Blocking Behaviour of Covalently Attached p-Substituted Phenyls Towards Solution-Based Redox Probes

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In this work, the electrochemical properties of glassy carbon (GC) electrodes modified with p-nitrobenzene diazonium tetrafluoroborate, p-tolyldiazonium tetrafluoroborate and 4-diazo-N-phenylaniline tetrafluoroborate have been investigated. A diazonium salt coupling procedure was used to covalently bind the various p-substituted phenyls to glassy carbon electrodes and the blocking properties of aryl-modified glassy carbon electrodes towards solution-based redox probes have been studied. The response of Fe(CN)₃⁻⁻⁻ redox probe at modified electrodes was monitored to give a measure of electrode grafting. The blocking action of GC grafted electrodes for Fe(CN)₃⁻⁻⁻ redox probe was studied using cyclic voltammetry (CV) and electrochemical impedance spectroscopy method (EIS). Electrochemistry of Fe(CN)₃⁻⁻⁻ was studied as a function of modification parameters. There were observed differences in blocking properties for the p-nitrophenyl, p-tolyl and N-phenylaniline groups: this points to an influence of the substituent of the phenyl rings either on the formation of the layer or on its resulting properties. The best results, in terms of blocking properties, are obtained with p-nitrophenyl groups.

Keywords: redox probe, diazonium salt, blocking properties, electrochemical grafting

The surface modifications with specific chemical functionalities at the molecular level are important providing specific properties to the interfaces [1]. The modified surfaces have found wide range of applications in several domains including molecular electronics [2], protection against corrosion [3, 4], reversible trapping of ionic waste on reactive electrografted surfaces as an alternative to ion-exchange resins [5], information storage [6], and sensing [7-10].

Most of the methods used for modifying the carbon surface involve oxidation processes leading to the formation of carboxylic, ketonic or hydroxyl groups on the surface that can then be coupled with the molecule to be attached. All of these procedures lead to the formation of oxygenated functional groups on the carbon surface whose nature and number are difficult to identify and control. It is therefore desirable to use more versatile and less drastic strategies for modifying carbon surfaces. The electrochemical grafting of substituted aryl groups by reduction of the corresponding diazonium salt was introduced in the early 90s by Saveant and Pinson [11], this modification procedure being an attractive way to modify carbon-based surfaces [11-14].

Electrochemical grafting of a monolayer of substituted aryl groups is a reductive process and involves the formation of phenyl radicals that react with a carbon atom of a glassy carbon electrode (GC) surface to form a covalent carbon-carbon bond. This technique has the advantage of controlling the functionalization of the electrode surface by the selection of the functional group in para position of the grafted molecule. The resulting interface can exhibit desirable qualities depending on the type of chemical modifier that was used.

This kind of functionalization of glassy carbon electrodes can be performed as a preliminary step for the functionalization of carbon nanotubes. The functionalization processes with diazonium salts can lead to further modifications of the nanotubes in order to facilitate their incorporation into polymer composite materials or their use in sensors applications. Identifying the grafting behaviour of diazonium salts on carbon surfaces should help in obtaining a certain degree of functionalization for carbon nanotubes that can be used in various sensing devices where the control of the grafting density must be assessed to ensure high sensitivity [15].

There has been a long-standing interest in studying the blocking properties of covalently attached aryl layers [13-17]. This is an important aspect of aryl-modified electrodes from both fundamental and practical points of view. 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. Electrochemistry is a useful characterization method when a redox active functional group is attached to the surface, in this case the surface concentration of aryl modifiers can be determined easily from cyclic voltammetry measurements [18, 19]. In this paper, the selection of the molecules to be grafted was done both for their electroactivity after grafting and the contrasted electronegativity (i.e., electro-withdrawing nitro group, electro-donating amino groups) of the substituents. In order to establish the blocking behaviour of covalently attached aryl layers obtained by different kinds of diazonium derivatives electrochemically reduced on the carbon substrate, the following diazonium salts were chosen: p-nitrophenyl diazonium tetrafluoroborate (NBTDFB); p-tolyldiazonium tetrafluoroborate (TDTFB) and 4-diazo-N-phenylaniline tetrafluoroborate (PADTFB), respectively. In addition to the character of the substituent of the diazonium salt, both the diazonium reduction potential and the time are varied. The cyclic voltammogram of soluble electroactive species provides a convenient tool to study the presence of grafted films.
and their blocking properties. In this paper we have studied the blocking action of the electrochemically grafted electrodes for Fe(CN)$_{3/4}$ redox probe using cyclic voltammetry (CV). Usually, the occurrence of the electrochemical processes after the chemical grafting can be indicative of pinholes or defects where the electron transfer between the electroactive probe and the metal surface can proceed. The slower kinetics and/or blocking effect of the grafted layer for the redox systems is conveyed by an increase of the separation of the anodic and cathodic peak potentials (ΔEp) and a decrease of the intensity of the anodic/cathodic peak current of the cyclic voltammograms. It was also of considerable interest to test whether the blocking properties observed during CV experiments could be confirmed by EIS studies.

**Experimental part**

The studied diazonium salts (2) were obtained as tetrafluoroborates (stable in solid state at room temperature) by diazotation of the aromatic amines (1) (p-nitroaniline, p-toluidine and N-phenylalanine) in fluoroboric acid 50% (scheme 1). The amines were added to 50% fluoroboric acid prediluted with water, and the solution was then cooled in an ice bath. A solution of sodium nitrite in water was added slowly to the stirred solution maintaining the temperature near 0-5°C. The mixture was then cooled to below 0°C in a salt/ice bath. The precipitate was collected on a filter which had been washed with cold 5% fluoroboric acid followed by ice-cold ethanol and ethylic ether. The products were air-dried and stored at room temperature in the dark in a vacuum desiccator.

![Scheme 1. The synthesis of the diazonium salts (2): (p-nitrophenyl diazonium tetrafluoroborate: NBDTFB, p-tolyldiazonium tetrafluoroborate: TDTFB, 4-diazo-N-phenylalanine tetrafluoroborate: PADTBF)](image)

**Results and discussions**

The cyclic voltammetry study of GC electrode in diazonium salts solutions (in ACN + 0.1 M TBATFB supporting electrolyte) allowed the establishment of the electrode potential to be used for electrodeposition and the electrochemical domain for characterisation of the grafted electrode. As shown in figure 1, cyclic voltammograms recorded in the diazonium salts solutions of NBDTFB, TDTFB and PADTBF, respectively (concentration 2mM, in ACN + 0.1 M TBATFB) at a GC electrode show as in all cases a broad irreversible wave, indicating that an irreversible reaction (i.e., the cleavage of the C-N bond and elimination of dinitrogen) is associated with the electron transfer. After the second scan, the wave disappears almost completely and indicates the blocking of the surface by the organic groups which become attached to the surface.
The reduction potential values correlate well with electron-donating or electron-withdrawing properties of the diazonium substituents in the way that the more electron-withdrawing is the substituent, the more shifted towards positive values is the reduction potential. The success of the derivatization of the carbon surfaces by electrochemical reduction of diazonium salts hinges upon the fact that the aryl radicals produced by this reaction are not reduced at the potential at which they are produced and may react with the surface [11]. Thus, the values of the potentials for the reduction peak (noted as Ep) for the studied salts on GC are around -150 mV for NBDTFB, -550 mV for PADTFB, respectively (values obtained for a potential scan rate of 20mV/s). It can be observed that TDTFB and PADTFB shows reduction potential peaks displaced more negatively in respect with NBDTFB salt. These peak values correlate the Hammett behaviour relative to the mesomeric and inductive effects of the substituents that influence the diazonium electroreduction [15]. This behaviour of TDTFB and PADTFB salts can indicate a lower reactivity of the radical with the electrode surface than for NBDTFB due to possible radical stabilization and solution diffusion with further coupling side reactions. Also, it was observed that peak current values are lower for NBDTFB reflecting a limitation of the reduction process of the diazonium salt, in this case. It can be seen that after the first scan the electrodes present a blocking effect toward the reduction of diazonium in solution because, in the potential range used for grafting, no electroactive relay continue to exist for the grafted molecules.

Grafting of p-nitrophenyl and N-phenylaniline functional groups at the electrode surface can be proved by the reversible wave observed in the cyclic voltammetry of the electrode transferred to a pure electrolyte solution. The voltammetric signal of the nitrophenyl group can be observed at rather low cathodic potential (approximately -1.6 V for a scan rate of 20 mV/s), nitrobenzene being reversibly reduced, in aprotic medium, by one electron to its stable radical-anion (fig. 2). Nevertheless, upon repetitive scans, this reversible wave gradually decreases due to the protonation of the radical-anion of the p-nitrophenyl group by residual water [20]. The cathodic and anodic peaks are located at the same potential leading to the conclusion that the p-nitrophenyl group is attached to the surface. The fact that the cathodic and anodic peaks are located at the same potential indicates that the species undergoing the redox process do not diffuse to and from the electrode and, therefore, are bonded to the surface.

The voltammograms acquired on the GC electrode after modification by N-phenylaniline groups exhibit during the first sweep in anodic potential range a very well defined oxidation process showing partial reversibility with a potential peak of approximately 0.6 V. The second scan shows decreased current intensity compared to the first peak, but the obtained waves present good reversibility and stability along the successive sweeps (fig. 3). This behaviour indicates that after the first oxidation scan, coupling reactions at the surface of the modified electrode may take place.

**Fig. 3.** Cyclic voltammograms (20mV/s) of N-phenylaniline/GC (PAGC) modified electrodes obtained by CPE for 10 min in 2 mM PAGC solution at -1.2V potential value, in the supporting electrolyte solution (ACN + 0.1 M TBA(TFB))

p-Tolyl functional group is not electroactive, hence it was not possible to pursue the surface modification steps by direct voltammetric methods. Therefore, for all substituted aryl layers grafted by electrochemical reduction of diazonium salts, the behavior of ferri/ferrocyanide redox system on the modified electrode was investigated. In addition to the nature of the substituent on the diazonium moiety, the influences of the electrochemical method used for grafting and diazonium reduction time at the potential corresponding to each diazonium cathodic peak (E<sub>p</sub>) were also studied.

The Fe(CN)<sub>3/4-</sub> couple in 0.1 M NaCl aqueous solution presents a reversible system with a peaks potentials separation (∆Ep) of 70mV on bare GC electrode. The various diazonium layers on the GC electrode exhibit different blocking behavior for oxidation and reduction reactions of the Fe(CN)<sub>3/4-</sub> redox system. The response of negatively charged redox probes as Fe(CN)<sub>3/4-</sub> on NBGC and TGC films is very different from that of PAGC films.

A strong increase of ∆Ep and decrease in current is observed for Fe(CN)<sub>3/4-</sub> at p-nitrophenyl grafted electrode surfaces, hence a blocking behavior of the grafted layer towards the Fe(CN)<sub>3/4-</sub> redox system (fig. 4). The suppression of the electrochemical response for hydrophilic species such as Fe(CN)<sub>3/4-</sub> at the p-nitrophenyl-modified electrode may be due to hydrophobicity of the film. The electrochemistry of nitroaromatic compounds has been widely studied in the past, and it is well-known that their electrochemical reduction leads to the formation of phenylhydroxylamine and aniline depending on the experimental conditions [14]. Although for the electrognerated nitrophenyl layer, the reduction of nitro to amino group can occur [14], and as a consequence, the p-nitrophenyl group is expecting to suffer some chemical modifications upon cycling in aqueous solutions, the obtained results suggest that the resulting film still preserve a significant hydrophobic character.

**Fig. 2.** Cyclic voltammograms (20mV/s) of NBGC modified electrodes obtained by CPE for 10 min in 2 mM NBDTFB solution at -1.2V potential value, in the supporting electrolyte solution (ACN + 0.1 M TBA(TFB))
Figure 5 shows a representative set of cyclic voltammograms with the responses of the ferri/ferrocyanide redox system on the TGC modified GC electrodes by CPE at \(E_p = -380\) mV for a grafting time of 1s and by CV in the potential range of \((0, -500)\) mV, at a scan rate of 10 mV/s, for 5 cycles. It was observed that after electrode modification with \(p\)-tolyl groups by CV method, the \(\text{Fe(CN)}_6^{3-/4-}\) response is strongly suppressed. Same results were obtained when the electrodes were grafted by CPE method at the same potential, for a grafting time higher than 60 s (not shown). At short electrolysis times, the films are less blocking and differences in blocking behaviours are more easily observed.

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The cyclic voltammetry data for the \(p\)-nitrophenyl modified electrodes suggest that the suppression of the response of \(\text{Fe(CN)}_6^{3-/4-}\) redox probe is stronger for this layer. This might be due to the fact that the \(p\)-nitrophenyl film is thicker or more compact than the tolyl film.

The obtained experimental data revealed that the responses at the studied modified electrodes are of two general types. For NBGC and TGC electrodes, at grafting potentials equal or more negative than \(E_p\), only very low currents are observed at large overpotentials. In contrast, for PAGC electrode obtained by CPE method, there is little difference between the behaviour of a bare GC electrode and the GC modified electrode (the same peak potentials and, sometimes, the peak currents are slightly higher compared to bare electrode), no matter what time has been used for grafting (fig. 6). It is important to note here that, contrary to surface modifications generated by the reduction of the diazonium salts such as NBDFTB and TDFTB, the layer obtained through the electroreduction of PADTFB diazonium salt behaves differently depending on the grafting conditions. Thus, for the PAGC modified electrode, generated using five electroreduction cycles between 0 and -0.9 V, as depicted in figure 1(c), no current is observed on the in the potential range where \(\text{Fe(CN)}_6^{3-/4-}\) reactions usually occur on bare electrodes. The organic layer totally blocks the electrode in such a potential window and an “irreversible” wave is observed with an oxidation peak at 430 mV. However, no reduction peak is observed. This is consistent with the behaviour mentioned in the recent literature [21,22]. According to these references, above some threshold potential, oxidation of soluble external probes is possible whereas the reduction of the oxidized form of this external probe remains impossible, the layer obtained through the electroreduction of PADTFB diazonium salt behaving like an electrochemical switch [21]. The PA layer has a blocking effect of the reduction process and could be considered as insulating layer toward this electrochemical reaction. Such behaviour is linked to the electroactivity of the grafted layer which acts as a dopable organic semiconductive material and switches from an insulating state to a conductive state above a potential threshold which is here close to 0.4 V/SCE.

It was found that the electrochemical switch behavior observed with PAGC electrodes generated by potential scanning disappears when CPE method was employed. The CV responses of these electrodes in \(\text{Fe(CN)}_6^{3-/4-}\) solutions, suggests that the PA layer has lost its blocking effect regarding to reduction processes and that the whole layer behaves as a metallic substrate. These results suggest the employing of such a derivatization methods leads to a continuous conductive chain bonded to the carbon electrode. It must be concluded that the electron transfer to these probes must take place at the surface of the film, which is conductive enough to act as an metallic electrode.
mV versus SCE. The peak-to-peak separation is around 80 mV (at 20 mV/s sweep rate), and the ratio of anodic to cathodic peak currents is close to unity. Also, it was observed a linear dependence of the current versus the scan rate indicating a surface process. This film electroactivity strongly suggests that PA moieties are grafted on the carbon surface. From the integrated charge of the electrochemical response (0.24 mC·cm⁻²), a surface coverage of approximately 2.5·10⁻⁹ mol·cm⁻² can be estimated (The electrical charge of the grafted layer, \( Q \), is calculated by integration of the voltammetric peak corresponding to the oxidation of the grafted groups. The surface coverage, \( \tilde{A} \), can be calculated as \( Q/nFA \) where \( F \) is the Faraday number, \( A \) is the geometric area of the electrode and \( n \) the number of the transferred electrons). From molecular models, a monolayer on a perfect plane would correspond to a surface concentration of 1.35·10⁹ mol cm⁻² [17]. Thus, the surface coverage of 2.5·10⁻⁹ mol·cm⁻² clearly indicates a surface coverage higher than a monolayer and, thus, that the GC electrode is covered with a thin film of PA or oligo(PA) molecules.

Electrochemical impedance spectroscopy measurements can be used to evaluate the effect of \( \text{p-nitrophenyl, } \text{p-tolyl and N-phenylaniline groups on the kinetics of the redox reaction of } \mathrm{Fe(CN)}_6^{3-/4-} \text{ at a GC electrode. Figures 8, 9 and 10 presents the complex impedance plots for NBGC, TGC and PAGC, respectively, modified GC electrodes for different grafting conditions at a potential of 0.21 V in the presence of \( \mathrm{Fe(CN)}_6^{3-/4-} \) redox couple. The impedance plot for the bare electrode is characterized by a semicircle at high frequency and a low-frequency Warburg line at an angle of 45°. The semicircle corresponds to a parallel combination of the charge-transfer resistance with the double layer capacitance, while the linear response is related to mass transport effects. The impedance plots for GC electrodes modified by electrochemical reduction of NBDTFB diazonium salts either by CPE method at \( E_p = -0.15 \text{V} \) for different grafting times or by potential scanning method differ significantly from that of the bare electrode (fig. 8). The diameter of the semicircle increases with an increase of the electrolysis time. Qualitatively, the increase of the semicircle indicates that the electrode kinetics become slower as the GC electrode is modified with a substituted phenyl group. The impedance data are in good agreement with the cyclic voltammetry results of figure 2. A similar trend is observed in the case of the \( \text{p-tolyl group (fig. 9).} \)

A similar study was performed on PAGC modified electrode. In contrast with the results obtained by CV where no significant changes were obtained between the bare and the PAGC modified electrode by CPE method, the results shown in figure 10 are characterized by a slight increase of the diameter of the semicircle obtained at high frequency for the grafted electrode. Clearly, some change in the permeability of the grafted layers occurred and the data suggest that electrochemical impedance spectroscopy is more sensitive to such modification than CV. In comparison with the others two studied systems the diameters of the semicircles were significantly lower. The Warburg diffusion line indicates that diffusion phenomena are occurring at these electrodes and that the grafted aryl groups does not appear to hinder the electron transfer of electroactive species. This is consistent with above discussion, according to the electron transfer to \( \mathrm{Fe(CN)}_6^{3-/4-} \) probe must take place at the surface of the grafted film, which is conductive enough to act as an electrode. The significant increase of the charge transfer resistance for the PAGC electrode modified by CV method demonstrates that the film is blocking to charge transfer at the formal potential of the \( \mathrm{Fe(CN)}_6^{3+/4-} \) redox probe (0.21 V).
Conclusions

Electrochemical reduction of aromatic diazonium salts appears to be a general and versatile method for derivatizing carbon surfaces with different substituted aromatic moieties.

The diazonium reduction potential values in the electrografting experiments correlated well with electron-donating or electron-withdrawing properties of the diazonium substituents: the more electron-withdrawing was the substituent, the more the reduction potential was shifted towards positive values. Among the three diazonium salts studied, PADTFB was the most difficult and NBDTFB was the most easy to reduce.

In an aqueous medium, the blocking effect of the grafted layer was assigned to hydrophilic/hydrophobic interactions preventing the redox probe from reaching the electrode. There were observed differences in blocking properties for the \( p \)-nitrophenyl, \( p \)-tolyl and \( N \)-phenylaniline groups: this points to an influence of the substituent of the phenyl rings either on the formation of the layer or on its resulting properties. The best results, in terms of blocking properties, are obtained with \( p \)-nitrophenyl groups. On the contrary, low modification of the electrochemical behaviour of the probe is visible in the case of \( N \)-phenylaniline film generated by CPE method. Probably in this case the electron transfer to \( \text{Fe(CN)}_{3/4}^{-} \) probe must take place at the surface of the grafted film, which is conductive enough to act as an electrode.

Further studies will be performed in order to evaluate the influence of different experimental parameters, such as diazonium salts concentration, applied potential or the charge used for grafting on the blocking behaviour of the resulting layers. These results should be very helpful for future studies concerning functionalization of carbon nanotubes and their use in sensors applications.

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