Electrochemical reduction of oxygen on anthraquinone-modified glassy carbon electrodes in alkaline solution

Ave Sarapuu\textsuperscript{a}, Katri Vaik\textsuperscript{a}, David J. Schiffrin\textsuperscript{b}, Kaido Tammeveski\textsuperscript{a,\textasteriskcentered*}

\textsuperscript{a} Institute of Physical Chemistry, University of Tartu, Jakobi 2, 51014 Tartu, Estonia
\textsuperscript{b} Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK

Received 6 May 2002; received in revised form 6 October 2002; accepted 26 October 2002

Abstract

The electrochemical reduction of oxygen on glassy carbon (GC) electrodes grafted with anthraquinone (AQ) has been studied using the rotating ring–disk electrode technique. Grafting was achieved by the electrochemical reduction of the corresponding diazonium salt and the effect of AQ surface concentration on the kinetics of oxygen reduction has been investigated. The two-electron reduction of oxygen to hydrogen peroxide was observed for all the quinone-modified electrodes studied and the catalytic activity of the electrodes for \( \text{O}_2 \) reduction was dependent on the AQ surface concentration. The kinetic parameters of oxygen reduction on GC/AQ electrodes in 0.1 M KOH were determined as a function of AQ surface concentration considering a surface redox catalytic cycle model for quinone-modified electrodes. The rate constant of the chemical reaction between the semiquinone radical anion of AQ and molecular oxygen has been determined.

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Keywords: Oxygen reduction; Electrocatalysis; Kinetic parameters; Anthraquinone; Diazonium salt; Surface modification

1. Introduction

The electrochemical reduction of oxygen on surface-confined quinones has been extensively investigated [1–12]. Most of these studies have been carried out with carbon electrodes and their modification with quinones has been found to enhance the rate of \( \text{O}_2 \) reduction. Several methods have been proposed for electrode surface modification by quinones. For instance, adsorptive attachment provides an easy preparation procedure for the study of the kinetics of \( \text{O}_2 \) reduction [3,6–11]. A disadvantage is that quinones tend to desorb from the surface during long-term operation, especially in alkaline solutions [9]. A better method is to attach the quinones covalently to the surface [4,5,7,12]. For example, it was found that covalently bound 9,10-phenanthrenequinone facilitated the rate of oxygen reduction [7]. Until now, only a few \( \text{O}_2 \) reduction investigations have been made with covalently modified electrodes because of the lack of simple grafting methods.

Native quinone-like groups present on the surface of GC are very active for oxygen reduction, as is shown by the reduction prewave observed on this electrode [12]. However, surface coverage by quinone groups was rather low on freshly polished GC electrodes and no clear quinone reduction waves could be observed even when strong electrocatalysis was in evidence. The surface concentration of active oxygen-containing groups (e.g. quinone-like species) can be increased by surface oxidation of carbon electrodes and the effect of this on \( \text{O}_2 \) reduction kinetics is well-established [13–19]. The chemical nature of carbon–oxygen functionalities depends on the pre-treatment conditions. For instance, naphthoquinone and phenanthrenequinone were considered the most likely species to be present on the surface of GC [20].

Several attempts have been made to elucidate the mechanism of \( \text{O}_2 \) reduction on quinone-modified electrodes. It has been proposed that the reduction rate is proportional to the surface semiquinone radical concentration [7,12]. The radical anion reacts with mole-
cicular oxygen to yield the superoxide anion \(O_2^-\). Further transformations of this radical anion are considered to be fast and this electrochemical-chemical (EC) mechanism can be represented by the following reactions:

\[
\begin{align*}
\text{Q} + e^- & \rightarrow Q^- & \text{(I)} \\
Q^- + O_2 & \rightarrow O_2^- + Q & \text{(II)}
\end{align*}
\]

where Q is the attached quinone species. Reaction (II) has been proposed as the rate-determining step (r.d.s.) [7]. The Tafel slope for this process should be \(-60 \text{ mV dec}^{-1}\) if either the rate of radical interception by \(O_2\) is faster than its subsequent reduction or the redox potentials of the \(Q/Q^-\) and \(Q^-/QH^-\) couples are very different. For the above EC mechanism the potential dependence of the \(O_2\) reduction current should correlate with that of the semiquinone surface concentration [7]. The more positive the redox potential of surface quinones the lower the \(O_2\) reduction overpotential would be.

The electrochemical grafting of glassy carbon by anthraquinone (AQ) has been used recently for the preparation of catalytically active surfaces for the two-electron reduction of oxygen to hydrogen peroxide [12]. This electrochemical reaction is depicted schematically in Scheme 1. The advantage of the quinone-modified electrode is that the reduction of \(O_2\) stops at the peroxide stage. The aim of this work was to determine the kinetic parameters of \(O_2\) reduction as a function of AQ surface concentration for AQ-modified electrodes prepared by electrochemical reduction of the AQ diazonium salt.

2. Experimental

A GC disk electrode (Pine Instruments) with a geometrical area (A) of 0.196 cm\(^2\) was employed for the rotating disk electrode (RDE) measurements. The rotating ring–disk electrode (RRDE) experiments were carried out on a GC disk–Au ring electrode (Pine Instruments, \(A = 0.164 \text{ cm}^2\)). The collection efficiency was 0.23 as determined by the reduction of hexacyanoferrate(III) [21]. The electrodes were polished before use to a mirror finish with 1.0 and 0.3 \(\mu\)m alumina slurries (Buehler) and cleaned by sonication in Milli-Q water (Millipore, Inc.) for 5 min. A Pine Instrument Company (Grove City, PA, USA) AFMSRX rotator and MSRX speed controller were used. The potential was applied with an Autolab potentiostat/galvanostat PGSTAT10 (Eco Chemie B.V.) and the experiments were controlled with General Purpose Electrochemical System (GPES) software. A Pt foil served as the counter electrode and a saturated calomel electrode (SCE) was used as the reference. All the potentials are referred to this electrode. All experiments were carried out at room temperature (\(23 \pm 1 ^\circ\text{C}\)).

The covalent attachment of AQ was performed by reducing the corresponding diazonium salt, Fast Red AL Salt (Acros Organics) [22]. The surface modification was carried out in MeCN (Riedel-de Ha¨ en) containing 1 mM of the diazonium salt and 0.1 M tetrabutylammonium tetrafluoroborate (TBABF\(_4\), Fluka). All chemicals were used as received. In order to alter the surface coverage of AQ, the reduction sweep was reversed at different potentials whilst keeping a constant sweep rate (\(v\)) of 0.05 \text{ V s}^{-1}. The starting potential was always -0.65 V. For comparison purposes, the GC surface modification by AQ was also performed in a 10 mM aqueous solution of Fast Red AL Salt containing 0.05 M H\(_2\)SO\(_4\). In this case, three potential cycles between -0.65 and -0.5 V were applied and the electrode was held at -0.5 V for 10 min after cycling. The electrodes modified with AQ are designated as GC/AQ.

The electrodes were characterised electrochemically by cyclic voltammetry and oxygen reduction was studied in 0.1 M KOH (BDH, AristaR) solution in Milli-Q water. The solutions were saturated with Ar (99.998%, AGA) or \(O_2\) (99.995%, AGA). For the RRDE experiments the Au ring electrode was activated before recording each scan to improve the reliability of the quantitative detection of peroxide by applying three potential cycles between \(-1.2\) and \(0.7 \text{ V}\) at 0.1 \text{ V s}^{-1}. The oxidation potential used to detect peroxide was set at 0.05 V.

3. Results and discussion

3.1. AQ grafting

The electrode functionalisation by AQ in acetonitrile was similar to that previously described [12]. The first sweep showed a high reduction current peak but very small currents were observed during the second sweep. The first sweep ensured almost complete monolayer
coverage with AQ. In order to achieve smaller surface coverages, the reduction scan was reversed at less negative potentials. It was desirable to ascertain how general the results of surface functionalisation obtained from acetonitrile were. For this reason, grafting was also carried out from an aqueous solution and the electrocatalytic properties resulting from both preparations were compared. Fast Red AL Salt had a limited solubility in 0.05 M aqueous H2SO4 and a poorly defined reduction wave was observed. To ensure complete surface coverage in this case the electrode was held at −0.5 V for 10 min.

The stability of covalently attached quinones was characterised by cycling the electrodes 100 times between 0 and −1.25 V in Ar-saturated 0.1 M KOH. The peak current decreased significantly during the initial stages of cycling, indicating desorption of non-covalently attached quinone molecules. All electrodes were treated before use as indicated above. Fig. 1 shows typical stable cyclic voltammetric responses of GC/AQ electrodes with different surface coverages. The peaks in the voltammograms correspond to:

\[ \text{AQ} + 2H^+ + 2e^- = \text{AQH}_2 \]  \hspace{1cm} (III)

The redox potential of surface-bound AQ shifted slightly to positive values at higher AQ coverages. The surface concentration of AQ \( (\Gamma_{\text{AQ}}) \) was calculated from [23]:

\[ \Gamma_{\text{AQ}} = \frac{Q}{nFA} \]  \hspace{1cm} (1)

where \( Q \) is the charge from the area under the quinone reduction peak corrected for the baseline; \( n \) is the number of electrons exchanged per reactant molecule \( (n = 2) \). The results were not corrected for surface roughness, which was assumed constant. Full coverage by AQ was obtained by cycling the potential between 0.65 and −0.45 V. The coverage obtained depended on the surface treatment and saturation was observed at a higher \( \Gamma_{\text{AQ}} \) value than that reported previously \( (\Gamma_{\text{AQ}} = 2.5 \times 10^{-10} \text{ mol cm}^{-2}) \) [12]. It is difficult to relate this accurately to molecular dimensions since neither orientation nor surface roughness are known.

3.2. Dependence of O2 reduction kinetic parameters on the surface concentration of AQ

Fig. 2 shows the RDE results for a GC/AQ electrode with \( \Gamma_{\text{AQ}} = 2.3 \times 10^{-10} \text{ mol cm}^{-2} \) at different rotation rates. These results are very similar to those obtained previously [12]. Typical oxygen reduction polarisation curves for various AQ surface concentrations are shown in Fig. 3 and the results are compared with those for an unmodified GC electrode. For the latter and for the GC/AQ electrodes at low surface coverage a current maximum at ca. −0.5 V was observed. It has been proposed that at the prewave potentials, oxygen reduction is mediated by quinone surface groups (reactions I–II) present on the native GC surface [7,12] and that the surface concentration of semiquinone follows the same potential dependence as the oxygen reduction current [12]. It is notable though (Fig. 3), that the current in this potential range is lower for higher surface concentrations of quinone, indicating that the attached AQ partially blocks native GC surface sites, therefore depressing the rate of O2 reduction at the prewave. The chemical nature of these native groups is unclear at present, but these are very good electrocatalysts for oxygen reduction.

At potentials \( E < -0.7 \text{ V} \) other GC surface sites appear to be active enough to catalyse oxygen reduction and therefore the current increases again on a bare GC electrode. The GC/AQ electrodes show a sharp current increase at much more positive potentials, clearly indicating the strong electrocatalytic effect of AQ on O2 reduction. A higher value of \( \Gamma_{\text{AQ}} \) causes a sharper current increase to its diffusion limited value, supporting the assumption that, at these potentials, the reduction
involves the reaction of oxygen with the AQ semiquinone intermediate.

The kinetic parameters of O$_2$ reduction as a function of AQ surface concentration have been calculated following the surface redox catalytic cycle model previously proposed [12]. According to this model, O$_2$ reduction proceeds in parallel on two different surface sites, at surface quinone groups (either native or covalently attached) and at a heterogeneous electrode surface. In this model, the current density is given by [12]:

$$\frac{1}{j} = \frac{1}{j_{dl}} - \left[ \frac{2Fc_{O_2}b\alpha e^{-f\alpha(E-E^\circ)}}{1 + e^{(E-E^\circ)/f2\Delta E_{0}}} + \frac{2Fc_{O_2}b\alpha e^{-f\alpha(E-E^\circ)}}{1 + e^{(E-E^\circ)/f2\Delta E_{0}}} \right]^{-1}$$  \hspace{1cm} (2)

where $i = 1$ corresponds to properties of the quinone groups in native GC and $i = 2$ to those of the attached AQ. $j_{dl}$ is the diffusionally controlled limiting current density; $k^0$ is the electrochemical rate constant on the free GC surface and $z$ is the corresponding transfer coefficient; $E^\circ$ is the standard potential of the O$_2$/HO$_2$ couple (−0.065 V vs. SHE); $k_i$ is the rate constant for the reaction (II); $\Gamma_i$ is the surface concentration of the quinone species; $E_0$ is the standard potential of surface Q/Q$^\circ$ complexes; $\Delta E_{0}$ is the difference between the standard potentials of the Q$^\circ$/Q$^\circ$ and the Q/Q$^\circ$ couples; $c_{O_2}$ is the concentration of oxygen in the bulk (1.2 × 10$^{-6}$ mol cm$^{-3}$) [24], $F$ is the Faraday constant and $f = F/RT$. The consideration of the surface as composed of both surface quinones and a free GC surface is an attempt to take into account the steric hindrance to full coverage by AQ of a highly heterogeneous surface.

The rate of the chemical reaction between the semiquinones formed on native GC and molecular oxygen is proportional to the product $k_1\Gamma_1$ (Reaction II). Unfortunately, it was not possible to determine $k_1$ and $\Gamma_1$. No quinone surface concentration data could be measured for the bare GC electrodes used since no clearly defined voltammetric peak was observed in this potential region. For GC/AQ electrodes, the covalently attached AQ molecules act as electrocatalytic sites and the rate of the chemical reaction between AQ$^\circ$ and O$_2$ is given by $k_2\Gamma_2c_{O_2}$. The increase in current for potentials more negative than −0.75 V was modelled according to the Butler–Volmer formalism [12]. Although the surface is heterogeneous, a single average value of $k^0$ and $z$ was used to represent electron transfer reactions occurring on a distribution of surface sites on the native GC surface that become available for electron transfer in this potential region. This is a simple device for parametrising a reaction occurring at multiple sites. The purpose of the present work is not to analyse this potential region but to investigate the kinetics at the quinone centres. The justification for this approach will become apparent when discussing the results obtained with it.

The oxygen reduction kinetic parameters were calculated by a non-linear regression (NLR) analysis of the current–potential curves at different rotation rates [12,25]. The values of the diffusion-limited current densities used were calculated from the Koutecky–Levich plots of O$_2$ reduction [23] and these were fixed during the analysis. Some dependence of the values of the parameters on rotation rate was observed and the averages obtained with their corresponding standard deviations are listed in Table 1. There was a slight tendency for $E^{(1)}$, to decrease with increasing AQ surface concentration. As previously observed this is most probably related to a change in the adsorption conditions on native GC quinone-type sites, which is due to the influence of AQ attached onto neighbouring sites. The value of $E^{(2)} = −0.88 ± 0.01$ V should be independent of $\Gamma_{AQ}$, as is indeed observed, if there is no interaction between the AQ molecules present on the surface. The value of $E^{(2)}$ is very close to the average peak potentials ($E_{\text{redox}}$) of the voltammetric response of the GC/AQ electrode in oxygen-free 0.1 M KOH. For instance, for $\Gamma_{AQ} = 2.3 × 10^{-10}$ mol cm$^{-2}$, $E_{\text{redox}} = −0.867$ V. This value compares well with that determined previously of $E_{\text{redox}} = −0.860$ V, measured at the same sweep rate [12]. (The value extrapolated to zero sweep rate is 15 mV more positive). The values of $\alpha$ ($\alpha = 0.19±0.01$), $\Delta E_{1}$ ($\Delta E_{1} = −0.23±0.02$ V) and $\Delta E_{2}$ ($\Delta E_{2} = −0.34±0.03$ V) showed no dependence on $\Gamma_{AQ}$. The values of these kinetic parameters at different coverages are very similar to those previously obtained for $\Gamma_{AQ} = 2.5 × 10^{-10}$ mol cm$^{-2}$ [12]. The differences in the errors of the various quantities calculated is a consequence of the different influence that each model parameter has on the goodness-of-fit.

The constancy of $\alpha$ indicates that the reaction occurring at the free GC is unaffected by coverage. Also, the constancy of $\Delta E_{1}$ and $\Delta E_{2}$ indicates that the
thermodynamic properties of the semiquinone of the
grafted AQ are independent of coverage in the range
investigated. Although there is some scatter in the data,
the rate constant \( k^0 \) decreased with increasing \( \Gamma_{AQ} \)
and this is most likely due to a site-blocking effect of AQ.
There was only a slight tendency for the parameter \( k_1 \Gamma_1 \)
to decrease at higher surface concentrations of AQ. Its
decrease is expected since the number of native quinone
sites on GC should decrease with increasing surface
functionalisation.

The most notable dependence on AQ surface coverage
was observed for the parameter \( k_2 \Gamma_2 \). According to the
proposed EC mechanism (Reactions (I–II)) the rate of
\( \text{O}_2 \) reduction is limited by the chemical step when the
rate of electron transfer to surface-confined AQ is fast.
Therefore, the reduction rate should increase at higher
AQ surface concentrations as can be seen in Fig. 3.
Importantly, the calculated parameter \( k_2 \Gamma_2 \) was linearly
dependent on \( \Gamma_{AQ} \), as is shown in Fig. 4. From the slope
of this graph, a value for the rate constant \( k_2 = (4.7 \pm 0.3) \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) was found.

3.3. RRDE studies on \( \text{O}_2 \) reduction

A comparison between surfaces functionalised in
aqueous solution and acetonitrile was carried out to
ensure that the conditions under which the electrode was
grafted did not affect the properties of the electroactive
groups. Typical ring–disk voltammetry results obtained
for the bare GC electrode and for electrodes grafted in an
aqueous solution and in acetonitrile are compared in Fig.

5. Both GC/AQ electrodes gave similar responses and
their diffusion limited current value was almost equal to
that of bare GC. The results of the non-linear regression
analysis for the electrode functionalised in an aqueous
solution are also shown in Table 1. A comparison of the
kinetic parameters measured for this electrode shows that
there is no significant difference when these two very
different solvents are employed. It can be concluded that
the grafting procedure is very robust.

The ring and disk current data were analysed according
to the RRDE treatment proposed in Refs. [26,27].
The dependence of \( N_i F/IR \) on \( \omega^{-1/2} \) was nearly
independent of potential and rotation rate for all the
quinone-modified electrodes investigated as is shown in
Fig. 6. These results were almost identical to those
obtained for a GC/AQ electrode grafted in an aceton-

Table 1
Average values of kinetic parameters for oxygen reduction on AQ-modified GC electrodes as a function of AQ surface concentration \( \Gamma_{AQ} \)

<table>
<thead>
<tr>
<th>( 10^{10} \Gamma_{AQ} \text{mol cm}^{-2} )</th>
<th>( E_{1/2}/V )</th>
<th>( E_{i/2}/V )</th>
<th>( 10^4 k^0/\text{cm s}^{-1} )</th>
<th>( a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.516 ± 0.004</td>
<td>-0.875 ± 0.012</td>
<td>(7.2 ± 1.9)</td>
<td>0.18 ± 0.01</td>
</tr>
<tr>
<td>0.52</td>
<td>-0.53 ± 0.01</td>
<td>-0.874 ± 0.013</td>
<td>(5.0 ± 2.6)</td>
<td>0.19 ± 0.02</td>
</tr>
<tr>
<td>0.73</td>
<td>-0.53 ± 0.01</td>
<td>-0.860 ± 0.006</td>
<td>(4.6 ± 2.5)</td>
<td>0.2 ± 0.03</td>
</tr>
<tr>
<td>1.9</td>
<td>-0.57 ± 0.02</td>
<td>-0.877 ± 0.006</td>
<td>(3.3 ± 1.8)</td>
<td>0.2 ± 0.02</td>
</tr>
<tr>
<td>2.3</td>
<td>-0.55 ± 0.02</td>
<td>-0.880 ± 0.003</td>
<td>(3.5 ± 2)</td>
<td>0.19 ± 0.02</td>
</tr>
<tr>
<td>3</td>
<td>-0.57 ± 0.02</td>
<td>-0.890 ± 0.006</td>
<td>(3.5 ± 2)</td>
<td>0.19 ± 0.01</td>
</tr>
<tr>
<td>3.7</td>
<td>-0.55 ± 0.02</td>
<td>-0.876 ± 0.009</td>
<td>(3.6 ± 2.2)</td>
<td>0.21 ± 0.02</td>
</tr>
<tr>
<td>4.3</td>
<td>-0.55 ± 0.02</td>
<td>-0.909 ± 0.008</td>
<td>(2.8 ± 1.1)</td>
<td>0.18 ± 0.01</td>
</tr>
<tr>
<td>2.2 (^a)</td>
<td>-0.57 ± 0.01</td>
<td>-0.909 ± 0.008</td>
<td>(2.8 ± 1.1)</td>
<td>0.18 ± 0.01</td>
</tr>
</tbody>
</table>

\(^a\) This GC/AQ electrode was modified in an aqueous solution of Fast Red AL Salt.

The parameters were calculated by non-linear regression analysis.

trile solution. The intercept of the extrapolated $N_{ID}/I_R$ lines was close to unity showing that $O_2$ reduction proceeds entirely by the two-electron pathway [26,27].

The percentage of peroxide formation on the disk ($F$) can be calculated from [28]:

$$F = \frac{200I_R/N}{I_D + I_R/N}$$

(3)

4. Conclusions

The proposed redox catalytic cycle model for oxygen reduction on quinone modified GC surfaces has been further verified. The observed dependence of the rate of the chemical step of the reaction between semiquinone and oxygen on surface coverage follows model predictions thus lending further support to the redox catalytic mechanism previously proposed [12]. In addition, the parameters defining the individual contributions to the reduction current, i.e. electrocatalytic groups on native GC, attached AQ and average free surface reactivities, are independent of coverage. The apparent rate constant for the latter decreases with an increase of $I_{AQ}^*$, as expected when the surface becomes crowded with attached AQ molecules.

Fig. 5. Oxygen reduction and hydrogen peroxide oxidation in $O_2$ saturated 0.1 M KOH on: (1) GC/AQ, modified in an aqueous solution, (2) GC/AQ, modified in acetonitrile; (3) GC; $v = 20$ mV s$^{-1}$; $\omega = 960$ rpm, $A$ (disk) = 0.164 cm$^2$; (a) disk and (b) ring currents.

Fig. 6. Dependence of $N_{ID}/I_R$ on $\omega^{-1/2}$ for oxygen reduction on a GC/AQ electrode in $O_2$ saturated 0.1 M KOH. The electrode was modified in aqueous solution. The solid line corresponds to the average of the $N_{ID}/I_R$ values.

Fig. 7. Dependence of the yield of peroxide formation ($\Phi$) on potential for: (▲) GC/AQ, modified in an aqueous solution, (●) GC/AQ, modified in acetonitrile and (■) GC.

The percentage yields of $H_2O_2$ were in the range 95–100% for all the GC/AQ electrodes studied (Fig. 7). A slight decrease observed at more negative potentials could result from a slightly non-quantitative detection of peroxide on the gold ring electrode.

$n$ was calculated from the Koutecky–Levich (K–L) equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_{dl}} = \frac{1}{nFkF_{O_2}^b} - \frac{1}{0.62nFD_{O_2}^{b/2}v^{-1/6}c_o^{b/2} \omega^{1/2}}$$

(4)

where $j_k$ and $j_{dl}$ are the kinetic and diffusion-limited current densities, respectively, $k$ is the rate constant for $O_2$ reduction, $D_{O_2}$ is the diffusion coefficient of oxygen ($1.9 \times 10^{-5}$ cm$^2$ s$^{-1}$) [24], $c_o^b$ is the concentration of oxygen in the bulk ($1.2 \times 10^{-6}$ mol cm$^{-3}$) [24] and $v$ is the kinematic viscosity of the solution ($0.01$ cm$^2$ s$^{-1}$). A value of $n = 2.1 \pm 0.1$ was found for all the electrodes investigated at potentials $-0.7 > E > -1.25$ V, showing the great promise of these materials as electrocatalysts for the production of hydrogen peroxide.
Acknowledgements

This research was partly supported by the Estonian Science Foundation (Grant No. 4623). Support from the European Union Framework V Growth programme, CLETEPEG project, Contract No G5RD-CT-2001-00463, is gratefully acknowledged.

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