity for oxygen reduction in alkaline solution in comparison to AQ-modified GC electrodes. The greater activity can be a result of both the positive shift of the redox potential and increased rate constant for the chemical step in the oxygen reduction reaction. The redox potential of surface bound phenanthraquinone was 300 mV more positive than that for covalently attached

Table 3. Comparison of Kinetic Parameters for Oxygen Reduction on Glassy Carbon Electrode Modified with Different Anthraquinone Substituted Podands at 25 °C [32]

Electrode	Γ (10^{-9} mol cm^{-2})	k (10^4 M^{-1} s^{-1})	$k\,\Gamma$ (10^{-3} cm s^{-1})
AQ5	1.17	2.9	33.9
AQ6	0.93	3.4	31.6
AQ7	1.18	2.6	30.7
AQ8	1.16	3.7	42.9
AQ9	1.12	2.4	26.9
AQ10	1.12	2.7	30.2

Table 4. Kinetic Parameters for Oxygen Reduction at Different Modified Glassy Carbon Electrodes Obtained from Cyclic Voltammetry Data [24]

Electrode	$k_1\Gamma_1$ (cm s^{-1})	$k_2\Gamma_2$ (cm s^{-1})
GC	0.025 ± 0.001	-
AQ-GC	0.011 ± 0.002	0.072 ± 0.004
PAQ-GC	-	0.170 ± 0.020

$k_1\,\Gamma_1$: the chemical rate parameter of oxygen reduction by quinone groups present on the unmodified glassy carbon surface.
$k_2\,\Gamma_2$: the chemical rate parameter of oxygen reductionon the quinone-modified glassy carbon surface.

anthraquinone. Consequently, the semiquinone radical anion of PAQ is generated at much more positive potentials as compared to AQ thus increasing the electrocatalytic activity of the surface for oxygen reduction. This is believed to be the main factor that increases the electrocatalytic activity for oxygen reduction on the GC electrode modified with PAQ. In Table 4 are shown the values of the chemical rate parameter for oxygen reduction, $k_2\ \Gamma_2$, at PAQ and AQ-modified GC electrodes measured for similar surface coverage of the two functionalised surfaces. Hence, it can be concluded that the rate constant of the chemical step, reaction (31), is approximately 2.5 times greater for the phenanthraquinone. The difference in the values of the chemical rate parameters for PAQ and AQ modified GC electrodes indicates that the rate of chemical reaction between the semiquinone radical anion and molecular oxygen is influenced by the quinone structure. The results show that it is possible to control the electrocatalytic properties of the surface in two ways, by controlling the quinone redox potential with appropriate substituents and by altering the reactivity of the radical intermediate towards oxygen.

The electrochemical behaviour and electrocatalytic activity toward oxygen reduction of GC electrodes covalently modified with PAQ was also compared to that of HOPG modified with adsorbed PAQ [6]. Oxygen reduction to peroxide was examined in aqueous alkaline solution on HOPG with adsorbed 9,10-phenanthraquinone and on OPG with chemically attached 2-aminoanthraquinone. On the adsorbed quinone surfaces, the kinetics of the initial electron transfer to the quinone is fast while the reaction of reduced quinone with dissolved oxygen is the rate-determining step. On the chemically attached quinone surface, the initial electron transfer is the RDS because the quinone is further from the surface and in an unfavourable configuration for electron tunnelling [6]. In a similar study with 1,4-naphthoquinone and 9,10-anthraquinone-2-sulfonate a considerable current hysteresis between the negative and positive potential sweeps was observed [4]. This behaviour was attributed to quinone desorption or to some irreversible changes in the adsorbed layer [4]. In contrast, no such hysteresis was seen for GC covalently modified with PAQ. The RDE voltammograms of modified electrode were stable after many potential cycles indicating a strong attachment of PAQ to the surface of GC. The oxygen reduction current for HOPG modified with adsorbed PAQ was significantly lower than the theoretical mass transport limiting current for the two-electron reduction of oxygen [6]. On the contrary, the oxygen reduction current maxima observed for PAQ-GC electrodes were very close to the diffusion controlled values calculated from Levich equation. The reason for this difference may be related to different surface concentrations of PAQ, as the surface coverage of PAQ was not given in [6]. Alternatively, the rate of the chemical reaction between the covalently attached and the adsorbed semiquinone species, and molecular oxygen, reaction (31) may also be different.

The oxygen reduction behaviour of HOPG modified with phenanthraquinone is very similar to that observed on unmodified OPG in alkaline solution in that the onset in the current occurs at approximately the same potential and the overall number of electrons transferred is very close to 2, indicating formation of peroxide. The polarisation curve of oxygen reduction on HOPG modified with physically adsorbed 9,10-PAQ in alkaline solution showed a large increase in the reduction current relative to bare basal plane. The current falls at more negative potentials, which is also behaviour typical for glassy carbon and OPG in alkaline solutions. The mass transport-corrected Tafel plot yielded a slope of -67 mV/decade at low current densities. A Tafel slope of -60 mV/decade would suggest a fast electron transfer reaction followed by a rate-determining chemical step, reaction (37).

The oxygen reduction on the OPG surface with chemically attached 2-aminoanthraquinone (AAQ) shows significantly higher currents than does the unmodified OPG surface. The currents are still well below those expected for pure diffusion control even at quite negative potentials, implying that step (37) becomes rate-controlling at these very negative potentials. The reduction proceeds quantitatively to peroxide on both physically and covalently modified surfaces. The mass transport-corrected Tafel plot yielded a slope of *ca.* -110 mV/decade. This implies an initial one-electron transfer as the rate-determining step. These results are in accordance with the following reaction mechanism:

$$Q_{ads} + e^- \rightarrow Q_{ads}^- \qquad (36)$$

$$Q^- + O_2 \rightarrow Q_{ads} - O_2^- \tag{37}$$

$$Q_{ads} - O_2^- + H_2O + e^- \Leftrightarrow Q_{ads} + HO_2^- + OH^- \tag{38}$$

where Q is a generic quinone species. If reaction (36) is RDS, the Tafel slope should be *ca.* -120 mV/decade, where if the RDS is reaction (37), the expected slope of Tafel curve is *ca.* -60 mV/decade. Therefore, one can concluded that RDS of ORR on HOPG modified with physically adsorbed PAQ is reaction (37), while on chemically attached AAQ on OPG is reaction (36). The fact that the reduction current on the AAQ-chemically modified surface does not decrease at more negative potentials is consistent with the idea that the first electron transfer continues to be rate-determining step as the diffusion-limiting current is approached.

The difference in the rate-determining steps between electrodes modified with quinones by physical adsorption and chemical attachment can be explained by the difference in the reaction of immobilised quinones and graphite surface [6]. Physically adsorbed quinone assumed to adsorb parallel to the surface might experience a greater electronic interaction with the graphite surface than does the chemically attached quinone. The electron transfer at electrodes with adsorbed layers may be sufficiently fast so that chemical step (35) becomes the rate-determining step. It is assumed that chemically attached molecules are at a longer distance from the surface and in a less favourable configuration for electron tunnelling. Also, the chemically bound layer may shift potential of zero charge that additionally contributes to a slower electron transfer step, reaction (36).

Šljukić *et al.* [20] have investigated the applicability of glassy carbon electrodes modified with 9,10-phenanthraquinone *via* solvent evaporation for catalysis of electrochemical reduction of oxygen. Solutions of 9,10-phenanthraquinone in acetonitrile were pippetted on to an anodically pre-treated glassy carbon surface allowing the solvent to evaporate off at room temperature leaving the quinone species physically adsorbed onto the electrode. Cyclic voltammograms of the modified electrode are characterised with characteristic redox peaks at *ca.* -0.22 V (*vs.* SCE) corresponding to the reversible reduction of the surface confined 9,10-phenanthraquinone. In comparison, edge plane and basal plane electrodes modified with PAQ *via* solvent evaporation were explored. The response of the edge plane modified electrode in alkaline solution showed a distinct reduction peak at *ca.* -0.36 V and a small corresponding oxidation peak that became clearer at higher scan rates. Cyclic voltammograms of a PAQ-modified BPPG electrode in alkaline solution exhibiting a single reduction peak at *ca.* -0.32 V, with no corresponding oxidation peak observed.

The expected Nernstian pH dependence of the voltammetric peak potentials was exhibited for all three modified electrodes in pH range from 2.0 to 8.0, with the peak potentials shifting towards more negative values with increase of the pH of the solution. The corresponding plots of peak potential against pH were found to produce a straight line with a slope of *ca.* 55 mV, per pH unit for the edge plane electrode and 60 mV per pH unit for the glassy carbon. In solutions of higher pH values, the curve levels level off, probably due to deprotonation of the hydroquinone. It was also found that at high pH's (>10) the surface coverage was low with poorly defined waves, similar to those observed by Salimi and co-workers [32].

The electrocatalytic activity of different electrode substrates modified with PAQ *via* solvent evaporation towards the oxygen reduction reaction was compared. GC and EPPG electrodes modified with PAQ showed an enhancement of the reduction peak current in the presence of oxygen, whereas the corresponding oxidation peak vanished on the reverse scan evidencing the benefits of the modified electrode for electrocatalysis. Furthermore, the oxygen reduction peak was shifted positively for modified GC and EPPG electrodes, compared to the bare GC and EPPG electrodes, respectively. The rate constant of the oxygen reduction on PAQ-modified GC electrode was calculated to be 0.9×10^3 M^{-1} s^{-1}, while the value obtained for PAQ-modified EPPG electrode was 3.9×10^3 M^{-1} s^{-1}. The chemical rate parameter was found to be 15×10^{-3} cm s^{-1} for 9,10-phenanthraquinone modified GC electrode and 4.4×10^{-3} cm s^{-1} for modified EPPG electrode, *i.e.* the oxygen reduction is *ca.* three times faster on the former electrode. A BPPG electrode modified with PAQ *via* solvent evaporation proved not to be suitable as oxygen reduction electrocatalyst. The oxygen reduction peak could be seen on first scan but disappeared with further cycling. This was probably the result of instability of modified BPPG electrode and fast elimination of PAQ adsorbed on its surface.

Therefore, 9,10-phenanthraquinone modified glassy carbon electrode proved to be more electrocatalytic active toward the oxygen reduction in comparison with modified EPPG and BPPG electrodes.

Different electrode substrates: glassy carbon, edge plane and basal plane pyrolytic graphite modified by electrochemical cycling in an aqueous solution of 9,10-phenanthraquinone were explored. Obtained cyclic voltammograms of each modified substrate were found, as expected, to be closely similar to that observed *via* solvent evaporation with the exception of the modified BPPG electrode which showed a small oxidation peak. In comparison to 9,10-phenanthraquinone immobilised at the same carbon electrodes *via* solvent evaporation, lower coverages were obtained.

OXYGEN REDUCTION USING A 9, 10-PHENANTHRAQUINONE MODIFIED RETICULATED CARBON ELECTRODE

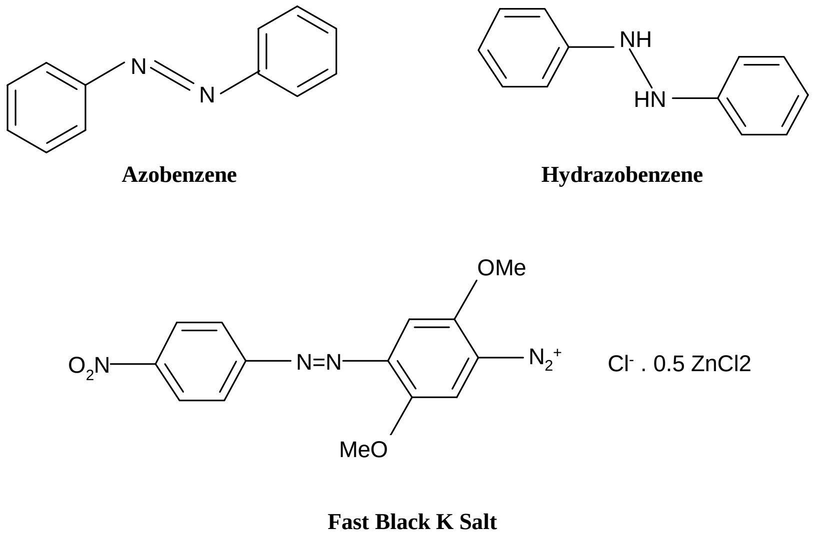
Electrocatalytic activity of reticulated vitreous carbon, RVC, electrode modified by 9, 10-phenanthraquinone have been reported by Šljukić *et al.* [20]. The RVC electrode was modified by immersing the electrode into a solution of 9,10-phenanthraquinone in acetonitrile for 2 minutes. Cyclic voltammogram of the RVC electrode in alkaline solution shows a large current increase in an oxygen-saturated solution compared to degassed one. The absence of any reverse peak suggests excellent electrocatalytic behaviour towards oxygen reduction. It was noteworthy that the currents were in the milli-ampere range. The rate of production of hydrogen peroxide on PAQ-modified RVC electrode (*ca.* 10 × 10 × 40 mm) was calculated from cyclic voltammetry data and found to be 2.1×10^{-6} M^{-1} s^{-1}.

OXYGEN REDUCTION ON CARBON ELECTRODES MODIFIED WITH NAPHTHOQUINONE AND ITS DERIVATIVES

1,2-Naphthoquinone and its derivatives (NQ) have been studied as mediators for oxygen reduction and hydrogen peroxide production. Golabi and Raoof [31] demonstrated the construction of the chemically modified carbon paste electrodes by incorporating 1,4-naphthoquinone and its derivatives: 5-hydroxy-, 5-hydroxy-2-methyl-2,3-dichloro-, and 2-amino-3-chloro-1,4-naphthoquinone and showed their activity toward the oxygen reduction to hydrogen peroxide. Their behaviour was similar to those of covalently bound and polymer-coated electrodes chemically modified by other quinone species. The value of slope of Koutecky-Levich plot of the oxygen reduction on NQCP electrodes was similar to that for two-electron oxygen reduction, indicating the reduction of oxygen to hydrogen peroxide. In addition, it was found that the further reduction of hydrogen peroxide on NQCP electrodes is not electrocatalysed. Under these conditions, the electron and proton exchange between the electrode and the electroactive sites, equation (34), were assumed to be fast enough compared to the irreversible homogeneous reaction between the reduced form of the modifier and oxygen, equation (35). It was observed that the electrocatalytic reduction of oxygen on NQCP electrodes in alkaline solution was irreversible and occurred at potentials about 350 to 550 mV less negative than at the unmodified CP electrode with a significant increase in the oxygen reduction peak current.

The electrocatalytic activity of a glassy carbon electrode modified with 1,2-naphthoquinone *via* solvent evaporation for the oxygen reduction reaction was subsequently examined [20]. The cyclic voltammograms of 1,2-naphthoquinone-modified glassy carbon electrode show a pair of the reduction waves at *ca.* -0.2 V (*vs.* SCE). In oxygen-saturated solution, the oxygen reduction peak is considerably increased whilst the oxidation peak virtually disappears on the reverse scan indicating excellent electrocatalysis. Kinetic parameters of the oxygen reduction reaction on the GC electrode modified with 1,2-naphthoquinone were evaluated from cyclic voltammetry data and the rate constant found to be 5.6×10^{2} M^{-1} s^{-1} for a surface coverage of 16.5×10^{-9} mol cm^{-2}.

Comparison of chemical rate parameters of the oxygen reduction reaction on the glassy carbon electrodes modified by two different quinone species, 9,10-phenanthraquinone and 1,2-naphthoquinone, by the same method of solvent evaporation, showed that catalytic activity of GC electrode modified by PAQ is slightly greater than the one modified by NQ. The chemical rate parameter was evaluated as 15×10^{-3} cm s^{-1} for PAQ-GC electrode compared to 10×10^{-3} cm s^{-1}



Scheme 3. The structure of azobenzene and its derivatives used for electrode modification.

obtained for NQ-GC electrode. Both values were greater than value of 4.4×10^{-3} cm s^{-1} obtained for Alizarin (1,2-dihydroxyanthraquinone) [40].

OXYGEN REDUCTION ON CARBON ELECTRODES MODIFIED WITH AZO-BENZENE AND ITS DERIVATIVES

The electrochemical reduction of oxygen using glassy carbon electrodes modified with azobenzene, hydro-azobenzene, or fast black K salt (2,5-dimethoxy-4-[(4-nitrophenyl)azo] benzenediazonium tetrachlorozincate), Scheme 3., have been explored [21]. The anodically pre-treated glassy carbon or polished edge plane pyrolytic graphite electrodes were modified with azobenzene and its derivatives *via* solvent evaporation. No voltammetric waves are seen if the glassy carbon electrode is simply placed into a solution of azobenzene for a few minutes and then removed to a fresh electrolyte solution. The catalytic activity of the immobilised species towards oxygen reduction was examined *via* cyclic, rotating disc and sono-voltammetry and kinetic parameters evaluated from the obtained data.

Distinctive for azobenzene and its derivatives is that they are adsorbed on the electrode surface simultaneously in the two different forms, as monolayers and microcrystals. Cyclic voltammograms of edge plane of pyrolytic graphite electrode modifies with azobenzene in acidic solution show a peak of reduction of azobenzene to hydroazobenzene, reaction (39), at *ca*. -0.60 V (*vs*. SCE) [21,107,108] with the corresponding oxidation peak observed at ca. +0.40 V:

$$C_6H_5 - N = N - C_6H_5 + 2e^- + 2H^+ \rightleftharpoons C_6H_5 - NH - NH - C_6H_5 \tag{39}$$

If cyclic voltammograms were run to more negative potentials, additional wave could be seen at *ca*. -1.2 V (*vs*. SCE) corresponding to the irreversible reduction of hydroazobenzene to aniline [21,107]:

$$C_6H_5\text{–}HN\text{–}NH\text{–}C_6H_5 + 2e^- + 2H^+ \longrightarrow 2C_6H_5\text{–}NH_2 \tag{40}$$

On the second scan only a single reduction wave of azobenzene reduction is seen, with continual scanning resulting in a decrease of the voltammetric response, consistent with literature reports that hydroazobenzene is reduced irreversibly to aniline [21,107,108] at high reduction potentials.

If a polished edge plane electrode was left in an acetonitrile solution of azobenzene for 12 hours, a small reduction wave, *ca*. 7 times smaller than that seen for the electrode modified *via* evaporation, could be seen at *ca*. -0.6 V (*vs*. SCE). The reduction of azobenzene at modified glassy carbon electrode is characterised by two reduction waves: at *ca*. -0.11 V associated to the reduction of azobenzene to hydroazobenzene with both species in the form of a monolayer and more broad one at -0.45 V corresponding to the reduction of azobenzene in the form of crystals which dissolve from the electrode surface when reduced, and a single oxidation wave on the reverse scan. The indication of existence of adsorbed azobenzene in two different forms was the large decrease in the peak current with further scanning. This implied that azobenzene is immobilised on GC electrode in two different forms: microcrystals, which dissolve from the GC electrode surface when reduced, so on the second scan the large broad peak is absent and only the monolayer (or less) response is left. This was consistent with the work of Komorsky-Lovrić [107] who studied the voltammetry of azobenzene microcrystals abrasively attached to a basal plane pyrolytic graphite electrode, observing a reduction peak at *ca*. -0.40 V at pH 2.

Oxidation of hydroazobenzene at an edge plane pyrolytic graphite modified electrode exhibits an oxidation wave corresponding to the oxidation of hydroazobenzene to azobenzene at *ca*. +0.2 V with a reverse reduction peak of azobenzene back to hydroazobenzene at -0.3 V which is analogous to that seen for the electrochemical reduction of azobenzene on the edge plane electrode.

The cyclic voltammograms of hydrazobenzene-modified glassy carbon electrodes in an acidic solution shows two reduction peaks, at *ca*. -0.13 V and -0.4 V (*vs*. SCE), which again can be accredited to the reduction of azobenzene as two different forms from the electrode surface. A peak is observed on the oxidation scan corresponding to the oxidation of hydroazobenzene to azobenzene. On the second scan the latter reduction peak has practically disappeared implying that hydroazobenzene in the form of crystals is dissolved from the electrode.

For the reduction of fast black K (FBK) salt at a modified glassy carbon electrode three reduction peaks and one oxidation peak appeared on the first scan. The peaks at -0.30 and -0.41 V (*vs*. SCE) were assigned to the reduction of the nitro group of the FBK salt adsorbed on the GC surface in two different forms, as a monolayer and as microcrystals, while the peak at +0.15 V can be attributed to the reduction of the azo linkages of the fast black K compound with the corresponding oxidation wave at +0.4 V [21,109]. The reduction peak at -0.30 V disappeared on the second scan and only two reduction waves at *ca*. +0.15 V and -0.41 V could be observed. It was observed that redox peaks were pH-dependent and shifted towards more negative potentials with increasing the solution pH. The potential of the reduction peak shifts by 57 mV/pH unit in case of glassy carbon electrodes modified with azobenzene and hydrazobenzene and by 51 mV/pH unit for FBK salt, confirming that a 2-proton 2-electron process takes place. A plot of peak current *vs*. scan rate was found to be linear, as expected for surface confined species

Comparison of oxygen reduction at the bare GC electrode and GC electrode modified with immobilised azobenzene, hydrazobenzene and salt, reveals that the waves corresponding to the reduction of oxygen shift to a more positive potential at modified surfaces (*ca*. 0.16 V for azobenzene-modified GC electrode). Oxygen reduction peak currents significantly increase, while the corresponding oxidation peaks disappear on the reverse scan suggesting excellent catalytic behaviour of GC electrodes modified with azobenzene, hydrazobenzene and FBK salt. The largest enhancement was observed in acidic solution at pH 2.

The kinetic parameters, catalytic rate constants and chemical rate parameters of oxygen reduction on GC electrodes modified *via* solvent evaporation with azobenzene, hydrazobenzene and FBK salt were evaluated from cyclic, rotating disc and sono-voltammetry data. Kinetic parameters obtained by different methods were consistent with each other. Table 5 shows the values of the rate constants and chemical rate parameters assessed from cyclic voltammetry data and it can be noted that the catalytic activity toward electroreduction of oxygen manifested for FBKS-modified GC electrode was somewhat greater than in case of azobenzene and hydrazobenzene-modified GC electrodes. In the same table are shown the calculated values of kinetic parameters for the oxygen reduction on glassy carbon electrodes modified by the same solvent evaporation procedure with quinone species [20]. Note that all the data refers to pH 2 and 25 °C; faster rates can be found at different pH’s [22]. The azobenzene-modified GC electrodes exhibited a more remarkable electro-

Table 5. Kinetic Parameters for Oxygen Reduction at Glassy Carbon Electrodes Modified by Solvent Evaporation Procedure with Various Compounds Obtained from Cyclic Voltammetry data [21]

Compund	Γ (10^{-10} mol cm^{-2})	k (10^3 M^{-1}s^{-1})	$k\,\Gamma$ (10^{-3} cm s^{-1})
Azobenzene	69	6.1	42.1
Hydrazobenzene	55	7.4	40.7
Fast black K salt	48	10.4	50.0
9,10-Phenanthraquinone	168	0.9	15.1
1,2-Naphthoquinone	165	0.6	9.9
Alizarin	2	22.0	4.4

catalytic activity toward oxygen reduction. Comparisons of the combined chemical rate parameters for azobenzene and derivatives with the quinone species reveal that the former is *ca*. five times faster.

OXYGEN REDUCTION UNDER ULTRASOUND USING QUINONE AND AZOBENZENE-MODIFIED CARBON ELECTRODES

The advantages of application of ultrasound in electrochemistry have been examined and recently established [110-112]. Extensive consideration has been dedicated to the understanding of the fundamental nature of the interaction of ultrasound with electrochemical processes [111,112]. Ultrasound was found to promote very high rates of local mass transport *via* a combination of acoustic streaming and cavitation [111]. This is exceptionally valuable in electrosynthesis [111,112] where the sustained mass transport can drastically reduce electrolysis times whilst cavitational activity can keep the electrode ‘active’ under circumstances where passivation otherwise takes place. An especially noteworthy effect of application of ultrasound to an aqueous media is the *in situ* production of hydrogen peroxide, although in small quantities [111,113,114]. It was found that the water molecules present inside cavitations bubbles dissociate and yield $OH^{\cdot}$ and $H^{\cdot}$ radicals. These radicals may react with other gaseous species within the cavitation bubble and diffuse out or alternatively the $OH^{\cdot}$ radicals can unite to generate hydrogen peroxide [111,113,114].

Applicability of glassy carbon electrodes modified with quinones and azobenzene and its derivatives as catalytic materials for oxygen reduction and hydrogen peroxide mediators under ultrasound have been explored. The behaviour of the modified electrodes under insonation was considered since it is known that some adsorbates are removed in great extent from electrode surface when exposed to ultrasound [115]. Different ultrasound powers were applied for various time periods with a fixed horn -to-electrode distance and stability was assessed *via* cyclic voltammetry, monitoring the CVs of the modified electrode in the appropriate solution and ascertaining the amount of adsorbed species left by the obtained peak height and surface coverage.

Investigation of the stability under ultrasound of different carbon electrodes: glassy carbon, edge plane pyrolytic graphite and basal plane pyrolytic graphite modified with 9,10-phenanthraquinone by electrochemical cycling showed that the GC electrode is more stable than modified EPPG and BPPG electrodes. This is summarised in Table 6. In contrast, for example, adsorbed PAQ was almost completely removed from the EPPG surface. Similarly, insonation of the PAQ-modified BPPG electrode under the same conditions resulted in a significant elimination of deposited PAQ. If GC electrode modified with PAQ by electrochemical cycling was subjected to insonation, it was observed that application of ultrasound decreased the peak height over approximately the first minute, *ca*. 50% of the initial signal, after which the current was stable indicating partial, but not complete removal of PAQ adsorbed

Table 6. Stability under Ultrasound (36 W cm^{-2} Intensity for 3 min at Horn-to Electrode Distance of 10 mm) of an Edge Plane and Basal Plane Pyrolytic Graphite and Glassy Carbon Electrodes Modified with 9,10-Phenanthraquinone by Electrochemical Cycling Obtained from Cyclic Voltammetry Data

Electrode	Edge plane pyrolytic graphite	Glassy carbon	Basal plane pyrolytic graphite
Γ_{initial} (10^{-10} mol cm^{-2})	33	2.6	0.15
$\Gamma_{\text{after insonation}}$ (10^{-10} mol cm^{-2})	1.6	1	0.04
$\delta\Gamma$ (%)	95	61	73
I_{initial} (μA)	13	4.9	0.15
$I_{\text{after insonation}}$ (μA)	0.8	2.2	0.05
δI (%)	94	55	67

$\Gamma_{initial}$: the surface coverage of 9,10-phenanthraquinone on GC electrode before insonation.
$\Gamma_{after\ insonation}$: the surface coverage of 9,10-phenanthraquinone on GC electrode after insonation.
$I_{initial}$: the reduction peak current at 9,10-phenanthraquinone-modified GC electrode before insonation.
$I_{after\ insonation}$: the reduction peak current at 9,10-phenanthraquinone-modified GC electrode after insonation.

Table 7. Stability under Ultrasound (36 W cm^{-2} Intensity for 3 min at Horn-to Electrode Distance of 10 mm) of an Edge Plane and Basal Plane Pyrolytic Graphite and Glassy Carbon Electrodes Modified with 9,10-phenanthraquinone *via* Solvent Evaporation Obtained Using Cyclic Voltammetry Data

Electrode	Edge plane pyrolytic graphite	Glassy carbon	Basal plane pyrolytic graphite
Γ_{initial} (10^{-10} mol cm^{-2})	15	71	10
$\Gamma_{\text{after insonation}}$ (10^{-10} mol cm^{-2})	0.8	48	0.74
$\delta\Gamma$ (%)	95	32	93
I_{initial} (μA)	16	11	2.3
$I_{\text{after insonation}}$ (μA)	1.4	6	0.3
δI (%)	91	45	87

$\Gamma_{initial}$: the surface coverage of 9,10-phenanthraquinone on GC electrode before insonation.
$\Gamma_{after\ insonation}$: the surface coverage of 9,10-phenanthraquinone on GC electrode after insonation.
$I_{initial}$: the reduction peak current at 9,10-phenanthraquinone -modified GC electrode before insonation.
$I_{after\ insonation}$: the reduction peak current at 9,10-phenanthraquinone-modified GC electrode after insonation.

on GC electrode surface.

The study of stability of different carbon electrodes modified with 9,10-phenanthraquinone *via* solvent evaporation showed once again that the modified glassy carbon electrode is the most stable under ultrasound, as shown in Table 7. Comparison of the stability under ultrasound of the glassy carbon electrode modified with 9,10-phenanthraquinone *via* solvent evaporation with the one modified by electrochemical cycling proved the former to be more stable.

Salimi *et al.* [40] unexpectedly found that physically adsorbed Alizarin remained surface bound under insonation in contrast to covalently attached 9,10-anthraquinone which was formed *via* reduction of the corresponding diazonium salt.

Table 8. Stability under Ultrasound (Maximum Intensity of 87 W cm^{-2} for 3 min at Horn -to Electrode Distance of 10 mm) of Glassy Carbon Electrode Modified with Quinones and Azobenzene and Derivates *via* Solvent Evaporation Obtained Using Cyclic Voltammetry Data

Compound	NQ	DAA	Alizarin	AB	HAB	FBKS
$\Gamma_{initial}$ (10^{-10} mol cm^{-2})	13	27	34	152	217	35
$\Gamma_{after\ insonation}$ (10^{-10} mol cm^{-2})	1.3	11	17	115	173	27
$\delta\Gamma$ (%)	90	59	50	24	20	23
$I_{initial}$ (μA)	5	5.3	5.2	11	16	13
$I_{after\ insonation}$ (μA)	0.6	3.6	2.3	9.4	14	11
δI (%)	88	32	56	14	12	15

NQ: 1,2-naphthoquinone; DAA: 1,2-diazonium-9,10-anthraquinone; AB: Azobenzene; HAB: Hydrazobenzene; FBKS: Fast Black K Salt.

$\Gamma_{initial}$: the surface coverage of quinones, azobenzene and their derivatives on GC electrode before insonation.

$\Gamma_{after\ insonation}$: the surface coverage of quinones, azobenzene and their derivatives on GC electrode after 3 min of insonation.

$I_{initial}$: the reduction peak current at GC electrodes modified with quinones, azobenzene and their derivatives before insonation.

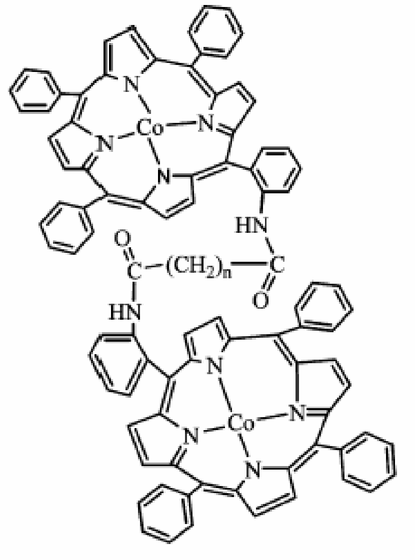
$I_{after\ insonation}$: the reduction peak current at quinones, azobenzene and their derivatives-modified GC electrode after 3 min of insonation.

Again, this likely reflects the different sites of attachment and /or orientation relative to the surface. The behaviour and stability under ultrasound of the glassy carbon electrodes modified *via* solvent evaporation with different compounds was considered. Comparison of the ultrasound stability of glassy carbon electrode modified by quinones and azobenzene and derivatives, Table 8, established that the azobenzene-, hydrazobenzene- and fast black K salt-modified GC electrodes are very stable under insonation and therefore potentially suitable for use as sonoelectrocatalysts for the oxygen reduction and hydrogen peroxide generation. On the other hand, the loss of adsorbed quinones was manifested to a greater extent. The species were continuously detached from the electrode surface for a certain period after which the current was stable indicating partial but not complete removal of adsorbed compounds.

The study of the electrocatalytic reduction of oxygen at glassy carbon electrodes modified with quinone and azobenzene *via* solvent evaporation under ultrasound showed significant enhancement of the catalytic currents under the high mass-transport conditions of ultrasound. The results are quantitatively consistent with a modified Koutecky-Levich equation [40] which was used for evaluation of kinetic parameters of oxygen reduction under insonation. Therefore, sono-electrodes provide a potential inexpensive and clean method for hydrogen peroxide production in which oxygen (air) is reduced with a high efficiency at an insonated electrode or sonotrode.

OXYGEN REDUCTION USING CARBON ELECTRODES MODIFIED WITH METAL-BASED CATALYSTS

The oxygen reduction reaction with metalloporphyrins as electrocatalysts has been extensively studied [116-123]. It was shown that porphyrins have high electrocatalytic activity toward the ORR. Most of the research was carried out with iron or cobalt porphyrins. Monomeric complexes of porphyrins catalyse the reduction of oxygen mainly to hydrogen peroxide. In contrast, metallodiporphyrins can catalyse the oxygen reduction to yield either water through a four-electron process, or hydrogen peroxide through a two-



n = 2, Co_2PP_2, **I**

n = 5, Co_2PP_5, **II**

n = 8, Co_2PP_8, **III**

Scheme 4. The structure of dicobalt diporphyrin complexes.

electron process [4]. Which process occurs depends on their geometric and electronic properties [124]. Liu *et al.* [125] have proposed that porphyrins with a *cis* configuration (two ligands attached to separate atoms that are connected by a double bond or are contained in a ring on the same side of a plane) improve oxygen reduction *via* a four-electron process, while *trans* configuration ones (ligands attached to separate atoms on the opposite sides of a plane) are much less active for this process. For example, different dicobalt diporphyrins complexes, CoPPx (Scheme 4.), studied by Lu and co-workers [126] could catalyze oxygen reduction only by a two-electron pathway to hydrogen peroxide. Polished glassy carbon electrodes were modified with absorbed CoPPx by immersing the electrode surface into solutions of complexes in dichloromethane, which were allowed to dry in air. The number of electrons exchanged for the reduction of oxygen was calculated to be *ca.* two for all four CoPPx and therefore it was concluded that on glassy carbon electrodes modified with CoPPx, the oxygen reduction reaction proceeds through two-electron process to hydrogen peroxide. Also, the electrogenerated ferrous form of iron tetrakis (M-methyl-4-pyridyl) porphyrin (bisulfate) has been shown to be an effective catalyst for the reduction of oxygen to hydrogen peroxide *via* two-electron pathway [117-119,127]. On the other hand, the reduced form of iron tetrakis (M-methyl-4-pyridyl) porphyrin, electrogenerated at a highly polished glassy carbon electrode has showed catalytic activity for electrochemical reduction of oxygen to water *via* a multistep mechanism [116]. Also, a glassy carbon electrode modified with iron(III) octaethylporphyrin chloride by a ‘dipcoating’ procedure showed clear, but modest electrocatalytic activity for the reduction of oxygen to a mixture of water and hydrogen peroxide in buffered solutions on both the acid and basic sides of neutral [128]. Several diporphyrins of cobalt [125,129-131]) have been shown to be efficient as catalysts for the four-electron reduction of oxygen to water. For example, Winnischofer *et al.* [131] showed that *meso*-tetrakis (4-pyridyl) porphynatocobalt(III), CoTCP, is acting as a four-electron transfer catalyst for oxygen reduction to water.

Yeager and co-workers [4] have examined the oxygen reduction at graphite discs with a range of adsorbed transition metal tetrasulfonated phthalocyanines (TsPc). It was established that Fe-TsPc in solution at pH greater than 4, catalyse the reduction of oxygen to water through a direct four -electron pathway with no peroxide production except at very high polarisation [132]. On the other hand, the oxygen reduction is catalysed to yield peroxide at Co-TsPc-modified graphite discs [132]. The different mechanisms of oxygen reduction at Fe-TsPc and Co-TsPc modified graphite discs can be explained by the difference in redox potentials.

Baez *et al.* [58] have examined the electrochemical reduction of oxygen on vitreous carbon electrode modified with titanium dioxide. The titanium dioxide coatings on vitreous carbon were made by spraying solutions of titanium(IV) n-butoxide, followed by thermal decomposition. The current-potential characteristic for oxygen reduction on modified vitreous carbon electrode in alkaline solutions shows two reduction waves as a result of the reduction process at two different sites on the carbon. The response at an RRDE demonstrates that all current corresponds to the two-electron reduction to HO_2^-, although the rate of reduction never reaches that expected for a two-electron reaction over the whole surface of the disc electrodes which may imply that titanium dioxide layer acts as partially permeable barrier to the reactants.

Besides depositing metal-based catalysts onto carbon electrodes, the doping of the bulk of carbon materials with a catalytic metal has also been applied [133-135]. The advantages of carbon paste electrodes have been reported as having low background currents and wide potentials windows, with possible miniaturisation and easy preparation, renewal and modification processes [133]. Additionally, metal-dispersed carbon paste electrodes, based on mixing an organic binder with metalised graphite, combine the efficient electrocatalytic activity of metal microparticles with the attractive properties of carbon paste matrices. Carbon paste doped with different metals such as platinum, palladium or ruthenium, exhibit different electrocatalytic activities, background current contributions, and hence analytical performances. For instance, Yao *et al.* [136] have examined chemically modified carbon paste electrodes for the reduction of oxygen to hydrogen peroxide. The cyclic voltammogram of tetrakis (μ-2-anilinopyridinato) dirhodium(II,III) chloride on a carbon paste electrode in degassed pH 7 buffer solution shows an irreversible wave at *ca*. -0.4 V which increases in intensity nine times in oxygen-saturated solution (when oxygen is bubbled into the solution).

Qu and co-workers [38] have made a hybrid thin film containing platinum nanoparticles and [tetrakis (N-methylpyridyl) porphyrinato} cobalt modified multi-walled carbon nanotubes on a glassy carbon electrode surface, which proved to be effective as catalyst for the electrochemical reduction of oxygen to water through four-electron process.

CONCLUSIONS

We have summarized the current thinking on the mechanism of oxygen reduction at carbon and modified carbon electrodes and show that the intelligent adaptation of the interface can control the reaction so as to catalyze the formation of hydrogen peroxide or water.

ACKNOWLEDGEMENTS

BŠ thanks the Clarendon Fund and the Physical and Theoretical Chemistry Laboratory for financial support.

REFERENCES

[1] E. Yeager, (1976) *in* Electroanalysis on Non-metallic Surfaces, pp. 203, NSB Special Publication 455.

[2] M. Tarasevich, A. Sadkowski, E. Yeager, in: B. Conway, J. Bockris, E. Yeager, S. Khan, R. White, (Eds.), Comprehensive Treatise of Electrochemistry Vol. 7, Plenum Press, New York, 1983.

[3] H.J. Lee, T.R. Lalk, J. Power Sources 73 (1998) 229.

[4] E. Yeager, Electrochim. Acta 29 (1984) 1527.

[5] E. Yeager, J. Mol. Catal. 38 (1986) 5.

[6] M.S. Hossain, D. Tryk, E. Yeager, Electrochim. Acta 34 (1989) 1733.

[7] D.T. Sawyer, G.J. Chlericato, C.T. Angelis, E.J.J. Nanni, T. Tsuchlya, Anal. Chem. 54 (1982) 1720.

[8] Z.W. Zhang, D. Tyrk, E. Yeager, in: S.A. Sarangapani, B. Schumm, (Eds.), Proceedings of the Workshop on the Electrochemistry of Carbon The Electrochemical Society, Pennington, NJ. 1984, p. 158.

[9] J.P. Randin, in: A.J. Bard (Ed.), The Encyclopedia of Electrochemistry of the Elements, Marcel Dekker, New York, 1976.

[10] A. Kuessner, J. Phys. E: Sci. Instrum. 20 (1987) 224.

[11] K.H. Mancy, D.A. Okun, C.N. Reilley, J. Electroanal. Chem. 4 (1962) 65.

[12] J.M. Hale, M.L. Hitchman, J. Electroanal. Chem. 107 (1980) 281.

[13] D.T. Sawyer, L.V. Interrnate, J. Electroanal. Chem. 2 (1961) 310.

[14] D.T. Sawyer, I.T. Seo, Inorg. Chem. 16 (1977) 499.

[15] I. Morcos, E. Yeager, Electrochim. Acta 15 (1970) 953.

[16] V.A. Garten, P.E. Weiss, Austral. J. Chem. 8 (1955) 81.

[17] V.A. Garten, P.E. Weiss, Rev. Pure Appl. Chem. 7 (1957) 69.

[18] M. Davies, M. Clark, E. Yeager, F. Hovorka, J. Electrochem. Soc. 106 (1959) 56.

[19] I. Morcos, E. Yeager, Electrochim. Acta 15 (1972) 257.

[20] B. Sljukic, C.E. Banks, S. Mentus, R.G. Compton, Phys. Chem. Chem. Phys. 6 (2004) 992.

[21] B. Sljukic, C.E. Banks, R.G. Compton, Phys. Chem. Chem. Phys. 6 (2004) 4034.

[22] K. Tammeveski, K. Kontturi, R.J. Nichols, R.J. Potter, D.J. Schiffrin, J. Electroanal. Chem. 515 (2001) 101.

[23] K. Vaik, D.J. Schiffrin, K. Tammeveski, Electrochem. Commun. 6 (2004) 1.

[24] K. Vaik, A. Sarapuu, K. Tammeveski, F. Mirkhalaf, D.J. Schiffrin, J. Electroanal. Chem. 564 (2004) 159.

[25] Z.W. Zhang, D. Tryk, E. Yeager, in: National Meeting, The Electrochem. Soc., Extended Abstracts, Vol. 83-2, Washington, 1983, p. Abst. 395.

[26] R.J. Taylor, A.A. Humffray, J. Electroanal. Chem. 64 (1975) 63.

[27] A.J. Appleby, J. Marie, Electrochim. Acta 24 (1978) 1243.

[28] A.R. Despic, Bull. T 46, Serb. Acad Sci. Arts, Maths Natural Ci. 12 (1969) 79.

[29] J. Xu, W. Huang, R.L. McCreery, J. Electroanal. Chem. 410 (1996) 235.

[30] M. Shamsipur, A. Salimi, H. Haddadzadeh, M. Fazlollah Mousavi, J. Electroanal. Chem. 517 (2001) 37.

[31] S.M. Golabi, J.B. Raoof, J. Electroanal. Chem. 416 (1996) 75.

[32] A. Salimi, H. Eshghi, H. Sharghi, S.M. Golabi, M. Shamsipur, Electroanalysis 11 (1999) 114.

[33] I. Bhugun, F. C.Anson, Inorg. Chem. 35 (1996) 7253.

[34] J. Yang, J.J. Xu, Electrochem. Commun 5 (2003) 306.

[35] S. Cere, M. Vazquez, S. R. de Sa´nchez, D.J. Schiffrin, J. Electroanal. Chem. 505 (2001) 118.

[36] D. van den Ham, C. Hinnen, G. Magner, M. Savyf, J. Phys. Chem 91 (1987) 4743.

[37] M.S. El-Deab, T. Ohsaka, J. Electroanal. Chem. 553 (2003) 107.

[38] J. Qu, Y. Shen, X. Qu, S. Dong, Chem. Commun. 1 (2004) 34.

[39] A. Sarapuu, K. Tammeveski, T.T. Tenno, V. Sammelselg, K. Kontturi, D.J. Schiffrin, Electrochem. Commun 3 (2001) 446.

[40] A. Salimi, C.E. Banks, R.G. Compton, Phys. Chem. Chem. Phys. 5 (2003) 3988.

[41] A. Sarapuu, K. Vaik, D.J. Schiffrin, K. Tammeveski, J. Electroanal. Chem. 541 (2003) 23.

[42] R.L. McCreery, in: A.J. Bard (Ed.), Electroanalytical Chemsitry Vol. 17, Dekker, New York, 1991.

[43] R. Bowling, R. Packard, R.L. McCreery, J. Am. Chem. Soc. 111 (1989) 1217.

[44] R. Bowling, R.L. McCreery, C.M. Pharr, R.C. Engstrom, Anal. Chem. 61 (1989) 2763.

[45] N.M. Pontikos, R.L. McCreery, J. Electroanal. Chem. 324 (1992) 229.

[46] I.F. Hu, T. Kuwana, Anal. Chem. 58 (1986) 3235.

[47] D.T. Fagan, I. Hu, T. Kuwana, Anal. Chem. 57 (1985) 2759.

[48] R.C. Engstrom, V.A. Strasser, Anal. Chem. 56 (1984) 136.

[49] J.F. Evans, T. Kuwana, Anal. Chem. 49 (1977) 1632.

[50] D.C.S. Tse, T. Kuwana, Anal. Chem. 50 (1978) 1315.

[51] G.E. Cabaniss, A.A. Diamantis, W.R. Murphy, R.W. Linton, T.J. Meyer, J. Am. Chem. Soc. 107 (1985) 1845.

[52] M.R. Deakin, K.J. Stutts, R.M. Wightman, J. Electroanal. Chem. 182 (1985) 113.

[53] C. Barbero, J.J. Silber, L. Sereno, J. Electroanal. Chem. 248 (1988) 321.

[54] F.A. Armstrong, A.M. Bond, H.A.O. Hill, B.N. Oliver, I. S. M. Psalti, J. Am. Chem. Soc. 111 (1989) 9185.

[55] H. Gerischer, S.D. McIntyre, J. Phys. Chem 91 (1987) 1930.

[56] R.K. Sen, J. Zegal, E. Yeager, Inorg. Chem. 16 (1977) 3379.

[57] C. Paliteiro, A. Hamnett, J.B. Goodenough, J. Electroanal. Chem. 233 (1987) 147.

[58] V.B. Baez, D. Pletcher, J. Electroanal. Chem. 382 (1995) 59.

[59] R. McIntyre, D. Scherson, W. Storek, H. Gerischer, Electrochim. Acta 32 (1987) 51.

[60] M.T. McDermott, K. Kneten, R.L. McCreery, J. Phys. Chem. 96 (1992) 3124.

[61] M.T. McDermott, R.L .McCreery, Langmuir 10 (1994) 4307.

[62] K.K. Cline, M.T. McDermott, R.L. McCreery, J. Phys. Chem. 98 (1994) 5314.

[63] J.P. Randin, E. Yeager, J. Electroanal. Chem. 36 (1972) 257.

[64] J.P. Randin, E. Yeager, J. Electrochem. Soc. 118 (1971) 711.

[65] J.F. Evans, T. Kuwana, Anal. Chem. 51 (1979) 358.

[66] T. Nagaoka, T. Sakai, K. Ogura, T. Yoshino, Anal. Chem. 58 (1986) 1953.

[67] I.F. Hu, D.H. Karwelk, T. Kuwana, J. Electroanal. Chem. 188 (1985) 59.

[68] J.F. Rusling, Anal. Chem. 56 (1984) 575.

[69] D.C. Thornton, K.T. Corby, V.A. Spendel, J. Jordan, A. J. Robbat, D.J. Rutstrom, M. Gross, G. Ritzler, Anal. Chem. 57 (1985) 150.

[70] R.C. Engstrom, Anal. Chem. 54 (1982) 2310.

[71] R.J. Taylor, A.A. Humffray, J. Electroanal. Chem. 42 (1973) 247.

[72] J. Wang, L.D. Hutchins, Anal. Chim. Acta 167 (1985) 325.

[73] C.W. Miller, D.H. Karweik, T. Kuwana, Anal. Chem. 53 (1981) 2319.

[74] R.M. Wightman, M.R. Deakin, P.M. Kovach, W. G. Kuhr, K.J. Shutts, J. Electroanal. Soc. 131 (1984) 1578.

[75] K.J. Shutts, P.M. Kovach, W.G. Kuhr, R.M. Wightman, Anal. Chem. 55 (1983) 1632.

[76] E. Hershenhart, R.L. McRerry, Anal. Chem. 56 (1984) 2256.

[77] J. Zak, T. Kuwana, J. Electroanal. Chem. 150 (1983) 645.

[78] S. Dong, T.J. Kuwana, J. Electroanal. Soc. 131 (1984) 813.

[79] P. Chen, R.L. McCreery, Anal. Chem. 68 (1996) 3958.

[80] M.T. McDermott, C.A. McDermott, R.L. McCreery, Anal. Chem. 65 (1993) 937.

[81] S. Mazur, T. Matasinovic, K. Camman, J. Am. Chem. Soc. 99 (1977) 3888.

[82] M.A. Fryling, J. Zhao, R.L. McCreery, Anal. Chem. 67 (1995) 967.

[83] P. Chen, M.A. Fryling, R.L. McCreery, Anal. Chem. 67 (1995) 3115.

[84] M. Delamar, R. Hitmi, J. Pinson, J.M. Saveant, J. Am. Chem. Soc. 114 (1992) 5883.

[85] M.R. Kagan, R.L. McCreery, Anal. Chem. 66 (1994) 4159.

[86] P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson, J. M.Saveant, J. Am. Chem. Soc. 119 (1997) 201.

[87] H. Gomathi, G.P. Rao, J. Electroanal. Chem. 190 (1985) 85.

[88] X. Chu, K. Kinoshita, Mater. Sci. Eng. B 49 (1997) 53.

[89] H.-H. Yang, R.L. McCreery, J. Electrochem. Soc. 147 (2000) 3420.

[90] K. Horita, T. Nishibori, T. Ohshima, Carbon 34 (1996) 217.

[91] A. Sarapuu, K. Vaik, D.J. Schiffrin, K. Tammeveski, J. Electroanal. Chem. 541 (2003) 23, and references cited within.

[92] M.P. Soriaga, A.T. Hubbard, J. Am. Chem. Soc. 104 (1982) 2735.

[93] P. He, R.M. Crooks, L.R. Faulkner, J. Phys. Chem 94 (1990) 1135.

[94] J. Zhang, F.C. Anson, J. Electroanal. Chem. 331 (1992) 945.

[95] A. Salimi, M.F. Mousavi, H. Eshghi, H. Sharghi, M. Shampsipur, Bull. Chem. Soc. Jpn. 72 (1999) 2121.

[96] T. Nagaoka, T. Sakai, K. Ogura, T. Yoshino, J. Chem. Soc., Faraday Trans. 1, 83 (1987) 1823.

[97] G.S. Galabrese, R.M. Buchanan, M.S. Wrighton, J. Am. Chem. Soc. 104 (1982) 5786.

[98] G.S. Galabrese, R.M. Buchanan, M.S. Wrighton, J. Am. Chem. Soc. 105 (1983) 5594.

[99] F. Mirkhalaf, K. Tammeveski, D.J. Schiffrin, Phys. Chem. Chem. Phys. 6 (2004)1321.

[100] R.L. Blankespoor, D.L. Schutt, M.B. Tubergen, R.L. De Jong, J. Org. Chem. 52 (1987) 2059.

[101] M.H. Pournaghi-Azar, S.M. Golabi, Talanta 35 (1988) 959.

[102] M.H. Pournaghi-Azar, F. Shemirani, S. Pourtork, Talanta 42 (1995) 677.

[103] P.W. Crawford, E. Carlos, J.C. Elleggod, C.C. Cheng, Q. Dong, D.F. Liu, Y.L. Luo, Electrochim. Acta 41 (1996) 2399.

[104] P. Tissot, A. Huissoud, Electrochim. Acta 41 (1996) 2451.

[105] J.K. Kariuki, M.T. McDermott, Langmuir 15 (1999) 6534.

[106] J.K. Kariuki, M.T. McDermott, Langmuir 17 (2001) 5947.

[107] S. Komorsky-Lovric, J. Solid State Electrochem. 1 (1997) 94, and references cited therein.

[108] L. Chuang, I. Fried, P.J. Elving, Anal. Chem. 37 (1965) 1528.

[109] H.C. Leventis, I. Streeter, G.G. Wildgoose, N.S. Lawrence, L. Jiang, Y.G.J. Jones, R.G. Compton, Talanta 6 (2004) 2989.

[110] C.E. Banks, R.G. Compton, Electroanalysis 15 (2003) 329.

[111] C.E. Banks, R.G. Compton, ChemPhysChem 4 (2003) 169.

[112] C.E. Banks, R.G. Compton, Chem. Anal. 48 (2003)159.

[113] M.E. Abdelsalam, P.R. Birkin, Phys. Chem. Chem. Phys. 4 (2002) 5340.

[114] C.E. Banks, A.H. Wylie, R.G. Compton, Ultrasonic. Sonochem. 11 (2004) 327.

[115] E. Maisonhaute, C. Prado, P.C. White, R.G. Compton, Ultrasonic. Sonochem. 9 (2002) 297.

[116] P.A. Forshey, T. Kuwana, Inorg. Chem. 22 (1983) 699.

[117] A. Bettelheim, T. Kuwana, Anal. Chem. 51 (1979) 2257.

[118] A. Bettelheim, R.J.H. Chan, T. Kuwana, J. Electroanal. Chem.Interfacial Electrochem. 99 (1979) 391.

[119] M. Fujihira, K. Sunakawa, T. Osa, T. Kuwana, J. Electroanal. Chem. 88 (1978) 299.

[120] K. Araki, H.E. Toma, Inorg. Chim. Acta 179 (1991) 293.

[121] C. Shi, F.C. Anson, Inorg. Chem. 29 (1990) 4298.

[122] C. Shi, F.C. Anson, Inorg. Chem. 37 (1998) 1037.

[123] S.L. Gojkovic, S. Gupta, R.F. Sanvinell, J. Electroanal. Chem. 462 (1999) 63.

[124] R. Karaman, S. Jeon, O. Almarsson, T.C. Bruice, J. Am. Chem. Soc. 114 (1992) 4899.

[125] H.Y. Liu, M. Weaver, C. Wang, C. Chang, J. Electroanal. Chem. 145 (1983) 439.

[126] W. Lu, C. Wang, Q. Lv, X. Zhou, J. Electroanal. Chem. 558 (2003) 59.

[127] A. Bettelheim, R.J.H. Chan, T. Kuwana, J. Electroanal. Chem.Interfacial Electrochem. 110 (1980) 93.

[128] M. Khorasani-Motlagh, M. Noroozifar, A. Ghaemi, N. Safari, J. Electroanal. Chem. 565 (2004) 115.

[129] J.P. Collman, P. Denesevich, Y. Konai, M. Marrocco, C. Koval, F.C. Anson, J. Am. Chem. Soc. 102 (1980) 6027.

[130] J.P. Collman, M. Marrocco, P. Denesevich, C. Koval, F.C. Anson, J. Electroanal. Chem. 101 (1979) 117.

[131] H. Winnischofer, V.Y. Otake, S. Dovidauskas, M. Nakamura, H.E. Toma, K. Araki, Electrochim. Acta 49 (2004) 3711.

[132] J. Zagal, P. Bindra, E. Yeager, J. Electrochem. Soc. 127 (1980) 1506.

[133] J. Wang, N. Naser, L. Angnes, H. Wu, L. Chen, Anal. Chem. 64 (1992) 1285.

[134] M.R. Callstrom, T.X. Neenan, R.L. McCreery, D.C. Alsmeyer, J. Am. Chem. Soc. 112 (1990) 4952.

[135] D. Ingersoll, D.H. Huskisson, J. Electroanal. Chem. Interfacial Electrochem. 307 (1991) 281.

[136] C.-L. Yao, K.H. Park, J.L. Bear, Anal. Chem. 61 (1989) 279.