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MARKO KULLAPER

Electrochemical properties
of glassy carbon, nickel and
gold electrodes modified with
aryl groups



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I. LIST OF ORIGINAL PUBLICATIONS

This thesis consists of nine original articles listed below and a review. The articles are referred in the text by Roman numerals I–IX.

- I. **M. Kullapere**, G. Jürmann, T.T. Tenno, J.J. Paprotny, F. Mirkhalaf, K. Tammeveski, Oxygen electroreduction on chemically modified glassy carbon electrodes in alkaline solution, *Journal of Electroanalytical Chemistry* 599 (2007) 183–193.
- II. **M. Kullapere**, F. Mirkhalaf, K. Tammeveski, Electrochemical behaviour of glassy carbon electrodes modified with aryl groups, (manuscript submitted).
- III. J.-M. Seinberg, **M. Kullapere**, U. Mäeorg, F.C. Maschion, G. Maia, D.J. Schiffrin, K. Tammeveski, Spontaneous modification of glassy carbon surface with anthraquinone from the solutions of its diazonium derivative: An oxygen reduction study, *Journal of Electroanalytical Chemistry* 624 (2008) 151–160.
- IV. **M. Kullapere**, J.-M. Seinberg, U. Mäeorg, G. Maia, D.J. Schiffrin, K. Tammeveski, Electroreduction of oxygen on glassy carbon electrodes modified with in situ generated anthraquinone diazonium cations, *Electrochimica Acta* 54 (2009) 1961–1969.
- V. **M. Kullapere**, K. Tammeveski, Oxygen electroreduction on anthraquinone-modified nickel electrodes in alkaline solution, *Electrochemistry Communications* 9 (2007) 1196–1201.
- VI. **M. Kullapere**, L. Matisen, A. Saar, V. Sammelselg, K. Tammeveski, Electrochemical behaviour of nickel electrodes modified with nitrophenyl groups, *Electrochemistry Communications* 9 (2007) 2412–2417.
- VII. **M. Kullapere**, M. Marandi, V. Sammelselg, H.A. Menezes, G. Maia, K. Tammeveski, Surface modification of gold electrodes with anthraquinone diazonium cations, *Electrochemistry Communications* 11 (2009) 405–408.
- VIII. **M. Kullapere**, J. Kozlova, L. Matisen, V. Sammelselg, H.A. Menezes, G. Maia, D.J. Schiffrin, K. Tammeveski, Electrochemical properties of aryl-modified gold electrodes, *Journal of Electroanalytical Chemistry* 641 (2010) 90–98.
- IX. **M. Kullapere**, M. Marandi, L. Matisen, F. Mirkhalaf, A.E. Carvalho, G. Maia, V. Sammelselg, K. Tammeveski, Blocking properties of gold electrodes modified with 4-nitrophenyl and 4-decylphenyl groups, (manuscript submitted).

Author's contribution

The author has performed all the electrochemical measurements and calculations for [I,II,V–IX] and participated in [III,IV]. The author is responsible for the interpretations and writing the papers [II–IX] and participated in [I].

2. ABBREVIATIONS AND SYMBOLS

A	geometric surface area of an electrode
ACN	acetonitrile
AFM	atomic force microscopy
Au/AQ	gold modified with 9,10-anthraquinone groups
Au/BP	gold modified with biphenyl groups
Au/DP	gold modified with 4-decylphenyl groups
Au/Naph1	gold modified with 1-naphthyl groups
Au/Naph2	gold modified with 2-naphthyl groups
Au/NP	gold modified with 4-nitrophenyl groups
Au/PhBr	gold modified with 4-bromophenyl groups
AQ	9,10-anthraquinone
B	Levich slope
BDD	boron-doped diamond
$c_{O_2}^b$	concentration of oxygen in the bulk solution
C_f	sensitivity factor of the crystal
CNTs	carbon nanotubes
CP	carboxyphenyl group
CV	cyclic voltammetry
DA	dopamine
DBD	4-decylbenzenediazonium tetrafluoroborate
D_{O_2}	diffusion coefficient of oxygen
ΔE	difference between the standard potentials of the $Q^{\cdot-}/Q^{2-}$ and the $Q/Q^{\cdot+}$ couples
ΔE_p	separation of redox peaks
E	electrode potential
E^0	standard potential
$E_{Q/Q^{2-}}^0$	standard potential of the Q/Q^{2-} couple
$E_{1/2}$	half-wave potential
E_f	redox potential
E_p	peak potential
EC	electrochemical–chemical
EIS	electrochemical impedance spectroscopy
EQCM	electrochemical quartz crystal microbalance
ET	electron transfer
F	Faraday constant
Δf	resonance frequency shift
FTIRRAS	Fourier transform infrared reflection absorption spectroscopy
GC	glassy carbon
GC/AAQ1	glassy carbon modified with <i>in situ</i> synthesised 1-anthraquinone diazonium cations

GC/AAQ2	glassy carbon modified with <i>in situ</i> synthesised 2-anthraquinone diazonium cations
GC/Anth1	glassy carbon modified with 1-anthracenyl groups
GC/Anth2	glassy carbon modified with 2-anthracenyl groups
GC/AQ	glassy carbon modified with 9,10-anthraquinone groups
GC/AQ-Ph	glassy carbon modified with AQ and phenyl groups
GC/BP	glassy carbon modified with biphenyl groups
GC/DP	glassy carbon modified with 4-decylphenyl groups
GC/Naph1	glassy carbon modified with 1-naphthyl groups
GC/Naph2	glassy carbon modified with 2-naphthyl groups
GC/NP	glassy carbon modified with 4-nitrophenyl groups
GC/Ph	glassy carbon modified with phenyl groups
GC/PhBr	glassy carbon modified with 4-bromophenyl groups
HOPG	highly oriented pyrolytic graphite
I	current
I_d	diffusion-limited current
I_D	disk current
I_k	kinetic current
I_p	peak current
I_R	ring current
j	current density
j_{dl}	diffusion-limited current density
k	heterogeneous electron transfer rate constant
k^0	standard electrochemical rate constant
$k^{0'}$	apparent electrochemical rate constant for O ₂ reduction
k_c	rate constant for the chemical reaction between Q ^{•+} and O ₂
$k_t \Gamma_i$	chemical rate parameter
K-L	Koutecky-Levich
LSV	linear sweep voltammetry
Δm	change of mass per unit area
MP	methylphenyl group
n	number of electrons transferred per O ₂ molecule
N	collection efficiency
NBD	4-nitrobenzenediazonium tetrafluoroborate
Ni/AQ	nickel modified with 9,10-anthraquinone groups
Ni/NP	nickel modified with 4-nitrophenyl groups
NLR	non-linear regression
NP	nitrophenyl group
OCP	open circuit potential
PPF	pyrolysed photoresist film
Q	quinone
R	universal gas constant
RBS	Rutherford backscattering spectroscopy
RDE	rotating disk electrode
RMS	root-mean-square

RRDE	rotating ring-disk electrode
SCE	saturated calomel electrode
SHE	standard hydrogen electrode
SWCNTs	single-walled carbon nanotubes
TBABF ₄	tetrabutylammonium tetrafluoroborate
ν	potential scan rate
XPS	X-ray photoelectron spectroscopy
α	transfer coefficient
Γ	surface concentration
Q	charge
ν	kinematic viscosity of the solution
Φ	percentage yield of peroxide formation
ω	electrode rotation rate
θ	surface coverage

3. INTRODUCTION

Modification of carbon and metal electrode surfaces is an important task in electrochemistry and material science. The electrochemical grafting of the electrodes by diazonium reduction has become a widely used method of surface modification [1–3].

It is of considerable interest to study the reduction of oxygen on carbon and metal electrodes modified with barrier layers of various organic compounds. The blocking behaviour of these films is of paramount importance in many fields, including electrocatalysis and electroanalysis.

In this work the modification of glassy carbon (GC), nickel and gold surfaces with aryl groups was performed by electrochemical reduction of the corresponding diazonium salts. The electrografting of anthraquinone (AQ) to GC surface was also achieved using *in situ* generated AQ diazonium cations. The *in situ* modification method is especially attractive since the synthesis of the diazonium salts is made via a standard diazotisation procedure and the modification of the electrodes is carried out from the reaction solution thus avoiding separation and purification steps.

In addition to electrochemical grafting, also surface grafting via spontaneous modification is used [4]. It provides a simpler and more versatile route for electrode functionalisation. A systematic study of spontaneously grafted anthraquinone on GC from the solutions of its diazonium derivative and the resulting electrocatalytic properties are reported. Surface modification was performed in acetonitrile and in aqueous solutions of various pH and a strong bonding of AQ to the surface is in evidence. The kinetic parameters for oxygen reduction were determined.

It is of special interest to find out whether the strong attachment of aryl groups could be extended to substrates other than carbon materials. Therefore one of the aims of the present work is to demonstrate the modification of nickel and gold with various modifiers by diazonium reduction and to study the barrier properties of modified Ni and Au electrodes.

The main purpose of this work was to explore the electrochemical properties of GC, Ni and Au electrodes modified with different aryl groups to investigate the resulting blocking of electron transfer reactions. The molecules were chosen to provide attached aromatic rings of different sizes and two examples of a phenyl group containing a polar group. The barrier properties of these electrodes were characterised using dopamine and $\text{Fe}(\text{CN})_6^{3-}$ redox probes.

The aryl film formation was studied with electrochemical quartz crystal microbalance (EQCM). The surface morphology and chemical composition of the modifier films was characterised by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The electrochemical experiments were performed using cyclic voltammetry (CV) and the rotating disk electrode (RDE) method.

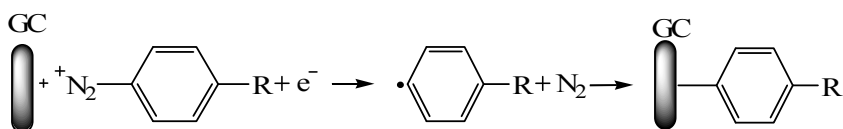
4. LITERATURE OVERVIEW

4.1. Surface modification of carbon materials by diazonium reduction

Aryldiazonium salts are very effective and diverse reagents for functionalising carbon surfaces with a variety of functional groups. The unique characteristics of the aryldiazonium cation are the very strong electron-withdrawing effect of diazonium moiety and high stability of dinitrogen as a leaving group [4].

4.1.1. Electrochemical grafting

There has been an increased research activity in the modification of carbon electrodes by electrochemical reduction of diazonium salts since the first report on the application of this method [5]. The details of this process and the properties of the modified electrodes have been reviewed by Downard [1] and by Pinson and Podvorica [2], and more recently by McCreery [3], Knigge et al. [6] and Gooding [7]. The surface modification by the electrochemical reduction of diazonium salts is shown in Scheme 1.



Scheme 1. Electrografting of GC surface with aryl groups by diazonium reduction [2].

The binding of aryl groups to carbon electrodes is a two-step process. The diazonium cation (ArN_2^+) is reduced and the formed aryl radical ($\text{Ar}^\bullet$) reacts with the carbon surface giving a strong covalent C–C bond [8–10]. It is likely that a short-lived neutral phenyl- N_2 species exist as an intermediate, but it rapidly and irreversibly dissociates to much more stable N_2 and phenyl radical [10]. In derivatisation of the carbon surfaces by electrochemical reduction of diazonium salts it is significant that the aryl radicals produced are not reduced at the potential at which they are produced and may thus react with the surface [10]. Formed radicals do not reduce further and not all radicals will attach to the surface, many will diffuse to the solution. Electrochemical reduction of diazonium salts has several features that make it an attractive surface modification method. As the radicals can be generated electrochemically, they are generated precisely where it is most likely to react with the electrode surface and even further the radicals are more likely to form near an uncovered region, thus the film would be with relatively even surface coverage [3].

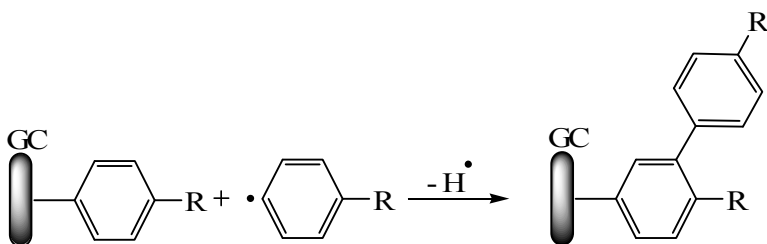
Glassy carbon (GC) [5,10–24], highly oriented pyrolytic graphite (HOPG) [9–11,25], boron-doped diamond (BDD) [25–27], carbon nanotubes (CNT) [28,29] and other carbon materials have been successfully grafted using the diazonium reduction method.

The attachment of aryl groups to graphene sheet has been investigated by Jiang et al., using first principles density functional theory methods [30]. They showed that the interaction between the basal plane and isolated phenyl groups is weak, but it could be strengthened significantly with two phenyl groups attached to the para positions of the same six-membered ring to form a pair on the basal plane. The strongest bonding was found at the graphene edges. A 1,2-addition pair is predicted to be most stable for the armchair edge, whereas the zigzag edge possesses a unique localized state near the Fermi level that shows a high affinity for the phenyl group [30].

A large variety of surface modifiers can be attached to carbon surfaces. Among other compounds, several quinones have been grafted to carbon electrodes [10,31–35]. The quinone-modified electrodes showed a high electrocatalytic activity for the two-electron reduction of oxygen as reported by Schiffrin and co-workers [25,31–35].

Alternatively, a radical generated at an unmodified carbon surface can attack an adjacent surface-bound molecule instead of the carbon surface itself. Since all diazonium reagents used for carbon surface modification so far have been aromatic, electron tunnelling through a monolayer is fairly efficient, thus permitting the generation of second equivalent radicals [3,36,37].

Multilayer growth can be explained by the following mechanism (Scheme 2):



Scheme 2. Schematic representation of multilayer formation by diazonium reduction [2].

The radical formed by diazonium ion reduction may attack an already attached group by abstracting H atom and this surface bound radical may react with another radical causing the second layer and subsequent layers to be formed [2]. The film resulting from this mechanism remains conjugated, although alternative mechanisms can result in termination of the chain reaction.

It was found that a longer deposition time (at least 10 min) at constant potential results in a thicker film formation. The preferential growth of the films

occurred on defect sites of HOPG. The formation of “humps” was also seen, which reveals the three-dimensional (3D) growth of the film on HOPG. The height of these features was 5–15 nm above the substrate surface [9].

In this respect, the structure of the modifier film is a major concern. It is important to know whether (sub)monolayer or multilayer films are formed [1,2]. In case of submonolayers the determination of the modifier orientation is a rather complicated task. There is also experimental evidence that in many cases multilayer films are formed [9,18,37–40].

A comparison of the amount of the electrografted material determined by charge integration and the data on film morphology measured by atomic force microscopy (AFM) was made by Brooksby and Downard [38]. An atomically flat pyrolysed photoresist film (PPF) was used as a substrate material and the authors concluded on the basis of their data that an incompact layer was formed. The experimentally determined surface concentration of nitrophenyl groups corresponded to 21% of a close-packed monolayer [38].

The tendency to form multilayers and the thickness of the modifier film depend on the nature of the surface, the particular diazonium reagent employed, and the deposition conditions, including scan rate and potential range, diazonium ion concentration, and number of deposition scans [3].

4.1.2. Spontaneous grafting

The spontaneous grafting from solutions of the diazonium derivatives was originally reported for carbon black and patented by the Cabot Corporation [41]. The attachment of aryl groups to electrode surfaces by reduction of aryldiazonium cations has attracted considerable interest in recent years, particularly, in relation to spontaneous grafting [23,42–50]. Various aspects of spontaneous modification have been recently highlighted in the review by Barriere and Downard [4]. Current interest in these reactions results from the desirability of the construction of nanostructures with carbon nanotubes employing simple chemical means [51,52].

Compared with electrochemical grafting, spontaneous modification provides a simpler and more versatile route for electrode functionalisation. For example, GC electrodes have been modified with nitrophenyl groups by immersion in the corresponding diazonium salt solution in acetonitrile, as shown by the typical cyclic voltammetric response of the $-\text{NO}_2$ group [42]. The formation of organic layers has also been clearly demonstrated by atomic force microscopy [42,43]. The AFM images revealed layer thicknesses above 5 nm, which is an indication of the formation of multilayers (a monolayer thickness is *ca* 1 nm). The presence of the $-\text{NO}_2$ substituent group was confirmed by FTIR [42,43] and X-ray photoelectron spectroscopy [43,47,48]. The studies show that the films grafted spontaneously have the same characteristics as those grafted electrochemically, but in general, films are thinner and form more slowly by the spontaneous route [50]. For example, in their study aimed at confirming

covalent bonding between GC and aryl groups, Combellas and co-workers employed time-of-flight secondary ion mass spectroscopy to examine films electrografted and spontaneously grafted from solutions of aryldiazonium salts (2 mM in 0.1 M TBABF₄-acetonitrile) [23]. The spontaneously grafted films of -C₆F₁₃ and bromophenyl derivatives gave qualitatively similar spectra to those grafted electrochemically, although for the same preparation times, signals were much weaker after spontaneous grafting.

Le Floch et al. studied a number of diazonium salts and observed that only the compound with electron withdrawing group was able to create spontaneous covalent bonding with the GC electrode. They concluded that for molecules with electron withdrawing groups, the reduction wave starts before the open-circuit potential of GC in ACN whereas for the other compounds the onset of the reduction waves starts at more cathodic potential values and then grafting occurs only by polarizing the electrode at higher cathodic potential [49].

4.2. Electrografting of metal surfaces by diazonium reduction

The attachment of organic layers to metals is an important process in many fields (protection against corrosion, preparation of functionalised materials, sensors, electrocatalysis and others) [53]. Coating of metals with paints, polymers and related organic materials is an industrial process of wide application and there exists a large variety of methods for this purpose: plasma deposition, spin coating, vapour deposition and self-assembly [54]. In these cases, only weak bonds are formed between the metal substrate and the organic layer [53,54].

Three methods are available for the formation of a strong bond between a metal and an organic molecule as has been reviewed by Palacin et al. [54]. One of these involves the electrochemical reduction of vinylic compounds (H₂C=CHR) in aprotic medium and it leads to a metal-polymer structure. Thin (~10 nm) polymeric layers can be grafted to a variety of metals (Fe, Ni, Au and Pt) [55]. The second method is based on the electrooxidation of diamines such as ethylenediamine on metal (Pt, Au) electrodes, which furnishes a polyethylenimine coating [56]. The third method is the reduction of diazonium salts [2,57], which has been frequently employed for the attachment of aryl layers to metal surfaces. Electrochemical reduction of diazonium salts can be used with oxidisable metals and the reduction potential is always set negative compared to the open circuit potential of the metal. This is made in order to prevent the oxidation of the metal electrode surface during the electrochemical grafting.

It is now well-established that the electrochemical reduction of diazonium salts on metals (iron and mild steel, zinc, nickel, cobalt, copper, palladium, gold, platinum) [45,53,57–60] and silicon leads to the covalent bonding of aryl groups bearing a terminal functionality such as alkyl, nitro, cyanide, carboxylic, hydroxylic, thiol and halogenated groups.

4.2.1. Modification of gold by diazonium reduction

Ahlberg et al. were the first to report on the irreversible adsorption of aryl groups to gold by electrochemical reduction of diazonium salts in acetonitrile [57]. In recent years, there has been an increased research activity in the electrografting of aryldiazonium derivatives to gold [7,53,59,61–79] since Au is considered to be the most inert of all metals [80]. The mechanism of attachment of aryl groups to gold is not entirely clear although there is good evidence for the formation of Au–C bonds [53,61,65,67]. Also the Au–C bonds formed yield layers that are more stable than those obtained by chemisorption of alkanethiols regarding long-term storage, ability to withstand repeated cycling and available potential window [68,79]. The modification of Au surface by diazonium reduction is different from that of carbon materials as modification peaks also depend on the crystallographic properties of substrate. Benedetto et al. explained the formation of multi-peaks in cyclic voltammograms during Au modification by the reduction of diazonium salts on different crystallographic sites of gold electrodes [62].

An attractive grafting approach is to use *in situ* synthesised diazonium derivatives [65,75,77]. This is especially attractive since the *in situ* synthesis of the diazonium salts is made via a standard diazotisation procedure and the modification of the electrodes is carried out from the reaction solution thus avoiding separation and purification steps. Aryl-modified Au electrodes can find applications in biochemical sensing [7] due to the possibility of performing additional chemical transformations to the attached film. Belanger and co-workers have systematically studied the electrochemical deposition of 4-substituted phenyl groups to gold by diazonium reduction [64].

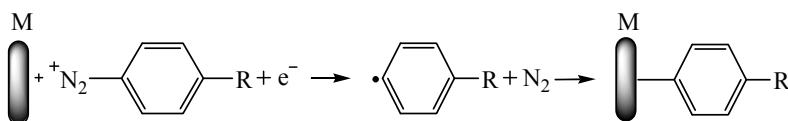
Spontaneous modification of gold surfaces at open circuit potential (OCP) in acetonitrile and aqueous acid solutions of diazonium salts has been reported in several works [81,82]. Films prepared at OCP show growth behaviour and composition that are very similar to those electrografted from acetonitrile solution, but their stability to sonication is significantly smaller [82]. Podvorica et al. reported spontaneous chemical and electrochemical grafting of diazotate salts to gold from aqueous solutions and a successful modification of Au surface with nitrophenyl and bromophenyl groups was achieved [83]. The diazonium chemistry can be used to attach alkylbenzene monolayer to gold nanoparticles [84].

The thickness of aryl layers can vary from a monolayer to thin films [59]. Surface polymerization of hydrophobic monomers could be a means to protect the surface. It is possible to form μm thick polyphenylene films by electrochemical reduction of benzenediazonium tetrafluoroborate on metals in acetonitrile [59]. It has been reported that aryl films on gold are less stable than those formed on carbon substrates [85,86].

4.2.2. Modification of nickel by diazonium reduction

So far there are only a few papers that focus directly on the modification of nickel surfaces by diazonium reduction [42,43,53]. The electrochemical modification of Ni electrodes with NP groups has been achieved and a typical electrografting behaviour has been observed [53]. Adenier et al. studied the spontaneous modification of Ni substrates from 4-nitrobenzenediazonium tetrafluoroborate solutions of various concentrations [42]. It was shown that NP layers can be grafted to Ni surfaces without electrochemical induction. In subsequent work the spontaneous grafting with aryldiazonium salts was further studied on nickel and zinc surfaces in order to compare the modification behaviour of two metals of different redox properties [43]. It appeared that spontaneous grafting with 4-nitrobenzenediazonium tetrafluoroborate was rather fast on the easily oxidised metal (Zn), but did not lead to a dense layer. The grafting of the nickel surface took a much longer time (a homogeneous NP layer was observed after 2 h immersion). These authors concluded that spontaneous grafting occurs when electrode substrate provides electrons for the reduction of a diazonium cation into an aryl radical. However, there is still a debate about the formation of thicker layers by spontaneous modification from diazonium salts.

Electrografting reactions are shown in Scheme 3.



Scheme 3. Electrografting of metal surface (M) with aryl groups by diazonium reduction.

4.3. Blocking properties of aryl-modified electrodes

Blocking behaviour of aryl-modified electrodes is an important aspect from both fundamental and practical points of view. These are of special interest due to the application of these modified electrodes in electroanalysis and other areas of electrochemistry [2,7].

4.3.1. Blocking properties of aryl-modified carbon electrodes

Blocking properties of electrochemically grafted aryl moieties have been of considerable interest during the recent decade [1,2,9,13,15–18,24,87–91]. Various compounds have been covalently attached to carbon electrode surfaces and their effect on the electron transfer kinetics has been investigated.

The barrier properties of covalently grafted phenyl layers have been studied in several laboratories [13–17,24]. This is the thinnest blocking layer which can be formed by the diazonium reduction method. The estimated thickness of the phenyl monolayer is 0.59 nm, however, the “average thickness” of the layer is less than that, due to defects and disorder in the modifier monolayer. The phenyl monolayer was found to decrease the rate of electron transfer reactions of certain redox species (for example, the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple [17,24]), whereas for others (e.g. methyl-viologen) the redox process was not significantly influenced by the surface modifier [17].

The modifier film structure is crucially important in the electron transfer kinetics research. If the layer is not compact enough, then the redox active species can reach the underlying substrate and therefore the modifier film does not provide an effective blocking of the electrode surface. By contrast, for a compact monolayer the electron transfer can occur only by tunnelling through the film and obviously its rate depends on the thickness of the monolayer film. Systematic investigations in this field using monolayer of variable thicknesses (from 0.59 to 1.4 nm) have been carried out by Yang and McCreery [15]. For several organic redox systems studied, the presence of a monolayer had little effect on the value of k^0 as compared to the one of the polished GC. For instance, only 50% decrease of k^0 was observed for methyl-viologen on the GC electrode modified with nitrophenyl groups. For chlorpromazine, the value of the tunnelling parameter (β) was found to be $0.2 \text{ \AA}^{-1}$. However, when interpreting these results, one must be concerned about the compactness and ordering of the chemisorbed monolayer on GC.

Downard proposed that electrolysis potential influences the barrier properties of the aryl films. Markedly different blocking behaviours towards solution-based redox probes have been reported for monolayer films of the same modifier. Apparently, different electrolysis potential of electrode modification leads to such variability [16].

The blocking action of aryl films depends on their thickness (monolayer vs. multilayer films) and compactness [17]. The blocking behaviour towards solution-based redox probes depends also on the charging of a film. For example, carboxyphenyl and aminophenyl groups behave in a different way in this regard. The charge of an ionisable group is pH dependent and the solution pH influences the barrier properties of a film [87]. Much work has been done to study the electrochemical response of various redox couples on aryl-modified electrodes. There is clear evidence that the blocking action depends on the chemical nature of the redox species and their hydrophile/lipophile properties [17,87]. For example, the electron transfer of the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox system is facilitated by interaction with carbon surface [89] and therefore the blocking effect of aryl films is rather strong, whereas for the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ redox couple the electron transfer process is less suppressed.

The blocking properties of the aryl films depend greatly on electrostatic and electrolyte/solvent effects (hydrophobic/hydrophilic properties and from the electrostatic interactions between the layer and the redox probe) [13].

Comparisons of various redox couples show that the electron-transfer kinetics of hydrophobic probes is inhibited to a lesser degree than those of hydrophilic probes. This observation indicates that hydrophobic/hydrophilic interactions between solution species and the modifier film restrict the approach of redox probes to the monolayer surface [17].

Indeed there are many aspects that affect the blocking behaviour of aryl films and some of these are connected with film properties. To obtain the highest blocking action the formed film should be as regular and compact as possible, also the thickness of the film is an important criteria. Modification conditions such as modification media, concentration of modifier, applied potential and modification time (or number of potential cycles) are the variables that affect the film properties and therefore also the blocking properties of the aryl films. Frequently, the multilayer films formed are loosely packed and this is an important consequence, when studying the blocking action of aryl films [90].

One of the main problems in studying the blocking properties of aryl films is related to the correct determination of surface concentration of aryl groups (Γ). There are only a few modifiers for which the value of Γ could be determined electrochemically, for instance nitrophenyl and quinone groups. An alternative approach is to employ various surface analytical techniques for this purpose.

4.3.2. Blocking properties of aryl-modified metal electrodes

It is of considerable interest to study metal electrodes modified with barrier layers of various organic compounds. The blocking behaviour of these films is of paramount importance in many fields (e.g. electrocatalysis, electroanalysis and protection against corrosion).

The barrier properties of aryl-modified Au electrodes for various solution-based redox species have been investigated and the blocking action depends on the properties of the modifier film [61,64,65,68].

The inhibition of electron transfer (ET) reactions by the attachment of aryl groups to gold electrodes have been studied using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) [65]. Typically, thicker and more compact films exhibit a stronger blocking behaviour but the nature of the modifier film and the ionisation of functional groups play an important role in determining the electrochemical response of these modified electrodes.

Laforgue et al. showed that a thin carboxyphenyl (CP) layer attached to gold did not alter the kinetics of ET for the $\text{Fe}(\text{CN})_6^{3-/4-}$ probe [64] and the peak potential separation was the same as for bare gold. Stronger inhibition was observed, however, by increasing the grafting time at a constant potential [64,74]. By contrast, Liu et al. observed that a CP film of submonolayer coverage suppressed electron transfer compared with bare gold [68]. Long-term sonication of the freshly prepared Au/CP electrode partially removed the modifier from the surface and the CV became similar to that of unmodified gold. Paulik

et al. studied the structure and properties of multilayer CP and methylphenyl (MP) films on gold [61]. The formation of porous films was in evidence. However, the voltammetric peaks of the $\text{Fe}(\text{CN})_6^{3-/4-}$ probe disappeared in the presence of an incomplete CP layer. This effect was explained by electrostatic repulsion between the $-\text{COO}^-$ groups and the $\text{Fe}(\text{CN})_6^{3-/4-}$ anions in solution. Both CP and MP multilayer films were affected by long time sonication, which changes their structure and electrochemical properties. Sonication of these functionalised Au electrodes in solvents of different polarities led to different interfacial electrochemistry and hydrophilicity, consistent with a dynamic surface structure that can reorganize in response to the environment [61]. The greater stability of functional residues attached using diazonium chemistry compared with thiol attachment has been recently demonstrated by Shewchuk and McDermott [79].

Surprisingly, the behaviour of the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple is not affected by the presence of a thick phenyl film on gold [59], whereas the CV response is completely inhibited on the Au electrodes modified with nitrophenyl (NP) groups [59]. Thick NP and diethylaniline films remarkably decrease the ferri/ferrocyanide electron transfer rate [64]. Electrode modification with aminophenyl groups appears to suppress the response of this redox probe even more strongly than the NP-modified Au electrodes [65]. In this case, AFM imaging showed that the thickness of the aminophenyl layer was approximately 25 nm. Modification of gold electrodes with (4-aminoethyl)benzenediazonium cations had little effect on the voltammetric response of the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple [69]. The degree of inhibition increases significantly by attaching glutathione to the modifier film. The EIS results indicate effective grafting of Au electrode surface with a fluorinated diazonium salt [62]. Some attempts have been made to obtain molecular level information regarding the binding of carbon to gold [92,93]. Similarly, electrografting of gold has also been achieved using iodonium salts [94].

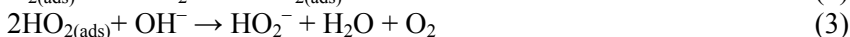
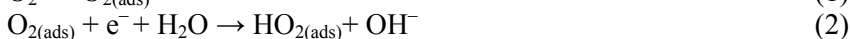
Aryl-modified gold electrodes provide a good platform for the development of biosensors [7]. Aminophenyl and carboxyphenyl groups are most suitable for the covalent attachment of DNA, enzymes, redox proteins, antibodies and cells. These techniques have been used, for example, for the immobilisation of horseradish peroxidase on a Au electrode surface [75,77] and therefore methods for the functionalisation of gold electrodes are of great current interest. Of these, spontaneous modification with aryl groups from diazonium salts solutions presents advantages in terms of simplicity and has been recently demonstrated [81–83].

The blocking behaviour of these films is of paramount importance in many fields, including electrocatalysis and electroanalysis. Up to now, there have been only a few studies of O_2 reduction on self-assembled monolayer-modified gold electrodes (SAM/Au) [95–99] and a single report on the reduction on 4-methylphenyl-modified GC electrodes [100]. The blocking action for O_2 reduction was also observed for fullerene monolayers on gold electrodes [101].

4.4. Oxygen reduction on bare carbon and on quinone-modified electrodes

The electrochemical reduction of oxygen on carbon materials generally yields hydrogen peroxide as the final product. The decomposition and reduction process of hydrogen peroxide on bare carbon surfaces which does not contain impurities or additives is very slow [102]. Oxygen reduction on bulk carbon electrodes in alkaline solution has been thoroughly investigated and several mechanisms have been proposed [103–112]. However, so far there is still no general agreement on the exact oxygen reduction mechanistic pathway.

Morcos and Yeager suggested a mechanistic scheme, where the reduction of adsorbed O_2 (Reaction (2)) is the rate-determining step, which is followed by disproportionation [103]:



Xu et al. have considered the following pathway [109]:



or



It was suggested that adsorption of $O_2^{\bullet-}$ on a carbon surface makes this species more basic and therefore accelerates its protonation (Reaction (5)), which is the rate determining step at $pH > 12$. At $pH < 10$, the first electron transfer (Reaction (4)) becomes rate-determining. At lower pH, adsorbed $HO_2^{\bullet}$ blocks the adsorption centres of O_2 and the reduction proceeds by the outer sphere route.

The electrocatalytic properties of carbon materials and also the proposed mechanism for the oxygen reduction reaction depend highly on the structure of a carbon material. On boron-doped diamond (BDD) and on the basal plane of highly ordered pyrolytic graphite (HOPG) this process is almost completely inhibited also in basic solution. However glassy carbon (GC) and pyrolytic graphite are quite active catalysts for the oxygen reduction reaction. The electrocatalytic properties also depend on the number of oxygen-containing functional groups, called as native quinone-type functionalities. It has been proposed that after oxidising the electrode the quantity of these groups arises, therefore also increasing the electrocatalytic activity of the electrode [106,107, 112]. The native quinone functionalities are present in a larger number on GC surface, but their concentration is very low on the basal plane of HOPG and on BDD. This could be the reason why the pre-wave of O_2 reduction is observed on GC, but not on BDD and HOPG and three orders of magnitude larger electron transfer rate constant for O_2 reduction on GC has been estimated [111].

Tryk et al. have reviewed the reduction of O_2 on different carbon materials and suggested that there are two distinct types of reduction processes [111]. In

the first process, the first electron transfer (Reaction (4)) is rate-determining and therefore it is not pH-dependent. The second process is considered to be electrocatalytically mediated by the quinone radical anions that are formed from native quinone-type functionalities on carbon surface at certain potentials [105].

Oxygen reduction on quinone-modified electrodes has been extensively studied and it has been demonstrated that they display excellent electrocatalytic properties [25,31–35,104,105,112–138]. Various quinones have been employed: 9,10-phenanthrenequinone (PQ) [25,33,105,121,124], 1,2-naphthoquinone (NQ) [124], 1,4-naphthoquinone and its derivatives [104,112,114,117,132–134], and most frequently, 9,10-anthraquinone (AQ) and its derivatives [25,31,32,34,104,105,116,118–125,131,135–138].

Detailed mechanistic aspects of this reaction have been obtained from quantum chemical calculations [127], which show that the anion radical of the quinone is responsible for their electrocatalytic activity [31,105]. In addition, entropic effects of the intermediates are important in determining the reaction channels followed. The reduction of O₂ on quinone-modified electrodes follows an electrochemical–chemical (EC) mechanism according to [31]:



followed by a chemical step:



The superoxide ion can undergo disproportionation



or further reduction to peroxide:



where Q is the surface quinone species. Reaction (9) is the rate determining step and in this reaction model, the overall rate is determined by the surface concentration of Q^{•−} [31,105]. Reactions (10) and (11) are considered to be fast and lead to the formation of peroxide although the preferred route to peroxide is most likely the further reaction of the O₂^{•−} intermediate [127]. Previous work demonstrated that the commercial diazonium salt of anthraquinone (AQ), Fast Red AL, could be easily used for surface grafting [31]. The resulting AQ-modified GC electrode showed a high electrocatalytic activity for oxygen reduction in alkaline solutions and as expected from the proposed mechanism (Reactions (8) and (9)), the rate of the chemical reaction between the semiquinone radical anion and molecular oxygen (Reaction (9)) depended linearly on the surface concentration of AQ [32]. It has been established that the electrocatalytic activity of surface-confined quinones greatly depends on their redox potential (*E*_f). For example the *E*_f of surface-bound phenanthrenequinone is higher by 300 mV as compared to that of AQ and as a consequence its O₂ reduction activity is significantly higher [33]. Various aspects of O₂ reduction electrocatalysis by quinones have been thoroughly reviewed by Sarapuu [139].

5. EXPERIMENTAL

5.1. Preparation of electrodes

For electrochemical measurements the following electrodes were used:

- A single-piece GC rotating disk electrode (Pine Research Instrumentation) with a geometric area of 0.196 cm^2 [I–IV]. RRDE measurements were carried out on a GC disk-Au ring electrode (Pine Research Instrumentation) [IV]. $A(\text{disk}) = 0.164\text{ cm}^2$. The collection efficiency (N) was 0.23 as determined by ferricyanide reduction.
- A nickel rotating disk electrode with a geometric area of 0.196 cm^2 . The disk was cut from Ni rod (99.995%, 5 mm in diameter, product of Alfa Aesar) and was pressed in a Teflon holder [V–VI].
- A gold rotating disk electrode with a geometric area of 0.196 cm^2 . The disk was cut from Au rod (99.99%, 5 mm in diameter, product of Alfa Aesar) and was pressed in a Teflon holder [VII–IX].

All the electrodes were polished before use to a mirror finish with 1.0 and $0.3\text{ }\mu\text{m}$ alumina slurries (Buehler) and cleaned by sonication in Milli-Q water (Millipore, Inc.) and isopropanol and/or in acetonitrile for 5 min.

The polished Au electrodes were electrochemically cleaned in Ar-saturated $0.5\text{ M H}_2\text{SO}_4$ by cycling the potential 50 times at 100 mV s^{-1} between -0.3 and 1.5 V vs. SCE. Sulphuric acid (96%, Suprapur) was supplied by Merck.

In some experiments, chemical polishing of Ni electrodes was carried out by immersing the electrodes in an etching solution, which consisted of 33 vol.% concentrated CH_3COOH , 33 vol.%. $(\text{CH}_3\text{CO})_2\text{O}$, 33 vol.% concentrated HNO_3 and 1 vol.% concentrated HCl for 2 min [V].

5.2. Modification procedures and aryl diazonium salts used

The following diazonium salts were used for surface grafting in this work: benzenediazonium tetrafluoroborate, biphenyldiazonium tetrafluoroborate, 1-naphthalenediazonium tetrafluoroborate, 2-naphthalenediazonium tetrafluoroborate, 1-anthracenediazonium tetrafluoroborate and 2-anthracenediazonium tetrafluoroborate (also AQ- N_2BF_4 and DBD salts mentioned below) were synthesised by Dr. Jerzy J. Paprotny at the University of Liverpool. The synthesis was made according to a published procedure [140]. Briefly, an ice-cooled solution of 50 mmol of NaNO_2 in 7.5 ml water was added slowly (dropwise $\sim 0.5\text{ h}$) to a mixture of 45 mmol of aryl amine in 30 ml of 48% HBF_4 cooled to $0\text{ }^\circ\text{C}$. The temperature was kept at $0\text{--}2\text{ }^\circ\text{C}$ while stirring the solution for an additional 0.5 h. The compound was filtered, washed once with ice cool HBF_4 , once with ice cool water, twice with ice cool ethanol and finally three

times with diethyl ether. The product was then dried in vacuum or air (yield up to 90%).

The synthetic procedure for the preparation of AQ-N₂BF₄ is as follows: 5 mmol of AQ-NH₂ is dissolved/suspended in 20 ml acetic acid and 10 ml of 48% HBF₄ is added. The suspension is cooled to 10–12 °C and 0.6 g of NaNO₂ is added in small portions within 30–60 min. The suspension is then stirred for 3 h. The off-white precipitate is filtered off, washed three times with water, then methanol and finally with diethyl ether and dried (yield 90%).

4-decylbenzenediazonium tetrafluoroborate (DBD) was synthesized according to a published procedure [84]. Briefly, DBD was prepared by the diazotization of 4-aminodecylbenzene (Aldrich) in fluoroboric acid and sodium nitrite [IX].

The covalent attachment of 4-nitrophenyl and 4-bromophenyl groups was performed using commercially available 4-nitrobenzenediazonium tetrafluoroborate, 97% (Aldrich) and 4-bromobenzenediazonium tetrafluoroborate (Aldrich) [II,VI,IX].

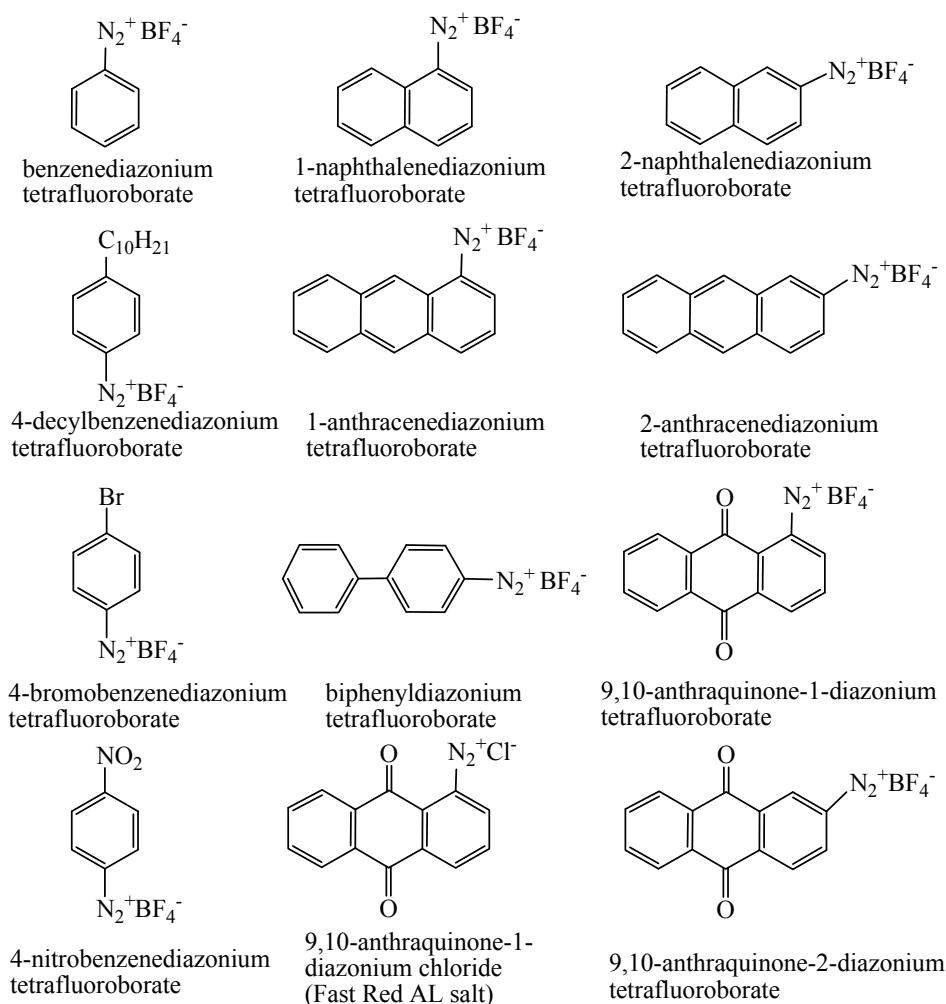
For some experiments (modification of nickel and spontaneous modification of GC) also commercially available 9,10-anthraquinone diazonium salt (Fast Red AL salt, Acros Organics) was used [III,V].

Chemical structures of the diazonium salts used are shown in Scheme 4.

Surface grafting was carried out in acetonitrile (ACN, Riedel-de Haën) containing 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄, Fluka) as base electrolyte. The concentration of the aryldiazonium salts was 1 mM [I,II,IV], 3 mM [VI,VII,VIII,IX] or 10 mM [V]. In some experiments modification was also carried out on acidic aqueous media (0.05 M H₂SO₄) where the diazonium salt concentration was 3 mM [VI,VII] or 10 mM [V].

The surface modification with *in situ* generated anthraquinone diazonium cations was performed in acetonitrile, ACN (Riedel-de Haën) containing 1 mM of 1-aminoanthraquinone, 1-AAQ (97%, Aldrich) or 2-aminoanthraquinone, 2-AAQ (84+%, Aldrich) and 0.1 M tetrabutylammonium tetrafluoroborate, TBABF₄ (Fluka) [IV]. Before use TBABF₄ was dried under vacuum at 80 °C for 24 h. 3 mM of *tert*-butyl nitrite (90%, Aldrich) was added 20 min before electrochemical grafting. The procedure for the covalent attachment of AQ using *in situ* generated diazonium cations in ACN was taken from Ref. [141].

In all cases, the electrografting was followed by sonication in acetonitrile for 5 min in order to remove the physically adsorbed material.



Scheme 4. Chemical structures of the diazonium salts used.

5.3. EQCM studies of film formation

The resonance frequency shifts were measured *in situ* with a Research Quartz Crystal Microbalance (RQCM, Maxtek). The working electrode used for the electrogravimetric measurements was a 5 MHz AT-cut quartz crystal with a gold film sputtered on a Ti layer ($A = 1.37 \text{ cm}^2$) (Maxtek). The microgravimetric studies were carried out in a GC-15 three-electrode glass cell that included a CHC-15 crystal holder, clamp, and stopper (Maxtek).

The surface was thoroughly cleaned before electrografting by cycling 30 times in N_2 -saturated 0.5 M H_2SO_4 between -0.2 and 1.5 V vs. SCE at

100 mV s⁻¹ and changing the solution three times. The surface modification of the working electrode for EQCM measurements was carried out in 0.1 M NaClO₄/ACN containing 3 mM 4-bromobenzenediazonium tetrafluoroborate (96%, Aldrich). [VIII] or 3 mM NBD [IX] or 3 mM Fast Red AL salt [VII]. NaClO₄·H₂O (99%) was supplied by Merck.

With Fast Red AL salt the surface modification was also carried out in 0.05 M H₂SO₄ containing 3 mM of the diazonium salt [VII]. Sulphuric acid p.a. quality was supplied by Merck.

The Sauerbrey equation was used assuming that the attached layer of AQ is rigid and no viscoelastic changes occur at electrode/solution interface: $\Delta m = -\Delta f/C_f$ [142], where Δm is the change of mass per unit area in g cm⁻²; Δf is the resonance frequency shift in Hz and C_f is the sensitivity factor of the crystal in Hz ng⁻¹ cm² [VII]. The EQCM measurements were carried out at the Federal University of Mato Grosso do Sul, Brazil.

5.4. Surface characterisation methods

All XPS measurements were carried out using SCIENTA SES-100 spectrometer. The pressure in the analysis chamber was below 10⁻⁹ Torr. For the X-ray photoelectron spectroscopy studies on gold, the gold Arrandee™ specimens (250±50) nm thick gold film deposited on a (2.5±1.5) nm chromium layer on borosilicate glass slides, (1.1×1.1 cm) were used [VIII,IX]. For the experiments on gold an unmonochromated Mg K α X-ray source energy (incident energy = 1253.6 eV), a take-off angle of 90° and a source power of 300 W, was used.

While collecting the survey scan of 4-bromophenyl film on gold, the following parameters were used: pass energy = 200 eV, step size = 0.5 eV, energy range = 600–0 eV [VIII]. For collecting the survey scan of 4-nitrophenyl film on gold energy range was 1100–0 eV and for the high-resolution scan in the N1s region: energy range = 415–380 eV, pass energy = 200 eV, step size = 0.1 eV [IX].

For the X-ray photoelectron spectroscopy studies on nickel, nickel plates of 12×12 mm² and 1 mm thick were used and an Al K α X-ray source (incident energy = 1486.6 eV), electron take-off angle = 90°. A source power of 400 W was used. While collecting the survey scan, the following parameters were used: energy range = 900–0 eV, pass energy = 200 eV, step size = 0.5 eV, and for the high resolution scan in the N1s region: energy range = 420–390 eV, pass energy = 200 eV, step size = 0.1 eV [VI]. The XPS measurements were performed by Dr. Leonard Matisen in the Institute of Physics, University of Tartu.

The surface morphology of AQ-modified [VII] Au(111) electrodes was studied by atomic force microscope 5500 Measurement System (Agilent Technologies) in non-contact mode using PPP-NCHR (Nanosensors™) cantilevers. The surface morphology of 4-bromophenyl-modified [VIII] and 4-nitrophenyl-modified [IX] Au(111) electrodes as well as that of the bare gold electrode was studied by AFM with a CP-II (PSI/Veeco) multimode microscope

in intermittent contact mode using a NSG01 series cantilevers (NT-MDT) under ambient conditions.

For all cases the Gwyddion™ free software (Czech Metrology Institute) was employed for image processing and surface roughness calculations. All images were processed by the first order flattening for background slope removal, and if necessary, the contrast and brightness were adjusted. A flat Au film deposited on mica sheets was used as a substrate for the AFM measurements. After annealing the Au film showed a preferential orientation of the (111) plane. Each AFM image presented is representative of numerous images taken on different locations of the sample [VII,VIII,IX]. The AFM measurements were performed by Jekaterina Kozlova [VIII] and Margus Marandi [VII,IX] in the Institute of Physics, University of Tartu.

5.5. Electrochemical instrumentation and measurements

The electrochemical studies of polished and aryl-modified electrodes were carried out by cyclic voltammetry in 0.1 M K_2SO_4 containing 1 or 5 mM $K_3Fe(CN)_6$ (Aldrich) and in 0.1 M H_2SO_4 containing 1 mM dopamine (Sigma).

The electrolyte solutions for studying O_2 reduction were prepared from KOH pellets (AristaR, BDH or pro analysi, Merck) in Milli-Q water and these were saturated with O_2 (99.999%, AGA or 99.95%, AGA) or deaerated with Ar gas (99.999%, AGA). An EDI101 rotator and a CTV101 speed control unit (Radiometer, Copenhagen) were used for the RDE experiments. A Pine Research Instrumentation (Grove City, PA, USA) AFMSRX rotator and MSRX speed controller were used for the RRDE experiments. A saturated calomel electrode (SCE) was employed as a reference and all the potentials are referred to this electrode. The counter electrode compartment of the three-electrode cell was separated from the main cell compartment by a glass frit and Pt wire served as a counter electrode. The potential was applied with an Autolab potentiostat PGSTAT10 or PGSTAT30 (Eco Chemie B.V., The Netherlands) and the experiments were controlled with General Purpose Electrochemical System (GPES) software. All experiments were carried out at room temperature ($23\pm 1^\circ C$).

6. RESULTS AND DISCUSSION

6.1. Electrochemical properties of modified GC electrodes

6.1.1. Oxygen electroreduction on chemically modified glassy carbon electrodes in alkaline solution

6.1.1.1. GC surface modification with aryl groups

The surface of GC electrodes was modified with phenyl (Ph), naphthyl (Naph) and anthracenyl (Anth) groups by electrochemical reduction of the corresponding diazonium salts. Figure 1 presents the cyclic voltammograms of electrografting of phenyl groups to the GC electrodes. The grafting behaviour of Ph to GC is very similar to previous observations [24]. The first potential scan showed a current peak of diazonium reduction at *ca* -0.17 V vs. SCE and the second reduction peak as a shoulder at more negative potentials. The first peak gradually disappeared during subsequent scans and the final voltammogram was featureless in the range of potentials from 0.6 to -1.2 V, indicating a complete blocking of the surface by phenyl layer. After such a potential program the GC electrode was held at -0.8 V for 10 min in order to improve the compactness of the Ph film. The electrografting behaviour of naphthalene and anthracene diazonium salts was qualitatively similar to that presented in Fig. 1. The peak potentials of the first cathodic scan were 0.04, 0.03, -0.02 and -0.06 V for the modification with Naph1, Naph2, Anth1 and Anth2, respectively. It appears that the reduction potential of all these aryldiazonium salts is rather similar, in agreement with previous studies [2].

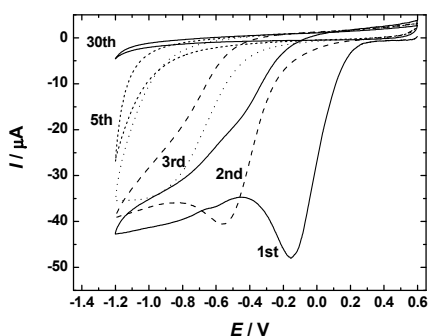


Figure 1. Electrochemical grafting of phenyl groups to GC in Ar saturated acetonitrile containing 1 mM $\text{C}_6\text{H}_5\text{N}_2^+$ and 0.1 M TBABF₄ at a sweep rate of 100 mV s^{-1} . The first, second, third, fifth and thirtieth potential scan are shown.

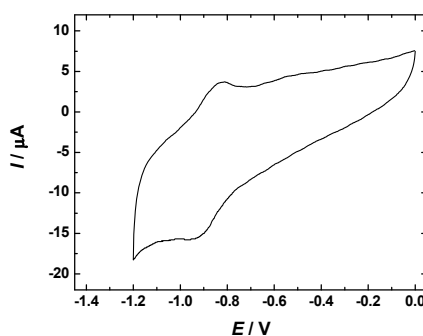


Figure 2. Cyclic voltammogram for a GC/AQ-Ph electrode in Ar saturated 0.1 M KOH. $\nu = 100 \text{ mV s}^{-1}$.

In addition, a mixed film of surface-bound anthraquinone and phenyl modifier was formed by the diazonium reduction method. In this case a submonolayer of AQ was formed first in 1 mM solution of AQ-N₂⁺ and then the GC/AQ electrode was further modified in ACN containing 1 mM Ph-N₂⁺. The grafting of AQ to GC was identical to that shown previously [31]. The potential profile used for the covalent attachment of Ph groups was different than that shown in Fig. 1. We found that the grafting of Ph in such a large potential region (between 0.6 and -1.2 V) led to a significant decrease in the current of AQ redox peaks in Ar-saturated 0.1 M KOH. We might speculate that at the reduction potential of AQ in ACN the formed AQ radical anion can react with phenyl radicals, therefore losing the quinone functionality in the mixed film. For this reason, the GC/AQ electrode was cycled only up to -0.6 V in the grafting experiment with Ph groups, followed by holding the electrode for 5 min at the same potential (-0.6 V). The cyclic voltammetric response of the GC/AQ-Ph electrode in Ar-saturated 0.1 M KOH is shown in Fig. 2. The redox potential of surface-bound AQ was found to be -0.86 V, very close to the value previously reported (-0.845 V [31]). The surface concentration of AQ was determined from charge integration under the CV peaks ($\Gamma_{AQ} = 1.6 \times 10^{-10}$ mol cm⁻²).

6.1.1.2. O₂ reduction on aryl-modified GC electrodes

In this work an attempt has been made to systematically investigate the oxygen reduction behaviour on GC electrodes modified with aryl layers. We started with oxygen reduction on an unmodified GC, which was used as a substrate material in further investigations. For comparison purposes, a set of RDE voltammetry curves of O₂ reduction on a bare GC electrode is presented in Fig. 3. This process has been studied by many groups [100,104,106,107,109] and the data are shown here because of the application of higher rotation rates than in the previous studies [31]. The application of higher values of ω is advantageous for the determination of kinetic parameters of O₂ reduction (Section 6.1.1.4.). As stated earlier, the reduction of oxygen follows a two-electron pathway on a polished GC electrode in alkaline solutions [31].

There are notable differences in the oxygen reduction behaviour on a GC/Ph electrode as compared to that of bare GC (Fig. 4). Most importantly, the first reduction peak at *ca* -0.5 V is remarkably suppressed and instead of a well-defined peak, a gradual increase of current is observed, which commences at more negative potentials than in Fig. 3.

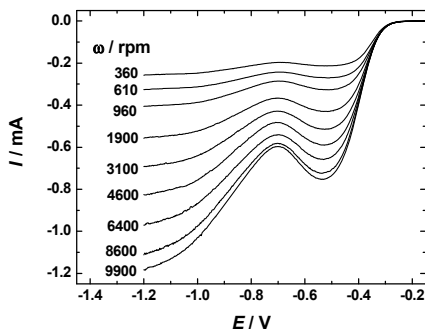


Figure 3. RDE voltammetry curves for oxygen reduction on a bare GC electrode in O_2 saturated 0.1 M KOH. $\nu = 20 \text{ mV s}^{-1}$.

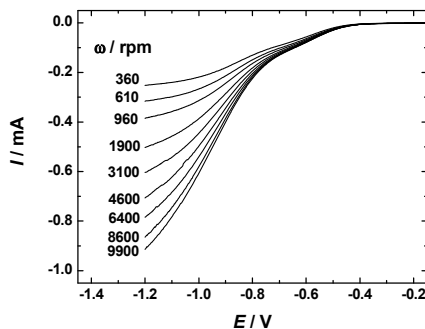


Figure 4. RDE voltammetry curves for oxygen reduction on a GC/Ph electrode in O_2 saturated 0.1 M KOH. $\nu = 20 \text{ mV s}^{-1}$.

Obviously, the phenyl layer blocks those active sites on the surface of GC, which are responsible for the high reduction current at pre-wave potentials. The exact nature of these sites is not clear at the moment, but according to the literature data, these could be quinone-type species [104]. It has been proposed recently that surface carbon-oxygen groups are not covalently modified by reduction of benzenediazonium ions [24]. Based on these considerations one cannot expect an essential change in the O_2 reduction behaviour caused by the phenyl layer. Nevertheless, we may assume that the interaction between surface functional groups and molecular O_2 is sterically hindered by neighbouring Ph groups and this could result in the decreased oxygen reduction activity of the most active GC surface sites.

Also, the second O_2 reduction wave is shifted to more negative potentials for the GC/Ph electrode. However, it should be noted that the barrier properties of Ph groups are not efficient enough to completely suppress the oxygen reduction activity of the modified electrode. Apparently, a part of the surface of the underlying GC electrode is available for O_2 molecules. It is difficult to estimate the uncovered area of GC and no such effort has been undertaken in the present work. There are two principle options to determine the surface coverage of covalently attached compounds. One can use an electrochemical determination, provided that the modifier molecule has an electroactive functionality (for instance, nitrophenyl group is frequently used) or alternatively, various surface analytical techniques can be employed [2].

The oxygen reduction behaviour of GC/Naph and GC/Anth electrodes is analogous to that of GC/Ph (see Figs. 5 and 6), however, some differences are also in evidence. It is clearly seen that the pre-wave current at -0.6 V is higher on GC/Naph1 and GC/Naph2 and even higher on GC/Anth1 and GC/Anth2 than on the GC/Ph electrode. These experiments have been repeated for several

times and we have always observed the same tendency. Such behaviour was not expected on the basis of barrier properties of monolayers of various thicknesses.

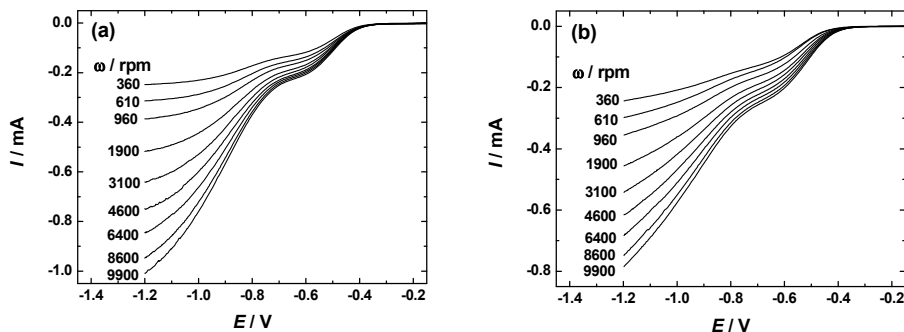


Figure 5. RDE voltammetry curves for oxygen reduction on GC/Naph electrodes in O_2 saturated 0.1 M KOH: (a) GC/Naph1 and (b) GC/Naph2 electrodes. $\nu = 20 \text{ mV s}^{-1}$.

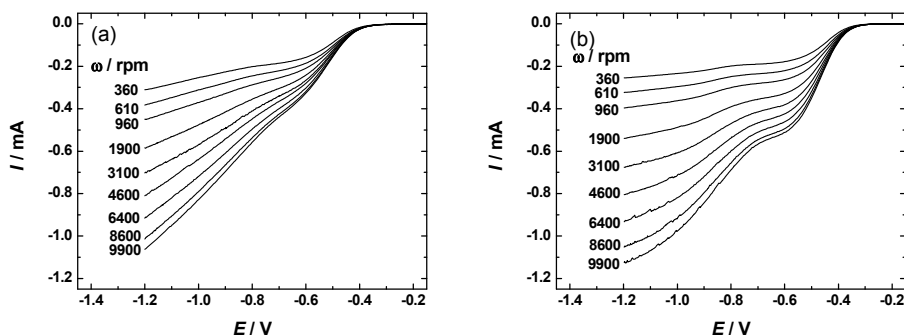


Figure 6. RDE voltammetry curves for oxygen reduction on GC/Anth electrodes in O_2 saturated 0.1 M KOH: (a) GC/Anth1 and (b) GC/Anth2 electrodes. $\nu = 20 \text{ mV s}^{-1}$.

The dependence of the electron transfer rate on film thickness should be observed for those systems in which the through-layer tunnelling is the only charge transfer mechanism. Surface-bound anthracene (monolayer thickness was calculated to be 0.99 nm for the attachment in position 2) is assumed to provide a thicker barrier towards solution based redox species than naphthyl (0.76 nm, attachment in position 2) and phenyl groups (0.54 nm) and therefore should inhibit the reduction of O_2 to a larger degree. However, the order of electrocatalytic activities of the GC electrodes modified with the aryl groups does not follow this assumption, i.e. the half-wave potential of O_2 reduction ($E_{1/2}$) decreases in the following sequence GC > GC/Anth2 > GC/Anth1 > GC/Naph1 > GC/Naph2 > GC/Ph (Fig. 7). The estimation of monolayer thicknesses for naphthyl and anthracenyl groups attached in position 1 is even

more difficult task, because the exact orientation of these moieties is unknown. Most of the previous reports have been concentrated on the study of phenyl layers. The surface concentration for a close-packed monolayer for Ph groups was estimated to be $1.35 \times 10^{-9} \text{ mol cm}^{-2}$ [2]. Unfortunately, the studying of the coverage of surface-bound naphthyl and anthracenyl groups is relatively scarce. Two groups of researchers have estimated the surface concentration of 1-naphthylmethyl groups ($\Gamma = 1.5 \times 10^{-10} \text{ mol cm}^{-2}$ [143] and $\Gamma = 1.6 \times 10^{-10} \text{ mol cm}^{-2}$ [144]). This layer was formed by the electrochemical oxidation of the carboxylate substituent. Note, that there is a $-\text{CH}_2-$ linkage between the naphthyl group and the electrode surface which allows rotation around the linkage group. Therefore, the surface area occupied by a naphthylmethyl group might be much higher than that in the absence of the linkage group. However, the formation of multilayers was in evidence on the basis of AFM results as shown by Brooksby *et al.* [144]. The most convenient method of the estimation of the modifier coverage is based on the application of solution redox species. The extent at which the response of these redox couples is suppressed is related to the surface coverage of the modifier.

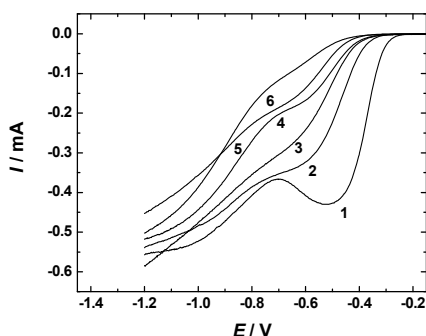


Figure 7. Comparison of current-potential curves for oxygen reduction on bare GC and electrochemically grafted GC electrodes in O_2 saturated 0.1 M KOH: (1) bare GC, (2) GC/Anth2, (3) GC/Anth1, (4) GC/Naph1, (5) GC/Naph2 and (6) GC/Ph. $\omega = 1900 \text{ rpm}$). Data from Figures 3–6.

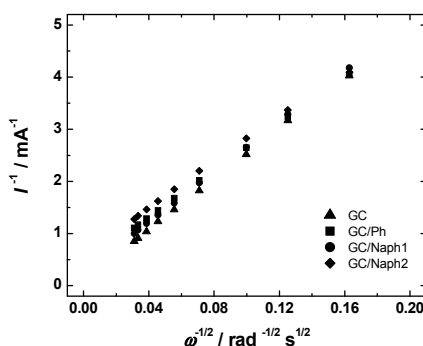


Figure 8. Comparison of Koutecky-Levich plots for oxygen reduction on bare GC, GC/Ph, GC/Naph1 and GC/Naph2 electrodes in O_2 saturated 0.1 M KOH. $E = -1.2 \text{ V}$.

The O_2 reduction results obtained with aryl-modified GC electrodes in the present work could be explained in a different way than that stated in the literature about the electron-transfer behaviour of larger redox couples (for instance, $\text{Fe}(\text{CN})_6^{3-/4-}$ [17,24]). We may assume that the covalently attached aryl film is disordered on the surface of GC. There is also a question about the surface coverage of these films as mentioned above. The formation of multi-

layers is another possibility, which may occur in the electrochemical reduction of aryldiazonium cations (Scheme 2). The presence of a multilayer does not necessarily mean that the underlying substrate surface is completely blocked by modifier molecules, even though their total amount may exceed the monolayer coverage. It has been proposed that the second layer may grow by the covalent binding of aryl radicals to aryl moieties already attached to the substrate surface [9,18], even in case of a submonolayer coverage in the first layer. The O₂ reduction results presented above can be interpreted as follows: phenyl groups cover the surface of GC to a larger extent as compared to those of Naph or Anth, or alternatively the films formed by covalent bonding of the latter modifiers are more disordered.

The RDE data of O₂ reduction were treated according to the Koutecky-Levich (K-L) method of analysis. The K-L lines of bare GC, GC/Ph, GC/Naph1 and GC/Naph2 electrodes were almost parallel (Fig. 8) and from the slope of these lines the number of electrons transferred per O₂ molecule (n) was calculated. The data were analysed using the K-L equation [145]:

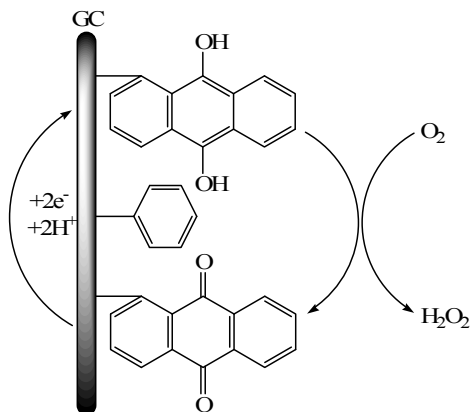
$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_d} = -\frac{1}{nFAkC_{O_2}^b} - \frac{1}{0.62nFAD_{O_2}^{2/3}\nu^{-1/6}C_{O_2}^b\omega^{1/2}} \quad (12)$$

where I is the measured current, I_k and I_d are the kinetic and diffusion-limited currents, respectively, k is the rate constant for O₂ reduction, F is the Faraday constant (96484 C mol⁻¹), A is the electrode area, ω is the rotation rate, $C_{O_2}^b$ is the concentration of oxygen in the bulk (1.2×10⁻⁶ mol cm⁻³ [146]), D_{O_2} is the diffusion coefficient of oxygen (1.9×10⁻⁵ cm² s⁻¹ [146]) and ν is the kinematic viscosity of the solution (0.01 cm² s⁻¹ [147]).

The value of n was close to two for all the electrodes shown in Fig. 8. However, for GC/Anth1 and GC/Anth2 electrodes $n > 2$ at high negative potentials. The kinetic component of current was obtained by the extrapolation of the K-L lines to the infinite rotation rate. As expected, the extent of inhibition of O₂ reduction estimated on the bases of the kinetic current data follows approximately the same order as that of the half-wave potential and could be explained by different coverage of covalently attached groups. The higher the modifier coverage, the smaller the number of GC sites available for O₂ reduction.

We have also tested the response of GC/AQ-Ph electrodes towards O₂ reduction (Fig. 9). These mixed films were prepared by two separate modifications using the diazonium salts of AQ and Ph, respectively. The reduction of oxygen on GC/AQ electrodes has been well documented [31,32] and the idea of using Ph groups was to further block the GC surface sites not covered by AQ molecules. Indeed, the effect of surface-bound Ph is clearly evident, because the prewave of O₂ reduction is almost entirely suppressed (Fig. 9). There are important consequences of this effect in the determination of kinetic parameters

of O_2 reduction (see Section 6.1.1.4.). In this electrode architecture the Ph groups act as spectator species and the electrocatalysis of O_2 reduction proceeds only on AQ sites (Scheme 5).



Scheme 5. Schematic representation for the electrochemical production of hydrogen peroxide on GC/AQ-Ph electrodes.

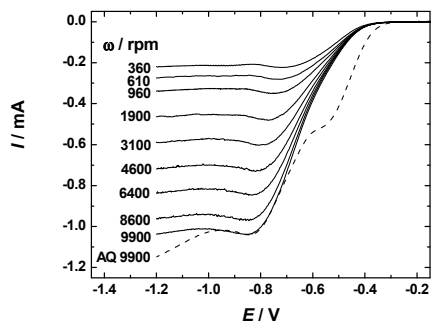


Figure 9. RDE voltammetry curves for oxygen reduction on a GC/AQ-Ph electrode in O_2 saturated 0.1 M KOH at a sweep rate of 20 mV s^{-1} . Electrode modified in a two-step procedure, first in 1 mM AQ- N_2^+ and then in 1 mM $C_6H_5N_2^+$ in acetonitrile containing 0.1 M TBABF₄. Curve AQ 9900 corresponds to GC/AQ. $\omega = 9900 \text{ rpm}$.

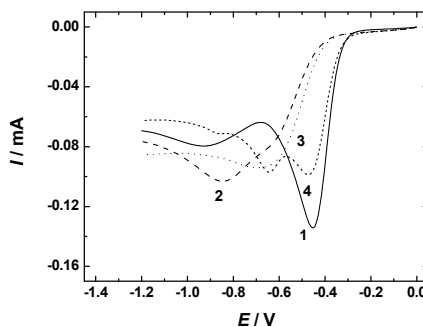


Figure 10. Comparison of linear sweep voltammograms for oxygen reduction in O_2 saturated 0.1 M KOH on: (1) bare GC, (2) GC/Ph, (3) GC/Anth1 and (4) GC/AQ electrodes. $\nu = 100 \text{ mV s}^{-1}$.

6.1.1.3. LSV studies of O₂ reduction

Linear sweep voltammetry (LSV) was also used in the O₂ reduction studies. LSV curves of O₂ reduction are shown in Fig. 10. There are two peaks observed on LSV voltammograms for the unmodified GC electrode. The first sharp peak appears at -0.45 V and the second peak of much lower current is seen at *ca* -0.9 V. Such LSV response is typical for a bare GC electrode and has been observed in many studies [100,109]. For the GC/AQ electrode the first peak appears at the same potential as for GC, but its current value is lower. The second peak is observed at much more positive potentials (at -0.65 V), which indicates about the involvement of the AQ sites in the reduction of oxygen. The LSV behaviour of GC/Ph and GC/Anth1 electrodes presented in Fig. 10 is significantly different than that of the unmodified GC electrode. The first sharp peak at -0.45 V is completely absent for these two electrodes. The LSV curve of the GC/Ph electrode is shifted to more negative potentials, in agreement with the RDE results of O₂ reduction presented above.

6.1.1.4. Determination of O₂ reduction kinetic parameters on GC modified with AQ and Ph groups

A redox-catalytic cycle model of quinone-modified electrodes developed by Schiffrin in 2001 [31] was used for the determination of kinetic parameters for oxygen reduction. It is assumed that the reactive species in the oxygen reduction reaction is the semiquinone radical anion ($Q^{\bullet-}$), which is formed in the one-electron reduction of surface-confined quinones (Reaction (8)). In the following chemical step the radical reacts with molecular oxygen yielding the superoxide radical anion (Reaction (9)). This reaction is considered to be the rate limiting step in the overall reduction of oxygen on quinone-modified electrodes. The following transformation of $O_2^{\bullet-}$ by either electrochemical reduction or disproportionation (Reactions (10) and (11)) are considered to be fast and both processes yield hydroperoxide anion (HO_2^-) as the final product of O₂ reduction in alkaline solutions. The overall O₂ reduction current is a function of the surface concentration of the semiquinone radical anion ($\Gamma_{Q^{\bullet-}}$). The expression for the potential dependence of $\Gamma_{Q^{\bullet-}}$ was derived in Ref. [31]. Besides

quinone-type sites there are also free carbon sites on the surface of GC and the reduction of O₂ is assumed to proceed on these sites according to the Butler-Volmer relationship. Therefore the model equation used for the calculation of kinetic parameters of O₂ reduction is as follows:

$$\frac{1}{j} = \frac{1}{j_{dl}} - \left[2Fc_{O_2}^b k^0 e^{-f\alpha(E-E^0)} + \frac{2Fc_{O_2}^b k_c \Gamma}{1 + e^{\frac{f(E-E^0_{Q/Q^{2-}})}{2}} + e^{\frac{-f(E-E^0_{Q/Q^{2-}})}{2}}} \right]^{-1} \quad (13)$$

where j_{dl} is the diffusionally controlled limiting current density; $k^{0'}$ is the apparent electrochemical rate constant for O_2 reduction on the free carbon surface and α is the corresponding transfer coefficient; E^0 is the standard potential of the O_2/HO_2^- couple (-0.065 V vs. SHE); k_c is the rate constant of the reaction between semiquinone and molecular oxygen; Γ is the surface concentration of the quinone species; $E_{Q/Q^{2-}}^0$ is the standard potential of the surface Q/Q^{2-} couple; ΔE is the difference between the standard potentials of the $Q^{\bullet-}/Q^{2-}$ and the $Q/Q^{\bullet-}$ couples; $c_{O_2}^b$ is the concentration of O_2 in the bulk, F is the Faraday constant and $f = F/RT$.

The kinetic parameters for O_2 reduction have been calculated by the non-linear regression (NLR) method [31,148]. For the GC/AQ electrode a two-quinone model was used in the previous studies in which the chemical rate parameter $k_1\Gamma_1$ corresponded to the native quinone-type sites on GC and $k_2\Gamma_2$ to those of the attached AQ [31,32,120,121]. In the present work the native sites are almost entirely blocked by phenyl groups on the GC/AQ-Ph electrode (see Fig. 9) and for this reason, the one-quinone model can be used for the determination of kinetic parameters of O_2 reduction. Therefore the chemical rate parameters $k_c\Gamma$ determined in this work should be compared with those of $k_1\Gamma_1$ and $k_2\Gamma_2$ for the native quinone sites of bare GC and surface-bound AQ, respectively. Table 1 lists the kinetic parameters of O_2 reduction for the bare GC and GC/AQ-Ph electrodes studied. The NLR results obtained for a bare GC electrode confirm our previous observations [31,32]. The only difference in experimental conditions used in this work is a much higher electrode rotation rate employed. Higher ω values should allow a more reliable determination of the kinetic parameters. For the first time, we have studied the reduction of oxygen on a mixed AQ and Ph film. As mentioned above, the grafting of GC/AQ electrodes with Ph groups further blocks the electrocatalytically active sites of the underlying GC electrode. As a result, the shape of the polarisation curve of O_2 reduction changes. The contribution of native GC sites to the overall reduction of oxygen at prewave potentials is negligible (cf. Figs. 3 and 9) and for this reason we could employ the one-quinone model in the determination of kinetic parameters for O_2 reduction. The parameter values that are related to surface-bound AQ ($E_{Q/Q^{2-}}^0$, ΔE , $k_c\Gamma$) are in a good agreement with those determined for GC/AQ electrodes of the same surface concentration of AQ using a two-quinone model [32] (see Table 1). The value of the chemical rate parameter ($k_c\Gamma$) is much higher for the GC/AQ-Ph and GC/AQ electrodes as compared to that of bare GC. The obvious reason for this difference relies on the remarkably higher surface coverage of covalently attached AQ. Unfortunately, we have not been able to determine the coverage of active carbon-oxygen groups on polished GC, because no cyclic-voltammetric peak is in evidence.

Table 1. The average values of kinetic parameters for oxygen reduction on polished GC and GC/AQ-Ph electrodes in O₂ saturated 0.1 M KOH ($\Gamma_{\text{AQ}} = 1.6 \times 10^{-10}$ mol cm⁻²).

Electrode	$E_{\text{Q/Q}^{2-}}^0$ (V)	$10^4 k^0$, (cm s ⁻¹)	α	ΔE (V)	$k_c \Gamma$ (cm s ⁻¹)
Bare GC	-0.53 ± 0.01	8.2 ± 1.6	0.21 ± 0.01	-0.23 ± 0.01	0.027 ± 0.001
GC/AQ-Ph	-0.81 ± 0.01	5.5 ± 1.8	0.17 ± 0.02	-0.29 ± 0.02	0.078 ± 0.003
GC/AQ	-0.86 ± 0.01	4.0 ± 2.0	0.19 ± 0.02	-0.29 ± 0.01	0.072 ± 0.004

The parameters were calculated by NLR analysis [31,148]. The parameter values for GC/AQ electrode ($\Gamma_{\text{AQ}} = 1.9 \times 10^{-10}$ mol cm⁻²) [32] are given for comparison purposes.

There have been many studies of O₂ reduction on quinone-modified carbon electrodes [25,31–35,104,105,112–138]. In most of these studies the electrodes with physically adsorbed quinones have been employed. However, these compounds tend to desorb from the electrode surface, especially in alkaline solutions. The main advantage of the covalent attachment of quinones is that the modified electrodes are stable for long-term application. The redox-catalytic cycle model presented above is an invaluable tool in order to determine the kinetic parameters of O₂ reduction for quinone-modified electrodes.

6.1.1.5. Fe(CN)₆^{3-/4-} redox process on aryl-modified GC electrodes

The Fe(CN)₆^{3-/4-} redox couple was used as a benchmark system in order to study the barrier properties of aryl layers on GC electrodes [149]. There is experimental evidence that the Fe(CN)₆^{3-/4-} couple should interact with the GC surface for a fast electron transfer (ET) to occur [89]. Apparently, blocking the surface by aryl moieties should inhibit the rate of ET of this couple. Fig. 11 presents the RDE voltammetry curves recorded in the solution of 1 mM Fe(CN)₆³⁻. It is clearly evident that all the aryl-modified electrodes used remarkably suppress the reduction current. However, we observed some scatter in the RDE data which primarily arises from fine differences in the preparation of aryl-modified electrodes, even though the same procedure of modification was used. Therefore we did not succeed in determining the correct order of blocking efficiencies for the aryl-modified GC electrodes studied. Fig. 12 shows the cyclic voltammetric response of GC/Ph, GC/Naph1, GC/Anth1, and bare GC electrodes towards the Fe(CN)₆^{3-/4-} redox couple. A quasi-reversible redox behaviour was observed for unmodified GC, whereas the CV curves of aryl-modified GC electrodes were almost featureless in agreement with previous observations [17–24].

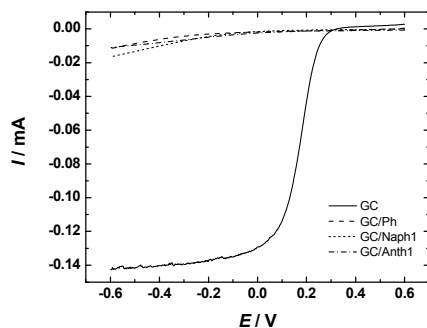


Figure 11. Representative RDE voltammetry curves for ferricyanide reduction on bare GC and aryl-modified GC electrodes in Ar-saturated 0.1 M K_2SO_4 containing 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$. $\nu = 20 \text{ mV s}^{-1}$. $\omega = 1900 \text{ rpm}$.

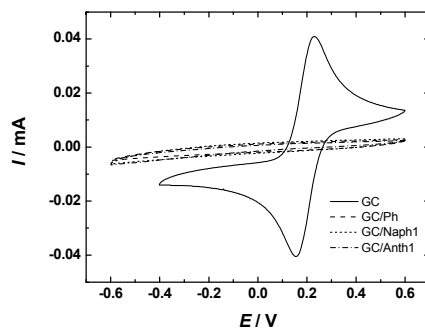


Figure 12. Cyclic voltammograms recorded in Ar-saturated 0.1 M K_2SO_4 containing 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ for bare GC, GC/Ph, GC/Naph1 and GC/Anth1 electrodes. $\nu = 100 \text{ mV s}^{-1}$.

Obviously, the electron transfer process is more efficiently inhibited by aryl groups for larger redox species. The size of the $\text{Fe}(\text{CN})_6^{3-}$ ion (diam. 0.62 nm) was calculated on the basis of the data on bond-length taken from the literature [150]. The disordered areas or defect sites of the aryl film formed by diazonium reduction are easily available for smaller molecules like O_2 (bond length 0.12 nm [147]) and therefore its reduction is less hindered by aryl groups as compared to that of ferricyanide.

6.1.2. Electrochemical behaviour of glassy carbon electrodes modified with aryl groups

6.1.2.1. Electrografting of GC surface with aryl groups

Glassy carbon surface was modified with biphenyl (BP), 1-naphthyl (Naph1), 2-naphthyl (Naph2), 4-bromophenyl (PhBr), 4-decylphenyl (DP) and 4-nitrophenyl (NP) groups by electrochemical reduction of the corresponding diazonium salts. Figure 13 presents the first modification cycle of electrografting of the aryl groups to the GC electrodes. In all cases the first peak gradually disappeared during subsequent scans and the final voltammogram was featureless in the range of potentials from 0.5 to -1.0 V , indicating a complete blocking of the surface by aryl layers. The electrografting behaviour of aryl diazonium derivatives used was qualitatively similar (Fig. 13).

The peak potentials of the first cathodic scan were as follows: $E_{p,\text{BP}} = -0.24 \text{ V}$, $E_{p,\text{Naph1}} = -0.23 \text{ V}$, $E_{p,\text{Naph2}} = -0.28 \text{ V}$, $E_{p,\text{PhBr}} = -0.39 \text{ V}$, $E_{p,\text{DP}} = -0.33 \text{ V}$ and $E_{p,\text{NP}} = 0.04 \text{ V}$ vs. SCE. It appears that the reduction potential of all

these aryldiazonium salts is rather similar, in agreement with previous studies, (GC/BP -0.15 V [15], GC/PhBr -0.35 V [89] and GC/NP 0.04 V [5,15]). The only exception is the positive potential of the reduction of nitrobenzenediazonium cations. This is due to the presence of nitro group. Due to the attachment of aryl groups the CV response is more complex than that of solution based redox species undergoing only electron transfer step at the electrode surface.

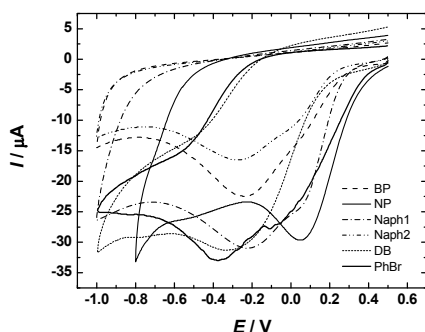


Figure 13. Electrochemical grafting of aryl groups to glassy carbon in Ar saturated acetonitrile containing 1 mM of the corresponding aryldiazonium salt and 0.1 M TBABF₄ at the sweep rate of 100 mV s^{-1} .

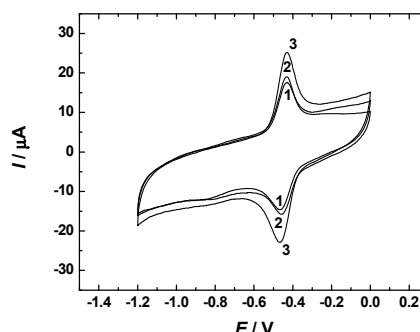


Figure 14. Stabilised CV curves for GC/NP electrodes in Ar-saturated 0.1 M KOH at a sweep rate of 100 mV s^{-1} . Modification conditions: (1) Procedure 1, (2) Procedure 2 and (3) Procedure 3. Electrodes were electrochemically modified in acetonitrile containing 1 mM of the corresponding diazonium salt and 0.1 M TBABF₄.

After modification the surface concentration (Γ) of nitrophenyl groups for GC/NP electrodes was estimated. Fig. 14 shows the CV response of the GC/NP electrodes in O₂-free 0.1 M KOH. Surface concentrations were determined by charge integration under the voltammetric peaks according to $\Gamma = Q/nFA$, where Q is the charge under the peak, n is the number of electrons involved (n is considered to be 2), F is the Faraday constant and A is the electrode area ($A = 0.196 \text{ cm}^2$). The procedure for the estimation of the Γ values was taken from ref. [151].

The surface modification by cycling the potential once between 0.5 and 0.1 V (Procedure 1), resulted in the value of $\Gamma = 3.3 \times 10^{-10} \text{ mol cm}^{-2}$. Modification with one full cycle (Procedure 2) and 20 cycles (Procedure 3) between 0.5 and -0.8 V gave surface concentrations of 3.5×10^{-10} and $5.8 \times 10^{-10} \text{ mol cm}^{-2}$, respectively. The theoretical monolayer coverage is $1.25 \times 10^{-9} \text{ mol cm}^{-2}$ [10]. Therefore, the surface coverage of NP groups is less than a monolayer. We may assume that the coverage of other aryl groups used in present work follow a similar trend to that of surface-bound NP groups. Unfortunately, the surface coverages of all other aryl films remain unknown, because these modifiers are not electroactive.

6.1.2.2. Oxygen reduction on aryl-modified GC electrodes

In the present work an attempt has been made to systematically study the oxygen reduction reaction on GC electrodes modified with aryl layers of different surface coverage. Figure 15 presents the RDE voltammetry curves of O_2 reduction on a GC/BP electrode in O_2 saturated 0.1 M KOH solution. For comparison purposes, a polarisation curve of O_2 reduction on a bare GC electrode at 9900 rpm is also shown in Fig. 15. The oxygen reduction behaviour of a GC/BP electrode differs notably as compared to that of bare GC. The first reduction peak at *ca* -0.5 V is remarkably suppressed and the reduction wave commences at more negative potentials than that of the unmodified GC electrode.

The Koutecky–Levich analysis (dependence of $I^{-1/2}$ on $\omega^{-1/2}$) of the RDE data on O_2 reduction is shown in Fig. 16. The number of electrons transferred per O_2 molecule (n) was calculated from these plots using the K–L equation [145].

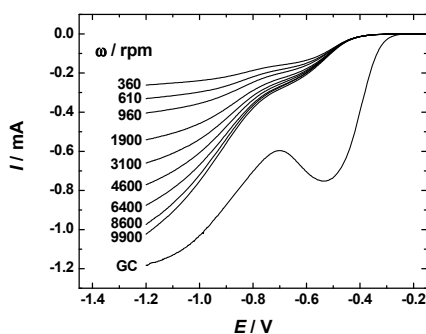


Figure 15. RDE voltammetry curves for oxygen reduction on a GC/BP electrode in O_2 saturated 0.1 M KOH. $v = 20 \text{ mV s}^{-1}$. Electrode was modified using Procedure 3. The curve GC corresponds to the reduction of O_2 on a polished GC electrode at $\omega = 9900 \text{ rpm}$.

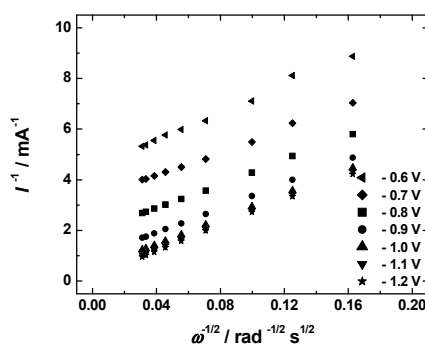


Figure 16. Koutecky–Levich plots for oxygen reduction on a GC/BP electrode in O_2 -saturated 0.1 M KOH solution. Data derived from Figure 15.

The value of n was close to two for GC/BP electrode for the entire range of potentials studied, indicating that the process of O_2 reduction on these electrodes yields hydrogen peroxide as the final product. It is also evident that the reduction of O_2 is under the mixed kinetic–diffusion control even at high negative potentials.

The effect of different modification procedures on the RDE voltammetry curves for oxygen reduction on aryl modified GC electrodes in O_2 saturated 0.1 M KOH is shown in Fig. 17.

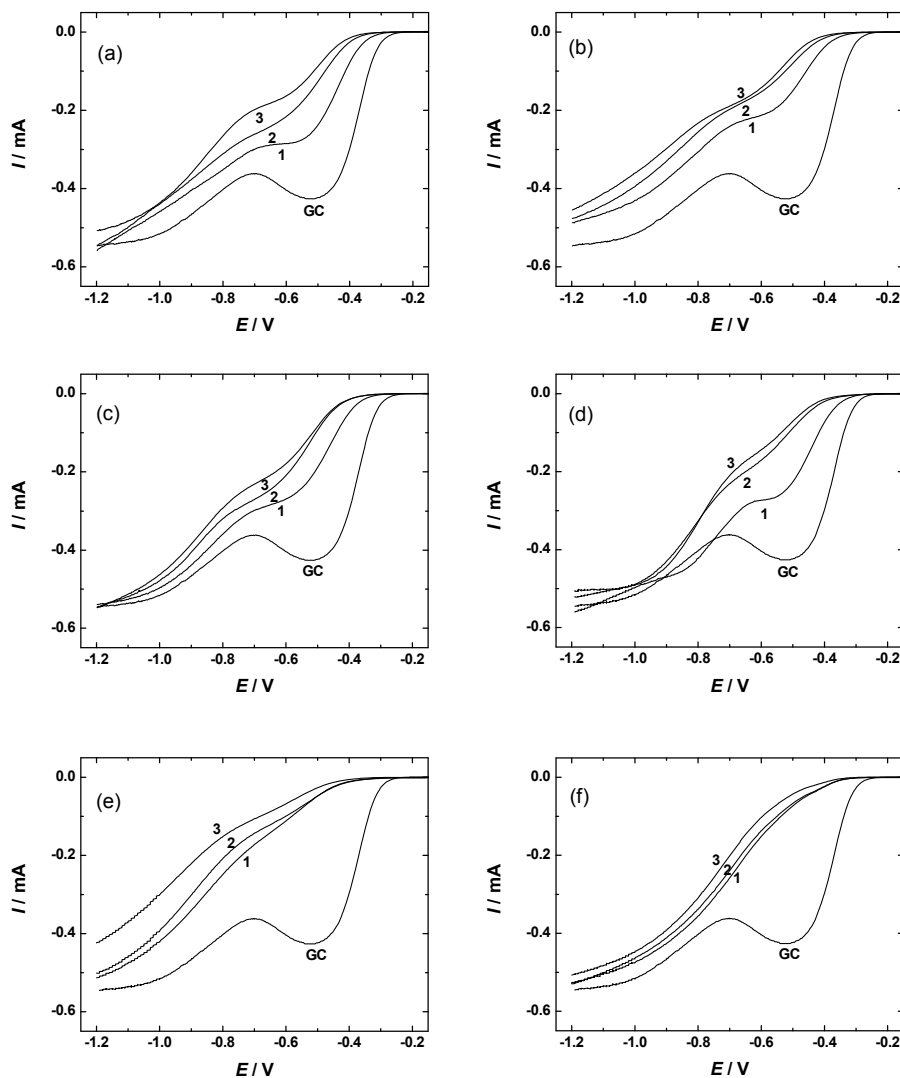


Figure 17. RDE voltammetry curves for oxygen reduction on: (a) GC/Naph1, (b) GC/Naph2, (c) GC/BP, (d) GC/DP, (e) GC/PhBr and (f) GC/NP electrodes in O_2 saturated 0.1 M KOH ($\omega = 1900$ rpm, $\nu = 20$ mV s $^{-1}$). Modification conditions: (1) Procedure 1, (2) Procedure 2 and (3) Procedure 3. Electrodes were electrochemically modified in acetonitrile containing 1 mM of the corresponding diazonium salt and 0.1 M TBABF $_4$. Curve GC corresponds to the voltammetry curve of O_2 reduction on a bare GC electrode.

It can be seen that already a very short modification program i.e. by applying Procedure 1 (Fig. 17, curve 1) suppresses the oxygen reduction current significantly and shifts the first reduction peak to more negative potentials as

compared to that of the bare GC electrode (Fig. 17, curve GC). Electrode surface modification by Procedure 2 (Fig. 17, curve 2) suppressed the reduction current even more.

Procedure 3 used for the modification of GC electrodes (Fig. 17, curve 3) suppresses the peak current even further and instead of a well-defined peak there is almost a gradual increase of reduction current. Twenty modification cycles seems to yield maximum surface coverage and no significant change in the shape of the oxygen reduction voltammetry curves could be observed with increasing the number of modification cycles.

Obviously, all the aryl layers studied even with quite low coverage block at least in part those active sites on the surface of GC, which are responsible for the high reduction current at pre-wave potentials. The exact nature of these sites is not clear at the moment, but according to the literature data, these could be quinone-type species [31,104,105]. It has been proposed recently that surface carbon-oxygen groups are not covalently modified by electrochemical reduction of benzenediazonium cations [24]. However, this claim is not justified. There are several reports on the modification of oxide surfaces by diazonium reduction [46,152].

We have recently proposed that the interaction between surface functional groups and molecular O₂ is sterically hindered by aryl groups attached to neighbouring sites and this could result in the decreased oxygen reduction activity of the most active GC surface sites [I].

Nevertheless, it is evident that even modification by 20 potential cycles (Procedure 3) does not give completely blocked surface and therefore we may assume that the formed aryl layer is not uniform and has defects through which the oxygen reduction can still take place, however, in a significantly lower rate. The formation of an incomplete or loosely packed film is the obvious reason why a relatively large reduction current is observed at high negative potentials. For several aryl-modified electrodes the value of current at -1.2 V is very close to that of bare GC.

Recently, it has been proposed that the aryl radicals (Ar[•]) formed during the diazonium reduction can react with the quinone groups [153]. One can also assume that such a reaction may occur with the centers on the GC surface and thereby lead to a decrease in the oxygen reduction current. This is an alternative explanation for a significantly lower O₂ reduction current at pre-wave potentials.

Although the different aryl-modified electrodes show similar electrocatalytic behaviour, the largest blocking effect towards oxygen reduction was observed for a GC/PhBr electrode. The half-wave potentials ($E_{1/2}$) of O₂ reduction were determined and the results are given in Table 2. There is a clear tendency for the $E_{1/2}$ value to shift negatively for more strongly modified electrodes. This is obviously related to an increase in surface concentration, even though the latter values could not be determined for five surface modifiers used, because these are not electroactive.

Table 2. Half-wave potentials of O₂ reduction for aryl modified GC electrodes in 0.1 M KOH at 1900 rpm. Data derived from Fig. 17. The $E_{1/2}$ value for a bare GC was -0.37 V.

Modification procedure	$E_{1/2} / \text{V}$					
	GC/Naph1	GC/Naph2	GC/BP	GC/DP	GC/PhBr	GC/NP
Procedure 1	-0.56	-0.71	-0.60	-0.63	-0.81	-0.70
Procedure 2	-0.73	-0.78	-0.70	-0.73	-0.85	-0.72
Procedure 3	-0.79	-0.79	-0.78	-0.75	-0.89	-0.75

6.1.2.3. Electrochemical response of $\text{Fe}(\text{CN})_6^{3-}$ on aryl-modified GC electrodes

The $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple was used to study further the blocking properties of aryl films. There is an experimental proof that the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple should interact with the GC surface for a fast ET to occur [89]. Therefore covering the electrode surface with aryl moieties should inhibit the rate of ET for this couple. Figure 18 shows that grafting the electrode surface in a narrow potential range between 0.1 and 0.5 V gives substantially smaller $\text{Fe}(\text{CN})_6^{3-/4-}$ redox peak currents (curve 1) and the peak potentials are shifted as compared to that of bare GC (curve GC). The peak potential separation (ΔE_p) values after modification by Procedure 1 are given in Table 3. It is evident that the same procedure of electrografting by different aryl groups results in different degrees of surface blocking. The blocking properties towards $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple using Procedure 1 increase in the following sequence:

GC < GC/NP < GC/Naph1 < GC/Naph2 < GC/DP < GC/BP < GC/PhBr. However the order of the blocking action of aryl films would change with the application of further modification procedures.

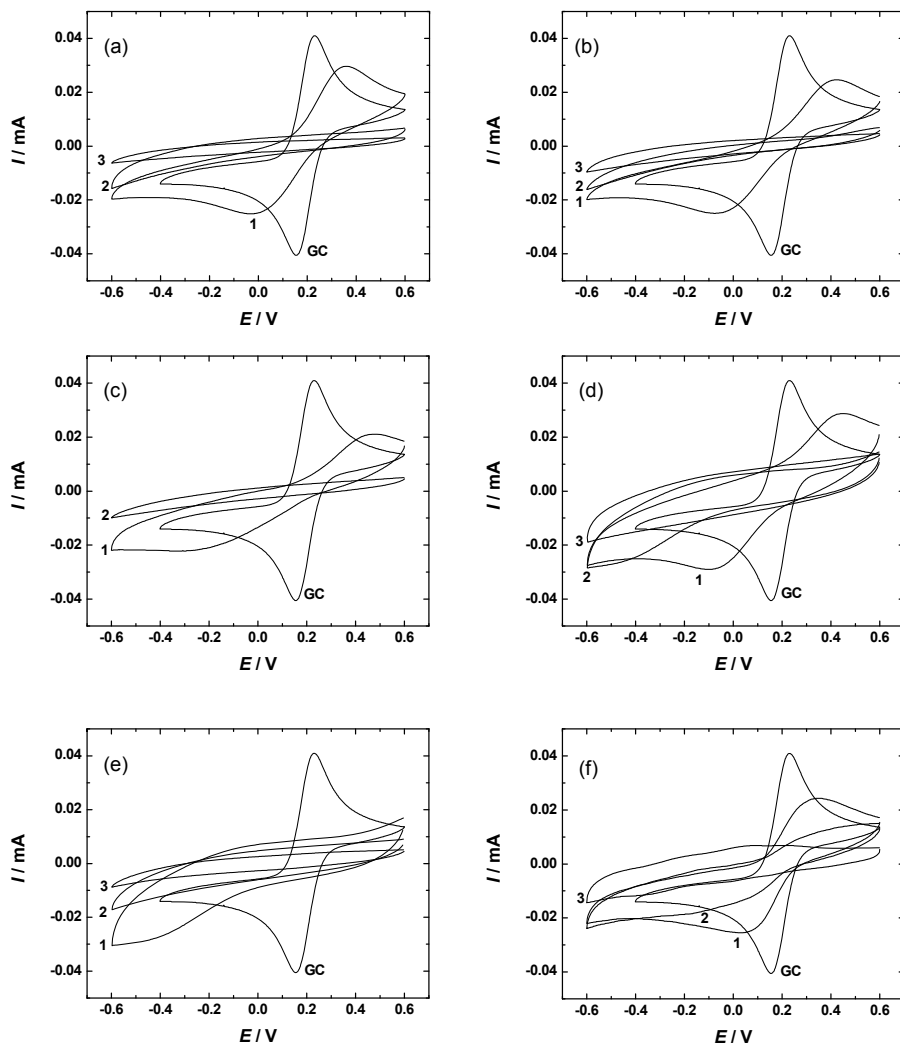


Figure 18. Electrochemical response of the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple on (a) GC/Naph1, (b) GC/Naph2, (c) GC/BP, (d) GC/DP, (e) GC/PhBr and (f) GC/NP electrodes in Ar-saturated 0.1 M K_2SO_4 containing 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ ($\nu = 100 \text{ mV s}^{-1}$). Modification conditions: (1) Procedure 1, (2) Procedure 2 and (3) Procedure 3. Electrodes were electrochemically modified in acetonitrile containing 1 mM of the corresponding diazonium salt and 0.1 M TBABF₄. Curve GC corresponds to the CV response of a bare GC electrode.

It has been previously demonstrated that it is possible to chemically modify the surface of GC electrodes with different para-substituted phenyl groups simply by dipping the GC electrode into 10 mM aryldiazonium salt solution in ACN [43]. In that work a similar electrochemical response was observed to our results obtained by applying modification Procedure 1. From six para-substituted phenyl groups studied the best blocking effect was found for the GC/PhBr electrode.

Modification with one cycle in the potential range between -1.0 and 0.5 V (curve 2) results in a drastic inhibition of the charge transfer process for all the aryl layers studied. For some aryl modified electrodes the blocking action was strong enough that the CV peaks were not discernible. For these electrodes we could not determine the separation of peak potentials (ΔE_p) in order to characterise their blocking properties. Further cycling improves the blocking effect even further and curve 3 shows that the ET through the film almost completely ceased.

Table 3. Comparison of ΔE_p values for aryl-modified GC electrodes determined in Ar-saturated 0.1 M K_2SO_4 containing 1 mM $K_3Fe(CN)_6$ and in Ar-saturated 0.1 M H_2SO_4 containing 1 mM dopamine. Electrodes were modified using Procedure 1. Data derived from Figures 18 and 19.

Redox probe	$\Delta E_p / V$						
	GC	GC/Naph1	GC/Naph2	GC/BP	GC/DP	GC/PhBr	GC/NP
$K_3Fe(CN)_6$	0.087	0.403	0.508	0.685	0.559	n.d.	0.292
Dopamine	0.054	0.504	0.755	0.881	0.429	0.952	0.097

n.d. – not detectable

6.1.2.4. Electrochemical response of dopamine on aryl-modified GC electrodes

In addition to anionic $Fe(CN)_6^{3-/4-}$ redox couple also oxidation of cationic dopamine was studied on aryl modified GC electrodes. Figure 19 presents the electrochemical behaviour of the modified electrodes of different surface concentrations in 0.1 M H_2SO_4 solution containing 1 mM dopamine.

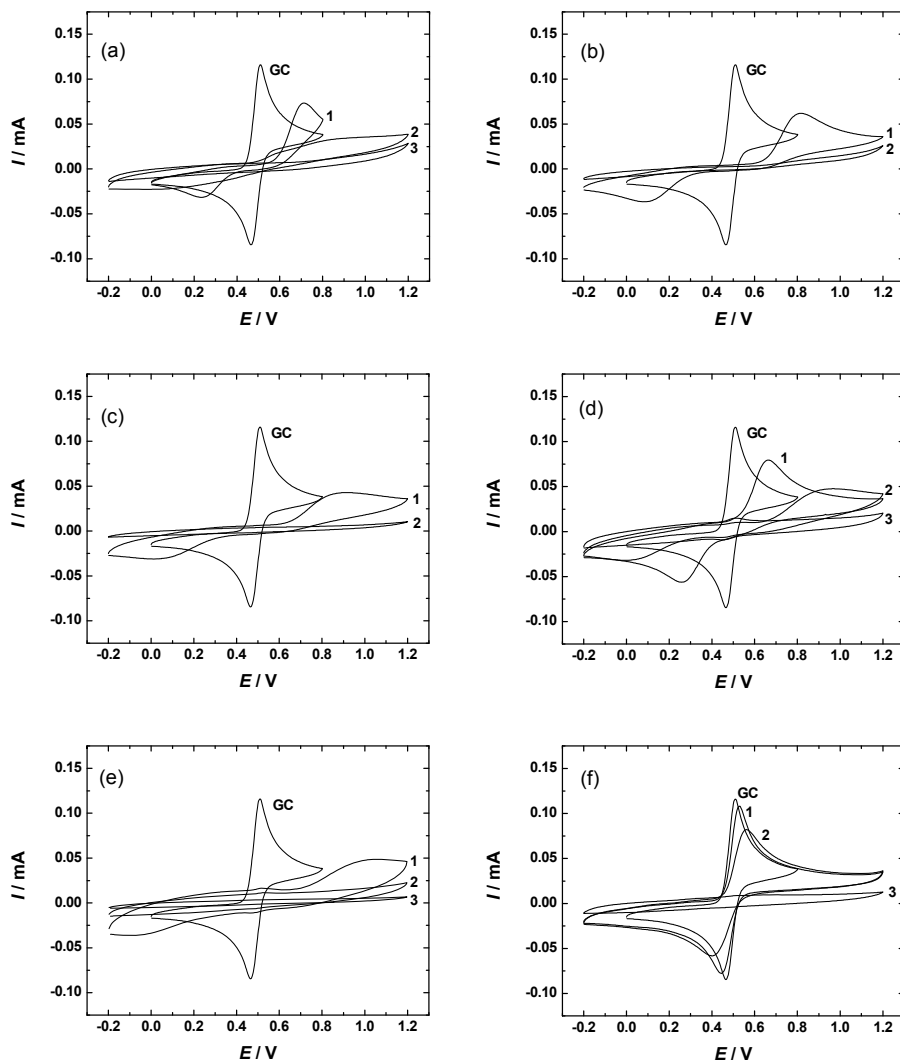


Figure 19. Electrochemical response of dopamine on (a) GC/Naph1, (b) GC/Naph2, (c) GC/BP, (d) GC/DP, (e) GC/PhBr and (f) GC/NP electrodes in Ar-saturated 0.1 M H_2SO_4 containing 1 mM dopamine ($v = 100 \text{ mV s}^{-1}$). Modification conditions: (1) Procedure 1, (2) Procedure 2 and (3) Procedure 3. Electrodes were electrochemically modified in acetonitrile containing 1 mM of the corresponding diazonium salt and 0.1 M TBABF₄. Curve GC corresponds to the CV response of a bare GC electrode.

The electrochemical behaviour of $\text{Fe}(\text{CN})_6^{3-/4-}$ and dopamine redox couple clearly shows, that with increasing the number of modification cycles the surface concentration of aryl groups increases and therefore improving also the barrier properties of the modified surface. The increase of the separation of peak

potentials indicates the inhibition of the charge transfer process. The results obtained for dopamine oxidation on aryl films are in agreement with the results reported by DuVall and McCreery on dopamine electrochemistry on trifluoromethylphenyl [154] and methylene blue [155] modified electrodes.

Ferricyanide reduction and dopamine oxidation is blocked on the modified electrodes to a much larger degree than O_2 reduction. This effect could be explained by the hydrophobic properties of the aryl films studied and by size differences between the $Fe(CN)_6^{3-}$ ions and dopamine and O_2 molecules. The values of ΔE_p are listed in Table 3 for substituted phenyl groups such as NP, DP and PhBr are higher for hexacyanoferrate redox probe than for dopamine redox probe. Indicating that these films are blocking the response towards the $Fe(CN)_6^{3-/4-}$ couple more effectively than that of dopamine. For Naph1, Naph2 and BP higher ΔE_p values were observed for dopamine redox probe.

6.1.3. Spontaneous modification of GC surface with AQ from the solutions of its diazonium derivative: An oxygen reduction study

6.1.3.1. Cyclic voltammetry of GC/AQ electrodes

The GC electrodes were spontaneously modified in various solutions containing 10 mM Fast Red AL salt for different periods of time. The cyclic voltammetry of the GC/AQ electrodes was recorded in O_2 -free 0.1 M KOH. Figure 20 shows that AQ spontaneously attached to GC by simple immersion in the diazonium salt solution. For comparison, the voltammogram for electrochemically grafted GC/AQ electrodes is shown in Fig. 20a, curve 1. This is a typical response for electrochemically grafted GC/AQ electrodes as previously observed [31–33,120,121], whereas the CV response of the bare GC electrode is completely featureless (Fig. 20a, curve 2).

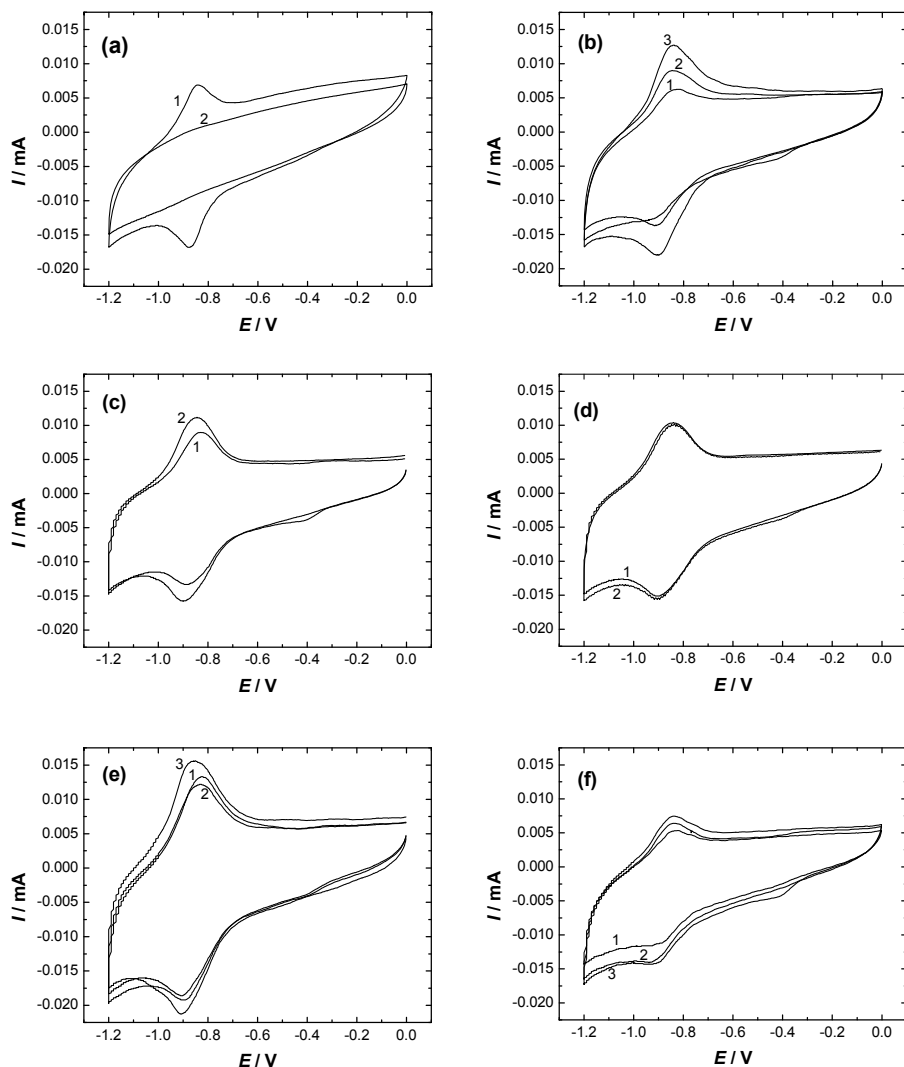


Figure 20. Cyclic voltammograms for GC/AQ electrodes in Ar saturated 0.1 M KOH. The electrodes were modified by: (a) electrochemically grafted (1) and unmodified GC (2); (b) immersion in 10 mM Fast Red AL salt/ACN for 0.5 h (1), 1 h (2) and 24 h (3); (c) immersion in 10 mM Fast Red AL salt/0.5 M HCl for 10 min (1) and 0.5 h (2); (d) immersion in 10 mM Fast Red AL salt/phosphate buffer (pH 7) for 0.5 h (1) and 1 h (2); (e) immersion in 10 mM Fast Red AL salt/H₂O for 0.5 h (1), 1 h (2) and 3 h (3); (f) immersion in 10 mM Fast Red AL salt/borate buffer (pH 10) for 10 min (1), 0.5 h (2) and 1 h (3). $A = 0.196 \text{ cm}^2$, $\nu = 100 \text{ mV s}^{-1}$.

A clear pair of peaks for the GC/AQ modified electrode obtained by immersion in the AQ- N_2^+ solutions is shown in Fig. 20b-f. The average redox potential (E_f)

of spontaneously attached AQ was -0.85 V, very close to the value reported for the electrochemically modified electrode ($E_f = -0.845$ V [31]). The spontaneously grafted electrodes withstand ultrasonication indicating a strong bonding between the AQ moieties and the electrode surface. Although the spontaneous attachment of AQ occurs for all solutions studied, the rate of attachment differs somewhat for the different media as shown by the different times required to achieve coverages close to a monolayer (see below). There was some scatter in the CV data (measurements with duplicate electrodes were made throughout this study) and the spontaneous modification technique is not very reproducible.

The surface concentration of covalently attached AQ (Γ_{AQ}) was calculated from $\Gamma_{AQ} = Q/nFA$ [145], where Q is the charge integrated under the CV peaks, n is the number of electrons involved per AQ molecule ($n=2$) and A is the geometric electrode area. The value of Γ_{AQ} was in the range between $(1-5) \times 10^{-10}$ mol cm^{-2} for all the modified electrodes studied. There is a clear trend for the surface concentration of AQ to increase with increasing immersion time for spontaneous grafting in acetonitrile. The grafting rate is faster in aqueous media and maximum coverage is nearly complete in 10–30 min, with a limited thickness of 2–3 monolayers. It is of particular interest that AQ grafting was also successful from slightly basic media (in borate buffer at pH 10) since only a few examples of grafting using the reduction of diazonium compounds have been reported in alkaline solutions [156,157] and it is known that diazonium salts are not very stable at $\text{pH} > 2$ [2]. Spontaneous modification with diazonium salts was previously achieved from acidic and neutral aqueous solutions [43,45,46] and the latter has been particularly attractive for the covalent modification of carbon nanotubes [51,156,158,159].

The modification time is important from a practical point of view and grafting times of the order of several minutes are desirable for many applications. The main advantage of spontaneous attachment is that no electrochemical equipment is required, the method is simple and versatile and enables the grafting of surfaces in conditions for which the electrochemical reduction procedure is difficult to employ.

6.1.3.2. Mechanism of spontaneous modification of GC with aryldiazonium derivatives

The purpose of this work was not to investigate the mechanism of the spontaneous grafting reaction and therefore the possible reaction pathways are given here in brief. The attachment of the radical formed in the dediazotation reaction to a graphitic surface, requires a change from an sp^2 to an sp^3 surface structure. It is recognised that the kinetics of substitution is much faster at edge plane sites than at the basal plane although grafting appears to be non-selective for oxygen terminated surfaces [6]. The loss of resonance stabilisation energy on functionalisation of an sp^2 surface would be too large for this process to occur on the terraces of the graphene sheets and therefore, attachment would

only be possible at edges, steps or defects. If attachment could only occur at sp^3 carbon sites already present on the surface, the functionalisation of HOPG or of carbon nanotubes could not take place. Since this is indeed observed, it is reasonable to consider that a highly reactive species is involved, i.e., an aryl radical ($Ar^\bullet$). Bahr and Tour attributed the increase in the relative intensity of the disorder mode of Raman spectra at 1290 cm^{-1} to an increased number of sp^3 carbon atoms upon derivatisation of single-walled carbon nanotubes with aryl groups demonstrating the changes in the graphene sheets on their spontaneous functionalisation [48].

The reaction of $Ar^\bullet$ obtained by reduction of ArN_2^+ with a carbon surface is very fast but in the absence of an applied potential, the reducing agent needs to be identified. Toupin and Bélanger [50] investigated the mechanism of the spontaneous chemical functionalisation of Vulcan carbon black by reaction with 4-nitrobenzenediazonium cations by varying the reaction conditions (carbon surface modification by *in situ* generated diazonium cations and in the presence of a reducing agent). They found that the grafting yield was not affected by a change in the reaction conditions. Therefore, they suggested that a galvanic process of the carbon surface could be responsible for the reduction of the diazonium salts and subsequent functionalisation. They did not discard diazonium ions decomposition in acidic solutions in the presence of a nucleophile such as electron-donating π -electron systems (the carbon π -electron system would be presumably the nucleophile, which transfers electrons needed for the reduction of the diazonium cations that leads to the formation of aryl radicals). This could be followed by the formation of a covalent C–C bond between the surface and the aryl radical. Toupin and Bélanger [50] proposed that the higher energy of the Fermi level in HOPG (and, presumably, in GC) could lead to electron transfer to ArN_2^+ but this still leaves open the question of which functional groups or reactions are responsible for the quenching of the hole produced after electron transfer. Considering the slow reaction rates in the heterolytic pathway, however, this appears a reasonable explanation for the spontaneous grafting in acid solutions and provides a common rationalisation for both the attachment of aryl groups and the spontaneous electroless metal deposition on HOPG in the absence of an added reducing agent.

Diazonium chemistry is, however, more complicated than the reduction of a metal ion, due to the involvement of an $Ar^\bullet$ radical. In neutral and alkaline solution, an additional source of radicals required for the homolytic mechanism could be the Gomberg–Bachmann reaction. This mechanism offers an interpretation of the complex behaviour of diazonium compounds in near neutral and alkaline solutions [160–163] due to the formation of radicals in solution that can couple the aryl moiety of the aryldiazonium cation with other aryl groups. Importantly, this coupling can also occur with the conjugated graphitic regions of the GC surface instead of reaction with solution species. OH^- can bind covalently to the aryldiazonium cation [162,164,165]:



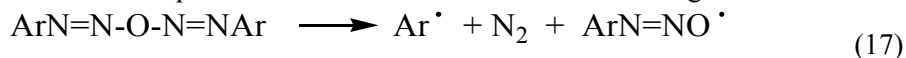
In alkaline solutions, the ArN=NOH species is ionized:



to give an aryldiazotate, which by reaction with an additional molecule of ArN₂⁺ yields a diazoanhydride:



Further decomposition leads to radical formation according to:



The Ar[•] radical is the arylating reagent [166]. Eliel et al. [166] further proposed that disproportionation of ArN=NO[•] gives the corresponding arylbenzene and regenerates ArN=NOH, thus providing a cyclic mechanism for radical generation. These reactions can take place in the pH range where steps (14) and (15) are feasible and hence, depends on the acid-base properties of the intermediates [167,168]. A similar analysis for the spontaneous grafting of single-walled carbon nanotubes (SWCNTs) from the aqueous solutions of aryldiazonium salts has been suggested by Tour and co-workers [51,158,159]. Recently, Doyle et al. have proposed the physisorption of diazoanhydride on the surface of SWCNTs, which could then cleave and yield a radical that attacks SWCNT and form a covalent bond [157]. Thus, Reactions (14), (15), (16) and (17) represent an alternative mechanism of spontaneous modification from one in which the substrate is directly involved in the formation of reactive intermediates from the diazonium salt at open-circuit potential [43,45,46].

It is difficult to understand the further growth of the aryl layers when the substrate surface is completely blocked by a monolayer film. It has been proposed that electron tunnelling or transfer through π -conjugated bonds to diazonium species in solution could occur [46] but the mechanism of multilayer formation by spontaneous grafting needs further elucidation. Although there are difficulties with a mechanism involving electron transfer from GC to aryldiazonium cations at open-circuit to produce, for example, AQ[•] leading to the multilayer growth as often observed, the latter process cannot be entirely ruled out. The surface of GC is highly heterogeneous and various surface sites can possess different electronic properties.

Spontaneous grafting of GC can be carried out in non-aqueous media, for example, in ACN solutions [42,43]. The formation of thicker layers would involve a further reaction of the diazonium reactive intermediates with attached material leading to further functionalisation of the aryl film [42,43]. D'Amours and Belanger have proposed an adsorption phenomenon considering that only a few layers would be concerned in electrografting and the growth of the film would be due to the adsorption of reaction products arising from aryl radicals. This could be a mixture of dimers or oligomers resulting from H-atom transfer from the solvent to the monomeric or oligomeric radicals [20]. The comple-

xities of the reaction mechanism leading to the formation of multilayers are beyond the scope of the present work.

Based on the above considerations, it is proposed that the most likely mechanism for spontaneous grafting with anthraquinone diazonium salt in aqueous solution (acidic or neutral pH) and in acetonitrile would be a combination of an electron transfer reaction from the graphene sheets in glassy carbon resulting in the rapid formation of aryl radicals. In neutral to alkaline solutions, the availability of ArN_2^+ decreases due to equilibrium (14) but besides the electron transfer process mentioned above, the intermediate could still be the aryl radical resulting from the Gomberg–Bachmann mechanism (Reactions (14), (15), (16) and (17)). The lower coverage by AQ observed at pH 10 may result from this lower concentration of the precursor of $\text{Ar}^\bullet$; the actual concentration of arylating agent will depend, in this case, on the stability of the $\text{ArN}=\text{NO}^\bullet$ and $\text{ArN}=\text{N}-\text{O}-\text{N}=\text{NAr}$ intermediates. Further growth leading to a multilayer film can also take place. The presence of much thicker films has been observed [42,43] and an alternative explanation for multilayer formation can be, for example, the addition of an aryl carbocation or an aryl radical to the already attached aryl group at the GC surface. The details of the mechanism require further investigation. The significance of non-electrochemical methods in carbon surface modification has been recently highlighted in the review by Barrière and Downard [4]. However, the mechanistic aspects of spontaneous grafting from the solutions of aryldiazonium derivatives are still under debate.

6.1.3.3. Oxygen reduction on GC/AQ electrodes

The electrochemical reduction of oxygen was studied in order to characterise the electrocatalytic properties of the spontaneously grafted AQ layers. For comparison, O_2 reduction on electrografted GC/AQ electrodes was also examined. Electrocatalysis of covalently attached AQ for this reaction is well established [31–33,120,121]. A typical feature of the polarisation curves for these electrodes is the suppression of the O_2 reduction pre-wave (c.f. curves 1 and 2 at -0.5 V in Fig. 21a), due to the presence of native quinone groups on the carbon surface. Electrocatalysis by surface-bound AQ starts at more negative potentials.

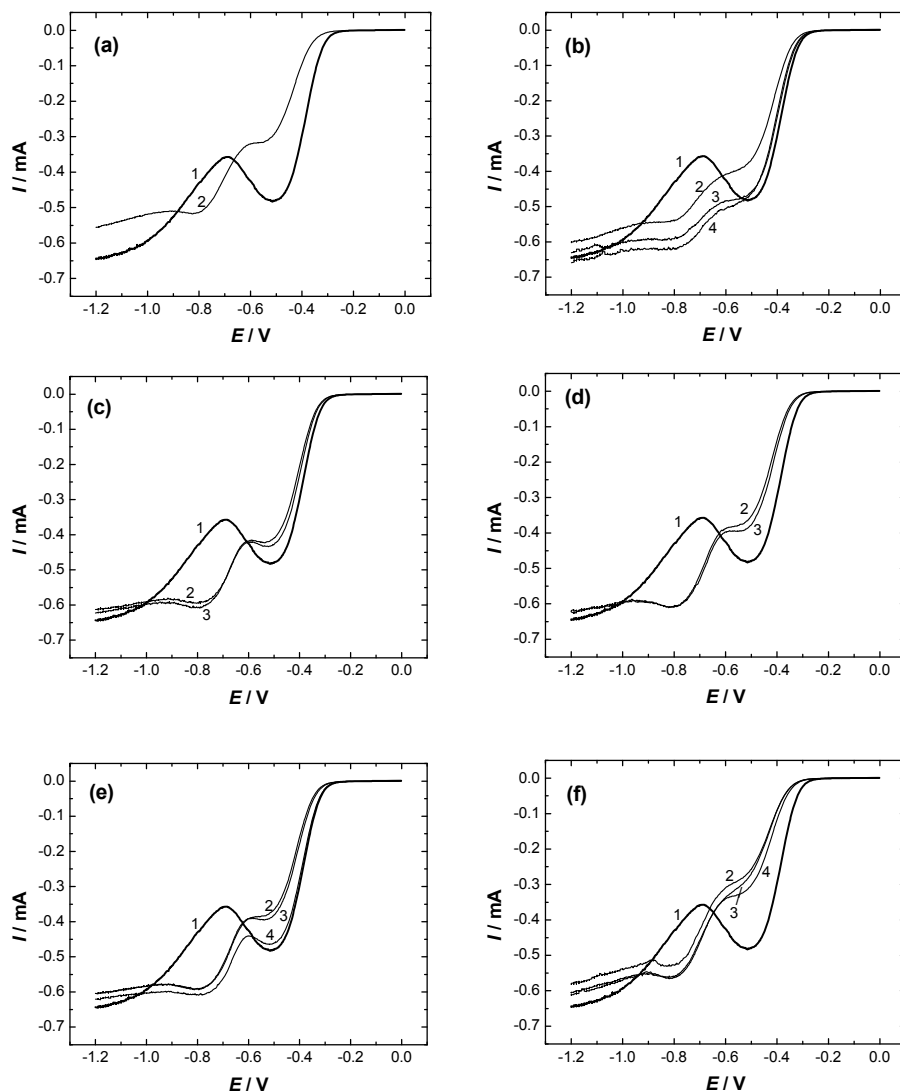


Figure 21. RDE voltammetry curves for oxygen reduction on GC/AQ electrodes in O_2 saturated 0.1 M KOH. The electrodes were: (a) electrochemically grafted (2); (b) immersion in 10 mM Fast Red AL salt/ACN for 0.5 h (2), 1 h (3) and 24 h (4); (c) immersion in 10 mM Fast Red AL salt/0.5 M HCl for 10 min (2) and 30 min (3); (d) immersion in 10 mM Fast Red AL salt/phosphate buffer (pH 7) for 0.5 h (2) and 1 h (3); (e) immersion in 10 mM Fast Red AL salt/ H_2O for 0.5 h (2), 1 h (3) and 3 h (4); (f) immersion in 10 mM Fast Red AL salt/borate buffer (pH 10) for 10 min (2), 0.5 h (3) and 1 h (4). For comparison, in all these figures the RDE voltammetry curve for a bare GC electrode is given (curve 1). $A = 0.196 \text{ cm}^2$, $\nu = 20 \text{ mV s}^{-1}$, $\omega = 1900 \text{ rpm}$.

The reduction of O₂ on spontaneously modified GC/AQ electrodes is shown in Fig. 21b–f. Although the polarisation curves of these electrodes are similar to those of electrografted GC/AQ, some subtle differences are in evidence. A much weaker suppression of the native quinone groups pre-wave is observed and therefore the binding of AQ occurs preferentially at surface sites that are not involved in the reduction of O₂ at pre-wave potentials. There is still controversy whether the covalent bond is formed only with surface carbon atoms or aryl groups are attached to oxygenated sites of the surface leading to the formation of C–O–C bonds. It appears that by spontaneous modification from acetonitrile solutions the catalytically active carbon–oxygen functionalities (most probably quinone-type groups) remain active on the surface of GC (Fig. 21b) as the suppression of the O₂ reduction pre-wave is much weaker as compared to that of the electrografted GC/AQ (Fig. 21a). A current peak is observed at *ca* –0.8 V, which is due to electrocatalysis by the attached anthraquinone and the reduction current reaches a value close to the diffusion control at this potential.

By contrast, for electrodes modified in borate buffer (pH 10), suppression of the pre-wave is clearly observed (Fig. 21f). The reason for such a difference in the O₂ reduction behaviour between the electrodes spontaneously modified from ACN and borate buffer is unclear at present. A possible explanation could be the different intermediates produced in solution and further bonded to the GC surface as was suggested in the previous section. If the Gomberg–Bachmann reaction made a significant contribution to the radical inventory present close to the GC surface, two radical species would be present, Ar[•] and ArN=NO[•]. The surface chemistry of the latter would be very different from that of the simple Ar[•] species. The polarisation curves of O₂ reduction presented in Fig. 21c–e are, however, similar and the effect of surface-confined AQ on the reduction rate is clear. The Koutecky–Levich analysis (dependence of $I^{-1/2}$ on $\omega^{-1/2}$) is shown in Fig. 22. The number of electrons transferred per O₂ molecule (*n*) was calculated from these plots using the K-L equation [145].

It is also evident that the reduction of O₂ is under mixed kinetic-diffusion control even at the potential of the current maximum at –0.8 V since there is a clear intercept of the K-L plot at infinite rotation rate. A lower intercept value for the GC/AQ electrodes of higher surface concentration of AQ was obtained by extrapolating the K-L lines at this potential indicating that there is a finite reaction rate limiting the surface reaction. Equation (12) was used to obtain the value of *n* since it reflects the changes in the thickness of the diffusion layer with ω and hence, the diffusional term is independent of the type of reaction taking place at the surface, e.g. under electron transfer control or by an EC mechanism, see below Equation (18). The value of *n* was close to two for all the AQ-modified electrodes studied (see Fig. 23), indicating that O₂ reduction on these electrodes yields hydrogen peroxide as the final product.

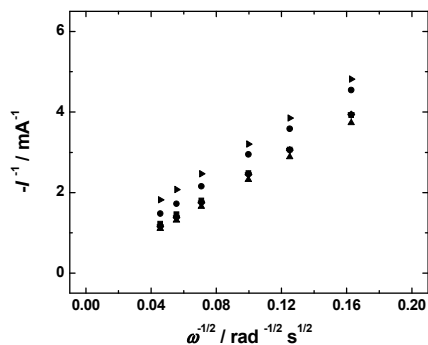


Figure 22. The dependence of I^{-1} on $\omega^{-1/2}$ for O_2 reduction on GC/AQ electrodes in 0.1 M KOH at -0.8 V. The electrodes were spontaneously modified in different solutions containing 10 mM Fast Red AL salt: (●) ACN; (▲) 0.05 M H_2SO_4 ; (▼) phosphate buffer (pH 7); (◆) water; (■) borate buffer (pH 10) and (►) bare GC electrode. All the results shown correspond to electrodes modified for 0.5 h.

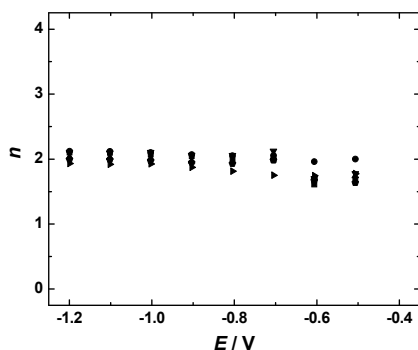


Figure 23. The potential dependence of n for O_2 reduction on GC/AQ electrodes in 0.1 M KOH. The electrodes were spontaneously modified in different solutions containing 10 mM Fast Red AL salt: (●) ACN; (▲) 0.05 M H_2SO_4 ; (▼) phosphate buffer (pH 7); (◆) water; (■) borate buffer (pH 10) and (►) bare GC electrode. All the results shown correspond to electrodes modified for 0.5 h.

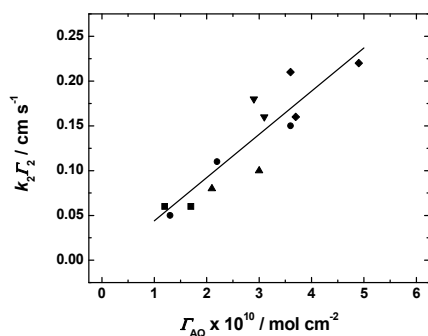


Figure 24. The dependence of $k_2\Gamma_2$ on AQ surface concentration for O_2 reduction on GC/AQ electrodes in 0.1 M KOH. The electrodes were spontaneously modified in different solutions: (●) ACN; (▲) 0.5 M HCl; (▼) phosphate buffer (pH 7); (◆) water and (■) borate buffer (pH 10).

The kinetics of O_2 reduction on the spontaneously modified GC/AQ electrodes was studied as a function of the immersion time and a direct correlation between the O_2 reduction rate and the surface concentration of AQ was found (Fig. 24).

6.1.3.4. Determination of kinetic parameters for O₂ reduction

The kinetic parameters were determined by non-linear regression (NLR) analysis using the surface redox catalytic cycle model previously described [31]. This model distinguishes between contributions to the current from native and grafted quinone groups, and from the free carbon surface, and considers that Reaction (9) is the rate determining step. The current density is given by:

$$\frac{1}{j} = \frac{1}{j_{dl}} - \frac{1}{2Fc_{O_2}^b k^0 e^{-f\alpha(E-E^0)} + \sum_i \frac{2Fc_{O_2}^b k_i \Gamma_i}{1 + e^{f(E-E_{(i)}^0)} e^{(f/2)\Delta E_{(i)}} + e^{-f(E-E_{(i)}^0)} e^{(f/2)\Delta E_{(i)}}}} \quad (18)$$

where $i = 1$ corresponds to properties of the quinone-type groups present on native GC and $i = 2$ to those of the attached quinones; j_{dl} is the diffusionally controlled limiting current density; k^0 is the standard electrochemical rate constant on the free GC surface and α is the corresponding transfer coefficient; E^0 is the standard potential of the O₂/HO₂⁻ couple (-0.065 V vs. SHE); k_i is the rate constant for the reaction between the quinone radical anion and oxygen (Reaction (9)); Γ_i is the surface concentration of the quinone species; $E_{(i)}^0$ is the standard potential of the surface Q/Q²⁻ couples; $\Delta E_{(i)}$ is the difference between the standard potentials of the Q^{•-}/Q²⁻ and the Q/Q^{•-} couple; F is the Faraday constant and $f = F/RT$. The two-quinone surface redox catalytic cycle model fits well the oxygen reduction data for quinone modified GC electrodes [31–33,120,121]. The main advantage of this method is that it can distinguish between the contributions of various surface sites to the overall rate of oxygen reduction without the need to use extrapolations to infinite rotation rates to calculate the chemical rate parameters ($k_i \Gamma_i$). In addition, the analysis of the extrapolated values of the K-L plots (the second term in Eq. (18)) would be very inaccurate. The use of the potential dependent currents allows employing the whole experimental dataset without the need to rely on data extrapolation.

The kinetic parameters obtained for the GC/AQ electrodes of various surface modifications are listed in Tables 4–8. The parameters determined for the polished GC electrode used are given for comparison purposes. These values are similar to those previously observed [31,32].

Table 4. Average values of kinetic parameters for O₂ reduction on GC/AQ electrodes in 0.1 M KOH. The electrodes were immersed in 10 mM Fast Red AL salt/ACN for different periods of time (t=0.5; 1 and 24 h).

t (h)	$10^{10} \Gamma$ (mol cm ⁻²)	$E_{(1)}^0$ (V)	$E_{(2)}^0$ (V)	$10^4 k^0$ (cm s ⁻¹)	α	$\Delta E_{(1)}$ (V)	$\Delta E_{(2)}$ (V)	$k_1 \Gamma_1$ (cm s ⁻¹)	$k_2 \Gamma_2$ (cm s ⁻¹)	$10^{-8} k_2$ (cm ³ mol ⁻¹ s ⁻¹)
0.5	1.3	-0.57 ± 0.02	-0.87 ± 0.01	5.3 ± 2.5	0.17 ± 0.01	-0.26 ± 0.03	-0.24 ± 0.02	0.018 ± 0.001	0.05 ± 0.01	3.8 ± 0.8
1	2.2	-0.56 ± 0.01	-0.83 ± 0.01	6.2 ± 3.2	0.21 ± 0.01	-0.26 ± 0.01	-0.24 ± 0.01	0.034 ± 0.002	0.11 ± 0.01	5.0 ± 0.5
24	3.6	-0.56 ± 0.01	-0.80 ± 0.01	5.9 ± 3.2	0.24 ± 0.01	-0.26 ± 0.02	-0.19 ± 0.02	0.033 ± 0.002	0.15 ± 0.03	4.2 ± 0.8
GC	–	-0.52 ± 0.01	–	8.3 ± 3.1	0.18 ± 0.01	-0.20 ± 0.01	–	0.031 ± 0.001	–	–

Table 5. Average values of kinetic parameters for O₂ reduction on GC/AQ electrodes in 0.1 M KOH. The electrodes were immersed in 10 mM Fast Red AL salt/0.5 M HCl for different periods of time (10 min and 30 min).

t (min)	$10^{10} \Gamma$ (mol cm ⁻²)	$E_{(1)}^0$ (V)	$E_{(2)}^0$ (V)	$10^4 k^0$ (cm s ⁻¹)	α	$\Delta E_{(1)}$ (V)	$\Delta E_{(2)}$ (V)	$k_1 \Gamma_1$ (cm s ⁻¹)	$k_2 \Gamma_2$ (cm s ⁻¹)	$10^{-8} k_2$ (cm ³ mol ⁻¹ s ⁻¹)
10	2.1	-0.56 ± 0.02	-0.87 ± 0.02	3.0 ± 1.7	0.19 ± 0.01	-0.25 ± 0.02	-0.33 ± 0.03	0.014 ± 0.002	0.08 ± 0.02	3.8 ± 0.9
30	3.0	-0.57 ± 0.02	-0.86 ± 0.02	3.7 ± 1.2	0.19 ± 0.01	-0.23 ± 0.02	-0.33 ± 0.02	0.011 ± 0.001	0.10 ± 0.02	3.3 ± 0.7
GC	–	-0.52 ± 0.01	–	8.3 ± 3.1	0.18 ± 0.01	-0.20 ± 0.01	–	0.031 ± 0.001	–	–

Table 6. Average values of kinetic parameters for O₂ reduction on GC/AQ electrodes in 0.1 M KOH. The electrodes were immersed in 10 mM Fast Red AL salt/phosphate buffer (pH 7) for different periods of time (0.5 h, 1 h).

t (h)	$10^{10} \Gamma$ (mol cm ⁻²)	$E^0_{(1)}$ (V)	$E^0_{(2)}$ (V)	$10^4 k^0$ (cm s ⁻¹)	α	$\Delta E_{(1)}$ (V)	$\Delta E_{(2)}$ (V)	$k_1 \Gamma_1$ (cm s ⁻¹)	$k_2 \Gamma_2$ (cm s ⁻¹)	$10^{-8} k_2$ (cm ³ mol ⁻¹ s ⁻¹)
0.5	3.1	-0.56 ± 0.01	-0.84 ± 0.02	3.7 ± 2.1	0.22 ± 0.01	-0.24 ± 0.01	-0.21 ± 0.02	0.014 ± 0.002	0.16 ± 0.02	5.2 ± 0.7
1	2.9	-0.55 ± 0.01	-0.82 ± 0.02	3.5 ± 1.3	0.23 ± 0.01	-0.22 ± 0.01	-0.22 ± 0.02	0.013 ± 0.002	0.18 ± 0.02	6.2 ± 0.7
GC	–	-0.52 ± 0.01	–	8.3 ± 3.1	0.18 ± 0.01	-0.20 ± 0.01	–	0.031 ± 0.001	–	–

Table 7. Average values of kinetic parameters for O₂ reduction on GC/AQ electrodes in 0.1 M KOH. The electrodes were immersed in 10 mM Fast Red AL salt/H₂O for different periods of time (0.5 h, 1 h and 3 h).

t (h)	$10^{10} \Gamma$ (mol cm ⁻²)	$E^0_{(1)}$ (V)	$E^0_{(2)}$ (V)	$10^4 k^0$ (cm s ⁻¹)	α	$\Delta E_{(1)}$ (V)	$\Delta E_{(2)}$ (V)	$k_1 \Gamma_1$ (cm s ⁻¹)	$k_2 \Gamma_2$ (cm s ⁻¹)	$10^{-8} k_2$ (cm ³ mol ⁻¹ s ⁻¹)
0.5	3.6	-0.55 ± 0.02	-0.82 ± 0.02	3.7 ± 2.2	0.23 ± 0.01	-0.23 ± 0.02	-0.22 ± 0.02	0.018 ± 0.001	0.21 ± 0.01	5.8 ± 0.3
1	3.7	-0.54 ± 0.01	-0.83 ± 0.02	4.1 ± 2.1	0.21 ± 0.01	-0.22 ± 0.01	-0.25 ± 0.03	0.019 ± 0.001	0.16 ± 0.02	4.3 ± 0.6
3	4.9	-0.52 ± 0.01	-0.83 ± 0.02	4.9 ± 2.9	0.22 ± 0.01	-0.19 ± 0.02	-0.26 ± 0.02	0.034 ± 0.002	0.22 ± 0.02	4.5 ± 0.4
GC	–	-0.52 ± 0.01	–	8.3 ± 3.1	0.18 ± 0.01	-0.20 ± 0.01	–	0.031 ± 0.001	–	–

Table 8. Average values of kinetic parameters for O₂ reduction on GC/AQ electrodes in 0.1 M KOH. The electrodes were immersed in 10 mM Fast Red AL salt/borate buffer (pH 10) for different periods of time (10 min and 30 min).

t (min)	$10^{10} \Gamma$ (mol cm ⁻²)	$E^0_{(1)}$ (V)	$E^0_{(2)}$ (V)	$10^4 k^0$ (cm s ⁻¹)	α	$\Delta E_{(1)}$ (V)	$\Delta E_{(2)}$ (V)	$k_1 \Gamma_1$ (cm s ⁻¹)	$k_2 \Gamma_2$ (cm s ⁻¹)	$10^{-8} k_2$ (cm ³ mol ⁻¹ s ⁻¹)
10	1.2	-0.57 ± 0.02	-0.85 ± 0.01	2.8 ± 1.9	0.20 ± 0.01	-0.26 ± 0.03	-0.28 ± 0.02	0.009 ± 0.001	0.06 ± 0.01	5.0 ± 0.8
30	1.7	-0.60 ± 0.02	-0.86 ± 0.01	4.3 ± 2.0	0.18 ± 0.01	-0.31 ± 0.02	-0.30 ± 0.01	0.010 ± 0.001	0.06 ± 0.01	3.5 ± 0.6
GC	–	-0.52 ± 0.01	–	8.3 ± 3.1	0.18 ± 0.01	-0.20 ± 0.01	–	0.031 ± 0.001	–	–

There is a clear change in the shape of the polarisation curve of O_2 reduction, when the electrode was immersed in the diazonium solution before the measurements. A notable feature is the appearance of a new peak at approximately -0.8 V indicating electrocatalysis by the attached anthraquinone. The values of $k_2\Gamma_2$ were significantly higher than those of the unmodified GC electrode ($k_1\Gamma_1$) in accordance with the increased coverage by the quinone.

The kinetic parameters related to the underlying GC substrate ($E_{(1)}^0$, k^0 , α , $\Delta E_{(1)}$, $k_1\Gamma_1$) did not significantly differ for the different preparations except for the result at 0.5 h (Table 4). The chemical rate constant k_i corresponding to the native quinone-type groups of GC ($k_1\Gamma_1$) for electrodes spontaneously modified in ACN show a similar value to that for unmodified GC (Table 4), indicating that the attached AQ groups do not affect the electrocatalytic properties of the most active native quinone sites. However, for most of the AQ/GC electrodes, the value of $k_1\Gamma_1$ decreased slightly for reaction times of 0.5 and 1 h. The value of k^0 shows a small decrease after surface modification. The other kinetic parameters ($E_{(1)}^0$, α , $\Delta E_{(1)}$) are almost unchanged for these particular electrodes. This is an unexpected result, because the AQ surface concentration was rather high and therefore it would be expected that this would influence the properties of the underlying substrate. It is proposed that, in accordance with previous observations for spontaneous attachment from the solutions of AQ carboxylic derivatives [122], the surface is unevenly covered by AQ probably with islets of AQ formed in the regions of favourable attachment.

The parameters characterising the properties of surface-confined AQ ($E_{(2)}^0$, $\Delta E_{(2)}$, and $k_2\Gamma_2$) are similar for the different electrode preparations. It can be concluded that the electrocatalytic activity for O_2 reduction resulting from the attached quinone depends mostly on the surface concentration of AQ and not on the particular media from which the spontaneous modification was carried out. There are differences, however, for oxygen reduction at the pre-wave (see Fig. 21). The product $k_2\Gamma_2$ should be linearly proportional to the surface concentration of AQ. Figure 24 shows these results for all the electrodes modified in different media. A clear linear tendency for the chemical rate parameter is observed for increasing Γ_{AQ} values. From the slope of this plot, the rate constant for the chemical reaction between the semiquinone radical and oxygen was determined ($k_2 = 4.9 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). This value is in excellent agreement with that previously determined for electrochemically grafted AQ [32]. In consequence, the bonding of anthraquinone moieties to GC is similar for both types of modification (spontaneous attachment vs. electrografting).

The bonding between AQ and GC is strong since the modified electrodes survived sonication for 10 min without alteration in their properties. In the case of spontaneous functionalisation, the AQ moiety (carbocation or radical) could attach to the surface of GC in a manner similar to that of electrochemical modification (i.e. the AQ radical formed reacts with the GC surface) [10]. These results are in line with previous investigations in which the grafting of aryl groups to GC was achieved without any external potential applied [42,43]. The

spontaneous attachment of AQ from the solutions of its diazonium derivative is much faster compared to the reaction of its carboxylic derivative [122] and is therefore more suitable for practical applications. The formation of multilayers (layer thickness above 5 nm) and islets was observed by AFM when carboxylic derivatives were used for spontaneous grafting [122] and it is very likely that these features would also be present for spontaneously modified GC surfaces.

6.1.4. Electroreduction of oxygen on GC electrodes modified with *in situ* generated AQ diazonium cations

6.1.4.1. GC surface modification with *in situ* synthesised AQ-N₂⁺

Figure 25 presents the first and the fifth potential scans for the electrochemical grafting of a GC electrode in the presence of *in situ* generated 9,10-anthraquinone-2-diazonium cations. The current peak of the diazonium ion reduction was observed at 0.28 and 0.17 V for the electrodes modified in acetonitrile (Fig. 25a) and in aqueous acidic media (Fig. 25b), respectively. This peak almost disappears on consecutive scans. Similar electrografting behaviour was observed for *in situ* synthesised 9,10-anthraquinone-1-diazonium cations.

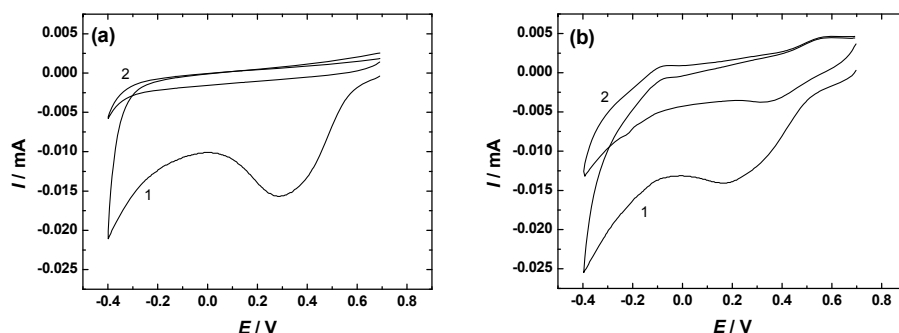


Figure 25. Electrochemical grafting of anthraquinone groups to glassy carbon using *in situ* generated diazonium derivatives. Electrode modified in: (a) Ar saturated ACN containing 1 mM of 2-aminoanthraquinone and 3 mM *tert*-butyl nitrite, (b) Ar saturated 0.5 M HCl containing 2 mM of 2-aminoanthraquinone and 4 mM NaNO₂. $\nu = 100 \text{ mV s}^{-1}$, $A = 0.196 \text{ cm}^2$. Trace (1) corresponds to the first and trace (2) to the fifth scan.

Anthraquinone coverage and stability of the grafted surfaces were characterised by cycling the electrode between 0 and -1.2 V 25 times in Ar saturated 0.1 M KOH. Characteristic cyclic voltammetric responses of these electrodes in 0.1 M KOH are shown in Fig. 26. The redox potential (E_f) of surface-bound AAQ1 obtained by functionalisation in ACN was -0.865 V , very close to the value

previously reported for 1-anthraquinonyl modified surfaces (-0.845 V [31]). The GC/AAQ1 electrode modified in 0.5 M HCl showed a similar redox potential ($E_f = -0.859$ V). The E_f values for surface-bound AAQ2 were -0.838 and -0.840 V for electrodes modified in ACN and 0.5 M HCl, respectively. The surface quinone concentration (Γ) was determined by charge integration under the CV peaks ($\Gamma = Q/nFA$ [145], where Q is the amount of charge consumed, n is the number of electrons involved ($n=2$), F is the Faraday constant and A is the geometric surface area). The Γ_{AAQ1} values were 4.0×10^{-10} and 5.1×10^{-10} mol cm $^{-2}$ for the electrodes modified in ACN and in aqueous 0.5 M HCl, respectively. For GC electrodes modified from solutions containing *in situ* generated 9,10-anthraquinone-2-diazonium cations, $\Gamma_{AAQ2} = 11.7 \times 10^{-10}$ mol cm $^{-2}$ (electrode modified in ACN) and $\Gamma_{AAQ2} = 4.6 \times 10^{-10}$ mol cm $^{-2}$ (electrode modified in 0.5 M HCl). The electrodes modified with previously synthesised AQ diazonium derivatives yielded surface concentrations of the same order: $\Gamma_{AQ1} = 8.9 \times 10^{-10}$ mol cm $^{-2}$ and $\Gamma_{AQ2} = 6.8 \times 10^{-10}$ mol cm $^{-2}$ (modification in ACN) and $\Gamma_{AQ1} = 4.1 \times 10^{-10}$ mol cm $^{-2}$ and $\Gamma_{AQ2} = 4.0 \times 10^{-10}$ mol cm $^{-2}$ (modification in aqueous media).

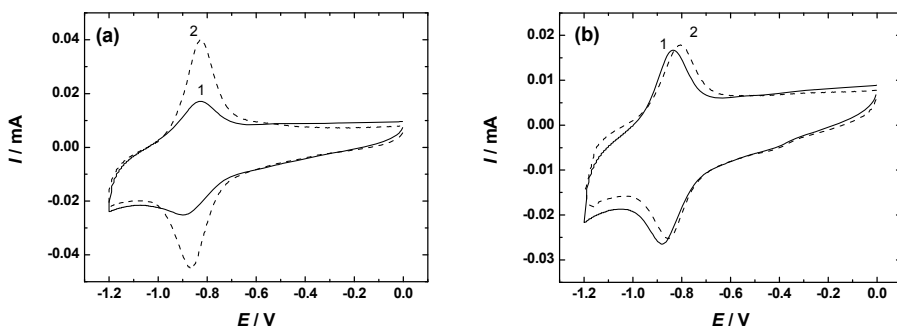


Figure 26. Cyclic voltammograms for GC/AAQ1 (1) and GC/AAQ2 (2) electrodes in Ar saturated 0.1 M KOH. $\nu = 100$ mV s $^{-1}$, $A = 0.196$ cm 2 . Electrode modified in ACN (a) and in 0.5 M HCl (b).

It was of special interest to test electrochemically the redox processes of surface bound anthraquinone at different potential scan rates. Figure 27 presents the representative CV responses for GC/AAQ2 modified in ACN and in 0.5 M HCl. As expected for a surface electron transfer reaction, the peak current corrected for the baseline (I_p) is linearly dependent on ν . The surface confined anthraquinone shows a quasi-reversible electron-transfer behaviour as the separation of anodic and cathodic peak potentials increases with the scan rate. These features are similar to those observed in a previous study for anthraquinone-modified GC [31]. No attempt has been made to determine the rate constant of electron transfer from the CV data shown in Fig. 27.

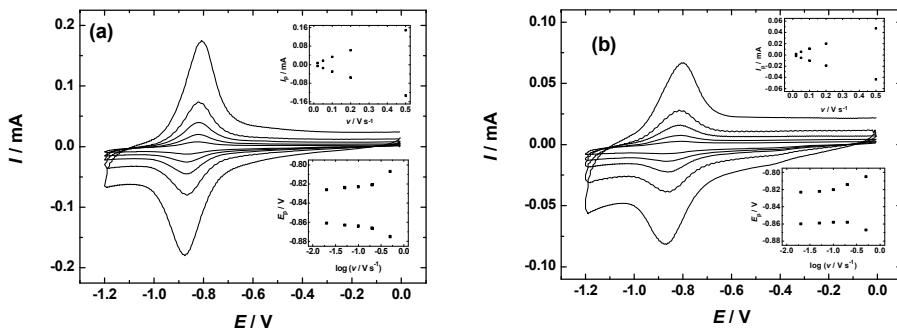


Figure 27. Cyclic voltammograms for GC/AAQ2 electrodes in Ar saturated 0.1 M KOH recorded at various sweep rates: 20, 50, 100, 200 and 500 mV s^{-1} . Electrode modified in ACN (a) and in 0.5 M HCl (b). The insets show the plots of I_p vs. ν and E_p vs. $\log \nu$.

6.1.4.2. O_2 reduction on GC modified with *in situ* synthesised AQ- N_2^+

Oxygen reduction on GC/AAQ electrodes was studied between 0 and -1.2 V at different rotations rates to establish the dependence of electrocatalytic activity on preparation conditions and point of attachment of the quinone to the carbon surface. Figure 28 shows the RDE results for the GC/AAQ2 electrodes modified in acetonitrile (Fig. 28a) and in aqueous acidic solution (Fig. 28b). These different grafting methods give very similar electrocatalytic properties. As observed before [31], the attached AQ groups partially block native GC surface sites, therefore suppressing the O_2 reduction pre-wave observed at -0.5 V due to the native quinone groups of GC. At potentials more negative than *ca* -0.6 V the attached quinone groups act as electrocatalysts for O_2 reduction and consequently, the reduction current increases sharply close to its diffusion-limited value.

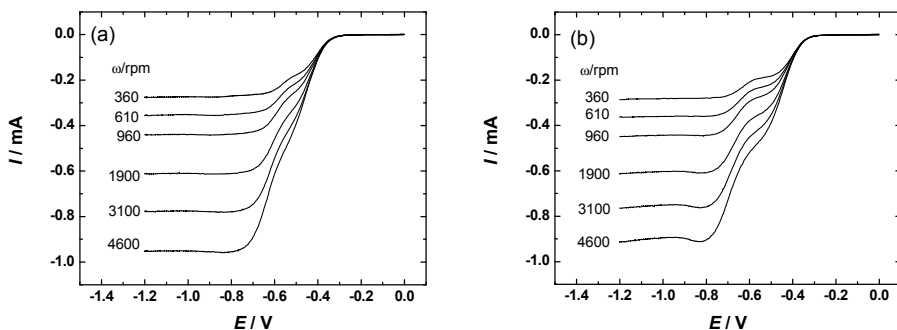


Figure 28. RDE voltammetry curves for oxygen reduction on a GC/AAQ2 electrode modified via *in situ* generated diazonium cations (a) in ACN and (b) in 0.5 M HCl in O_2 saturated 0.1 M KOH. $\nu = 20 \text{ mV s}^{-1}$. $A = 0.196 \text{ cm}^2$.

The Koutecký–Levich analysis for these results is shown in Fig. 29. The number of electrons transferred per O₂ molecule (n) was calculated from these plots using the K-L equation [145].

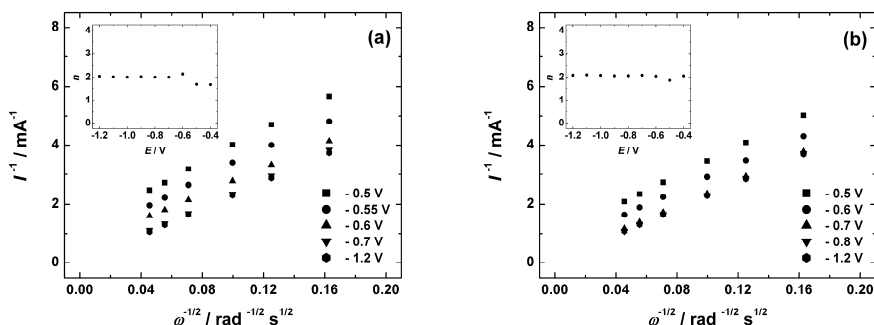


Figure 29. Koutecký–Levich plots for oxygen reduction on GC/AAQ2 electrodes in 0.1 M KOH (a) modified in ACN and (b) modified in 0.5 M HCl. The inset shows the potential dependence of the number of electrons transferred per O₂ molecule. Data derived from Figure 28.

Figure 29 shows that the reduction of O₂ is under mixed kinetic-diffusion control even at the potential of the current maximum at -0.8 V . The intercept obtained by extrapolating the K-L lines at this potential depends on the surface concentration of the attached anthraquinone as previously observed [32]. The value of n was close to two for all the AQ-modified electrodes studied (see insets to Fig. 29), indicating that O₂ reduction on these electrodes stops at the peroxide stage. Figure 30 compares the RDE results obtained for the bare GC electrode and for the electrodes electrografted with anthraquinone in ACN and in an aqueous solution. Both GC/AAQ electrodes gave similar responses towards O₂ reduction, similarly to results previously obtained [32]. The limiting current was almost equal to that for bare GC. Small differences between the polarisation curves could be explained by differences in surface coverage (see Section 6.1.4.1.). It appears that the electrodes modified with 2-anthraquinonyl groups show slightly better electrocatalytic properties (for example, the current plateau starts at a more positive potential), regardless of the media from which the modification was carried out. A quantitative analysis of these results is presented below.

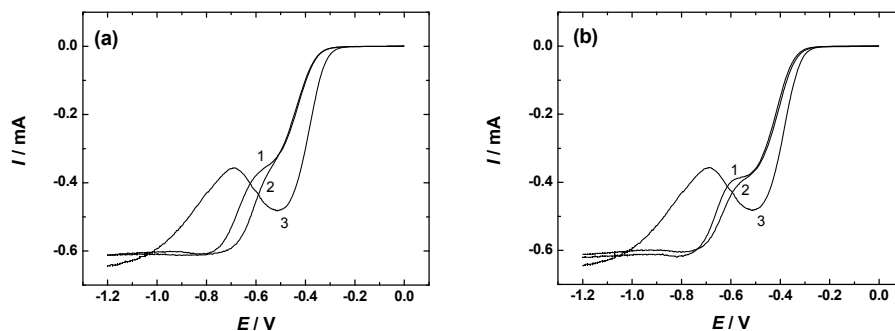


Figure 30. Comparison of current-potential curves for oxygen reduction on bare GC and electrochemically grafted electrodes in O₂ saturated 0.1 M KOH: (1) GC/AAQ1, (2) GC/AAQ2 and (3) bare GC. $\omega = 1900$ rpm, $A = 0.196$ cm². Electrodes modified in ACN (a) and in 0.5 HCl (b).

6.1.4.3. O₂ reduction on GC modified with previously synthesised AQ diazonium salts

In order to evaluate the electrocatalytic properties of these electrodes, a comparison between electrodes modified with *in situ* generated AQ-N₂⁺ and those modified with previously synthesised diazonium salts was made. Figures 31 and 32 present typical RRDE voltammetry results for a bare GC electrode (curve 3) and for GC/AQ1 (curve 1) and GC/AQ2 (curve 2) electrodes grafted in acetonitrile (Fig. 31) and in an aqueous acidic solution (Fig. 32). Both GC/AQ electrodes modified by previously synthesised AQ diazonium salts gave similar responses and their diffusion limiting current was almost equal to that for bare GC. Earlier studies have shown that the reduction of oxygen on GC/AQ electrodes follows a two-electron pathway [31,32]. In previous work the RRDE data were analysed using Wroblowa method [169]. The percentage of peroxide formation on the disk (Φ) can be calculated from [170]:

$$\phi = \frac{200I_R / N}{I_D + I_R / N} \quad (19)$$

where I_R and I_D are the ring and disk currents, respectively and N is the collection efficiency. Figure 33 shows the potential dependence of Φ for all the GC/AQ electrodes studied. All these electrodes showed a 95–100% yield for peroxide production. The slight decrease observed at more negative potentials could be caused by the adsorption of impurities on the gold ring during the RRDE measurements that may result in a slightly non-quantitative detection of peroxide.

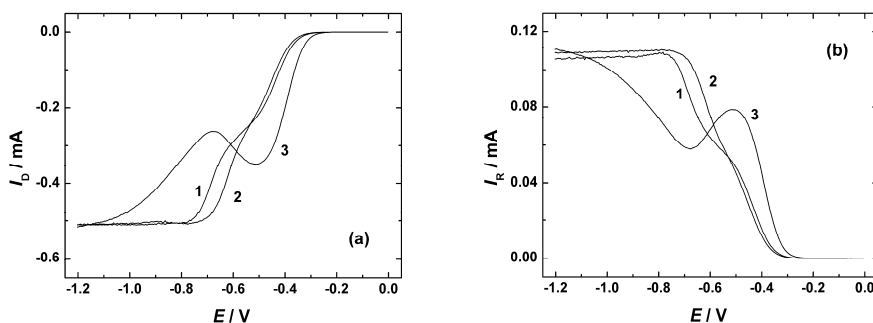


Figure 31. Ring and disk currents for oxygen reduction in O_2 saturated 0.1 M KOH on: (1) GC/AQ1, (2) GC/AQ2 and (3) bare GC. GC electrodes modified in ACN containing 1 mM of the corresponding diazonium salt. $\nu = 20 \text{ mV s}^{-1}$, $\omega = 1900 \text{ rpm}$ and A (disk) = 0.164 cm^2 ; (a) disk and (b) ring currents.

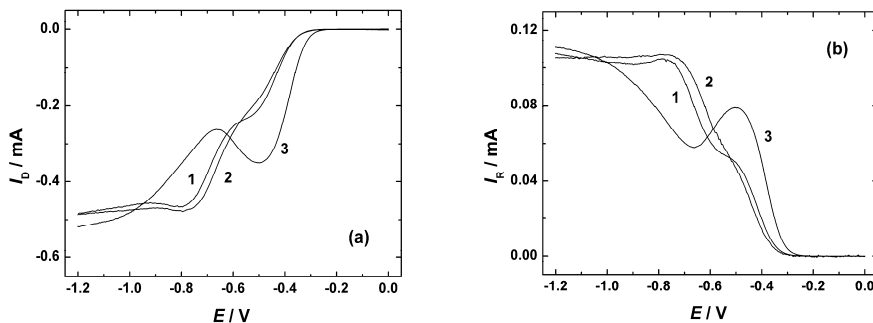


Figure 32. Ring and disk currents for oxygen reduction in O_2 saturated 0.1 M KOH on: (1) GC/AQ1, (2) GC/AQ2 and (3) bare GC. GC electrodes modified in 0.05 M H_2SO_4 containing 2 mM of the corresponding diazonium salt. $\nu = 20 \text{ mV s}^{-1}$, $\omega = 1900 \text{ rpm}$ and A (disk) = 0.164 cm^2 ; (a) disk and (b) ring currents.

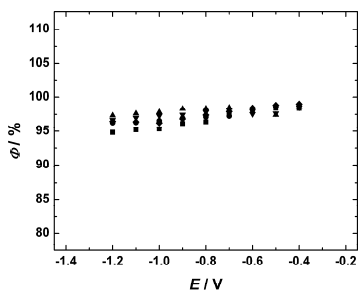


Figure 33. Dependence of the yield of peroxide formation (Φ) on potential for: (■) GC/AQ1, (●) GC/AQ2 (GC electrodes modified in ACN); (▲) GC/AQ1, (▼) GC/AQ2 (GC electrodes modified in 0.05 M H_2SO_4) and (◆) bare GC. $\omega = 1900 \text{ rpm}$. Data derived from Figures 31 and 32.

6.1.4.4. Determination of O₂ reduction kinetic parameters

The kinetic parameters for oxygen reduction were calculated by a non-linear regression analysis of the current–potential curves at different rotation rates using the surface redox catalytic cycle model for quinone-modified electrodes previously described [31]. This model distinguishes between contributions to the current from native and grafted quinone groups and from the free carbon surface, and considers that Reaction (9) is the rate determining step.

The values of the diffusion-limited current densities used were calculated from the Koutecky–Levich plots and these were fixed during the analysis. The results of the NLR analysis for the electrodes modified with *in situ* generated AQ diazonium cations are listed in Table 9. The kinetic parameters corresponding to the GC substrate ($E_{(1)}^0$, k^0 , α , $\Delta E_{(1)}$, $k_1\Gamma_1$) are similar to those observed in previous investigations [31,32]. The value of $E_{(1)}^0$ of the modified electrode is slightly more negative than that of unmodified GC. The k^0 value of the electrode decreases when the surface of GC becomes crowded with covalently attached AQ. This is expected since this parameter relates only to the free GC surface and therefore, it should decrease as the surface becomes covered with attached quinone groups. For the same reason, the chemical rate parameter $k_1\Gamma_1$ has a lower value as compared to bare GC because some active sites of GC are blocked by surface-bound AQ groups. These results are as expected for the division of current contributions described above and provide additional evidence for the usefulness of the NLR method adopted.

An important conclusion from these results is the observation that these kinetic parameters characterising the properties of the covalently bound anthraquinone groups do not depend on the point of attachment in the molecule. A rather small positive shift of the $E_{(2)}^0$ values for AQ attached in position 2 is observed as compared to that attached in position 1. The values of $\Delta E_{(2)}$ are similar for both AQ derivatives studied regardless of the grafting method employed.

The maximum rate of peroxide production on a quinone-modified electrode is proportional to the product $k_2\Gamma_2$. As shown in previous work [32] this product is linearly dependent on the quinone coverage. The values of the rate constant k_2 (Reaction 9) calculated from the coverage measured was of the same order for the different preparation methods and the average value for all the results obtained in the present work was $k_2 = (3.5 \pm 1) \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This compares reasonably well with a previous determination for AQ1 of $(4.7 \pm 0.3) \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [32].

Table 9. Average values of the kinetic parameters for oxygen reduction on GC/AAQ electrodes in O₂ saturated 0.1 M KOH. The GC electrodes were modified with *in situ* generated AQ diazonium cations.

Quinone	Media	$E^0_{(1)}$ (V)	$E^0_{(2)}$ (V)	$10^4 k^0$ (cm s ⁻¹)	α	$\Delta E_{(1)}$ (V)	$\Delta E_{(2)}$ (V)	$k_1 \Gamma_1$ (cm s ⁻¹)	$k_2 \Gamma_2$ (cm s ⁻¹)	k_2 (cm ³ mol ⁻¹ s ⁻¹)
AAQ1	ACN	-0.59 ± 0.01	-0.89 ± 0.01	2.8 ± 1.6	0.20 ± 0.01	-0.29 ± 0.02	-0.37 ± 0.01	0.013 ± 0.002	0.11 ± 0.01	2.8 × 10 ⁸
AAQ2	ACN	-0.56 ± 0.02	-0.83 ± 0.01	2.6 ± 1.5	0.26 ± 0.01	-0.22 ± 0.04	-0.32 ± 0.01	0.013 ± 0.002	0.40 ± 0.02	3.4 × 10 ⁸
AAQ1	0.5 M HCl	-0.56 ± 0.01	-0.90 ± 0.01	2.7 ± 1.5	0.20 ± 0.01	-0.24 ± 0.02	-0.39 ± 0.01	0.013 ± 0.002	0.13 ± 0.01	2.6 × 10 ⁸
AAQ2	0.5 M HCl	-0.55 ± 0.01	-0.86 ± 0.01	4.9 ± 2.3	0.20 ± 0.01	-0.23 ± 0.02	-0.37 ± 0.01	0.017 ± 0.002	0.17 ± 0.01	3.8 × 10 ⁸

Table 10. Average values of the kinetic parameters for oxygen reduction on GC/AQ electrodes in O₂ saturated 0.1 M KOH. The GC electrodes were modified with previously synthesised AQ diazonium salts.

Quinone	Media	$E^0_{(1)}$ (V)	$E^0_{(2)}$ (V)	$10^4 k^0$ (cm s ⁻¹)	α	$\Delta E_{(1)}$ (V)	$\Delta E_{(2)}$ (V)	$k_1 \Gamma_1$ (cm s ⁻¹)	$k_2 \Gamma_2$ (cm s ⁻¹)	k_2 (cm ³ mol ⁻¹ s ⁻¹)
AQ1	ACN	-0.58 ± 0.02	-0.86 ± 0.01	3.6 ± 1.9	0.26 ± 0.01	-0.27 ± 0.04	-0.37 ± 0.02	0.008 ± 0.002	0.51 ± 0.02	5.7 × 10 ⁸
AQ2	ACN	-0.55 ± 0.02	-0.86 ± 0.01	3.1 ± 1.7	0.21 ± 0.01	-0.20 ± 0.04	-0.39 ± 0.01	0.012 ± 0.002	0.16 ± 0.01	2.4 × 10 ⁸
AQ1	0.05 M H ₂ SO ₄	-0.59 ± 0.02	-0.87 ± 0.01	4.4 ± 2.1	0.21 ± 0.01	-0.24 ± 0.04	-0.29 ± 0.01	0.008 ± 0.002	0.13 ± 0.01	3.2 × 10 ⁸
AQ2	0.05 M H ₂ SO ₄	-0.55 ± 0.01	-0.86 ± 0.01	3.1 ± 1.8	0.21 ± 0.01	-0.21 ± 0.03	-0.39 ± 0.01	0.014 ± 0.002	0.16 ± 0.01	4.0 × 10 ⁸

The kinetic parameters for O₂ reduction on GC/AQ electrodes modified with previously synthesised AQ diazonium tetrafluoroborates are listed in Table 10. These values are similar to those obtained for the electrodes modified with *in situ* generated AQ diazonium compounds. The parameters characterising the properties of covalently attached AQ ($E_{(2)}^0$, $\Delta E_{(2)}$ and k_2) do not depend greatly on the point of attachment of the quinone (i.e. whether it is attached in position 1 or 2) although the value of k_2 for the 2-derivative is slightly larger than that for the 1-anthraquinone derivative. This is a surprising observation since at first sight, these two substitutions could lead to very different steric constraints for the attached molecule and hence different configurations for the activated state for the reaction between Q^{•-} and O₂ [127]. Since no such large difference is observed, it has to be concluded that the support plays a secondary role in the activated state configuration. The reason for this might be related to the type of bond formed on grafting. In all cases, an sp³ configuration must result when grafting takes place on an sp² domain on the GC surface [6]. Therefore, the steric constraints that may result from the different points in the quinone molecule bound to a carbon atom on the surface are minimised. This is particularly important for a highly disordered surface such as that of GC where the different configurations that may prevail in the grafted layer cannot distinguish between attachments at position 1 or 2 in the quinone molecule. The slightly higher value of k_2 could be ascribed to an increase in steric hindrance of the attached molecule leading to an increase in the activation energy for the first step of the reaction between the semiquinone and O₂ [127].

Although this was not the purpose of present work, the values of $\Delta E_{(2)}$ require some comments. This parameter is the difference between the standard potentials for the Q/Q^{•-} and the Q^{•-}/Q²⁻ redox couples. An average value of the order of -0.35 V has been calculated from the oxygen reduction results. However, a single voltammetric wave is observed in the absence of oxygen. The observation of a single voltammetric wave indicates that the value of $\Delta E_{(2)}$ should be close to zero but a much larger value of $\Delta E_{(2)}$ is observed. The difference in behaviour of quinones in aqueous and non-aqueous solvents has been known for a long time. Quan et al. [171] have provided a rationalisation based on solvation effects for the observation of a single voltammetric wave in alkaline aqueous solutions in many systems, including complex quinones such as ubiquinone [172]. The values of the width at half maximum are of the order of 140 mV but this could simply be a consequence of a small difference in the potentials of the two redox processes but cannot account for the larger values of $\Delta E_{(2)}$ observed.

The model used assumes that the quinone/quinone radical anion redox process is not dependent on the presence of oxygen in the system, i.e. the rates for this equilibrium are much faster than the rate of reaction of oxygen with the radical anion. It is difficult to see how the thermodynamics of the Q/Q^{•-} redox couple can be influenced by the presence of oxygen. A more complete analysis should include the individual rate constants for the Q/Q^{•-} couple in competition with the chemical rate constant and these questions will be analysed further in

the future. It should be stressed that the model used is an oversimplification in an attempt to extract kinetic information from a very complex system; the value of the parameter $\Delta E_{(2)}$ contains more information than a simple difference in standard potentials. These observations do not alter the conclusions of the present work.

6.2. Electrochemical properties of modified Ni electrodes

6.2.1. Oxygen electroreduction on anthraquinone-modified nickel electrodes in alkaline solution

6.2.1.1. Cyclic voltammetry of Ni/AQ electrodes

Modified nickel electrodes were cycled in Ar saturated 0.1 M KOH solution in the range of potentials from -0.3 to -1.0 V using sweep rate of 100 mV s^{-1} . During potential cycling the peak area decreased, because the physically adsorbed AQ remaining on the surface desorbs into solution. This is due to the fact that in alkaline solution, anthrahydroquinone is in anionic form and repulsion takes place between anionic species and the negatively charged electrode surface. The stabilised cyclic voltammetric response of Ni/AQ electrodes in O_2 free 0.1 M KOH is shown in Fig. 34. Cyclic voltammograms of Ni/AQ electrodes modified in different grafting solutions are similar, nevertheless, one can observe a slight difference in redox potentials ($E_f = -0.835$ V for the electrode modified in ACN and $E_f = -0.812$ V for the electrode modified in H_2SO_4). Figure 34 shows that modification in ACN yields a larger surface concentration of anthraquinone than modification in H_2SO_4 . For comparison purposes, the CV response of an unmodified nickel electrode in O_2 free 0.1 M KOH is also shown. It can be seen that at $E < -0.9$ V there is an increase of current, which could be associated with the reduction of Ni surface oxides. The hydrogen evolution reaction starts at more negative potentials on the bare nickel electrode. These results are in agreement with previous reports on the CV behaviour of Ni electrodes in alkaline solution [173–175].

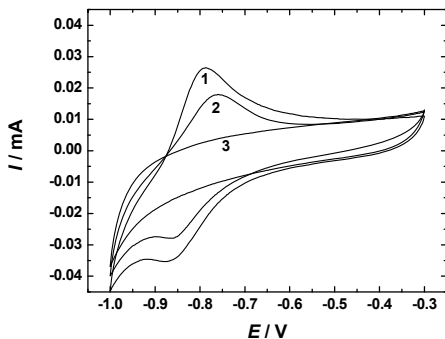


Figure 34. Cyclic voltammograms recorded in Ar saturated 0.1 M KOH for bare Ni (3) and Ni/AQ electrodes modified in acetonitrile (1) and in acid solution (2). $\nu = 100 \text{ mV s}^{-1}$.

The surface concentration of anthraquinone (Γ_Q) was determined by integration of the charge under the CV peaks ($\Gamma_Q = Q/nFA$ [145]). The values of Γ_Q of 6.5×10^{-10} and $5.3 \times 10^{-10} \text{ mol cm}^{-2}$ were found for Ni/AQ electrodes modified in ACN and H_2SO_4 , respectively. These values are higher than the surface concentrations of AQ on GC electrodes of similar modification [32]. The precise determination of Γ_Q is a complicated task because of the difficulties in baseline correction. Note also that the electrode roughness factor has not been taken into account for calculating Γ_Q for either of the electrodes. Therefore the actual surface coverages by AQ are not known. The higher value of surface concentration obtained in ACN as compared to that obtained in H_2SO_4 is in agreement with previous observations [58].

6.2.1.2. Oxygen reduction on Ni/AQ electrodes

The polarisation curves of oxygen reduction on Ni/AQ electrodes were registered in the same potential range as CV curves (from -0.3 to -1.0 V) at different rotation rates. Figures 35 and 36 present the oxygen reduction results for Ni/AQ electrodes modified in ACN and H_2SO_4 , respectively. Figure 35 also shows that Ni electrodes modified with AQ are significantly more active for oxygen reduction than a polished Ni electrode. It is evident that the electrocatalytic activity of the bare Ni electrode is rather low. It was found that the O_2 reduction current on the latter electrode was almost independent of rotation rate. These results obtained for polished nickel are in a good agreement with those obtained by Bagotzky et al. for oxidised Ni electrodes [173,174]. A poor performance towards O_2 reduction in alkaline solution was also observed for Ni catalysts supported on Vulcan XC-72R (the exchange current density (j_0) was found to be rather low: $j_0 = 8 \times 10^{-10} \text{ mA cm}^{-2}$) [176].

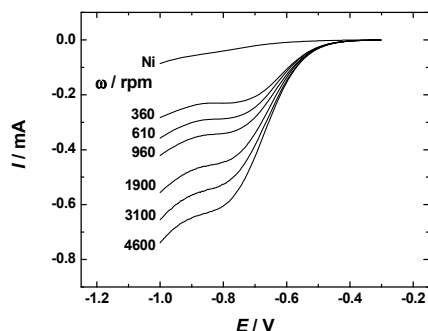


Figure 35. RDE voltammetry curves for oxygen reduction in O_2 saturated 0.1 M KOH on a Ni/AQ electrode modified in acetonitrile solution. $\nu = 20 \text{ mV s}^{-1}$. The curve (Ni) corresponds to the reduction of O_2 on a polished Ni electrode at $\omega = 360 \text{ rpm}$.

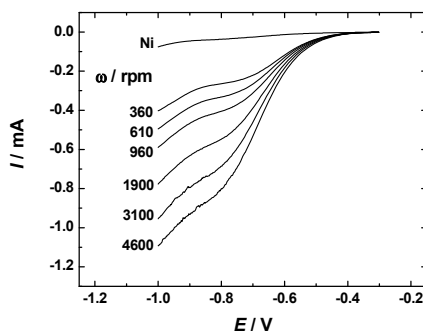


Figure 36. RDE voltammetry curves for oxygen reduction in O_2 saturated 0.1 M KOH on a Ni/AQ electrode modified in acid media. $\nu = 20 \text{ mV s}^{-1}$. The curve (Ni) corresponds to the reduction of O_2 on a polished Ni electrode at $\omega = 360 \text{ rpm}$.

On both Ni/AQ electrodes, the O_2 reduction wave commences at *ca* -0.4 V , which is 0.1 V more negative than that of the AQ-modified GC electrodes [31,32]. This could be explained by the electrocatalytic effect of the native quinone-type species on the surface of GC. The electrocatalysis by surface-bound AQ starts at a more negative potential as compared to GC sites [31]. It is also evident that Ni/AQ electrodes modified in H_2SO_4 showed slightly higher reduction currents than Ni/AQ electrodes modified in ACN. Further work is needed in order to explain the peculiarities caused by modification in different grafting solutions. It is interesting to note that chemical polishing of the Ni electrode surfaces did not noticeably alter the electrocatalytic properties of the anthraquinone-modified electrodes towards O_2 reduction.

The Koutecky–Levich analysis is shown in Figs. 37 and 38. The number of electrons transferred per O_2 molecule (n) was calculated from the K–L equation [145].

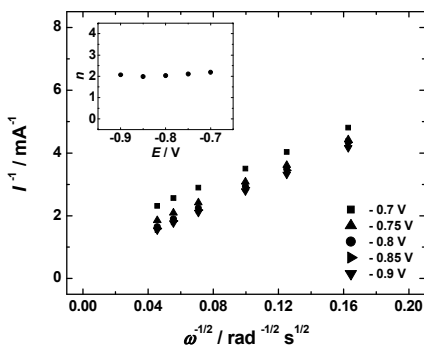


Figure 37. Koutecky–Levich plots for oxygen reduction on Ni/AQ electrodes in 0.1 M KOH (electrode modified in ACN). The inset shows the potential dependence of the number of electrons transferred per O_2 molecule. Data derived from Figure 35.

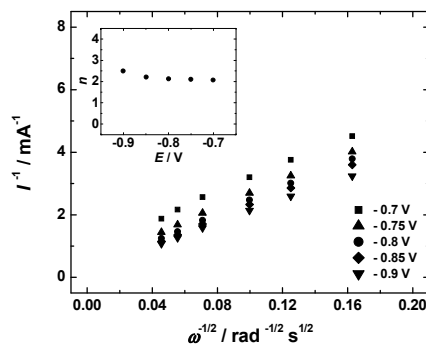


Figure 38. Koutecky–Levich plots for oxygen reduction on Ni/AQ electrodes in 0.1 M KOH (electrode modified in H_2SO_4). The inset shows the potential dependence of the number of electrons transferred per O_2 molecule. Data derived from Figure 36.

The value of n was close to two for both AQ-modified Ni electrodes (see insets to Figs. 37 and 38), indicating that the process of O_2 reduction on these electrodes yields hydrogen peroxide as the final product. It is also evident that the reduction of O_2 is under mixed kinetic–diffusion control even at high negative potentials. By extrapolating the K–L lines at -0.8 V, we obtain a lower intercept value for the Ni/AQ electrode modified in H_2SO_4 , which indicates the faster kinetics of O_2 reduction on this electrode.

The value of the rate constant k obtained from the intercept at -0.8 V (i.e., at the potential very close to the redox potential of surface-bound AQ) could be compared with the chemical rate parameter ($k_c\Gamma$) determined in our previous studies using GC/AQ electrodes of different values of Γ_Q [31,32]. In this case, we assume that $k = k_c\Gamma$ using the following equation:

$$k = \frac{I_k}{nFAC_{O_2}} \quad (20)$$

The simplified approach used in the present work for the determination of $k_c\Gamma$ is due to the fact that there are other sites contributing to the reduction current besides quinone sites. The increase of current at $E < -0.9$ V (Figs. 35 and 36) is associated with the reduction of O_2 on Ni sites. For this reason, we could not use the surface redox-catalytic cycle model which has been employed in the determination of kinetic parameters of O_2 reduction on GC/AQ electrodes in our previous studies [25,31–35,120,121].

In case of Ni/AQ electrode modified in ACN, $k_c\Gamma = 0.035 \text{ cm s}^{-1}$ and for the electrode modified in H_2SO_4 , the value of the chemical rate parameter was higher ($k_c\Gamma = 0.081 \text{ cm s}^{-1}$). By using the surface concentrations of AQ determined from the cyclic voltammograms, the rate constant for a chemical reaction between $\text{AQ}^{\bullet-}$ and molecular oxygen (k_c) was calculated to be $5.4 \times 10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $1.5 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for Ni/AQ electrodes modified in ACN and in acid media, respectively. It should be noted that the value of rate constant reported for the AQ-modified GC electrode in the same solution (0.1 M KOH) was significantly higher ($k_c = 4.7 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [32]). The reason for this discrepancy is not clear. We may assume that there could be different orientation of AQ moieties on GC and Ni electrodes. There is also an intriguing question whether quinone groups are attached to metal surface or to oxide film of the latter electrode. There is a controversy in the literature in this respect. Some groups claim that a covalent bond is formed between metal surface and aryl groups [53,58], other authors argue that the attachment could also occur via surface oxides [46]. By comparing the surface modification of Ni electrodes in ACN and in aqueous acidic solution, one could expect the reduction of surface oxides during electrochemical grafting in 0.05 M H_2SO_4 (the Ni electrode was held at -0.4 V for 10 min). In this way, at least in part, the covalent attachment of AQ species to metallic surface may occur. It appears that the higher O_2 reduction activity of the electrode modified in 0.05 M H_2SO_4 is related to such a difference in surface grafting. A sophisticated surface analytical approach is needed in order to clarify this essential aspect of surface modification. Such an investigation was outside the scope of the present work.

6.2.2. Electrochemical behaviour of nickel electrodes modified with nitrophenyl groups

6.2.2.1. Electrografting of Ni electrodes with NP groups

The surface of Ni electrodes was modified with nitrobenzene layers by electrochemical reduction of the corresponding diazonium salt. Figure 39 presents the linear potential scans of electrografting of nitrophenyl groups to the Ni electrode surface in acetonitrile. The grafting behaviour of NP to Ni is rather similar to that previously observed [53]. The first potential scan shows a current peak of diazonium reduction at *ca* 0.1 V vs. SCE and the peak disappeared on the second scan, indicating a complete blocking of the surface by nitrophenyl layer. To improve the compactness of the NP film altogether 10 cycles were carried out followed by holding the electrode at -0.3 V for 10 min.

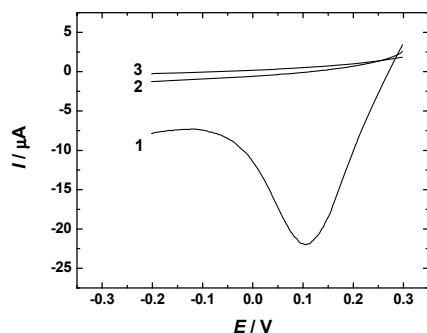


Figure 39. Electrochemical grafting of nitrophenyl groups to nickel electrode in Ar-saturated acetonitrile containing 3 mM 4-nitrobenzenediazonium tetrafluoroborate and 0.1 M TBABF₄, $\nu = 100 \text{ mV s}^{-1}$. The first (1), second (2) and tenth (3) potential scan are shown.

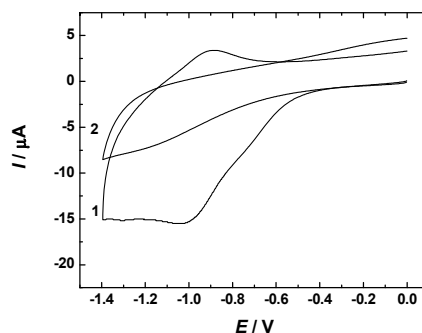


Figure 40. Cyclic voltammograms for nitrophenyl modified Ni (1) and polished Ni (2) electrodes in Ar-saturated ACN + 0.1 M TBABF₄, $\nu = 100 \text{ mV s}^{-1}$.

Figure 40 shows a cyclic voltammogram obtained after the electrochemical grafting with nitrophenyl groups (curve 1). A cathodic peak is observed at -1.05 V on the grafted electrode, which corresponds to the reduction of nitrophenyl groups [42,53] confirming the presence of these groups on the Ni electrode after ultrasonic rinsing. The peak decreases on subsequent scans, indicating the formation of protonated species by reaction of radical anions ($-\text{NO}_2^{\bullet-}$) with residual water. The CV response of an unmodified Ni electrode in the same solution is given for comparison purposes (Fig. 40, curve 2).

6.2.2.2. XPS analysis of Ni/NP samples

The modified electrode surfaces were further characterised by XPS. The XPS survey spectrum of the nitrophenyl modified nickel is shown in Fig. 41. A large decrease of the Ni2p peak was observed upon surface modification with NP groups, but still it is clearly visible. The XPS peaks of underlying nickel (Ni2p, Ni3s, Ni3p) are detected either because the organic layer is very thin or because it is incomplete in places. Similar behaviour has been reported by Adenier et al. [43]. Other large peaks are that of carbon (C1s) originating from the organic layer and of oxygen (O1s) related to nitro groups and surface oxides and most importantly the N1s peak confirming the presence of nitrophenyl groups on the surface. This peak is totally absent on the survey spectra of an unmodified nickel surface (data not shown). The inset of Fig. 41 reveals two peaks in the N1s region similar to the XPS spectra of nitrophenyl modified nickel electrodes previously observed [42]. The first peak with the higher binding energy around

406 eV is attributed to $-\text{NO}_2$ functionality. The second peak with a lower binding energy around 400 eV is attributed to amines. It has been demonstrated that the second peak can come from chemical transformations of $-\text{NO}_2$ groups under the X-ray beam during the XPS experiment [42,177].

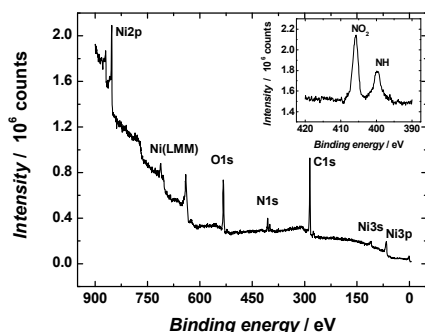


Figure 41. XPS survey spectrum of a nitrophenyl modified nickel. The inset shows the XPS spectrum of N1s region of nitrophenyl modified nickel.

6.2.2.3. Electrochemical reduction of $\text{Fe}(\text{CN})_6^{3-}$ on bare Ni electrodes

The passivation of the nickel surfaces after the modification with nitrobenzene diazonium salt was investigated using potassium ferricyanide as a redox probe. In order to describe the blocking effect of aryl films, $\text{Fe}(\text{CN})_6^{3-}$ reduction was first studied on a polished nickel electrode for comparison purposes. Figure 42 presents the RDE voltammetry curves recorded on an unmodified Ni electrode in 0.1 M KOH containing 5 mM $\text{Fe}(\text{CN})_6^{3-}$. A large diffusion-limited current plateau is observed analogous to that of carbon and noble metal electrodes in the same solution. The half-wave potential independence of rotation rate reveals close to the reversible behaviour, which is an indication of a fast redox transition process. It is interesting to note that these experiments cannot be carried out on Ni electrodes in a neutral solution (for instance in 0.1 M K_2SO_4 containing ferricyanide), because the oxidation potential of nickel is more negative than the redox potential of the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple [42]. However, these measurements can be performed in alkaline solution because the Ni surface oxidation is pH dependent. It is well-known that nickel electrodes are much more stable when the oxide layer is covering their surface. It has been estimated by XPS that the thickness of the oxide film is *ca* 1–2 nm when a polished Ni electrode is immersed in 0.1 M KOH. Obviously, the different behaviour of Ni electrodes in the solution of high pH could be related to the presence of an oxide film.

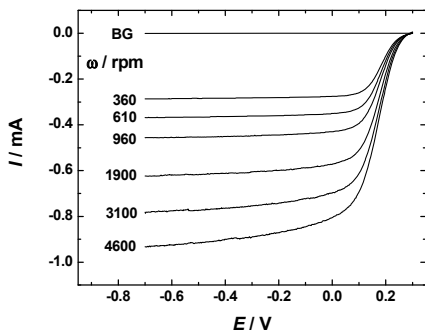


Figure 42. RDE voltammetry curves for ferricyanide reduction on a polished Ni electrode in Ar-saturated 0.1 M KOH containing 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ at different rotation rates. $\nu = 20 \text{ mV s}^{-1}$. Curve BG is recorded in the absence of ferricyanide and represents the background current.

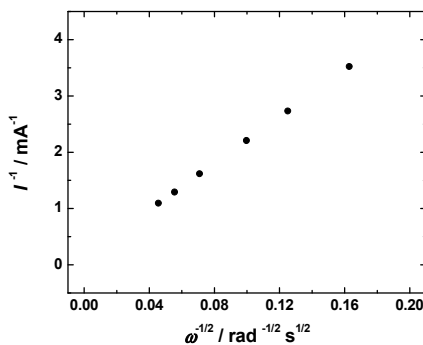


Figure 43. Koutecky–Levich plots of ferricyanide reduction on a polished Ni electrode in Ar-saturated 0.1 M KOH solution containing 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ at $E = -0.5 \text{ V}$. Data derived from Figure 42.

The Koutecky–Levich plot for ferricyanide reduction on the polished Ni electrode is shown in Fig. 43. The extrapolated K–L line yields intercept close to the origin at -0.5 V , which indicates that the process is primarily controlled by mass-transfer at this potential. The Levich slope determined from Fig. 43 is $0.0483 \text{ mA rad}^{-1/2} \text{ s}^{1/2}$, which is in a good agreement with a theoretical Levich slope ($B = 0.0499 \text{ mA rad}^{-1/2} \text{ s}^{1/2}$), calculated using Eq. (21) [145].

$$I_d = 0.62nFAC^0 D^{2/3} \nu^{-1/6} \omega^{1/2} = B\omega^{1/2} \quad (21)$$

where I_d represents diffusion-limited current, n is the number of electrons involved ($n=1$), F is the Faraday constant ($96\,485 \text{ C mol}^{-1}$), C^0 is the concentration of ferricyanide in the bulk ($5 \times 10^{-6} \text{ mol cm}^{-3}$), D is the diffusion coefficient of ferricyanide ($7.63 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) [178], ν is the kinematic viscosity of the solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$) [147] and ω is the rotation rate.

6.2.2.4. Electrochemical response of the $\text{Fe}(\text{CN})_6^{3-/4-}$ probe on Ni/NP electrodes

It can be assumed that the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple should interact with the Ni surface for a fast electron transfer to occur. Apparently, blocking the surface by aryl moieties should inhibit the rate of electron transfer of this couple. Figure 44 presents the RDE voltammetry curves for Ni/NP modified electrodes recorded in the solution of 5 mM $\text{Fe}(\text{CN})_6^{3-}$. It is clearly evident that compared with polished Ni electrode (shown in Fig. 41) the nitrophenyl film on the Ni

electrode surface suppresses the reduction current to a great extent. The reduction current is almost independent of rotation rate, which is an indication of relatively small fraction of the surface at which the reaction proceeds. However, we observed some scatter in the RDE data, which primarily arises from fine differences in the preparation of Ni/NP modified electrodes, even though the same procedure of modification was used. Nevertheless, it is clearly observed that the nitrophenyl layer attached to the Ni electrode surface strongly inhibits the ET kinetics of the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple.

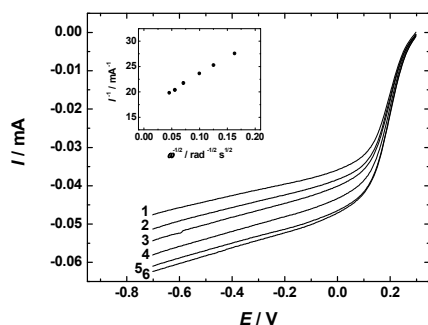


Figure 44. RDE voltammetry curves for ferricyanide reduction on a NP-modified Ni electrode in Ar-saturated 0.1 M KOH containing 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$. $\nu = 20 \text{ mV s}^{-1}$. ω : (1) 360, (2) 610, (3) 960, (4) 1900, (5) 3100 and (6) 4600 rpm. The inset shows the K-L plot for ferricyanide reduction on a Ni/NP electrode at -0.5 V .

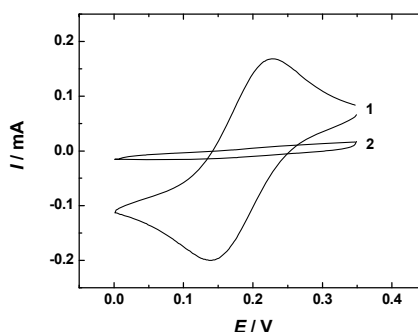


Figure 45. Cyclic voltammograms recorded in Ar-saturated 0.1 M KOH containing 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ for polished Ni (1) and Ni/NP electrodes (2). $\nu = 100 \text{ mV s}^{-1}$.

The Koutecky–Levich analysis was made and the K–L plot was inserted in Fig. 44. At this stage of work we are not able to determine unequivocally, what is the percentage of the Ni electrode surface blocked. It appears to be too speculative to determine the uncovered area from the response of the $\text{Fe}(\text{CN})_6^{3-/4-}$ probe. The kinetic current (I_k) was obtained from the intercept of the extrapolated K–L lines shown in the inset of Fig. 44. However, we can only calculate from $I_k = nFkAC$ the product $k \times A$ and cannot distinguish between their contributions (i.e. the decrease in the heterogeneous electron transfer rate constant (k) and the decrease in the surface area available for the redox species (A) cannot be separated). Moreover, the application of other redox couples might give significantly different response when the same modified electrode (Ni/NP) is used.

Obviously, the main reason for the retardation of the electron transfer process is that these ions (*ca* 0.62 nm in size) cannot penetrate through the NP

film. Apparently, there is a relatively small number of defects or uncovered areas at which the interaction between hexacyanoferrate ions and Ni surface could occur (the Ni2p peak observed in the XPS survey spectrum gives further evidence for that). The requirement for the direct interaction is analogous to that proposed for GC electrodes [89].

Figure 45 shows the cyclic voltammograms of nickel electrodes before (polished Ni) and after surface modification with nitrophenyl groups in 5 mM ferricyanide in 0.1 M KOH solution at a scan rate of 100 mV s^{-1} . At low sweep rates the peak separation of the polished Ni electrode cyclic voltammogram is close to the theoretical value for a reversible electron transfer process ($\Delta E = 59 \text{ mV}$) [145], however, the ΔE value slightly increases with increasing sweep rate. As expected, the dependence of I_p vs $v^{1/2}$ yields a linear relationship. The electrochemical behaviour of the unmodified Ni electrode towards this redox couple is similar to that of GC and noble metal electrodes [179]. The cyclic voltammograms of Ni/NP modified electrodes in the same solution were almost featureless showing a strong blocking effect of the modifier film (Fig. 45, curve 2). Also, the ΔE value was higher for the Ni/NP electrode. The extent of blocking can be estimated on the bases of the normalised current ($I_{p(\text{film})}/I_{p(\text{bare})}$) [20]. The CV peak current decreases by a factor of approximately 50 in the presence of the NP film. These results are in line with those obtained using NP-modified GC electrodes [13,14,16,20,42,180]. The CV and RDE results obtained with Ni/NP electrodes modified in aqueous acidic solution were similar to those modified in acetonitrile. The versatility of the diazonium reduction method makes it a promising tool in the modification of nickel surface with aryl groups for various applications, including molecular electronics.

6.3. Electrochemical properties of modified Au electrodes

6.3.1. Surface modification of gold electrodes with anthraquinone diazonium cations

6.3.1.1. Surface modification of gold with AQ by diazonium reduction

Figure 46 shows $i - E$ and $\Delta m - E$ potentiodynamic profiles for Au electrodes during five repetitive cycles in 0.1 M $\text{NaClO}_4/\text{ACN}$ and in 0.05 M H_2SO_4 containing 3 mM of the AQ diazonium salt. As can be seen in Fig. 46 the first potential scan shows a current peak corresponding to the reduction of AQ diazonium cations. These peaks are centered at 0.22 and 0.29 V vs. SCE in $\text{NaClO}_4/\text{ACN}$ and in H_2SO_4 , respectively. At the same time an increase in mass is observed with the displacement of the potential at negative direction. It is important to note that the peak current density of the reduction of AQ diazonium cations is significantly higher in $\text{NaClO}_4/\text{ACN}$ as compared to that obtained in H_2SO_4 . However, the mass increases by almost the same value in

both solutions. It should be mentioned that in both solutions the mass increase starts only at more negative potentials than the potential of the first CV peak. When the potential scan is reversed, the mass continues to increase slowly. During the further cycling the increase of mass is rather gradual. By comparing the mass change between the first and the fifth scans, an increase in mass around 200 and 70 ng cm^{-2} was observed for the reduction of the AQ diazonium salt in $\text{NaClO}_4/\text{ACN}$ and in H_2SO_4 , respectively. This type of behaviour was observed previously by other groups studying the covalent grafting of gold with other aryldiazonium compounds [62,64,70]. The behaviour of mass increase only after the potential of the first CV peak and a slow mass increase on the reverse scan can be attributed to the formation of charge-transfer complexes that precipitate on the electrode surface [181].

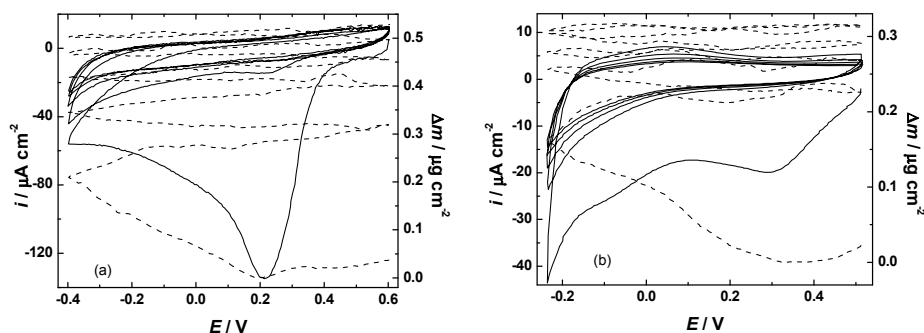


Figure 46. $i - E$ (solid line) and $\Delta m - E$ (dashed line) potentiodynamic profiles for five repetitive potential cycles for electrografting of AQ groups to Au electrodes in: (a) 0.1 M $\text{NaClO}_4/\text{ACN}$ and (b) 0.05 M H_2SO_4 . Both solutions contained 3 mM AQ diazonium salt. $v = 100 \text{ mV s}^{-1}$.

After recording five consecutive $i - E$ and $\Delta m - E$ profiles the electrodes were held at a constant potential (-0.2 V in both solutions) for 5 min and a relatively small reduction current was observed during the chronoamperometric experiments (data not shown). Surprisingly, at the same time the mass continues to increase indicating that a thicker modifier layer is formed reinforcing the multilayer growth as observed in Fig. 47 (see the section of AFM studies). The faradaic efficiency was calculated from the slope of the $\Delta m - \Delta q$ plots for different experimental conditions and the efficiency in ACN was close to 0.5 during the first electrografting scan. The faradaic efficiency was higher in H_2SO_4 .

6.3.1.2. Surface characterisation of AQ-modified Au electrodes by AFM

Surface morphology of AQ-modified gold electrodes was studied with AFM. Typical topographical images of the AQ-modified and bare Au surfaces are presented in Fig. 47. It can be seen from these images that a uniform granular AQ film is formed on the electrode surface in both modification media. The mean granule size in both cases is approximately the same (*ca* 15–17 nm). A certain distribution of granule sizes and the appearance of larger AQ grains are also notable. These features are bigger (50–55 nm in diameter) than the size of typical granules and sparse on the surface of electrode modified in ACN (Fig. 47b). For the samples modified in acid media the size of large AQ granules is smaller, 35–45 nm in diameter, but they appear rather frequently on the surface (Fig. 47c).

It is evident from Fig. 47 that in both cases the AQ films formed are relatively smooth: the RMS (root mean square) roughness value of both AQ films is almost the same, 1.30 nm for the film modified in ACN and 1.32 nm for the film modified in acid media. For comparison, the RMS roughness value for the unmodified Au(111) surface was determined to be 0.26 nm (Fig. 47a).

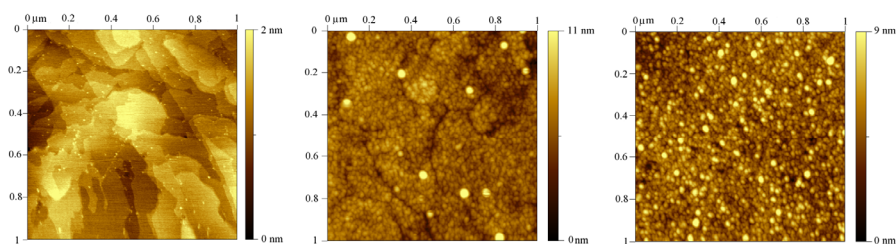


Figure 47. AFM images of AQ-modified (b,c) and bare gold (a) electrodes. Electrodes were modified in 0.1 M TBABF₄/ACN (b) and 0.05 M H₂SO₄ (c) containing 3 mM AQ diazonium salt. Note that the z-axis scale for image (a) is different than that used for the other two images.

6.3.1.3. Electrochemical behaviour of AQ-modified Au electrodes

Anthraquinone coverage and stability of the grafted surfaces were characterised by cycling the electrodes between -0.4 and -1.1 V for 25 times in Ar saturated 0.1 M KOH. Characteristic CV responses of these electrodes at various potential scan rates are shown in Fig. 48.

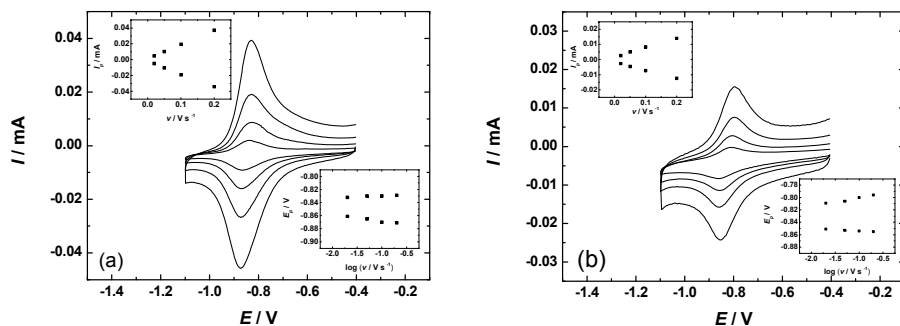


Figure 48. Cyclic voltammograms recorded in Ar saturated 0.1 M KOH for Au/AQ electrodes at different potential scan rates ($\nu = 20; 50; 100$ and 200 mV s^{-1}). $A = 0.2 \text{ cm}^2$. The electrodes were modified in ACN (a) and in acid solution (b). The insets show the plots of I_p vs. ν and E_p vs. $\log \nu$.

The redox potential (E_f) of surface-bound AQ obtained by modification in ACN was -0.85 V , close to the value previously reported for an AQ-modified GC electrode (-0.845 V [31]). The electrode modified in $0.05 \text{ M H}_2\text{SO}_4$ showed a similar redox potential ($E_f = -0.83 \text{ V}$). The surface concentration of anthraquinone (Γ) was determined by charge integration under the CV peaks ($\Gamma = Q/nFA$ [145], where Q is the amount of charge consumed, n is the number of electrons involved ($n=2$), F is the Faraday constant and A is the geometric area). The Γ_{AQ} values were 8.1×10^{-10} and $2.9 \times 10^{-10} \text{ mol cm}^{-2}$ for the electrodes modified in ACN and in $0.05 \text{ M H}_2\text{SO}_4$, respectively. The scan rate dependence of the peak current (I_p) and potential (E_p) was also analysed. The insets to Fig. 48 present the I_p vs. ν and E_p vs. $\log \nu$ responses for the AQ-modified Au electrodes. As expected for a surface ET process, the peak currents for both Au/AQ electrodes are linearly dependent on ν . The surface-confined AQ shows a quasi-reversible ET behaviour as the separation of anodic and cathodic peak potentials increases with the scan rate. These features are similar to those observed for GC/AQ electrodes in our previous studies [31,I,III,IV]. The significance of this work is to have demonstrated that electrografting from the solutions of AQ diazonium derivatives provides a good means for the preparation of Au/AQ electrodes. These electrodes could be employed for various applications, including electrochemical biosensors. It is highly challenging to develop biosensors based on aryl-modified Au electrodes [7,63].

6.3.2. Electrochemical properties of aryl-modified Au electrodes

6.3.2.1. Electrografting of aryldiazonium cations to Au electrodes

Figure 49 shows cyclic voltammograms for a gold electrode in the solutions of the aryldiazonium salts studied. The voltammograms show multiple peaks. The first sharp peak can be associated with the reduction of diazonium cations on Au(111) facets and the second peak, at more negative potentials, with reduction on Au(100) domains [62]. For the attachment of 1-naphthyl groups a third and broader peak was observed and this was more marked in the case of PhBr. This can be attributed to the convolution of reduction on Au(110), Au(311) and other crystal faces [62]. The peak potentials for the first cathodic scan were 0.25 and 0.08 V for Naph1, 0.24 and 0.14 V for Naph2, 0.23 and 0.09 V for BP, and 0.34 and 0.15 V for PhBr. These peaks disappear on consecutive scans and the cyclic voltammogram becomes featureless indicating maximum coverage.

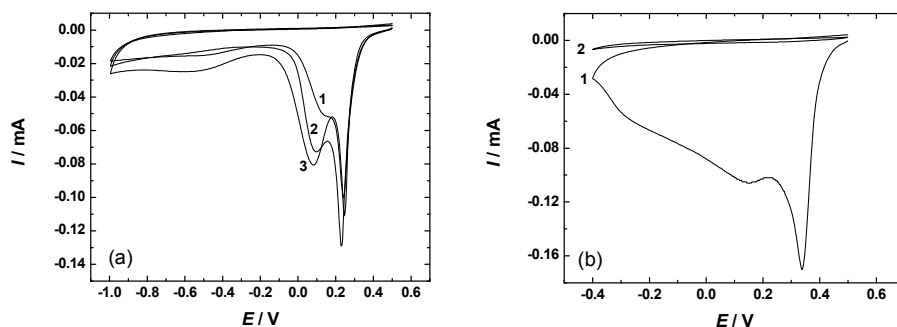


Figure 49. Electrografting of aryl groups to gold in Ar-saturated ACN containing 3 mM aryldiazonium cations and 0.1 M TBABF₄ at 100 mV s⁻¹. (a) 2-Naph-N₂⁺ (1); BP-N₂⁺ (2); 1-Naph-N₂⁺ (3) showing the first scan and (b) PhBr-N₂⁺. The 1st (1) and 10th (2) scans are shown.

As suggested by Benedetto et al. [62], although the exact nature and peak potential for the reduction of diazonium salts is not fully understood yet, the reduction of electroactive species in the solution leads to the formation of a strongly adsorbed layer (chemisorbed product) on the electrode surface. The diffusion peak corresponding to the reduction of the species in solution is preceded by a pre-peak which corresponds to the formation of the strongly adsorbed layer.

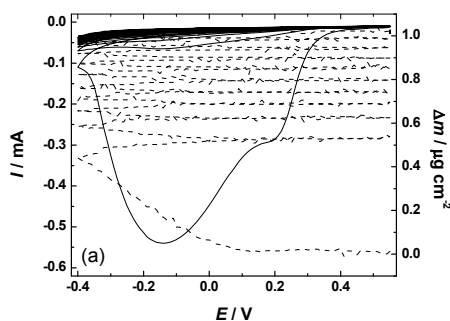


Figure 50a. I - E (solid line) and Δm - E (dashed line) potentiodynamic profiles for 10 repetitive potential cycles for electrografting of PhBr groups to Au electrode in 0.1 M $\text{NaClO}_4/\text{ACN}$ containing 3 mM 4-bromobenzenediazonium cations. $\nu = 100 \text{ mV s}^{-1}$.

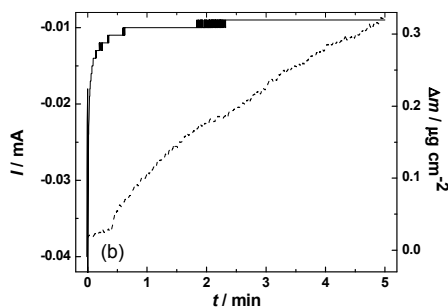


Figure 50b. I - t (solid line) and Δm - t (dashed line) dynamic profiles for the chronoamperometric experiment at -0.2 V vs. SCE for Au electrode in 0.1 M $\text{NaClO}_4/\text{ACN}$ containing 3 mM of 4-bromobenzenediazonium cations (after 10 potential scans presented in Fig. 50a).

Figure 50a presents I - E and Δm - E potentiodynamic results for a Au electrode during 10 repetitive cycles in 0.1 M $\text{NaClO}_4/\text{ACN}$ containing 3 mM of the 4-bromobenzenediazonium salt. The current response in Fig. 50a differs from that in Fig. 49b. The 0.34 V peak for bulk Au is absent from the voltammograms recorded during the EQCM experiments. This can be attributed to differences in crystallographic orientation of the Au/quartz oscillator compared with a polished bulk gold electrode. The first potential scan shows two current peaks at 0.2 and -0.15 V (see Fig. 50a) corresponding to the reduction of the 4-bromobenzenediazonium cation. An increase in mass is observed for potentials more negative than 0.1 V, which does not necessarily mean that no grafting occurs during the first reduction wave. If at the first stage of the attachment of aryl groups the molecules of the modifier replace adsorbed solvent molecules on the surface of gold film in equivalent mass could be the reason why we do not observe a total mass change at potentials between 0.4 and 0.1 V of the first electrografting scan. When the potential scan is reversed, the mass continues to increase slowly. A gradual mass increase is observed on further cycling the potential. Comparing the mass change of the 1st and 10th scans, an increase in mass of approximately 550 ng cm^{-2} is observed for a layer that blocks completely the reduction of the diazonium compound. This behaviour has been previously observed for the covalent grafting of gold with other aryldiazonium compounds [62,64,70]. The slow mass increase in the reverse scan has been attributed to the formation of charge-transfer complexes that precipitate on the electrode surface [181,VII], but further growth from the radicals generated and diffusing to the electrode surface cannot be ruled out. The faradaic efficiency was calculated from the slope of the $\Delta m - \Delta q$ plots for different experimental

conditions and a value of 24% was found for the first electrografting scan. By assuming a surface concentration of $10 \times 10^{-10} \text{ mol cm}^{-2}$ for a monolayer [64], the corresponding mass expected for a monolayer of PhBr is 156 ng cm^{-2} . The surface concentration of PhBr on Au surface can be calculated as $28.2 \times 10^{-10} \text{ mol cm}^{-2}$ (440 ng cm^{-2}), indicating the presence of more than a monolayer for the first potential half cycle.

After recording 10 consecutive $I-E$ and $\Delta m-E$ profiles the electrode was held at a constant potential of -0.2 V for 5 min and a relatively small reduction current was observed during the chronoamperometric transient (Fig. 50b). Surprisingly, although the current is very small, the mass continues to increase indicating further growth of the grafted layer (i.e. multilayer growth).

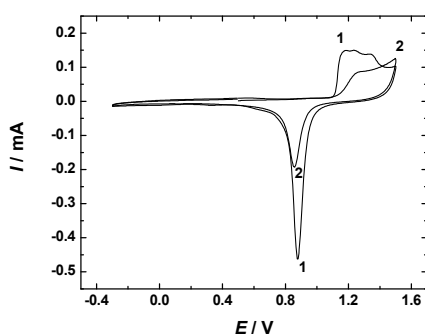


Figure 51. Cyclic voltammograms recorded in Ar-saturated $0.5 \text{ M H}_2\text{SO}_4$ for polished gold (1) and Au/PhBr (2) electrodes. $\nu = 100 \text{ mV s}^{-1}$. Electrode was modified by potential cycling between 0.5 and -0.4 V (10 scans in total) in ACN + 0.1 M TBABF_4 containing 3 mM 4-bromobenzenediazonium cations, followed by holding the potential at -0.2 V for 10 min.

The surface coverage by bromophenyl groups (θ) was characterised by cycling the polished gold (1) and Au/PhBr (2) electrodes between -0.3 and 1.5 V in Ar-saturated $0.5 \text{ M H}_2\text{SO}_4$ (Figure 51). The charge under the cathodic reduction peak (Q) for the Au/PhBr electrode was $221 \mu\text{C}$, which is lower by a factor of two compared to unmodified gold ($Q = 459 \mu\text{C}$). Even though the bromophenyl film appears to be rather thick (see Section 6.3.2.3. of AFM measurements), there are still some areas of the underlying gold substrate that are exposed to the solution. For this Au/PhBr electrode the value of θ was 0.52 . The exposed surface area (A_r) of gold was determined by integration of the current under the oxide reduction peak, assuming a charge of $400 \mu\text{C cm}^{-2}$ for an oxide monolayer [182]. The value of surface coverage of the modified electrodes may vary with the state of organic layers and substrate due the fact that different crystallographic orientation of gold surface may result in the formation of adsorbed layer of various strength and structures.

6.3.2.2. XPS analysis of Au/PhBr electrodes

Figure 52a and b compare the XPS survey spectra of 4-bromophenyl modified gold surfaces prepared by cycling and cycling followed by further reduction of the diazonium precursor at -0.2 V, respectively. The ratio of the Au4f to the Br3d peaks is larger for the former, confirming the results in Fig. 50a and b that, although the current is low, the 4-bromophenyl layer continues growing at -0.2 V. No detectable N1s peak at *ca* 400 eV is observed and therefore no reduction to other nitrogen containing groups is in evidence [42]. Also, no satellite peak on the high resolution C1s spectrum indicating the formation of a Au–C covalent bond on the surface is detectable (data not shown). The presence of Au–C bonds has been difficult to detect unambiguously by XPS [65,68].

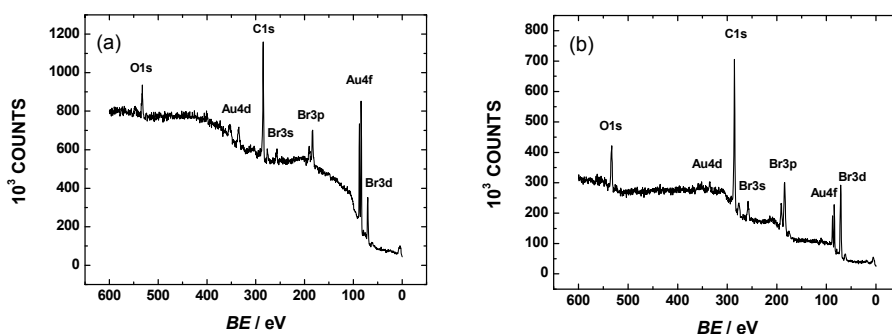


Figure 52. XPS survey spectra of 4-bromophenyl modified Au samples: (a) thin layer and (b) thick layer. Electrodes were modified: (a) by applying 10 potential cycles between 0.5 and -0.4 V at 100 mV s^{-1} in ACN + 0.1 M TBABF₄ containing 3 mM 4-bromobenzenediazonium cations and (b) followed by holding the potential at -0.2 V for 10 min.

6.3.2.3. Surface characterisation of Au/PhBr electrodes by AFM

AFM was used to study the surface morphology of the 4-bromophenyl-modified gold on a mica substrate. Figure 53 presents typical topographical images obtained in intermittent contact mode and their height profiles.

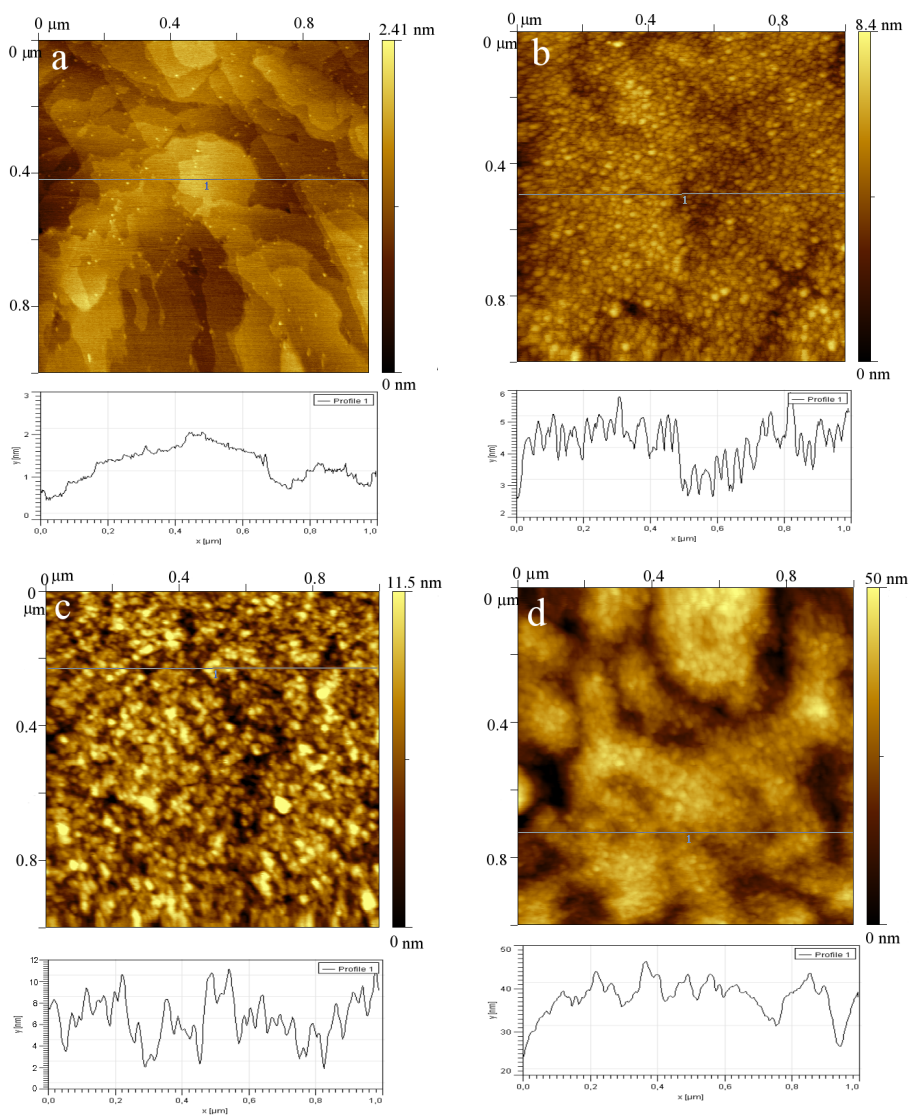


Figure 53. AFM images of bare gold (a) and Au/PhBr electrodes (b–d). Au electrodes were modified in 0.1 M TBABF₄/ACN containing 3 mM 4-bromobenzenediazonium cations, (b) 3 cycles between 0.5 and –0.4 V, (c) 10 cycles between 0.5 and –0.4 V and (d) 10 cycles between 0.5 and –0.4 V, followed by holding the electrode at –0.2 V for 10 min.

The bare Au film topography consists of atomically flat (111) terraces separated by (mono)atomic steps (Fig. 53a). The AFM images of aryl-modified electrodes exhibited a granular morphology (Fig. 53b–c). The film roughness and thickness increases with the number of potential cycles: three voltammetric cycles between 0.5 and –0.4 V (Fig. 53b) yielded a relatively smooth surface with a root mean square (RMS) roughness of 0.89 nm compared to 2.3 nm for the

same surface after 10 potential cycles (Fig. 53c). After holding the electrode at -0.2 V for 10 min the RMS surface roughness increased even more drastically, up to 7.5 nm (Fig. 53d). For comparison, the RMS roughness of the unmodified Au(111) surface was 0.26 nm. For additional comparison, the RMS roughness ratio obtained from the value after three voltammetric cycles between 0.5 and -0.4 V during the modification of Au(111) surface (Fig. 53b) and the unmodified Au(111) surface was 3.5 and the calculated surface concentration of PhBr on a Au surface after three voltammetric cycles between 0.5 and -0.4 V was 45×10^{-10} mol cm $^{-2}$ (700 ng cm $^{-2}$, see Fig. 50a). The granular features on the electrode modified by three potential cycles (Fig. 53b) were highly uniform with a 14 – 16 nm average diameter, whereas after 10 voltammetric scans, their dimensions varied markedly, with a maximum diameter of 35 nm. When the electrode potential was further held at -0.2 V for 10 min, their diameter became more uniform, but their mean size still remained larger (18 – 25 nm) than that of the granules formed after three potential cycles.

6.3.2.4. Electrochemical response of the $\text{Fe}(\text{CN})_6^{3-/4-}$ probe on modified Au electrodes

The blocking behaviour of aryl layers was investigated using the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple [61]. Figure 54 compares the cyclic voltammetric behaviour of aryl-modified gold electrodes in 0.1 M K_2SO_4 containing 1 mM $\text{Fe}(\text{CN})_6^{3-}$. For comparison, the response of a bare gold electrode is also shown (Fig. 54, curve 1). A pair of well-defined peaks is observed, with a peak to peak separation (ΔE_p) of 65 mV confirming the well-known fast one-electron transfer kinetics for this couple, close to the theoretical value of 60 mV expected for a reversible one-electron transfer process. In contrast to a bare gold electrode, electron transfer at the aryl-modified electrodes is almost completely blocked. The observed inhibition of ET between the metal and the redox species is in agreement with results for GC [24,183,I], and Ni [VI] electrodes functionalised with aryl layers.

Earlier studies of aryl-modified Au electrodes showed that ET inhibition by a 4-carboxyphenyl film was much lower than that observed here [68]. The difference is probably due to the different layer thickness employed; a sub-monolayer film was studied in Ref. [68] since the functionalisation of an electrode with a monolayer of phenyl groups does not decrease significantly the hexacyanoferrate ET rate [89]. These results can be rationalised considering the high value of the single molecule conductance associated with a phenyl group [184]. However, thicker aryl films on gold (aminophenyl [64,65], 4-nitrophenyl [65], 4-carboxyphenyl [64] and 4-diethylaniline [64] multilayer films) block ET to the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox system. In the present work, a much stronger inhibition is observed (Fig. 54). There are only slight differences in the CV response among the different aryl-modified Au electrodes studied. The hexacyanoferrate reduction current at 0.15 V increases in the sequence: Au/Naph2 < Au/Naph1

$< \text{Au/BP} < \text{bare Au}$. The hexacyanoferrate response of the Au/PhBr electrode was very close to that of Au/Naph2 (data not shown).

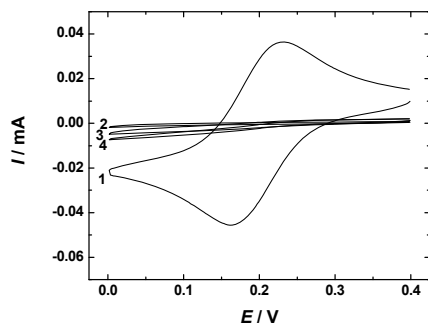


Figure 54. Cyclic voltammograms recorded in Ar-saturated 0.1 M K_2SO_4 containing 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ for polished gold (1) and aryl-modified Au electrodes at 100 mV s^{-1} ; (2) Au/Naph2; (3) Au/Naph1 and (4) Au/BP. Au electrodes were modified in 0.1 M TBABF₄/ACN containing 3 mM of the corresponding diazonium salt by applying 10 potential cycles between 0.5 and -1.0 V , followed by holding the electrode at -0.2 V for 10 min.

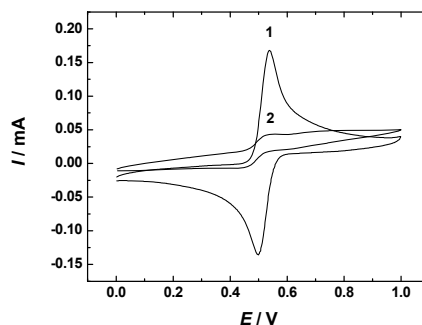


Figure 55. Cyclic voltammograms recorded in Ar-saturated 0.1 M H_2SO_4 containing 1 mM dopamine on (1) bare Au and (2) Au/PhBr electrodes at 100 mV s^{-1} .

Both probe size and hydrophobic/hydrophilic interactions between the surface and redox probes affect the kinetics of ET [17]. All the aryl layers studied are expected to give rise to hydrophobic surfaces and therefore, these would be expected to limit the approach of redox probes from the aqueous phase to the electrode surface. Thus, on hydrophobic surfaces, hydrophilic redox species such as $\text{Fe}(\text{CN})_6^{3-/4-}$ are forced to undergo electron transfer at greater distances to the surface than hydrophobic probes [17]. The blocking behaviour of different aryl layers has been widely investigated on GC surfaces [20,180,I] and shown to inhibit severely the electrochemical response of hexacyanoferrate ions. For 4-nitrophenyl films, blocking of ET increased when grafting was carried out at more negative potentials and/or for longer film growth times [180]. Although the formation of aryl layers on gold is less effective than that at glassy carbon, the general ET blocking trends are similar for both aryl-modified electrodes. The Au/PhBr electrode results may indicate the influence of the localised dipole moment of this molecule. Organisation and close packing of the organic residues in this film is likely to be influenced by intermolecular interactions between the residues attached to the Au surface. In particular, the local orientation of a molecule containing dipolar groups will tend to be

adjusted to minimise energy and hence, an end-on orientation will be disfavoured. The film in the case of this molecule is expected to be tilted or show free domains, as is discussed later on for the dopamine oxidation experiments.

6.3.2.5. Electrochemical response of dopamine on Au/PhBr electrodes

The oxidation of catechol derivatives has been studied widely due to the importance of catecholamine neurotransmitters and related compounds in biology. Dopamine (3,4-dihydroxy phenethylamine, DA) is an example of a catechol with heterogeneous electron transfer strongly dependent on the electrode surface properties [154,155]. In particular, the oxidations on GC are catalysed by adsorbed dopamine [154]. Figure 55 shows a comparison of the cyclic voltammetry of dopamine on a bulk Au electrode and on a Au/PhBr modified electrode. For the former, the half-wave potential was (0.520 ± 0.002) V and the peak separation was (38 ± 5) mV in the whole range of sweep rates investigated, thus corresponding to a fast two-electron oxidation mechanism.

The response of the PhBr filmed electrode is very different and is characteristic of a microelectrode array or that of a partially recessed and blocked electrode [185]. Since the film thickness is approximately 30–50 nm (data from AFM images), the diffusional contribution across the film will be negligible [185] and therefore the behaviour can be modelled as that of a microelectrode array. Thus, due to its open structure, the film partially blocks the transport of the dopamine molecules to the gold surface. DA oxidation is fully restored if a monolayer of anthraquinone instead of trifluoromethylphenyl covers the electrode surface, as shown in Ref. [154]. The catalytic effect was attributed to the presence of hydrogen bonding sites on the surface, which assists DA oxidation by bonding to the catechol hydrogen to effect a proton-assisted electron transfer mechanism [154]. On a bare carbon surface lacking hydrogen bonding sites, the catechol itself can adsorb on the surface to allow a self-catalytic mechanism by hydrogen bonding to quinones from solution [154].

The different activation procedures employed for GC led to the inference that an active electrode will exhibit fast electron transfer kinetics for all redox systems considered, when in fact the sensitivity of k° to various activation procedures depends strongly on the redox system considered. This variation with electrode surface condition has been exploited to impart selectivity of carbon surfaces for particular analytes. For example, an anionic carbon surface is much more sensitive to dopamine at pH 7 when dopamine is present in its cationic form, than to ascorbate, due to electrostatic repulsion of the ascorbate anion by the surface. Clearly the activation of a GC electrode by surface modification must be considered in the light of the particular redox system being considered [154]. As will be discussed in Section 6.3.2.6. polished GC surfaces generally have a 8–15% surface O/C ratio, while vacuum heat treatment reduces oxide coverage to a few percent. The example of dopamine oxidation cited illustrates that some redox processes have an enhanced ET rate

due to the presence of surface oxides, but in some other cases due to other functionalities such as carbonyl or carboxylate moieties [154].

A second low current redox process can be seen at *ca* 0.75 V for the Au/PhBr electrode. No indication of this feature is observed for the free Au surface, in accordance with literature data [154,155,186]. It is not the purpose of this work to analyse in detail dopamine oxidation but it is proposed that this additional process reflects the difference in environments between a free Au electrode and an electrode containing a strong hydrophobic film attached to it. Thus, for the latter, a non aqueous environment is present at the surface, stabilising the radical intermediates and allowing the oxidation reaction to follow a complex mechanism. The many different reactions sequences are described in [186] and in references cited therein.

The interest of the results shown in Fig. 55 is to demonstrate that the pathway of complex electrochemical reactions can be strongly influenced by electrode functionalisation not only in inhibiting direct electron transfer but also in providing a different local dielectric environment.

6.3.2.6. Oxygen reduction on aryl-modified Au electrodes

The oxygen reduction behaviour for aryl-modified gold electrodes was studied in 0.1 M KOH using the RDE and Fig. 56 shows some representative results. The attachment of 4-bromophenyl, 1-naphthyl and 2-naphthyl groups on the Au surface inhibits the electrochemical reduction of oxygen. It is well-known that on bare gold in the range of potentials studied, the number of electrons transferred per O₂ molecule is higher than two [187] indicating the further reduction of the intermediate HO₂⁻ ion formed [101,188].

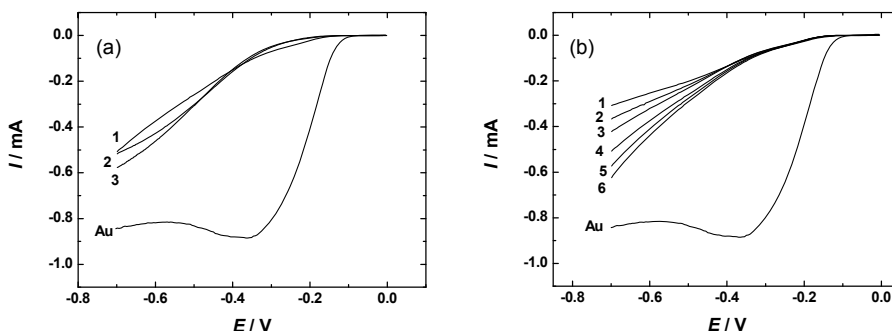


Figure 56. (a) Comparison of current–potential curves for oxygen reduction on bare Au and electrochemically grafted Au electrodes in O₂ saturated 0.1 M KOH at 1900 rpm: (1) Au/PhBr, (2) Au/Naph2 and (3) Au/Naph1. (b) RDE voltammetry curves for oxygen reduction on a bare gold (Au) electrode ($\omega = 1900$ rpm) and on a Au/PhBr electrode at different rotation rates: (1) 360, (2) 610, (3) 960, (4) 1900, (5) 3100 and (6) 4600 rpm in O₂ saturated 0.1 M KOH. $\nu = 20$ mV s⁻¹.

A bare polycrystalline gold electrode is an active electrocatalyst for O_2 reduction in alkaline solutions [101,151,187,188]. The oxygen reduction wave commences at *ca* -0.1 V on bare Au. The oxygen reduction current is remarkably suppressed on the aryl-modified Au electrodes but not to such an extent as to suppress completely oxygen reduction activity and a gradual increase of current at potentials more negative than -0.3 V is observed. A change in the O_2 reduction pathway by 4-methylphenyl groups on GC has been previously observed by Yang and McCreery [100]. Even though the oxygen reduction behaviour is analogous for all modified surfaces, there are some subtle differences. Oxygen reduction is similar for the different electrodes studied up to a potential of -0.45 V but at more negative potentials, the reduction current increases in the order: Au/PhBr < Au/Naph2 < Au/Naph1 < bare Au. The blocking efficiency of aryl films towards the $Fe(CN)_6^{3-/4-}$ redox couple is significantly higher compared to that for oxygen reduction. The oxygen molecule is small and therefore can easily penetrate into the modifier film, whereas the $Fe(CN)_6^{3-/4-}$ ion is larger and strongly hydrophilic and for this reason, ET is strongly inhibited in this case by the aryl films studied.

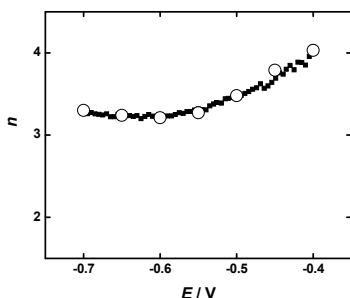


Figure 57. Potential dependence of n (■) for the results in Figure 56b; (○) data taken from Figure 6 in Ref. [101] corresponding to oxygen reduction on a bare Au electrode in 0.1 M KOH.

The value of n on the PhBr modified surface can be calculated from the results shown in Fig. 56b using the Koutecky–Levich equation as described in Ref. [101]. Figure 57 compares the potential dependence of n for the functionalised surface with that for bare Au. A very good agreement between these two surfaces is observed. It should be noted that, as discussed in Ref. [185], for a recessed and partially blocked electrode, there is a range of pore sizes and thickness of the porous film covering the electrode surface for which the value of n calculated from the K–L equation is independent of the surface available for reaction since changes in the current with rotation rate are determined only by the changes of the thickness of the diffusion layer [185]. It was argued in this work that when a fullerene film covers the electrode surface, oxygen reduction changed from a $4e^-$ to a $2e^-$ mechanism due to the suppression of the bridge

adsorption of oxygen on Au. The severe geometrical constraints in the close-packed fullerene films are not present in the PhBr films studied here and hence, the blocking effect due to the chemically bonded organic groups do not change the reduction product distribution.

6.3.3. Blocking properties of gold electrodes modified with 4-nitrophenyl and 4-decylphenyl groups

6.3.3.1. Electrografting of aryldiazonium cations to Au electrodes

Figure 58 presents electrografting behaviour of aryldiazonium derivatives on a gold electrode. The voltammograms show multiple peaks. The first sharp peak is attributed to the reduction of diazonium cations on Au(111) facets and the second peak observed at more negative potentials corresponds to the reduction on Au(100) domains [62]. The peak potentials for the first cathodic scan were 0.48 and 0.27 V for 4-nitrobenzenediazonium cations. These peaks completely disappear for the second scan. The first grafting scan of 4-decylbenzenediazonium cations shows a sharp peak at 0.15 V, which disappears on consecutive scans. A second peak appears at *ca* -0.8 V and the current of this peak decreases during repetitive potential cycling. The true origin of this peak is not clear, however this could be attributed to the reduction of aryldiazonium cations on Au(110), Au(311) and other crystal faces [62]. However, even after holding the electrode at -0.25 V for 5 min, the residual of this peak is still observed.

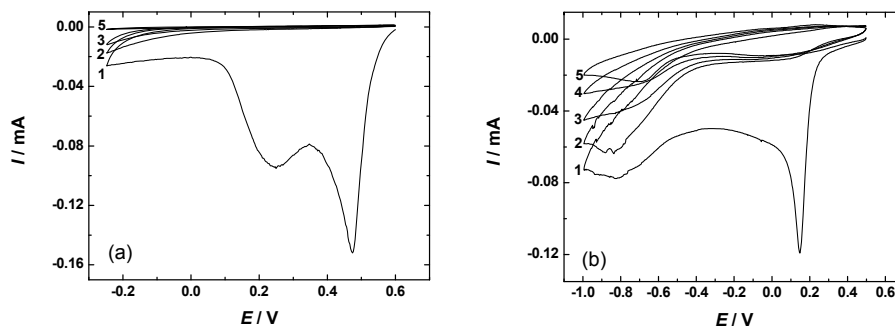


Figure 58. Electrografting of (a) 4-nitrophenyl and (b) 4-decylphenyl groups to gold in Ar saturated ACN containing 3 mM of the corresponding aryldiazonium cations and 0.1 M TBABF₄ at 100 mV s⁻¹. The 1st (1), 2nd (2) 3rd (3) and 5th (4) potential scans are shown. Curve (5) corresponds to the CV response of an electrode hold at -0.25 V for 5 min.

Figure 59a shows *I*-*E* and Δm -*E* potentiodynamic results for an Au electrode during 10 repetitive cycles in 0.1 M NaClO₄/ACN containing 3 mM of the

4-nitrobenzenediazonium salt. The current response is similar to that presented in Fig. 58a. The first potential scan shows two current peaks at 0.3 and 0.12 V (see Fig. 59a) corresponding to the reduction of the 4-nitrobenzenediazonium cation. An increase in mass is observed for potentials more negative than 0.53 V, which coincides with the increase of current for the first CV scan. This increase in mass (340 ng cm^{-2}) is linear until around 0.35 V which is very near to the potential of the first reduction peak potential and the first stage of the attachment of nitrophenyl (NP) groups on the surface of gold film is evident. After this potential, in negative potential scan direction, a second increase in mass ($150 (=490-340) \text{ ng cm}^{-2}$) with smaller inclination ($\text{ng cm}^{-2} \text{ V}^{-1}$) is observed until around 0.0 V (second stage of the attachment of NP groups on the surface of gold film). In the end of the first potential half cycle the increase in mass was 520 ng cm^{-2} and in the end of the first potential cycle was 540 ng cm^{-2} . When the potential scan is reversed, the mass continues to increase slowly. A gradual mass increase is observed on further potential cycling. Comparing the mass change of the first and tenth scans, an increase in mass of approximately 500 ng cm^{-2} is observed for a layer that blocks completely the reduction of the diazonium compound. This behaviour has been previously observed for the covalent grafting of gold with other aryldiazonium compounds [62,64,70]. The slow mass increase in the reverse scan has been attributed to the formation of charge-transfer complexes that precipitate on the electrode surface [181,VII,VIII], but further growth from the radicals generated and diffusing to the electrode surface cannot be ruled out. The faradaic efficiency was calculated from the slope of the $\Delta m - \Delta q$ plots for different experimental conditions and a value of 20% was found for the first electrografting half scan.

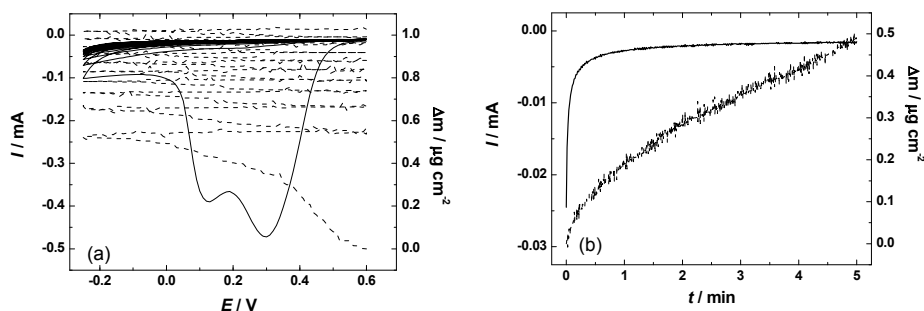


Figure 59. $I-E$ (solid line) and $\Delta m-E$ (dashed line) potentiodynamic profiles for ten repetitive potential cycles (a) and dynamic profiles for the chronoamperometric experiment (b) at -0.25 V for Au electrode in $0.1 \text{ M NaClO}_4/\text{ACN}$ containing 3 mM of 4-nitrobenzenediazonium cations (after 10 potential scans presented).

By assuming a surface concentration of $10 \times 10^{-10} \text{ mol cm}^{-2}$ for a monolayer [64], the corresponding mass expected for a monolayer of NP is 122 ng cm^{-2} .

The surface concentration of NP on Au surface can be calculated as $42.6 \times 10^{-10} \text{ mol cm}^{-2}$ (520 ng cm^{-2}), indicating the presence of more than a monolayer for the first potential half cycle.

After recording ten consecutive $I-E$ and $\Delta m-E$ profiles the electrode was held at a constant potential of -0.25 V for 5 min and a relatively small reduction current was observed during the chronoamperometric transient (Fig. 59b). Surprisingly, although the current is very small, the mass continues to increase indicating further growth of the grafted layer (i.e. multilayer growth).

6.3.3.2. Surface characterization of Au/NP electrodes by AFM

Surface morphology of the 4-nitrophenyl-modified gold film on a mica substrate was examined using AFM. Typical topographical images obtained in intermittent contact mode and their height profiles are presented in Fig. 60.

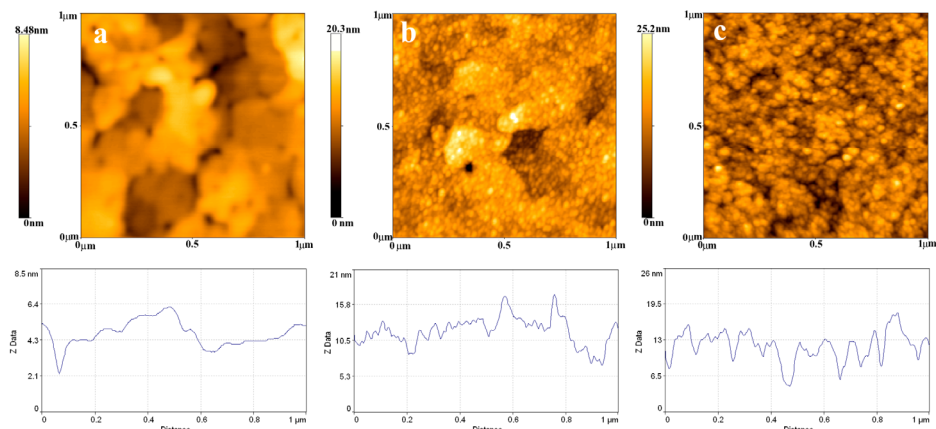


Figure 60. AFM images ($1 \times 1 \mu\text{m}$) and line analysis profiles for a bare gold substrate (a), thin Au/NP film (b) and thick Au/NP film (c). Au electrodes were modified in $0.1 \text{ M TBABF}_4/\text{ACN}$ containing 3 mM 4-nitrobenzenediazonium cations by applying three potential cycles between 0.6 and -0.25 V (b) and ten cycles between 0.6 and -0.25 V , followed by holding the electrode at -0.25 V for 5 min (c).

It can be seen that bare Au film surface is formed by atomically flat (111) terraces separated by monoatomic steps (Fig. 60a). The AFM images of aryl-modified electrodes show clearly that the surfaces of the electrodes are fully covered with granular NP layer (Fig. 60b,c). The granular features of the electrode modified by three potential cycles (Fig. 60b) were uniform with a $15\text{--}30 \text{ nm}$ average diameter, whereas after 10 voltammetric scans and holding the electrode at -0.25 V , their dimensions varied markedly, with a maximum diameter of 100 nm . Essential increase of the root-mean-square (RMS) roughness values from 1.9 nm for electrode modified with three voltammetric cycles

to 3.2 nm for electrode modified with 10 potential cycles and after holding the same electrode at -0.25 V for 5 min (Fig. 60c), confirms the film roughness and thickness increase with the number of potential cycles. For comparison, the RMS roughness of the unmodified Au(111) surface was 0.5 nm.

6.3.3.3. XPS analysis of Au/NP electrodes

Figure 61a presents the XPS survey spectrum of 4-nitrophenyl modified gold electrode grafted by 10 cycles between 0.6 and -0.25 V, followed by holding the electrode at -0.25 V for 5 min. A large decrease of the Au4f peak was observed upon surface modification with NP groups, but it was still visible. The latter can be explained either due to the formation of a non-uniform thin film or the presence of defect sites. Carbon (C1s) and oxygen (O1s) and most importantly the N1s peaks confirm the presence of nitrophenyl groups on the surface. On an unmodified gold surface survey spectra the N1s peak is totally absent (data not shown). The peak with the binding energy close to 406 eV is attributed to $-\text{NO}_2$ functionality, whereas the peak with the binding energy around 400 eV is attributed to amines. It has been demonstrated that X-ray beam during the XPS experiment can chemically transform $-\text{NO}_2$ groups to $-\text{NH}_2$ groups [42,177]. Alternatively, the XPS peak at 400 eV can be explained by the presence of azo-linkages within the NP film [64].

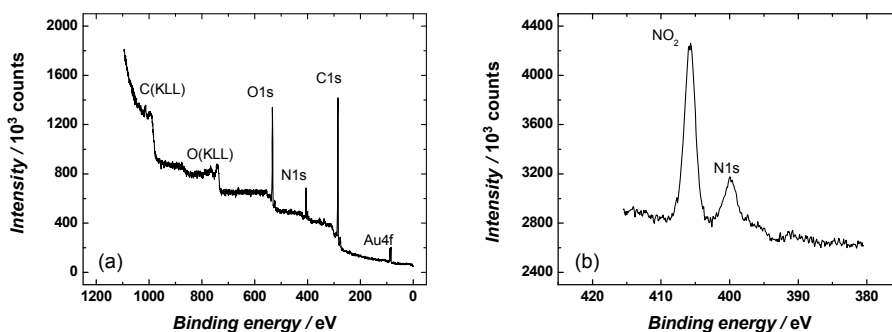


Figure 61. (a) XPS survey spectrum of a nitrophenyl modified gold electrode, (b) XPS spectrum of N1s region of nitrophenyl modified gold. Au electrodes were modified in 0.1 M TBABF₄/ACN containing 3 mM 4-nitrobenzenediazonium cations by applying ten potential cycles between 0.6 and -0.25 V, followed by holding the electrode at -0.25 V for 5 min.

6.3.3.4. Cyclic voltammetry of Au/NP electrodes

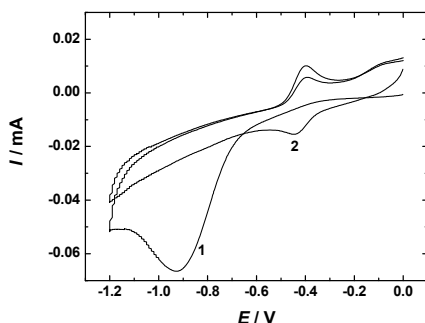
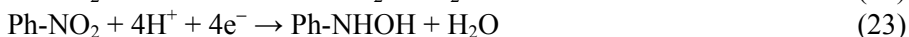
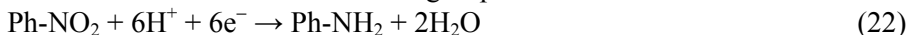


Figure 62. Cyclic voltammetric response of an Au/NP electrode in Ar saturated 0.1 M KOH at 100 mV s⁻¹. (1) first scan and (2) second scan.

Figure 62 shows repetitive cyclic voltammograms of Au/NP electrode in Ar saturated 0.1 M KOH. The first scan shows the characteristic, irreversible reduction ($E_p = -0.93$ V) of the NP group to aminophenyl (Reaction (22)) and hydroxyaminophenyl groups (Reaction (23)) and on the return scan, oxidation ($E_p = -0.4$ V) of hydroxyaminophenyl to nitrosophenyl groups (Reaction (24)) [151]. On the second cycle, the only significant feature is the nitrosophenyl/hydroxyaminophenyl redox couple. This provides further evidence that the gold surface has been modified with NP groups.



6.3.3.5. Oxygen reduction on aryl-modified Au electrodes

The oxygen reduction behaviour of aryl-modified gold electrodes was studied in 0.1 M KOH using the RDE method and Fig. 63 shows the representative RDE results. The attachment of 4-nitrophenyl groups (Fig. 63a) and 4-decylphenyl groups (Fig. 63b) to the Au surface inhibits the electrochemical reduction of oxygen. It is well-known that on bare gold in the range of potentials studied, the number of electrons transferred per O₂ molecule is higher than two [187] indicating the further reduction of the peroxide intermediate formed [187,188].

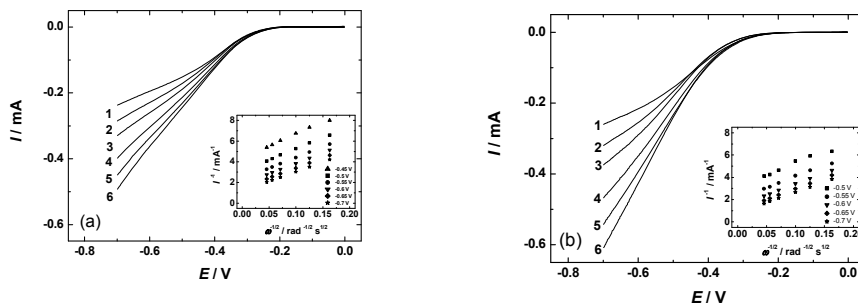


Figure 63. RDE voltammetry curves for oxygen reduction on (a) Au/NP and (b) Au/DP electrodes at different rotation rates: (1) 360, (2) 610, (3) 960, (4) 1900, (5) 3100 and (6) 4600 rpm in O_2 saturated 0.1 M KOH. $\nu = 20 \text{ mV s}^{-1}$. The insets show the Koutecky–Levich plots for oxygen reduction on modified Au electrodes.

The electrochemical reduction of oxygen is strongly influenced by the presence of the modifier film (Fig. 63). The half-wave potential of O_2 reduction shifted to negative direction as compared to that of a polished Au electrode. A typical feature of O_2 reduction on polycrystalline gold in alkaline solution is the presence of reduction current peak at *ca* -0.3 V . Both Au/NP and Au/DP electrodes show negligible reduction current at this potential. At more negative potentials the rate of O_2 reduction increases and current is dependent on the electrode rotation rate (Fig. 63a,b). Obviously, some parts of the catalytically active sites of the underlying gold electrode are not blocked and the reduction of O_2 occurs on these sites. A comparison of the RDE results on O_2 reduction of 4-nitrophenyl and 4-decylphenyl modified gold electrodes is presented in Fig. 64. Both modified electrodes have comparable behavior and are similar to those observed for Au electrodes modified with bromophenyl groups in our previous investigation [VIII].

The Koutecky–Levich analysis is shown in the insets of Fig. 63a,b. It is evident that the reduction of O_2 is under the mixed kinetic-diffusion control over the entire range of potentials studied, since there is a clear intercept of the K-L plots at infinite rotation rate. The intercept value other than zero for both modified electrodes gives further evidence for surface blocking and indicates that there is only a limited number of surface sites for oxygen reduction to occur.

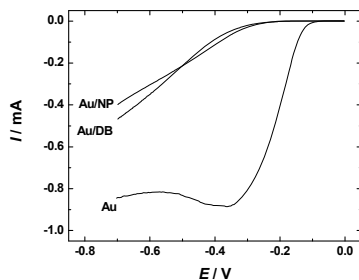


Figure 64. A comparison of current–potential curves for oxygen reduction on bare Au and electrochemically grafted Au/NP and Au/DP electrodes at $\omega = 1900$ rpm, $\nu = 20$ mV s⁻¹.

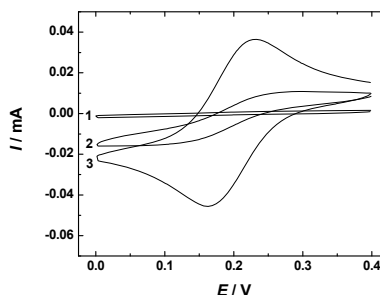


Figure 65. Cyclic voltammograms recorded in Ar-saturated 0.1 M K₂SO₄ containing 1 mM K₃Fe(CN)₆ for (1) Au/NP, (2) Au/DP and (3) polished gold electrodes at 100 mV s⁻¹.

6.3.3.6. Electrochemical response of the Fe(CN)₆^{3-/4-} probe on modified Au electrodes

The blocking properties of NP and DP films towards Fe(CN)₆^{3-/4-} redox probe were studied to further investigate the effect of film structure on the electrochemical behaviour of aryl modified Au electrodes. The CV response of the Fe(CN)₆^{3-/4-} redox probe is significantly suppressed on the Au/DP electrode (Fig. 65, curve 2) and totally suppressed on Au/NP electrode (Fig. 65, curve 1), indicating that the ET rate is much slower for Au/NP electrode. Apparently, for the Au/DP electrode there are pinholes or defects in the modifier film and therefore a sigmoidal shape of CVs is observed. For comparison, the response of a bare gold electrode is also shown (Fig. 65, curve 3). A pair of well-defined peaks is observed, with a peak to peak separation (ΔE_p) of 65 mV confirming the well-known fast one-electron transfer kinetics for this couple, close to the theoretical value of 60 mV expected for a reversible one-electron transfer process. In our earlier study we have demonstrated that grafting the Au electrodes with 1- and 2-naphthyl, biphenyl and 4-bromophenyl groups yielded strongly attached layers with high blocking efficiency toward Fe(CN)₆^{3-/4-} redox probe [VIII]. Recently, the barrier effect of 4-sulfophenyl layer on gold toward Fe(CN)₆^{3-/4-} redox probe was studied and it was concluded that the modified film on Au is not as closely packed as on glassy carbon [86]. These aspects are important for the development of electrochemical (bio)sensors based on aryl-modified gold electrodes.

7. SUMMARY

In this work the electrochemical behaviour of aryl modified glassy carbon (GC) [I–IV], nickel [V–VI] and gold [VII–IX] electrodes was studied. The electrodes were modified using the diazonium reduction method.

Glassy carbon electrodes electrografted with phenyl [I], naphthyl [I,II], anthracenyl [I], biphenyl [II], 4-bromophenyl [II], 4-decylphenyl [II] and 4-nitrophenyl [II] groups were used in the oxygen reduction studies. The blocking behaviour of the aryl films was in evidence. The highest blocking efficiency was observed for phenyl-modified GC electrodes. For comparison purposes the electrochemical response of the $\text{Fe}(\text{CN})_6^{3-}$ probe on aryl modified GC electrodes was studied. Ferricyanide reduction was blocked on the modified electrodes to a much larger degree than O_2 reduction and this effect can be explained by differences in size and hydrophilic/hydrophobic properties between the $\text{Fe}(\text{CN})_6^{3-}$ ion and O_2 molecule [I,II].

The spontaneous grafting of GC with 9,10-anthraquinone (AQ) was achieved by immersion of the substrate in the solutions of its diazonium derivative for different periods of time [III]. A strong attachment of AQ to GC was observed. There was a general tendency for the surface concentration of AQ to increase with increasing immersion time. The grafting reaction, however, depended on the solvent. The electrocatalytic activity of spontaneously grafted AQ for O_2 reduction was similar to that of the electrochemically grafted electrodes [III]. The kinetic parameters for this reaction were determined.

The GC surface modification with *in situ* generated anthraquinone diazonium cations is similar to that observed for previously synthesised anthraquinone diazonium salts. The GC electrodes modified in acetonitrile and in aqueous acidic solution showed similar electrocatalytic activity for O_2 reduction [IV].

The reduction of oxygen was studied on anthraquinone modified Ni electrodes and a high electrocatalytic activity for this reaction was observed [V]. The electrochemical grafting of nickel electrodes with nitrophenyl groups is easily feasible by the reduction of the corresponding diazonium salt. The surface modification was performed in acetonitrile and in aqueous acidic solution. The presence of the modifier film on the substrate surface was confirmed by the XPS analysis. The blocking effect of the nitrophenyl film towards the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple was in evidence [VI].

Electrografting of Au electrodes with diazonium compounds in acetonitrile yielded strongly attached films. The modified Au electrodes were characterised using AFM, EQCM and XPS techniques. The EQCM results gave insight into the growth of aryl films on gold. Cyclic voltammetry revealed a quasi-reversible response of surface-confined AQ in 0.1 M KOH [VII]. The blocking properties of gold electrodes modified with various aryl groups have been investigated [VIII,IX]. The aryl-modified Au surface showed an electrochemical behaviour towards dopamine oxidation corresponding to a microelectrode array.

The electrochemical response of the $\text{Fe}(\text{CN})_6^{3-}$ probe was completely suppressed on aryl-modified Au electrodes. The electrochemical reduction of oxygen was inhibited to a lesser extent by the modifier films [VIII]. AFM studies revealed that the film does not grow uniformly and a rather granular growth is evident, which does not result in compact, but rather loosely packed film. This finding is also supported by the XPS data where the Au4f peaks are clearly seen for the electrodes of high surface concentration of 4-bromophenyl and 4-nitrophenyl groups. The electrochemical response of the $\text{Fe}(\text{CN})_6^{3-}$ probe was completely suppressed on 4-nitrophenyl modified Au electrodes and less suppressed on 4-decylphenyl modified Au electrodes. The kinetics of O_2 reduction was inhibited to a lesser extent on both modified electrodes as compared to that of the $\text{Fe}(\text{CN})_6^{3-}$ probe [IX].

8. REFERENCES

- [1] A.J. Downard, *Electroanalysis* 12 (2000) 1085.
- [2] J. Pinson, F. Podvorica, *Chem. Soc. Rev.* 34 (2005) 429.
- [3] R.L. McCreery, *Chem. Rev.* 108 (2008) 2646.
- [4] F. Barriere, A.J. Downard, *J. Solid State Electrochem.* 12 (2008) 1231.
- [5] M. Delamar, R. Hitmi, J. Pinson, J.-M. Savéant, *J. Am. Chem. Soc.* 114 (1992) 5883.
- [6] D. Knigge, P. Kaur, G. Swain, in: A.J. Bard, M. Stratmann, M. Fujihira, I. Rubinstein, J.F. Rusling (Eds.), *Encyclopedia of Electrochemistry*, vol. 10, Wiley-VCH, Weinheim, 2007, pp. 236–260.
- [7] J.J. Gooding, *Electroanalysis* 20 (2008) 573.
- [8] R.L. McCreery, in: A. Wieckowski (Ed.), *Interfacial Electrochemistry: Theory, Experiment, and Applications*, Marcel Dekker, New York, 1999, pp. 631–647.
- [9] J.K. Kariuki, M.T. McDermott, *Langmuir* 15 (1999) 6534.
- [10] P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson, J.-M. Saveant, *J. Am. Chem. Soc.* 119 (1997) 201.
- [11] Y.-C. Liu, R.L. McCreery, *J. Am. Chem. Soc.* 117 (1995) 11254.
- [12] Y.-C. Liu, R.L. McCreery, *Anal. Chem.* 69 (1997) 2091.
- [13] C. Saby, B. Ortiz, G.Y. Champagne, D. Belanger, *Langmuir* 13 (1997) 6805.
- [14] B. Ortiz, C. Saby, G.Y. Champagne, D. Belanger, *J. Electroanal. Chem.* 455 (1998) 75.
- [15] H.-H. Yang, R.L. McCreery, *Anal. Chem.* 71 (1999) 4081.
- [16] A.J. Downard, *Langmuir* 16 (2000) 9680.
- [17] A.J. Downard, M.J. Prince, *Langmuir* 17 (2001) 5581.
- [18] J.K. Kariuki, M.T. McDermott, *Langmuir* 17 (2001) 5947.
- [19] T. Itoh, R.L. McCreery, *J. Am. Chem. Soc.* 124 (2002) 10894.
- [20] M. D'Amours, D. Belanger, *J. Phys. Chem. B* 107 (2003) 4811.
- [21] C.P. Andrieux, J. Pinson, *J. Am. Chem. Soc.* 125 (2003) 14801.
- [22] O. Ghodbane, G. Chamoulaud, D. Belanger, *Electrochem. Commun.* 6 (2004) 254.
- [23] C. Combellas, F. Kanoufi, J. Pinson, F.I. Podvorica, *Langmuir* 21 (2005) 280.
- [24] H.-G. Hong, M.D. Porter, *J. Electroanal. Chem.* 578 (2005) 113.
- [25] A. Sarapuu, K. Helstein, D.J. Schiffrin, K. Tammeveski, *Electrochem. Solid-State Lett.* 8 (2005) E30.
- [26] T.C. Kuo, R.L. McCreery, G.M. Swain, *Electrochem. Solid-State Lett.* 2 (1999) 288.
- [27] J. Wang, M.A. Firestone, O. Auciello, J.A. Carlisle, *Langmuir* 20 (2004) 11450.
- [28] J.L. Bahr, J. Yang, D.V. Kosynkin, M.J. Bronikowski, R.E. Smalley J.M. Tour, *J. Am. Chem. Soc.* 123 (2001) 6536.
- [29] C.E. Banks, T.J. Davies, G.G. Wildgoose, R.G. Compton, *Chem. Commun.* (2005) 829.
- [30] D. Jiang, B.G. Sumpter, S. Dai, *J. Phys. Chem. B* 110 (2006) 23629.
- [31] K. Tammeveski, K. Kontturi, R.J. Nichols, R.J. Potter, D.J. Schiffrin, *J. Electroanal. Chem.* 515 (2001) 101.
- [32] A. Sarapuu, K. Vaik, D.J. Schiffrin, K. Tammeveski, *J. Electroanal. Chem.* 541 (2003) 23.
- [33] K. Vaik, A. Sarapuu, K. Tammeveski, F. Mirkhalaf, D.J. Schiffrin, *J. Electroanal. Chem.* 564 (2004) 159.

- [34] F. Mirkhalaf, K. Tammeveski, D.J. Schiffrin, *Phys. Chem. Chem. Phys.* 6 (2004) 1321.
- [35] K. Vaik, D.J. Schiffrin, K. Tammeveski, *Electrochem. Commun.* 6 (2004) 1.
- [36] A.O. Solak, L.R. Eichorst, W.J. Clark, R.L. McCreery, *Anal. Chem.* 75 (2003) 296.
- [37] F. Anariba, S.H. DuVall, R.L. McCreery, *Anal. Chem.* 75 (2003) 3837.
- [38] P.A. Brooksby, A.J. Downard, *Langmuir* 20 (2004) 5038.
- [39] P.A. Brooksby, A.J. Downard, *J. Phys. Chem. B* 109 (2005) 8791.
- [40] P.A. Brooksby, A.J. Downard, *Langmuir* 21 (2005) 1672.
- [41] C. Galloway, J.A. Belmont, R.M. Amici, *US Patent No. CA2207414*, Cabot Corporation (1996).
- [42] A. Adenier, E. Cabet-Deliry, A. Chausse, S. Griveau, F. Mercier, J. Pinson, C. Vautrin-UI, *Chem. Mater.* 17 (2005) 491.
- [43] A. Adenier, N. Barre, E. Cabet-Deliry, A. Chausse, S. Griveau, F. Mercier, J. Pinson, C. Vautrin-UI, *Surf. Sci.* 600 (2006) 4801.
- [44] C. Combellas, M. Delamar, F. Kanoufi, J. Pinson, F.I. Podvorica, *Chem. Mater.* 17 (2005) 3968.
- [45] M.P. Stewart, F. Maya, D.V. Kosynkin, S.M. Dirk, J.J. Stapleton, C.L. McGuinness, D.L. Allara, J.M. Tour, *J. Am. Chem. Soc.* 126 (2004) 370.
- [46] B.L. Hurley, R.L. McCreery, *J. Electrochem. Soc.* 151 (2004) B252.
- [47] S.Y. Chang, C.C. Wan, Y.Y. Wang, *Electrochem. Solid-State Lett.* 10 (2007) D43.
- [48] J.L. Bahr, J.M. Tour, *Chem. Mater.* 13 (2001) 3823.
- [49] F. Le Floch, J.-P. Simonato, G. Bidan, *Electrochim. Acta* 54 (2009) 3078.
- [50] M. Toupin, D. Belanger, *Langmuir* 24 (2008) 1910.
- [51] C.A. Dyke, M.P. Stewart, F. Maya, J.M. Tour, *Synlett* (2004) 155.
- [52] C.A. Mitchell, J.L. Bahr, S. Arepalli, J.M. Tour, R. Krishnamoorti, *Macromolecules* 35 (2002) 8825.
- [53] M.-C. Bernard, A. Chausse, E. Cabet-Deliry, M.M. Chehimi, J. Pinson, F. Podvorica, C. Vautrin-UI, *Chem. Mater.* 15 (2003) 3450.
- [54] S. Palacin, C. Bureau, J. Charlier, G. Deniau, B. Mouanda, P. Viel, *ChemPhys Chem.* 5 (2004) 1468.
- [55] J. Charlier, C. Bureau, C. Lecayon, *J. Electroanal. Chem.* 465 (1999) 200.
- [56] G. Herlem, C. Goux, B. Fahys, F. Dominati, A.-M. Gonçalves, C. Mathieu, E. Sutter, A. Trokourey, J.-F. Penneau, *J. Electroanal. Chem.* 435 (1997) 259.
- [57] E. Ahlberg, B. Helgée, V.D. Parker, *Acta Chem. Scand. B* 34 (1980) 181.
- [58] A. Adenier, M.-C. Bernard, M.M. Chehimi, E. Cabet-Deliry, B. Desbat, O. Fagebaume, J. Pinson, F. Podvorica, *J. Am. Chem. Soc.* 123 (2001) 4541.
- [59] A. Adenier, C. Combellas, F. Kanoufi, J. Pinson, F.I. Podvorica, *Chem. Mater.* 18 (2006) 2021.
- [60] J. Ghilane, M. Delamar, M. Guilloux-Viry, C. Lagrost, C. Mangeney, P. Hapiot, *Langmuir* 21 (2005) 6422.
- [61] M.G. Paulik, P.A. Brooksby, A.D. Abell, A.J. Downard, *J. Phys. Chem. C* 111 (2007) 7808.
- [62] A. Benedetto, M. Balog, P. Viel, F. Le Derf, M. Sallé, S. Palacin, *Electrochim. Acta* 53 (2008) 7117.
- [63] J.C. Harper, R. Polsky, D.R. Wheeler, S.M. Brozik, *Langmuir* 24 (2008) 2206.
- [64] A. Laforgue, T. Addou, D. Belanger, *Langmuir* 21 (2005) 6855.
- [65] J. Lyskawa, D. Belanger, *Chem. Mater.* 18 (2006) 4755.
- [66] A. Ricci, C. Bonazzola, E.J. Calvo, *Phys. Chem. Chem. Phys.* 8 (2006) 4297.

- [67] G. Liu, J. Liu, T. Böcking, P.K. Eggers, J.J. Gooding, *Chem. Phys.* 319 (2005) 136.
- [68] G. Liu, T. Böcking, J.J. Gooding, *J. Electroanal. Chem.* 600 (2007) 335.
- [69] S. Griveau, F. Mercier, C. Vautrin-UI, A. Chaussé, *Electrochem. Commun.* 9 (2007) 2768.
- [70] J. Haccoun, C. Vautrin-UI, A. Chaussé, A. Adenier, *Prog. Org. Coat.* 63 (2008) 18.
- [71] D. Alamarguy, A. Benedetto, M. Balog, S. Noël, P. Viel, F. Le Derf, F. Houzé, M. Sallé, S. Palacin, *Surf. Interface Anal.* 40 (2008) 802.
- [72] J.C. Harper, R. Polsky, S.M. Dirk, D.R. Wheeler, S.M. Brozik, *Electroanalysis* 19 (2007) 1268.
- [73] J.C. Harper, R. Polsky, D.R. Wheeler, D.M. Lopez, D.C. Arango, S.M. Brozik, *Langmuir* 25 (2009) 3282.
- [74] R. Polsky, J.C. Harper, D.R. Wheeler, S.M. Brozik, *Electroanalysis* 20 (2008) 671.
- [75] A.-E. Radi, V. Lates, J.-L. Marty, *Electroanalysis* 20 (2008) 2557.
- [76] A.-E. Radi, X. Muños-Berbel, M. Cortina-Puig, J.-L. Marty, *Electrochim. Acta* 54 (2009) 2180.
- [77] A.-E. Radi, X. Muños-Berbel, M. Cortina-Puig, J.-L. Marty, *Electroanalysis* 21 (2009) 696.
- [78] A. Ricci, C. Rolli, S. Rothacher, L. Baraldo, C. Bonazzola, E.J. Calvo, N. Tognalli, A. Fainstein, *J. Solid State Electrochem.* 11 (2007) 1511.
- [79] D.M. Shewchuk, M.T. McDermott, *Langmuir* 25 (2009) 4556.
- [80] G.C. Bond, *Gold Bull.* 34 (2001) 117.
- [81] F.-R.F. Fan, J. Yang, L. Cai, D.W. Price, S.M. Dirk, D.V. Kosynkin, Y. Yao, A.M. Rawlett, J.M. Tour, A.J. Bard, *J. Am. Chem. Soc.* 124 (2002) 5550.
- [82] J. Lehr, B.E. Williamson, B.S. Flavel, A.J. Downard, *Langmuir* 25 (2009) 13503.
- [83] F.I. Podvorica, F. Kanoufi, J. Pinson, C. Combella, *Electrochim. Acta* 54 (2009) 2164.
- [84] F. Mirkhalaf, J.J. Paprotny, D.J. Schiffrin, *J. Am. Chem. Soc.* 128 (2006) 7400.
- [85] G. Liu, M. Chockalingam, S.M. Khor, A.L. Gui, J.J. Gooding, *Electroanalysis* 22 (2010) 918.
- [86] A.L. Gui, G. Liu, M. Chockalingam, G. Le Saux, J.B. Harper, J.J. Gooding, *Electroanalysis* 22 (2010) 1283.
- [87] S. Schauff, M. Ciorca, A. Laforgue, D. Belanger, *Electroanalysis* 21 (2009) 1499.
- [88] J.K. Kariuki, M.T. McDermott, *Langmuir* 17 (2001) 5947.
- [89] P. Chen, R.L. McCreery, *Anal. Chem.* 68 (1996) 3958.
- [90] A.J. Downard, *Int. J. Nanotechnol.* 6 (2009) 233.
- [91] M. Ceccato, L.T. Nielsen, J. Iruthayaraj, M. Hinge, S.U. Pedersen, K. Daasberg, *Langmuir* 26 (2010) 10812.
- [92] E. de la Llave, A. Ricci, E.J. Calvo, D.A. Scherlis, *J. Phys. Chem. C* 112 (2008) 17611.
- [93] D. Jiang, B.G. Sumpter, S. Dai, *J. Am. Chem. Soc.* 128 (2006) 6030.
- [94] T. Matrab, C. Combella, F. Kanoufi, *Electrochem. Commun.* 10 (2008) 1230.
- [95] E.R. Vago, K. de Weldige, M. Rohwerder, M. Stratmann, *Fresen. J. Anal. Chem.* 353 (1995) 316.
- [96] M.S. El-Deab, T. Ohsaka, *Electrochem. Commun.* 5 (2003) 214.
- [97] M.S. El-Deab, K. Arihara, T. Ohsaka, *J. Electrochem. Soc.* 151 (2004) E213.
- [98] M.S. El-Deab, T. Ohsaka, *Electrochim. Acta* 49 (2004) 2189.
- [99] M.I. Muglali, A. Bashir, M. Rohwerder, *Phys. Status Solidi A* 207 (2010) 793.

- [100] H.-H. Yang, R.L. McCreery, *J. Electrochem. Soc.* 147 (2000) 3420.
- [101] A. Kuzume, E. Herrero, J.M. Feliu, E. Ahlberg, R.J. Nichols, D.J. Schiffrin, *Phys. Chem. Chem. Phys.* 7 (2005) 1293.
- [102] E. Yeager, *J. Mol. Catal.* 38 (1986) 5.
- [103] I. Morcos, E. Yeager, *Electrochim. Acta* 15 (1970) 953.
- [104] Z.W. Zhang, D.A. Tryk, E.B. Yeager, in: S. Sarangapani, J.R. Akridge, B. Schumm (Eds.), *Proceedings of the Workshop on the Electrochemistry of Carbon*, The Electrochemical Society, Pennington, New Jersey, 1984, pp. 158–178.
- [105] M.S. Hossain, D. Tryk, E. Yeager, *Electrochim. Acta* 34 (1989) 1733.
- [106] R.J. Taylor, A.A. Humffray, *J. Electroanal. Chem.* 64 (1975) 63.
- [107] C. Paliteiro, A. Hamnett, J.B. Goodenough, *J. Electroanal. Chem.* 233 (1987) 147.
- [108] X. Chu, K. Kinoshita, *Mater. Sci. Eng., B* 49 (1997) 53.
- [109] J. Xu, W.H. Huang, R.L. McCreery, *J. Electroanal. Chem.* 410 (1996) 235.
- [110] B. Šljukić, C.E. Banks, R.G. Compton, *J. Iran. Chem. Soc.* 2 (2005) 1.
- [111] D.A. Tryk, C.R. Cabrera, A. Fujishima, N. Spataru, in: J. Prakash, D. Scherson, I. Tae Bae, D. Chu, M. Enayetullah (Eds.), *Fundamental Understanding of Electrode Processes in Memory of Professor Ernest B. Yeager*, The Electrochemical Society Proceedings, PV 2003–30, Pennington, New Jersey, 2005, pp. 45–57.
- [112] T. Nagaoka, T. Sakai, K. Ogura, T. Yoshino, *Anal. Chem.* 58 (1986) 1953.
- [113] E. Lobyntseva, T. Kallio, N. Alexeyeva, K. Tammeveski, K. Kontturi, *Electrochim. Acta* 52 (2007) 7262.
- [114] E. Yeager, *Electrochim. Acta* 29 (1984) 1527.
- [115] V.A. Bogdanovskaya, M.R. Tarasevich, M.L. Hidekel, G.I. Kozub, S.B. Orlov, *Elektrokhimiya* 20 (1984) 164.
- [116] C. Degrand, *J. Electroanal. Chem.* 169 (1984) 259.
- [117] T. Nagaoka, T. Sakai, K. Ogura, T. Yoshino, *J. Chem. Soc., Faraday Trans.* 1 (1987) 1823.
- [118] A. Salimi, H. Eshghi, H. Sharghi, S.M. Golabi, M. Shamsipur, *Electroanalysis* 11 (1999) 114.
- [119] A. Salimi, M.F. Mousavi, H. Sharghi, M. Shamsipur, *Bull. Chem. Soc. Jpn.* 72 (1999) 2121.
- [120] K. Vaik, U. Mäeorg, F.C. Maschion, G. Maia, D.J. Schiffrin, K. Tammeveski, *Electrochim. Acta* 50 (2005) 5126.
- [121] G. Jürmann, D.J. Schiffrin, K. Tammeveski, *Electrochim. Acta* 53 (2007) 390.
- [122] G. Maia, F.C. Maschion, S.T. Tanimoto, K. Vaik, U. Mäeorg, K. Tammeveski, *J. Solid State Electrochem.* 11 (2007) 1411.
- [123] A. Salimi, C.E. Banks, R.G. Compton, *Phys. Chem. Chem. Phys.* 5 (2003) 3988.
- [124] B. Šljukić, C.E. Banks, S. Mentus, R.G. Compton, *Phys. Chem. Chem. Phys.* 6 (2004) 992.
- [125] B. Šljukić, C.E. Banks, R.G. Compton, *Electroanalysis* 17 (2005) 1025.
- [126] T. Wilson, J. Zhang, C.C. Oloman, D.D.M. Wayner, *Int. J. Electrochem. Sci.* 1 (2006) 99.
- [127] J.R.T.J. Wass, E. Ahlberg, I. Panas, D.J. Schiffrin, *Phys. Chem. Chem. Phys.* 8 (2006) 4189.
- [128] J.C. Forti, R.S. Rocha, M.R.V. Lanza, R. Bertazzoli, *J. Electroanal. Chem.* 601 (2007) 63.
- [129] G. Zhang, W. Yang, F. Yang, *J. Electroanal. Chem.* 602 (2007) 163.

- [130] G. Zhang, F. Yang, *Electrochim. Acta* 52 (2007) 6595.
- [131] A.A. Abdelwahab, O.-S. Jung, Y.-B. Shim, *J. Electroanal. Chem.* 632 (2009) 102.
- [132] G.S. Calabrese, R.M. Buchanan, M.S. Wrighton, *J. Am. Chem. Soc.* 105 (1983) 5594.
- [133] S.M. Golabi, J.B. Raoof, *J. Electroanal. Chem.* 416 (1996) 75.
- [134] G.S. Calabrese, R.M. Buchanan, M.S. Wrighton, *J. Am. Chem. Soc.* 104 (1982) 5786.
- [135] P. Manisankar, A. Gomathi, *J. Power Sources* 150 (2005) 240.
- [136] P. Manisankar, A. Gomathi, *Electroanalysis* 17 (2005) 1051.
- [137] P. Manisankar, A. Gomathi, *Bull. Chem. Soc. Jpn.* 78 (2005) 1783.
- [138] P. Manisankar, A. Gomathi, D. Velayutham, *J. Solid State Electrochem.* 9 (2005) 601.
- [139] A. Sarapuu, *PhD Thesis*, University of Tartu, Tartu, 2008.
- [140] M.F.W. Dunker, E.B. Starkey, G.L. Jenkins, *J. Am. Chem. Soc.* 58 (1936) 2308.
- [141] S. Baranton, D. Bélanger, *Electrochim. Acta* 53 (2008) 6961.
- [142] D.A. Buttry, M.D. Ward, *Chem. Rev.* 92 (1992) 1355.
- [143] C.P. Andrieux, F. Gonzalez, J.-M. Savéant, *J. Am. Chem. Soc.* 119 (1997) 4292.
- [144] P.A. Brooksby, A.J. Downard, S.S.C. Yu, *Langmuir* 21 (2005) 11304.
- [145] A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, 2nd ed., Wiley, New York, 2001.
- [146] R.E. Davis, G.L. Horvath, C.W. Tobias, *Electrochim. Acta* 12 (1967) 287.
- [147] D.R. Lide (Ed.), *CRC Handbook of Chemistry and Physics*, 82nd ed., CRC Press, Boca Raton, 2001.
- [148] Origin® software, Version 7.5, OriginLab Corporation.
- [149] R.L. McCreery, in: A.J. Bard (Ed.), *Electroanalytical Chemistry*, Vol. 17, Dekker, New York, 1991, pp. 221–374.
- [150] W.R. Fawcett, M. Hromadova, G.A. Tsirlina, R.R. Nazmutdinov, *J. Electroanal. Chem.* 498 (2001) 93.
- [151] F. Mirkhalaf, K. Tammeveski, D.J. Schiffrin, *Phys. Chem. Chem. Phys.* 11 (2009) 3463.
- [152] S. Maldonado, T.J. Smith, R.D. Williams, S. Morin, E. Barton, K.J. Stevenson, *Langmuir* 22 (2006) 2884.
- [153] B. Batanero, R. Saez, F. Barba, *Electrochim. Acta* 54 (2009) 4872.
- [154] S.H. DuVall, R.L. McCreery, *J. Am. Chem. Soc.* 122 (2000) 6759.
- [155] S.H. DuVall, R.L. McCreery, *Anal. Chem.* 71 (1999) 4594.
- [156] L. An, Q. Fu, C. Lu, J. Liu, *J. Am. Chem. Soc.* 126 (2004) 10520.
- [157] C.D. Doyle, J.-D.R. Rocha, R.B. Weisman, J.M. Tour, *J. Am. Chem. Soc.* 130 (2008) 6795.
- [158] C.A. Dyke, J.M. Tour, *Nano Lett.* 3 (2003) 1215.
- [159] M.S. Strano, C.A. Dyke, M.L. Usrey, P.W. Barone, M.J. Allen, H. Shan, C. Kittrell, R.H. Hauge, J.M. Tour, R.E. Smalley, *Science* 301 (2003) 1519.
- [160] M.B. Smith, J. March, *March's Advanced Organic Chemistry Reactions, Mechanisms and Structure*, 5th Edition, John Wiley & Sons, New York, 2001.
- [161] H. Zollinger, *Angew. Chem. Int. Ed.* 17 (1978) 141.
- [162] M. Gomberg, W.E. Bachmann, *J. Am. Chem. Soc.* 46 (1924) 2339.
- [163] C. Rüchardt, E. Merz, *Tetrahedron Lett.* (1964) 2431.
- [164] C. Galli, *Chem. Rev.* 88 (1988) 765.
- [165] R. Bolton, G.H. Williams, *Chem. Soc. Rev.* 15 (1986) 261.
- [166] E. Eliel, J.G. Saha, S. Meyerson, *J. Org. Chem.* 30 (1965) 2451.

- [167] E.S. Lewis, H. Suhr, *J. Am. Chem. Soc.* 80 (1958) 1367.
- [168] W. Schwarz, H. Zollinger, *Helv. Chim. Acta* 64 (1981) 513.
- [169] H.S. Wroblowa, Y.-C. Pan, G. Razumney, *J. Electroanal. Chem.* 69 (1976) 195.
- [170] U.A. Paulus, T.J. Schmidt, H.A. Gasteiger, R.J. Behm, *J. Electroanal. Chem.* 495 (2001) 134.
- [171] M. Quan, D. Sanchez, M.F. Wasylikiw, D.K. Smith, *J. Am. Chem. Soc.* 129 (2007) 12847.
- [172] G.J. Gordillo, D.J. Schiffrin, *J. Chem. Soc., Faraday Trans.* 90 (1994) 1913.
- [173] N.A. Shumilova, V.S. Bagotzky, *Electrochim. Acta* 13 (1968) 285.
- [174] V.S. Bagotzky, N.A. Shumilova, G.P. Samoilov, E.I. Khrushcheva, *Electrochim. Acta* 17 (1972) 1625.
- [175] S.L. Medway, C.A. Lucas, A. Kowal, R.J. Nichols, D. Johnson, *J. Electroanal. Chem.* 587 (2006) 172.
- [176] H. Cheng, K. Scott, *J. Electroanal. Chem.* 596 (2006) 117.
- [177] P. Mendes, M. Belloni, M. Ashworth, C. Hardy, K. Nikitin, D. Fitzmaurice, K. Critchely, S. Evans, J. Preece, *ChemPhysChem* 4 (2003) 884.
- [178] J. Heyrovsky, J. Kuta, *Principles of Polarography*, Academic Press, New York, 1966.
- [179] K. Tammeveski, T. Tenno, J. Niinistö, T. Leitner, G. Friedbacher, L. Niinistö, *Appl. Surf. Sci.* 156 (2000) 135.
- [180] S. Baranton, D. Bélanger, *J. Phys. Chem. B* 109 (2005) 24401.
- [181] H.A. Menezes, G. Maia, *J. Electroanal. Chem.* 586 (2006) 39.
- [182] H. Angerstein-Kozłowska, in: E. Yeager, J.O'M. Bockris, B.E. Conway, S. Sarangapani (Eds.), *Comprehensive Treatise of Electrochemistry*, vol. 9, Plenum Press, New York, 1984, pp. 15–59.
- [183] M. Khoshroo, A.A. Rostami, *J. Electroanal. Chem.* 624 (2008) 205.
- [184] C.A. Xu, H. Zalinge, J.L. Pearson, A. Glidle, J.M. Cooper, D.R.S. Cumming, W. Haiss, J.L. Yao, D.J. Schiffrin, M. Proupin-Perez, R. Cosstick, R.J. Nichols, *Nanotechnology* 17 (2006) 3333.
- [185] E. Ahlberg, F. Falkenberg, J.A. Manzanares, D.J. Schiffrin, *J. Electroanal. Chem.* 548 (2003) 85.
- [186] S. Corona-Avendaño, G. Alarcón-Angeles, M.T. Ramírez-Silva, G. Rosquete-Pina, M. Romero-Romo, M. Palomar-Pardavé, *J. Electroanal. Chem.* 609 (2007) 17.
- [187] A. Sarapuu, M. Nurmik, H. Mändar, A. Rosental, T. Laaksonen, K. Kontturi, D.J. Schiffrin, K. Tammeveski, *J. Electroanal. Chem.* 612 (2008) 78.
- [188] R.W. Zurilla, R.K. Sen, E.B. Yeager, *J. Electrochem. Soc.* 125 (1978) 1103.

9. SUMMARY IN ESTONIAN

Arüülrühmadega modifitseeritud klaassüsinik-, nikkel- ja kuldelektroodide elektrokeemilised omadused.

Käesolevas doktoritöös uuriti arüülrühmadega modifitseeritud elektroodide elektrokeemilist käitumist. Klaassüsinik- [I–IV], nikkel- [V–VI] ja kuldelektroodide [VII–IX] pinna modifitseerimiseks kasutati vastavate diasooniumisoolade elektrokeemilist redutseerumist.

Hapniku redutseerumist uuriti fenüül- [I], naftüül- [I,II], antratsenüül- [I], bifenüül- [II], 4-bromofenüül- [II], 4-detsüülfenüül- [II] ja 4-nitrofenüülrühmadega [II] modifitseeritud klaassüsinikelektroodidel. Täheledatai arüülkilede blokeerivate omaduste esinemist ning kõige tugevamat inhibeerimist hapniku redutseerumisel näitas fenüülrühmadega modifitseeritud klaassüsinikelektrood. Võrdleval eesmärgil uuriti ka $\text{Fe}(\text{CN})_6^{3-/4-}$ redokspaari elektrokeemilist käitumist. Tulemustest selgus, et heksatsüanoferraat(III)ioonide redutseerumine oli palju suuremal määral blokeeritud, kui hapniku redutseerumine. Saadud efekti võivad põhjustada $\text{Fe}(\text{CN})_6^{3-}$ iooni ja O_2 molekuli suuruste erinevus ning erinevused hüdrofoobsetes/hüdrofiilsetes omadustes [I,II].

Klaassüsinikelektroodi spontaanseks modifitseerimiseks 9,10-antrakinooniga (AQ) sukeldati elektroode erinevateks ajavahemikeks vastava diasooniumisoola lahustesse [III]. Antrakinooni kile seondus tugevalt klaassüsiniku pinnale ja AQ pindkontsentratsioon sõltus elektroodi hoidmise ajast diasooniumisoola lahustes. Leiti, et modifitseerimise efektiivsus sõltub olulisel määral modifitseerimiskeskonnast. Spontaanselt modifitseeritud elektroodidel oli antrakinooni elektrokatalüütiline efekt hapniku redutseerumisele klaassüsinikelektroodidel võrreldav elektrokeemiliselt modifitseeritud elektroodide puhul saadud tulemustega [III]. Sarnased tulemused saadi ka *in situ* sünteesitud antrakinooni diasooniumisooladega elektrokeemiliselt modifitseeritud klaassüsinikelektroodidel. Atsetonitriilis ja happelises vesilahuses modifitseeritud elektroodid näitasid sarnast elektrokatalüütilist aktiivsust hapniku redutseerumisel 0,1 M KOH lahuses [IV]. Määrati kineetilised parameetrid sellele reaktsioonile erinevates tingimustes modifitseeritud elektroodide korral.

Hapniku elektrokeemilist redutseerumist uuriti ka antrakinooniga modifitseeritud nikkelelektroodidel ning täheledatai kõrget elektrokatalüütilist aktiivsust [V]. Nikkelelektroodi pinda modifitseeriti ka 4-nitrofenüülrühmadega vastava diasooniumisoola elektrokeemilise redutseerimise teel. Pinna modifitseerimine viidi läbi atsetonitriilis ja happelises vesikeskkonnas. Nitrofenüülkile seondumist nikli pinnale kinnitasid ka röntgenfotoelektronspektroskoopilised mõõtmised. Modifitseeritud elektroodid näitasid häid blokeerivaid omadusi $\text{Fe}(\text{CN})_6^{3-/4-}$ redokspaari laenguülekandeprotsessile [VI].

Diasooniumisoola redutseerumise meetodil modifitseeriti ka kuldelektroode ning saadi tugevalt seondunud arüülkiled. Arüülrühmadega modifitseeritud kuld-

elektroodide iseloomustamiseks kasutati kvartsmikroaalude, aatomjõumikroskoopia ja röntgenfotoelektronspektroskoopia meetodeid.

0,1 M KOH lahuses registreeritud antrakinooniga modifitseeritud kuld-elektroodide tsüklilised voltamperogrammid osutasid kvaasipöörduvale elektro-keemilisele käitumisele [VII].

Uuriti mitmete kullale seondatud arüülkilede blokeerivaid omadusi [VIII, IX]. Arüülkilede kasvamist kullal iseloomustati kvartsmikroaalude meetodiga. Kilede uurimine aatomjõumikroskoobiga näitas, et moodustunud arüülkile ei ole kompaktne, vaid pigem teraline ning hõredalt pakitud. Saadud tulemusi kinnitasid ka röntgenfotoelektronspektroskoopilised mõõtmised, mis näitasid Au4f piigi esinemist ka kõrge 4-bromofenüül- ja 4-nitrofenüülrühmade pindkontsentratsiooni korral. Arüülrühmadega modifitseeritud kullal toimus dopamiini oksüdatsioon sarnaselt mikroelektroodide rivi käitumisele ning $\text{Fe}(\text{CN})_6^{3-/4-}$ redokspaari laenguülekandeprotsess oli täielikult blokeeritud [VIII]. Hapniku redutseerumine arüülkiledega modifitseeritud kuldelektroodidel oli inhibeeritud väiksemal määral kui $\text{Fe}(\text{CN})_6^{3-/4-}$ ja dopamiini redokspaaride laenguülekandeprotsess [VIII, IX].

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II. PUBLICATIONS

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- surface with anthraquinone from the solutions of its diazonium derivative: An oxygen reduction study, *Journal of Electroanalytical Chemistry* 624 (2008) 151–160.
5. **M. Kullapere**, J.-M. Seinberg, U. Mäeorg, G. Maia, D.J. Schiffrin, K. Tammeveski, Electroreduction of oxygen on glassy carbon electrodes modified with in situ generated anthraquinone diazonium cations, *Electrochimica Acta* 54 (2009) 1961–1969.
 6. **M. Kullapere**, M. Marandi, V. Sammelselg, H.A. Menezes, G. Maia, K. Tammeveski, Surface modification of gold electrodes with anthraquinone diazonium cations, *Electrochemistry Communications* 11 (2009) 405–408.
 7. **M. Kullapere**, J. Kozlova, L. Matisen, V. Sammelselg, H.A. Menezes, G. Maia, D.J. Schiffrin, K. Tammeveski, Electrochemical properties of aryl-modified gold electrodes, *Journal of Electroanalytical Chemistry* 641 (2010) 90–98.
 8. R.Reilson, **M. Kullapere**, K. Tammeveski, Blocking behavior of covalently attached anthraquinone towards solution-based redox probes, *Electroanalysis* 22 (2010) 513–518.
 9. **M. Kullapere**, M. Marandi, L. Matisen, F. Mirkhalaf, A.E. Carvalho, G. Maia, V. Sammelselg, K. Tammeveski, Blocking properties of gold electrodes modified with 4-nitrophenyl and 4-decylphenyl groups, (manuscript submitted).
 10. **M. Kullapere**, F. Mirkhalaf, K. Tammeveski, Electrochemical behaviour of glassy carbon electrodes modified with aryl groups, (manuscript submitted).

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Tähtsamad teaduspublikatsioonid

1. **M. Kullapere**, G. Jürmann, T.T. Tenno, J.J. Paprotny, F. Mirkhalaf, K. Tammeveski, Oxygen electroreduction on chemically modified glassy carbon electrodes in alkaline solution, Journal of Electroanalytical Chemistry 599 (2007) 183–193.
2. **M. Kullapere**, K. Tammeveski, Oxygen electroreduction on anthraquinone-modified nickel electrodes in alkaline solution, Electrochemistry Communications 9 (2007) 1196–1201.
3. **M. Kullapere**, L. Matisen, A. Saar, V. Sammelselg, K. Tammeveski, Electrochemical behaviour of nickel electrodes modified with nitrophenyl groups, Electrochemistry Communications 9 (2007) 2412–2417.
4. J.-M. Seinberg, **M. Kullapere**, U. Mäeorg, F.C. Maschion, G. Maia, D.J. Schiffrin, K. Tammeveski, Spontaneous modification of glassy carbon sur-

- face with anthraquinone from the solutions of its diazonium derivative: An oxygen reduction study, *Journal of Electroanalytical Chemistry* 624 (2008) 151–160.
5. **M. Kullapere**, J.-M. Seinberg, U. Mäeorg, G. Maia, D.J. Schiffrin, K. Tammeveski, Electroreduction of oxygen on glassy carbon electrodes modified with in situ generated anthraquinone diazonium cations, *Electrochimica Acta* 54 (2009) 1961–1969.
 6. **M. Kullapere**, M. Marandi, V. Sammelselg, H.A. Menezes, G. Maia, K. Tammeveski, Surface modification of gold electrodes with anthraquinone diazonium cations, *Electrochemistry Communications* 11 (2009) 405–408.
 7. **M. Kullapere**, J. Kozlova, L. Matisen, V. Sammelselg, H.A. Menezes, G. Maia, D.J. Schiffrin, K. Tammeveski, Electrochemical properties of aryl-modified gold electrodes, *Journal of Electroanalytical Chemistry* 641 (2010) 90–98.
 8. R.Reilson, **M. Kullapere**, K. Tammeveski, Blocking behavior of covalently attached anthraquinone towards solution-based redox probes, *Electroanalysis* 22 (2010) 513–518.
 9. **M. Kullapere**, M. Marandi, L. Matisen, F. Mirkhalaf, A.E. Carvalho, G. Maia, V. Sammelselg, K. Tammeveski, Blocking properties of gold electrodes modified with 4-nitrophenyl and 4-decylphenyl groups, (manuscript submitted).
 10. **M. Kullapere**, F. Mirkhalaf, K. Tammeveski, Electrochemical behaviour of glassy carbon electrodes modified with aryl groups, (manuscript submitted).

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