A study of glassy carbon electrodes modified with azobenzene derivatives

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Three different azobenzene derivatives (azobenzene diazonium tetrafluoroborate, Fast Garnet GBC sulphate salt and Fast Black K salt) were covalently attached to glassy carbon (GC) electrodes by electrochemical grafting. The grafting of GC surfaces was controlled by varying the number of potential cycles during the modification procedures. The presence of azo groups on the modified electrode surfaces was confirmed by X-ray photoelectron spectroscopy. The electrochemical properties of the modified electrodes were characterised by cyclic voltammetry and the rotating disc electrode (RDE) technique using the Fe(CN)6 3/4 redox system. The blocking behaviour of aryl films towards oxygen reduction was studied by linear sweep voltammetry and the RDE method. The blocking action of the aryl-modified electrodes for ferricyanide reduction was significantly greater than for O2 reduction. By estimating the parameter of relative blocking efficiency the best barrier properties were observed for azobenzene-modified GC electrodes.

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1. Introduction

Carbon materials such as glassy carbon (GC), pyrolytic graphite, carbon nanotubes and graphene are widely used as substrates for many important electrochemical applications, including electrocatalysis and electroanalysis [1]. Various nanocarbons have been considered as electrode materials in (bio)fuel cells, supercapacitors and in recent years, these nanomaterials have been also used as a support to develop biosensors and biomedical devices. The main advantages of the electrodes based on carbon materials are low cost compared to metals, mechanical stability and a wide potential window in electrochemistry [1,2]. Among bulk carbon electrodes, GC has been most frequently used as a substrate material in electrochemistry research. GC provides a stable surface to attach organic and biomolecules. Also, it has a reproducible surface for film formation, which is extremely important in the field of surface modification.

Modification of the carbon electrode surfaces is very important task in material science and electrochemistry. There are several reports and overviews involving different approaches in modifying carbon surfaces. For example, oxidation of amines or arylacetates, physical adsorption and electrochemical reduction of aryl diazonium salts [3–10]. Recently, spontaneous modification has become an increasingly popular method for surface grafting [10,11]. However, the electrochemical reduction of diazonium compounds is probably most extensively studied method since the pioneering work by Pinson and co-workers in the early 1990s [12]. It is known that the electrochemical reduction of diazonium salts in protic (aqueous solutions) or aprotic medium (for instance in acetonitrile) enables the formation of covalent carbon–carbon (C–C) bond between the carbon substrate and aryl radicals [12–15]. Also, a large variety of surface modifiers, for example nitrophenyl, carboxyphenyl, nitroazobenzene, anthraquinone groups can be bound to the substrate by electrochemical reduction of the corresponding diazonium salt [5,16–20]. In general, it is a simple and facile procedure to yield a strong covalent bond between carbon substrate and the organic layer. Therefore, this method has attracted a great deal of attention in recent years.

Aromatic azo compounds are known as a basis for the production of dyes [8,21]. One of the most common azo compounds is azobenzene. Because of its characteristic colour and photoresponsive properties, azobenzene and its derivatives have received considerable attention. In addition, azobenzene and its derivatives are known for their reversible trans–cis photoisomerisation [22]. Thus, these compounds have a wide variety of potential applications such as optical storage media, chemosensors and photochemical molecular switches [23,24].

However, molecular species that are attached to an electrode surface may have a great impact to the material, therefore it is important to study the properties of these functional layers [25]. In some cases electrocatalytic effects and in other cases blocking
effects on the electron transfer reactions have been observed for modified electrodes. Therefore, it is of considerable interest to study the blocking behaviour of ary1-modified carbon electrodes towards solution-based redox probes \[6,16,20,26–34\].

In this work, we have modified the GC electrode surfaces via electrochemical reduction of aryldiazonium salts: azobenzene diazonium tetrafluoroborate, Fast Garnet GBC sulphate salt and Fast Black K salt (see Scheme 1). These specific diazonium salts were chosen due to the differences in the structure of these compounds and therefore the aim of this work was to compare the electrochemical behaviour of the modified GC electrodes. After GC surface derivatisation, the electrochemical testing was performed to investigate the barrier properties of the obtained aryl films. As the blocking effect of the aryl film depends on the charge and the hydrophobicity of the redox probe, the ferri/ferrocyanide redox system was used to evaluate the barrier properties. In addition, the study of oxygen reduction on ary1-modified GC electrodes was conducted because of its paramount importance in many fields, including electrocatalysis and electroanalysis.

2. Experimental

2.1. Electrodes and surface modifiers

Glassy carbon (GC) electrodes with a geometric area (A) of 0.2 cm\(^2\) were prepared by pressing GC discs (GC-20SS, Tokai Carbon) into Teflon holders. The electrodes were polished to a mirror finish using 1.0 and 0.3 µm alumina slurries (Buehler) followed by sonication in Milli-Q water (Millipore, Inc.), isopropanol (Sigma–Aldrich) and acetonitrile (HPLC grade, Sigma–Aldrich) for 5 min.

The surface of GC electrodes was modified by the electrochemical reduction of aryldiazonium salts. Pre-synthesised azobenzene diazonium tetrafluoroborate and commercially available Fast Garnet GBC sulphate salt and Fast Black K salt (2,5-dimethoxy-4-(4-nitrophenyl)azo) were used. Azobenzene diazonium tetrafluoroborate was synthesised from 4-aminoazobenzene hydrochloride (97%, TCI) according to previously established procedures \[35–37\]. Briefly, the corresponding aniline (0.01 mol) was dissolved in 100 mL of the mixture of water and acetone (1:1 by volume). Acetone was supplied from Lach-Ner.

The obtained solution was maintained at 0–5 °C in an ice bath. A mixture of sodium nitrite (Merck) (0.01 mol), hydrochloric acid (37%, Sigma–Aldrich) (0.01 mol) and 50 mL of water and acetone (1:1 by volume) was added to the previously prepared solution. The solution was filtered and sodium tetrafluoroborate (98%, Sigma–Aldrich) (0.01 mol) was added. The slurry was cooled below 0 °C, filtered by suction and washed with ice water and cold ether. The synthesised azobenzene diazonium tetrafluoroborate was dried in a desiccator.

2.2. Electrografting of ary1 groups to GC electrodes

The covalent attachment of azobenzene, 2-methyl-4-((2-methy1phenyl)azo)benzene and 2,5-dimethoxy-4-((4-nitrophenyl)azo)benzene groups to the GC surface was carried out in acetonitrile containing 1 mM of the corresponding diazonium salt and 0.1 M tetrabutylammonium tetrafluoroborate (TBABF\(_4\), Fluka) as a base electrolyte. In what follows these modified GC electrodes are designated as GC/AB, GC/GBC and GC/FBK, respectively. Saturated calomel electrode (SCE) and a Pt foil were used as the reference and counter electrodes, respectively. All the potentials reported in this work are given with respect to the SCE electrode. In order to vary the modification conditions, three different procedures were used with each diazonium compound: (1) 1 cycle, (2) 10 cycles and (3) after 10 potential cycles the electrode was held at −0.2 V for 10 min. In all cases, the potential cycling was performed between 0.6 and −0.4 V with a scan rate of 100 mV s\(^{-1}\). After derivatisation, the modified electrodes were sonicated in acetonitrile for 3 min to remove the physically adsorbed material.

2.3. Electrochemical instrumentation and measurements

An EDI101 rotator and a CTV101 speed control unit (Radiometer, Copenhagen) were employed for the rotating disc electrode (RDE) experiments. The potential was applied with an Autolab potentiostat/galvanostat PGSTAT30 (Eco Chemie B.V., The Netherlands) and the experiments were controlled with the General Purpose Electrochemical System (GPES) software. All experiments were carried out at room temperature (23 ± 1 °C). The electrochemical response of modified electrodes towards the Fe(CN)\(_6\)^{3−/4−} redox couple was studied in Ar-saturated 1 mM K\(_3\)Fe(CN)\(_6\) (Aldrich) solution, containing 0.1 M K\(_2\)SO\(_4\) (Merck) as supporting electrolyte and using cyclic voltammetry (CV) and the RDE technique. Oxygen reduction was studied on the modified GC electrodes employing the RDE method and linear sweep voltammetry (LSV). The oxygen reduction measurements were carried out in 0.1 M KOH (p.a. quality, Merck) solution saturated with O\(_2\) (99.999%, AGA).

2.4. X-ray photoelectron spectroscopy studies

After GC surface grafting, the organic moieties present on the surface were characterised by X-ray photoelectron spectroscopy (XPS). For the XPS investigations, the electrochemical modification was performed on GC plates of 1.1 × 1.1 cm using the same procedures described in Section 2.2. The XPS data were obtained with a SCIENTA SES-100 spectrometer using an unmonochromated MgK\(_\alpha\) radiation (incident energy = 1253.6 eV), a take-off angle of 90° and a source power of 300 W. The base pressure in the analysis chamber was below 10\(^{−9}\) Torr. The survey spectra were scanned between 0 and 700 eV with a pass energy of 200 eV and a step size of 0.5 eV. High-resolution N1s scans (396–408 eV) were carried out with 200 eV pass energy and 0.1 eV step size.

3. Results and discussion

3.1. Electrochemical reduction of aryldiazonium salts on GC electrodes

Fig. 1a–c presents the cyclic voltammograms of surface modification of GC electrodes via electrochemical reduction of three compounds.
different aryldiazonium salts used. In case of electrografting with AB groups in acetonitrile solution (Fig. 1a), the first sweep between 0.6 and −0.4 V exhibited two reduction peaks at \( E_p \approx 0.31 \) V and 0.05 V, respectively. It appears that the reduction potential of AB diazonium salt is rather similar to that reported by Takashi and McCreery [38]. In the present study, similar electrografting behaviour of aryldiazonium salts was observed. Sadowska et al. proposed that azo compounds are electroactive and therefore the surface concentration can be estimated by cyclic voltammetry [42]. According to Brooksbys and Downard, the azobenzene groups have no detectable electroactivity in aqueous acid solution [43]. Slijukić et al. have evaluated the surface concentration of physically adsorbed azobenzene in acidic solution [44]. In the present research, CV peaks were not reproducible and therefore the surface coverage of all the azobenzene derivatives used remained unknown.

3.2. XPS characterisation of AB, GBC and FBK modified GC electrodes

XPS analysis was used to study the composition of the modifier films. As all the azobenzene derivatives used include azo groups (−N=N−), then it is relevant to note that the presence of azo linkages in aryl layers was studied by Saby et al. [20]. They attributed the XPS peak in the N1s region at 400 eV to \( N\equiv N \). Furthermore, Liu and McCreery [45] used the electrochemical reduction method to modify GC electrodes with aryl groups, using azobenzene as well as nitroazobenzene (NAB) diazonium salts. They investigated the aryl layers with Raman spectroscopy and also with XPS. As NAB includes nitro group besides the azo group, the high-resolution XPS spectra showed N1s peaks at 400 and 406 eV, which correspond to the azo and the nitro groups, respectively.

In this study, the XPS core-level spectrum in the N1s region of AB, GBC and FBK modified GC is shown in Fig. 2. It should be noted that the XPS data for the corresponding diazonium salts using different modification procedures was rather similar. As can be seen in Fig. 2, only one peak (BE = 400 eV) was observed upon surface modification with AB and GBC groups, which can be associated with the azo bonds. Meanwhile, for FBK modified surfaces, the XPS spectrum in the N1s region revealed two peaks (Fig. 2). The first peak around 406 eV is attributed to \( NO_2 \) functionality and the second one at 400 eV corresponds to azo linkage. Since all covalent C−C bond [40]. However, the origin of the first reduction peak (it is assigned also as a pre-peak) is not fully understood [2,8,15,18,41].

Overall, it was evident that the peak current decreased with the number of potential cycles and the first reduction peaks gradually disappeared on consecutive scans. This is a typical electrografting behaviour of aryldiazonium salts. The disappearance of the reduction wave refers to the progressive blocking of the electrode surface by corresponding aryl layer. There has been a disagreement in determining the surface concentration of azobenzene groups. Sadowska et al. proposed that azo compounds are electroactive and therefore the surface concentration can be estimated by cyclic voltammetry [42]. According to Brooksbys and Downard, the azobenzene groups have no detectable electroactivity in aqueous acid solution [43]. Slijukić et al. have evaluated the surface concentration of physically adsorbed azobenzene in acidic solution [44]. In the present research, CV peaks were not reproducible and therefore the surface coverage of all the azobenzene derivatives used remained unknown.

![Fig. 1. Electrochemical grafting of GC electrodes by diazonium reduction using 1 mM of (a) azobenzene diazonium salt, (b) Fast Garnet GBC sulphate salt and (c) Fast Black K salt in Ar-saturated acetonitrile containing 0.1 M TBABF₄, \( v \times 100 \text{ mV s}^{-1} \).](image)

![Fig. 2. The XPS spectrum in the N1s region for AB (solid line), GBC (dashed line) and FBK (dotted line) modified GC electrodes. The electrodes were modified using procedure (2).](image)
studied compounds contain azo linkage and additionally, FBK contains nitro group (Scheme 1), these XPS results were rather expected.

3.3. Electrochemical response of the Fe(CN)$_6^{3-/4-}$ probe on modified GC electrodes

The blocking behaviour of aryl-modified GC electrodes was investigated in the presence of the Fe(CN)$_6^{3-/4-}$ redox system. Fig. 3a–c shows representative sets of CVs obtained for all the modified GC electrodes in Ar-saturated 1 mM K$_3$Fe(CN)$_6$. The CV curve for polished GC is given for comparison. Two main parameters, $\Delta E_p$ and $I_{rel}$, were used to characterise the barrier properties of the aryl films studied. $\Delta E_p$ is the peak potential separation between the anodic and cathodic peak, whereas, the parameter of relative blocking efficiency ($I_{rel}$) is defined according to [39]:

$$I_{rel}(\%) = \frac{I_{pc} \text{ with a film}}{I_{pc} \text{ for bare GC}} \times 100$$

(1)

where $I_{pc}$ is the intensity of the cathodic peak current.

The blocking effect depends greatly on the modification procedure. In the present study, modification with one cycle in the potential range between 0.6 and -0.4 V leads to a considerable increase in the $\Delta E_p$ value for all the aryl layers studied compared to polished GC electrode (see Table 1). The increase in the value of $\Delta E_p$ reflects a significant decrease in the electron transfer rate due to the blocking action of the grafted AB, GBC and FBK layers. It is well-known that the Fe(CN)$_6^{3-/4-}$ ions should interact with GC surface for an effective electron transfer process to occur [30]. Therefore, it is evident that the formation of an aryl layer on the GC surface should inhibit the electron transfer kinetics of this redox couple. Also, it has been previously demonstrated that using the same procedure of modification by different aryl groups results in different degrees of surface blocking [33]. As can be seen from Table 1, the Fe(CN)$_6^{3-/4-}$ redox probe exhibits a significant increase of the $\Delta E_p$ and decrease of the CV peak current following GC modification with AB groups. Smaller peak separation values were observed for GBC and FBK modified electrodes. However, taking into account the $\Delta E_p$ values and comparing to those of polished GC, notable differences were observed. The increase in $\Delta E_p$ values can be ascribed to the AB, GBC and FBK films coated on the GC surface. It can be stated that the enlargement in the $\Delta E_p$ indicates the inhibition of the electron transfer rate and also it refers to the stronger blocking action. Khoshroo and Rostami have grafted the GC surface with FBK via electrochemical reduction using different diazonium reduction times and compared the electrochemical behaviour with 4-diazophenylaceticacid tetrafluoroborate (PAA) modified GC electrodes [46]. They concluded that the blocking action was less pronounced for FBK modified electrode towards Fe(CN)$_6^{3-/4-}$ redox couple compared to PAA modified GC electrode. However, both aryl layers showed a significant blocking effect for oxidation and reduction reactions of the Fe(CN)$_6^{3-/4-}$ redox system compared to polished GC electrode. For example, using the modification time of 30 s to obtain FBK layer on the GC surface, the parameter $I_{rel}$ was evaluated as 55.6%. In this study, according to the value of $I_{rel}$, the best blocking action was observed for GC/AB electrode and the lowest for GC/FBK electrode (see Table 1).

Kariuki and McDermott [47] reported that the longer electrolysis time of diazonium salt yielded larger $\Delta E_p$ for several redox systems. In the present study, we also used different modification conditions (i.e. by applying 10 potential cycles beside the one cycle and furthermore, for the third modification procedure the electrode was held 10 min at a constant potential in order to improve the compactness of the aryl film). Earlier studies have revealed that the blocking action increased with increasing the modification time [46]. However, the electrochemical response of the Fe(CN)$_6^{3-/4-}$ probe was strongly suppressed by applying modifica-

Table 1

<table>
<thead>
<tr>
<th></th>
<th>$I_{pc}$ (µA)</th>
<th>$I_{rel}$ (%)</th>
<th>$\Delta E_p$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>44</td>
<td>-</td>
<td>0.076</td>
</tr>
<tr>
<td>GC/AB</td>
<td>10</td>
<td>22.8</td>
<td>0.863</td>
</tr>
<tr>
<td>GC/GBC</td>
<td>12.5</td>
<td>28.4</td>
<td>0.597</td>
</tr>
<tr>
<td>GC/FBK</td>
<td>18</td>
<td>40.9</td>
<td>0.377</td>
</tr>
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Fig. 3. Electrochemical response of the Fe(CN)$_6^{3-/4-}$ probe on: (a) AB, (b) GBC and (c) FBK modified GC electrodes in Ar-saturated 0.1 M K$_3$SO$_4$ containing 1 mM K$_3$Fe(CN)$_6$. V = 100 mV s$^{-1}$. GC electrodes were modified by procedures (1–3). CV curve for a polished GC electrode (solid line) is given for comparison.
tion procedures (2) and (3) and therefore the CV peaks were not discernible (see Fig. 3). For these electrodes, the electrochemical data for the Fe(CN)$_6^{3-/4-}$ couple using CV could not be determined in order to characterise their barrier properties. The results shown in Fig. 3 imply that the use of subsequent cycles and duration time during the grafting procedure would result in larger aryl film thickness and more compact film.

In addition to CV experiments, the RDE method was employed to investigate the blocking action towards ferricyanide reduction in the potential range between 0.6 and 0.6 V. The RDE voltammetry curves for polished and differently modified GC electrodes are presented in Fig. 4a–c. Similar tendency was observed for all aryl grafted electrodes using the same modification procedure. For instance, using the procedure (3), AB, GBC and as well as FBK modified electrodes remarkably suppress the reduction current. Meanwhile, the Fe(CN)$_6^{3-}$ reduction behaviour of GC/AB, GC/GBC and GC/FBK electrodes by applying procedure (1) differs notably as compared to the above mentioned electrodes. It can be seen that in a case of GC/AB1 (see Fig. 4a) a short modification program suppresses the reduction current significantly. However, some differences were observed for GBC and FBK modified GC electrodes using the modification procedure (1). Multiple scans used in the grafting procedure have a significant effect on the current values and on the blocking action. From these results it can be concluded that for this procedure the electrode surface is not completely covered with AB, GBC or FBK layer. The GC surface grafted with aryl layers has still some pinholes and defect sites.

From the RDE data, the half-wave potential ($E_{1/2}$) of Fe(CN)$_6^{3-}$ reduction on polished and aryl-modified GC electrodes was calculated. The $E_{1/2}$ value for a polished GC electrode was found to be 0.16 V. In case of aryl-modified electrodes, the value of $E_{1/2}$ shifted to more negative potentials compared to polished GC which additionally refers to the inhibition of the electron transfer rate. For GC electrodes modified by procedure (3) the process of ferricyanide reduction was completely suppressed.

3.4. Oxygen reduction on AB, GBC and FBK modified GC electrodes

The electrochemical behaviour of AB, GBC and FBK grafted GC electrodes was further investigated towards O$_2$ reduction. These experiments were performed in O$_2$-saturated 0.1 M KOH and two methods were employed: LSV and RDE techniques. The polarisation curves for oxygen reduction were registered in the potential range between 0 and 1.2 V. In earlier reports, the LSV response of unmodified GC electrode has been studied [48–50]. Two CV peaks of O$_2$ reduction were observed, which are in agreement with our observations. In the present study, the reduction peaks appeared at ca. −0.4 and −0.9 V, respectively. The first O$_2$ reduction peak with a larger current can be associated with quinone-type centres which are present on the surface of polished GC. These groups are catalytically active in the solutions of high pH [51]. It is also known that the reduction of O$_2$ proceeds by a two-electron pathway at these potentials. At lower potentials (approximately at −0.9 V), the process of oxygen reduction is catalysed by other type of centres, the nature of which is not clearly understood. However, it is also considered that the two-electron reduction of oxygen to HO$_2$ takes place at these potentials.

Only some reports have been published in which the reduction of oxygen has been studied on azobenzene-modified electrodes. It should be noted that the optimum pH for electrocatalysis of oxygen reduction for azobenzene and FBK modified GC electrodes is two, according to the results reported by Šljukić et al. [44]. They used the solvent evaporation method to modify the GC electrodes with azobenzene and FBK. The reduction of oxygen was studied in acidic media (phosphate buffer solution, pH = 2) and they observed an electrocatalytic effect for modified electrodes compared to polished GC. Also, they investigated the electrochemical behaviour of azobenzene and FBK modified GC electrodes in an O$_2$-free solution. They suggested that the first reduction peak at −0.11 V is attributed to the reduction of azobenzene to hydrazobenzene in case of azobenzene modified GC electrode. For FBK grafted electrode, the CV showed three reduction peaks at 0.15, −0.30 and −0.41 V and one oxidation peak (0.40 V) at first scan, while at the second cycle two reduction waves (0.15 and −0.41 V) were observed. The reduction peaks at −0.30 and −0.41 V can be assigned to the reduction of the nitro group of the FBK salt and the first one at 0.15 V can be attributed to the reduction of the azo linkages of the FBK with the corresponding oxidation wave at 0.40 V [44,52].
Forti et al. studied the azobenzene redox reactions on GC electrode in 0.1 M dimethylformamide and NaClO₄ solution (pH 7) containing 60 mM of azobenzene. They proposed that the reduction peak at −0.79 V (vs. Ag/AgCl) corresponds to the reduction of azobenzene to hydrazobenzene. They also studied the reduction of oxygen in the same solution using CV and a remarkable increase in the peak current was observed compared to the results without azobenzene, which also refers to the electrocatalytic effect in the presence of azobenzene [53].

Interesting LSV results of O₂ reduction were obtained in this study as can be seen in Fig. 5a–c. In contrast to polished GC, all aryl-modified electrodes were rather inactive towards oxygen reduction in alkaline solution. The first peak shifted to more negative potentials and the $E_p$ values were as follows: −0.51, −0.47 and −0.46 V for the AB, GBC and FBK modified electrodes, respectively using the modification procedure (1). Some differences were observed depending on the diazonium salt and modification procedure used. For instance, the second LSV peak also shifted to more negative potentials for GC/AB electrodes (see Fig. 5a). In case of GC/GBC and GC/FBK electrodes, the second peak was rarely observed (Fig. 5b and c). Using different modification procedures, notable differences were not observed in case of GC/AB. The LSV behaviour of GC/GBC and GC/FBK electrodes in the presence of

![Fig. 5. Linear sweep voltammograms (LSV) for oxygen reduction in O₂-saturated 0.1 M KOH at a sweep rate of 100 mV s⁻¹ on polished and aryl-modified GC electrodes: (a) GC/AB, (b) GC/GBC and (c) GC/FBK. GC electrodes were modified by procedures (1–3).](image)

![Fig. 6. RDE voltammetry curves of oxygen reduction in O₂-saturated 0.1 M KOH at various rotation rates and using a sweep rate of 20 mV s⁻¹. The GC electrodes were modified with: (a) AB, (b) GBC and (c) FBK groups. In all cases, the modification procedure (3) was used. The insets show the Koutecky–Levich plots for oxygen reduction at different potentials.](image)
oxygen indicated that the blocking action depends greatly on the modification procedure. In order to evaluate the degree of blocking action, the parameter \( I_{\text{KB}} \) was used in case of the short modification program (procedure (1)). Hence, the blocking efficiency of the AB, GBC and FBK modified electrodes was estimated as 65%, 72% and 64%, respectively.

Besides LSV measurements, the oxygen reduction reaction on aryl-modified GC electrodes was also studied using the RDE method. The polarisation curves of oxygen reduction were registered in the same potential range as the LSV curves. In general, using different modification procedures, the obtained electrodes gave rather similar responses to \( \text{O}_2 \) reduction. But notable differences were observed for the GBC and FBK modified electrodes compared to the attached AB film. Fig. 6a–c presents the data for AB, GBC and FBK modified GC electrodes using the procedure (3). The most different behaviour was observed for GC/AB modified electrodes (see Fig. 6a–c). For GC/AB electrodes, the pre-wave started at more negative potentials compared to other electrografted and polished GC electrodes (see Fig. 7). Also the first reduction peak shifted to more negative direction and it was more suppressed. Surprisingly, the current values of the second reduction wave increased for this particular electrode compared to polished GC (Fig. 7). Further work is needed in order to explain the reduction current increase at these more negative potentials. As can be seen in Fig. 7, the pre-wave at \(-0.5\) V for unmodified GC was in evidence and the reduction wave shifted at ca \(-0.25\) V. It has been suggested that the reduction of \( \text{O}_2 \) at these potentials is catalysed by quinone-type groups that are present on the polished GC surface [51,54–57]. The onset potential of oxygen reduction shifted by up to 50 mV to more negative potentials for the GC electrodes modified with different azobenzene derivatives (see Figs. 6a–c and 7). In case of modified GC electrodes, the pre-wave was not strongly suppressed indicating that the GC surface is not completely covered with corresponding aryl groups. However, it is difficult to estimate the uncovered area. But to a certain extent, the native quinone groups are still blocked by the AB, GBC and FBK films. Recently, it has been proposed that the aryl radical formed by diazonium reduction can react with carboxyl groups [58]. This might be an alternative explanation for a decrease in the \( \text{O}_2 \) reduction current at pre-wave potentials, besides steric hindrance caused by an aryl layer.

Subsequently, the Koutecky–Levich (K–L) analysis (dependence of \( I^{1/2} \) on \( \omega^{1/2} \)) was made using the K–L equation:

\[
\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_d} = \frac{1}{nFakC_{O_2}} + \frac{1}{0.62nFAD_{O_2}^{1/2}v^{1/2}C_{O_2}^{1/2}D_{O_2}^{1/2}}
\]

where \( I \) is the measured current, \( I_k \) and \( I_d \) are the kinetic and diffusion-limited currents, respectively, \( n \) is the number of electrons exchanged, \( F \) is the Faraday constant (\( 96485 \text{C mol}^{-1} \)), \( A \) is the geometric electrode area, \( k \) is the electrochemical rate constant for \( \text{O}_2 \) reduction, \( C_{O_2} \) is the concentration of oxygen in bulk (\( 1.2 \times 10^{-5} \text{mol m}^{-3} \)) [59], \( D_{O_2} \) is the diffusion coefficient of oxygen (\( 1.9 \times 10^{-5} \text{cm}^2 \text{s}^{-1} \)) [59], \( v \) is the kinematic viscosity of the solution (0.01 \text{cm}^2 \text{s}^{-1} [60]) and \( \omega \) is the electrode rotation rate. According to these K–L plots (see Fig. 6a–c insets), the process of oxygen reduction is under the mixed kinetic–diffusion control.

The number of electrons (\( n \)) transferred per \( \text{O}_2 \) molecule was calculated from the K–L plots. It is well-known that the reduction of oxygen follows a two-electron pathway on polished GC electrodes in alkaline media [55,56]. In the same way, the value of \( n \) was close to two for GBC and FBK electrografted electrodes using different modification procedures. It indicates that on these electrodes the reduction of \( \text{O}_2 \) yields hydrogen peroxide as the final product. By contrast, for AB modified GC electrodes, the number of electrons was close to two at the pre-wave potentials, but it increased at higher negative potentials (the value of \( n \) was close to three at \(-1.2\) V).

Comparing the results between ferricyanide and oxygen reduction, the response of the \( \text{Fe(CN)}_6^{3-/-4-} \) redox couple was blocked on all the modified electrodes to a much larger degree (see Section 3.3) than \( \text{O}_2 \) reduction. This effect can be due to the variation of size between the reacting species (\( \text{Fe(CN)}_6^{3-/-4-} \) and \( \text{O}_2 \) molecule) and also the hydrophobic properties of the modifier films play a substantial role in this regard. The \( \text{O}_2 \) molecule is hydrophobic and therefore the hydrophobic film does not provide a suitable barrier to completely suppress the process of \( \text{O}_2 \) reduction. The \( \text{Fe(CN)}_6^{3-/-4-} \) probe is hydrophilic and its redox transformations are strongly inhibited by a thick enough and compact aryl films.

4. Conclusions

In this work, different diazonium derivatives of azobenzene (AB, GBC and FBK) were covalently attached to GC surfaces to compare the electrochemical behaviour of obtained aryl films. These aryl layers on the GC substrate greatly inhibited the electron transfer process of ferricyanide. The electrochemical response of the \( \text{Fe(CN)}_6^{3-/-4-} \) redox couple was strongly blocked on GC/AB and GC/GBC electrodes and completely suppressed on the GC/AB electrode using multiple potential scans and longer holding time at a constant potential during surface modification. However, using a short electrografting program, the oxidation and reduction waves were observed for all aryl-modified GC electrodes. The blocking action was far more evident for the ferricyanide redox probe than for oxygen reduction. For all the aryl-modified electrodes, the barrier properties of the modifier films were not efficient enough to completely suppress the process of oxygen reduction. This can be explained by differences in size between the \( \text{Fe(CN)}_6^{3-/-4-} \) ions and \( \text{O}_2 \) molecule. Also, hydrophobic properties of the aryl films play a great role in this regard. In general, the blocking properties of aryl-modified electrodes are influenced by the diazonium salt and modification procedures used.

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References
