



## COMPARATIVE STUDIES ON THE REDOX REACTION OF $\text{Fe}(\text{CN})_6^{4-/3-}$ AT MODIFIED GLASSY CARBON ELECTRODES VIA DIAZONIUM SALTS ELECTROREDUCTION

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In this paper, the electrochemical properties of glassy carbon (GC) electrodes modified with different functional groups have been investigated. A diazonium salt coupling procedure was used to covalently bind the various *p*-substituted aryl groups to GC surface. In order to establish suitable grafting conditions enforceable to all kinds of diazonium derivatives, the selection of the molecules to be grafted was done for the contrasted electronegativity of the substituents. We obtained that grafting density could be controlled by varying the concentration of the diazonium, the duration and the value of the applied potential. The surface modification was checked by the blocking action of GC modified electrodes for  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox probe in cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements.

### INTRODUCTION

The derivatization of surfaces is often required to improve the performance of many materials or change their surface properties and is also often critical for some particular applications.<sup>1</sup> The grafting process has been applied in order to induce reactivity to the surface of various conducting substrates which are then appropriate for the anchoring of a large variety of molecules. The electrochemical grafting of specific organic molecules has become a method of choice since the deposition conditions can be easily controlled and adapted to the substrate.<sup>2</sup> In this context, a technique based on the electroreduction of diazonium salts has been developed.<sup>3-16</sup> Electroreduction of diazonium salts provides a convenient way of covalently bonding the organic molecules through the formation of an aryl radical on different substrates. Diazonium salts are either commercially available or can be easily obtained in one step from widely available aromatic amines. Savéant and Pinson were the first to demonstrate that the reduction of an aryl diazonium cation

afforded the corresponding aryl radical,<sup>1</sup> which can further react with a carbon atom of the carbon substrate to yield the covalent bonding of this aryl group according to Scheme 1. Pinson and Andrieux have demonstrated that the generation of the aryl radical is a concerted process, which involves the electron transfer and the cleavage of dinitrogen before the formation of the covalent bond.<sup>2</sup> This modification procedure is very attractive because it allows the presence of selected functional groups on the electrode surface.

Changing the substituents on the aryl ring allows introduction of a large variety of chemical functions on the metallic or carbon surface in order to ensure a controlled grafting of molecules for applications in biological field or chemical sensors. This modification process is also very attractive because it avoids the use of oxidative conditions which can lead to the damaging oxidation of the carbon substrate.<sup>2</sup> Electrochemistry is a useful characterization choice 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

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(CV) measurements.<sup>17,18</sup> Also, indirect proof of grafting can be provided by cyclic voltammetry experiments using redox systems, which can show blocking effects that can be revealed by an increase of the peak potential separation and decrease of the peak current due to the presence of a layer at the electrode surface. This is an important point to assess the grafting behaviour when the subsequent grafted molecules are not responsive in electrochemistry as in the case for many biological receptors.

The present study was performed by electrochemical grafting of diazonium salts with different substituents on the phenyl group to a glassy carbon (GC) surface and investigation of  $\text{Fe}(\text{CN})_6^{3-/4-}$  behavior at the modified electrode surface. For this purpose, the following diazonium salts were chosen: 4-nitrobenzene diazonium tetrafluoroborate, *p*-tolylidiazonium tetrafluoroborate and 4-diazo-*N,N*-dimethylaniline fluoroborate. The influence of the GC electrode modification conditions on the cyclic voltammetric response of  $\text{Fe}(\text{CN})_6^{3-/4-}$  couple was investigated for different layers. The slower kinetics and/or blocking effect of the grafted layer for the redox systems was conveyed by an increase of the separation of the anodic and cathodic peak potentials ( $\Delta E_p$ ) and a decrease of the intensity of the anodic/cathodic peak current of the cyclic voltammograms. Electrochemical impedance spectroscopy (EIS) was also used to investigate the presence of the grafted layers.

## EXPERIMENTAL

### Reagents, solutions and instrumentation

All aqueous solutions were prepared with bidistilled water. Anhydrous acetonitrile (99.8%, noted ACN), tetra-*n*-

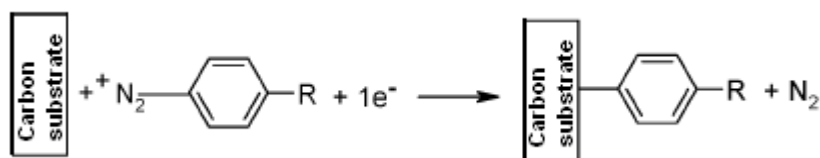
butylammonium tetrafluoroborate (99%, noted  $\text{Bu}_4\text{NBF}_4$ ),  $\text{K}_3\text{Fe}(\text{CN})_6$  (99%),  $\text{NaCl}$  (99%), were obtained from Aldrich and were used as received.

All electrochemical measurements including CV and EIS were performed with a computer-controlled GillAC potentiostat/galvanostat (ACM Instruments). A three-electrode configuration consisting of bare or modified GC (Metrohm, electrode disk diameter 2 mm) as working electrode,  $\text{Hg}/\text{Hg}_2\text{Cl}_2$  (3M KCl) and  $\text{Ag}/10\text{ mM AgNO}_3$ , 0.1 M  $\text{Bu}_4\text{NBF}_4$  as reference electrodes for electrochemical experiments in aqueous and organic solvents, respectively, and a Pt wire as counter electrode was used.

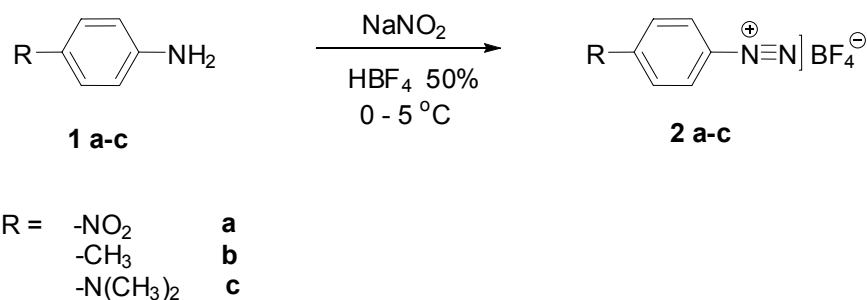
EIS measurements were carried out in the range of 10 kHz–10 mHz by superimposing a sine wave with 5mV amplitude on a constant potential of 0.21 V, which is the formal potential of the  $\text{Fe}(\text{CN})_6^{4-/3-}$  redox probe vs  $\text{Hg}/\text{Hg}_2\text{Cl}_2$  (3M KCl). The experimental impedance data were analyzed by Z-view impedance software. The experimental data of the electrochemical impedance plot were analyzed by applying nonlinear least squares fitting to the theoretical model represented by a Randles equivalent electrical circuit. All solutions were deoxygenated by bubbling high purity Ar for 15 min prior to experiments.

### Synthesis of arylidiazonium tetrafluoroborate salts

The studied diazonium salts (**2**) were obtained as tetrafluoroborates (stable in solid state at room temperature) by diazotization of the aromatic amines (**1**) (*p*-nitroaniline, *p*-toluidine and *p*-(*N,N*-dimethylamino)aniline) in fluoroboric acid 50% (Scheme 2). The amines (5 mmol) were added to 2mL of 50% fluoroboric acid prediluted with 2 mL of water, and the solution was then cooled in an ice bath. A solution of 5 mmol 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 sintered glass filter which had been cooled and 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 – Electrochemical reduction of an aryl diazonium salt, giving a reactive radical that covalently attaches to a carbon surface.



Scheme 2 – The synthesis of the diazonium salts **2 a-c**: (4-nitrobenzene diazonium tetrafluoroborate: NBDBF<sub>4</sub>, *p*-tolylidiazonium tetrafluoroborate: TDBF<sub>4</sub>, 4-diazo-*N,N*-dimethylaniline tetrafluoroborate: DMADBF<sub>4</sub>).

### Modification of glassy carbon electrode surface

Prior to electrode modification, the electrode surface was polished in 0.05  $\mu\text{m}$  alumina slurry on a microcloth pad. After polishing the electrode was thoroughly rinsed with water and sonicated in ACN for 5 min. The surface derivatization of the GC electrode was carried out in millimolar solutions of diazonium salts in ACN. The electrochemical derivatization was performed first by repetitive cyclic scanning in order to obtain information regarding the reduction potential of the diazonium salt and then the derivatization was performed by controlled potential electrolysis (CPE). The electrodes were then removed and rinsed with large volumes of ACN, followed by ultrasonication for 5 min to remove any loosely bounded species. The resulting modified electrode was thoroughly rinsed with water and transferred into a aqueous solution of 0.1 M NaCl + 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6$ . The  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox systems was used to evaluate the film integrity. A compact or blocking film will inhibit the redox reaction of the probe as investigated by CV. The presence of defects in the film will be evidenced by the apparition of sizable current that may reach that observed at a bare electrode if the grafted layer is very loosely. The redox systems were also used to evaluate the integrity of the film by EIS. A compact and blocking film will inhibit the redox reaction of the redox probe and will cause an increase of the charge-transfer resistance ( $R_{CT}$ ) of the impedance data. The presence of defects in the film will be monitored by a sizable diminution of the  $R_{CT}$  of the Nyquist representation. If the grafted layer is very loosely, a  $R_{CT}$  similar to a bare electrode should be observed.

The relative electroactivity of the modified electrode, which is inversely related to its blocking properties, was quantified by CV in the presence of redox probe species. The parameter of  $I_{rel}$  is defined as:  $I_{rel}(\%) = (I_{pa} \text{ for the grafted electrode} / I_{pa} \text{ for a bare electrode}) \times 100$ ; where  $I_{pa}$  is the intensity of the anodic peak current. Also, the increase in the charge transfer resistance can be related to the electrode coverage and is given by the following equation:  $(1 - \theta) = R_{CT}^0 / R_{CT}$ , where  $\theta$  is the apparent electrode coverage, assuming that all currents are passed via bare spots on the electrode, and  $R_{CT}^0$  and  $R_{CT}$  represent the charge transfer resistance measured by EIS method on a bare and on a modified GC electrode, respectively.

The grafted electrodes were denominated as NBGC, TGC or DMAGC when the grafting was done using 4-nitrobenzene diazonium tetrafluoroborate, *p*-tolyl diazonium tetrafluoroborate and 4-diazo-*N,N*-dimethylaniline fluoroborate, respectively.

## RESULTS AND DISCUSSION

### Electrochemical grafting of *p*-substituted aryl groups on GC electrode

The electrochemical study of the NBDBF<sub>4</sub>, TDBF<sub>4</sub>, DMADBF<sub>4</sub> salts allowed the establishment of the electrode potential to be used for electrodeposition. Cyclic voltammograms recorded in solutions of 2mM of the specified diazonium salts (+ 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> in ACN) at a GC electrode (Fig. 1) show an irreversible cathodic process assigned to the reduction of the diazonium species. The reduction potential values correlate well with electron-donating or electron-withdrawing properties of the diazonium substituents: the more electron-withdrawing is the substituent, the more shifted towards positive values is the reduction potential. From the studied diazonium salts, DMADBF<sub>4</sub> is the most difficult to reduce. It can be seen that after the first scan the electrode presents a blocking effect toward the reduction of diazonium in solution because, in this potential range, no electroactive relay continue to exist for the grafted molecules. In fact, in the case of DMADBF<sub>4</sub> salt, because of the electronic transfer, diazonium reduction is still observed after the first scan but the signal is displaced towards more negative values. This may denote a lower reactivity of the radical with the electrode surface than for NBDBF<sub>4</sub> and TDBF<sub>4</sub> attributed to a radical stabilization and solution diffusion with further coupling side reactions. Performing several scans leads to a more difficult electron transfer induced by thicker layers formed on the electrode surface. The values of the potentials for the reduction peak (noted as  $E_p$ ) for studied salts on GC are around -530 mV for DMADBF<sub>4</sub>, -380mV for TDBF<sub>4</sub> and -150mV for NBDBF<sub>4</sub>, respectively (values obtained for a potential scan rate of 20 mV/s).

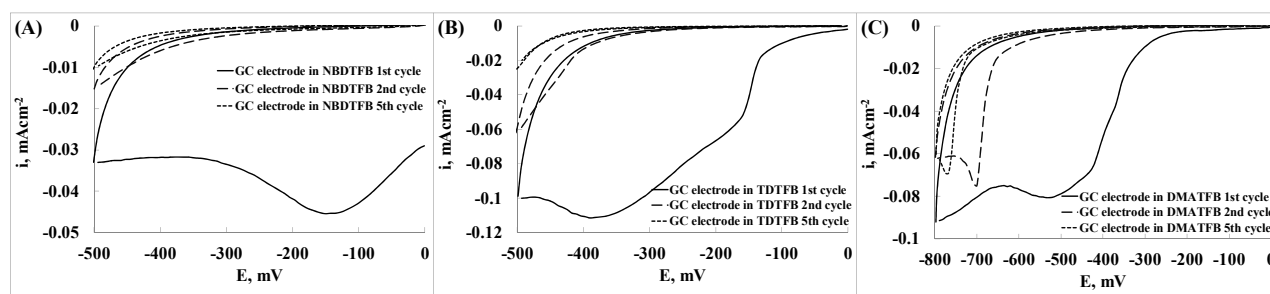


Fig. 1 – Successive cycling (20mV/s, 5 cycles) of GC electrode in (A) 2 mM NBDBF<sub>4</sub>, (B) 2mM TDBF<sub>4</sub> and (C) 2 mM DMADBF<sub>4</sub> solutions + 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> in CAN.

### Electrochemical response of the redox probes on grafted electrodes

The behavior of ferri/ferrocyanide redox system on the GC electrode was investigated for different layers grafted by electrochemical reduction of diazonium salts. In addition to the nature of the substituent on the diazonium moiety, the diazonium reduction time at the potential corresponding to each diazonium cathodic peak ( $E_p$ ), the grafting potential and the concentration were varied.

The ferri/ferrocyanide couple in 0.1 M NaCl aqueous solution presents a reversible system with  $\Delta E_p = 70$  mV on bare GC electrode. The various diazonium layers obtained at different deposition time on the GC electrode exhibit different blocking behavior for oxidation and reduction reactions of the  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox system. A strong increase of  $\Delta E_p$  and decrease in current is observed for  $\text{Fe}(\text{CN})_6^{3-/4-}$  at the TGC grafted electrode surface, hence a blocking behavior of the grafted layer towards the ferricyanide (Fig. 2). It was observed that after modification with 4-nitrobenzene and p-tolyl groups for a grafting time higher than 60 seconds the  $\text{Fe}(\text{CN})_6^{3-/4-}$  response is strongly suppressed. At short electrolysis times, the films are less blocking and differences in blocking behaviors are more easily observed. Fig. 2 shows a representative set of cyclic voltammograms for such an experiment with the responses of the ferri/ferrocyanide redox system on the TGC electrodes obtained by CPE at  $E_p = -380$  mV for different grafting times. However, when the

N,N-dimethylaniline group has been grafted, the CV resembled that of a bare GC electrode although the intensity of the peak currents remained slightly smaller and  $\Delta E_p$  slightly larger (not shown).

Results from Fig. 2 show that the blocking effects increase with increasing reduction time. This trend is observed for all grafted layers and demonstrates that it is possible to obtain relative control of the layer thickness by controlling the diazonium reduction time.

Fig. 3 shows the responses of the ferri/ferrocyanide redox system on the NBGC electrodes by CPE at different potentials for a grafting time of 1s. In agreement with previous studies,<sup>4-7</sup> the electrochemical reaction of  $\text{Fe}(\text{CN})_6^{3-/4-}$  is significantly blocked by the grafted layer at potentials more negative than  $E_p$ . The same is true for the modified electrode by p-tolyl group. Based on the shifts in  $\Delta E_p$  and changes in peak currents, NBGC and TGC films have very similar electrochemical blocking properties. On the other hand, DMAGC films have no measurable effect on the  $\text{Fe}(\text{CN})_6^{3-/4-}$  response. Although quantitative analysis of the  $\text{Fe}(\text{CN})_6^{3-/4-}$  response at the modified surfaces is not possible because the detailed structure of the films (i.e., the topography and number, size, and shape of defects) is unknown, the most important finding is that the 4-nitrobenzene and p-tolyl films exhibit similar effects on the  $\text{Fe}(\text{CN})_6^{3-/4-}$  response, even though the p-tolyl films appear to have much lower surface coverages than the 4-nitrobenzene films.

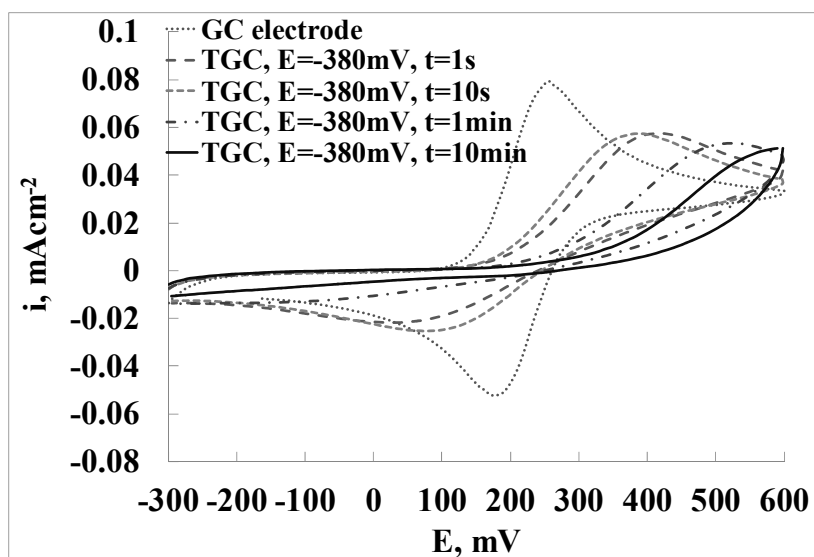


Fig. 2 – CV plots for TGC electrode in aqueous 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  + 0.1M NaCl obtained at  $E_p = -380$  mV for different grafting times.

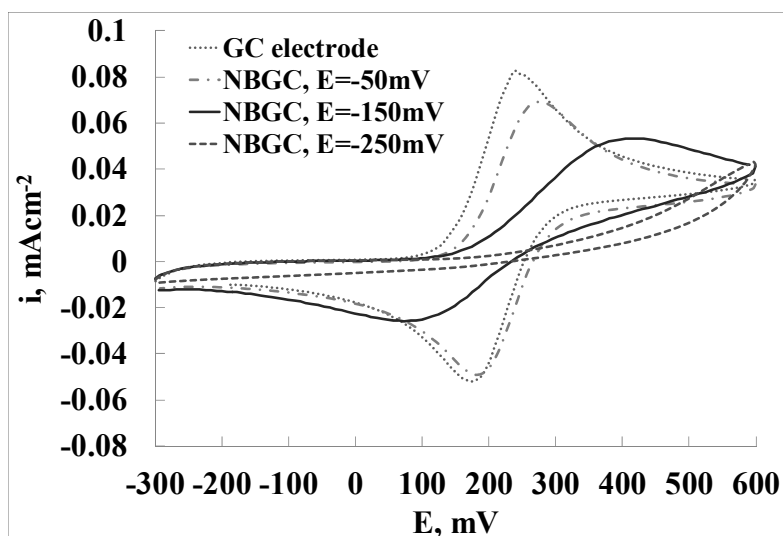


Fig. 3 – CV plots for a NBGC electrode in aqueous 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6 + 0.1\text{M NaCl}$  obtained at various reduction potentials for a grafting time of 1s.

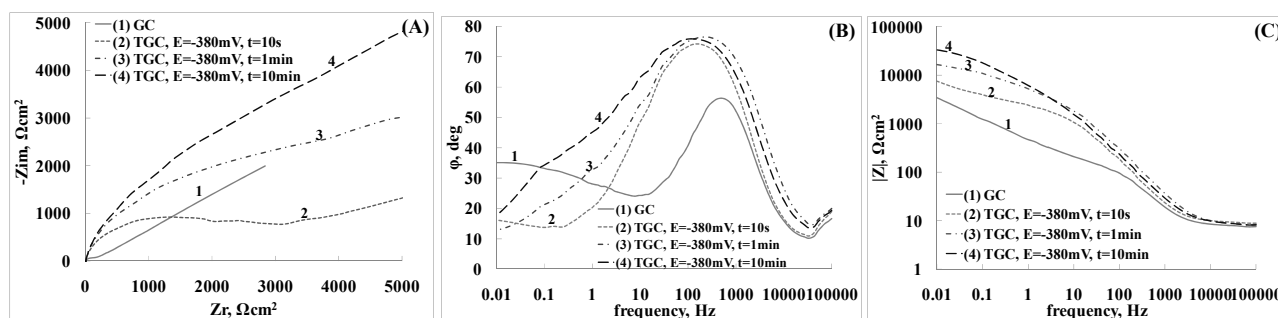


Fig. 4 – EIS plots for TGC electrode in aqueous 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6 + 0.1\text{M NaCl}$  at various reduction times.

Inspection of the measured data revealed that the responses at the modified electrodes are of two general types. For NBGC and TGC electrodes, at grafting potentials more negative than  $E_p$ , only very low currents are observed at large overpotentials. In contrast, for DMAGC electrode significant currents are observed at modest overpotentials and there is a peak in each voltammogram, no matter what potential has been used for grafting. Table 1 lists the shifts in peak potentials on the forward scan for the probe species at the modified electrodes.

The assessment on the blocking efficiency of the grafted layers on GC electrode at various times was also evaluated by EIS in a 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  solution. Fig. 4 presents the complex impedance plots for a bare GC electrode and TGC modified electrodes by CPE at  $E_p = -380\text{mV}$  for different grafting times.

The impedance plot for the bare electrode is characterized by a very small semicircle at high frequency and a low frequency Warburg line at an angle of  $45^\circ$ . The impedance plots for GC electrodes modified by electrochemical reduction of a p-tolyl diazonium salt at  $E_p = -380\text{mV}$  for different times differ significantly from that of the bare electrode. The diameter of the semicircle increases with increasing electrolysis time (see Fig. 4A). Qualitatively, the increase of the semicircle indicates that the electrode kinetics becomes slower as the GC electrode is modified with a substituted phenyl group. The impedance data are in good agreement with the CV results of Fig. 2. To give more detailed information about the electrode/solution interface, the Randles circuit was chosen to fit the obtained impedance data. The electrical equivalent circuits for bare and modified electrodes are shown in Fig. 5.

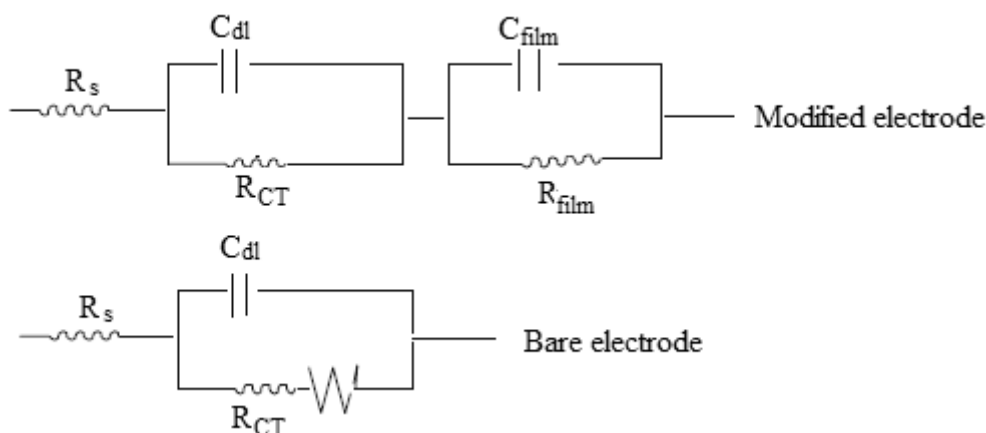


Fig. 5 – Equivalent circuits used for analysis of the electrochemical impedance data. The presented circuit elements are: the solution resistance,  $R_s$ ; the charge transfer resistance,  $R_{CT}$ ; the double layer capacitance,  $C_{dl}$ ; the capacitance of the grafted film,  $C_{film}$  and resistance of the grafted film,  $R_{film}$ .

Table 1

Relative electroactivity ( $I_{rel}$ ) and surface coverage ( $\theta$ ) obtained for aryl-modified GC electrodes for different grafting conditions

Electrode	Grafting potential	Grafting time	$I_{pa}$ , $\text{mAcm}^{-2}$	$I_{rel}$ , %	$R_{CT}$ , $\Omega\text{cm}^2$	$\theta$
GC bare	-	-	0.082	-	50	-
NBGC	-50mV	1s	0.068	83	2408	0.979
	$E_p = -150\text{mV}$	1s	0.053	64.6	6071	0.992
	-250mV	1s	0.04	48.8	7828	0.994
TGC	-150mV	1s	0.08	97.6	227	0.780
	$E_p = -380\text{mV}$	1s	0.057	69.5	1436	0.965
	-500mV	1s	0.05	61	2556	0.980
	$E_p = -380\text{mV}$	10s	0.056	68.3	2168	0.977
	$E_p = -380\text{mV}$	1min	0.053	64.6	4756	0.989
	$E_p = -380\text{mV}$	10min	0.05	61	16640	0.997
DMAGC	-150mV	1s	0.077	94	165	0.697
	-350mV	1s	0.075	91.5	172	0.709
	$E_p = -530\text{mV}$	1s	0.067	81.7	230	0.783
	-700mV	1s	0.08	97.6	62	0.194

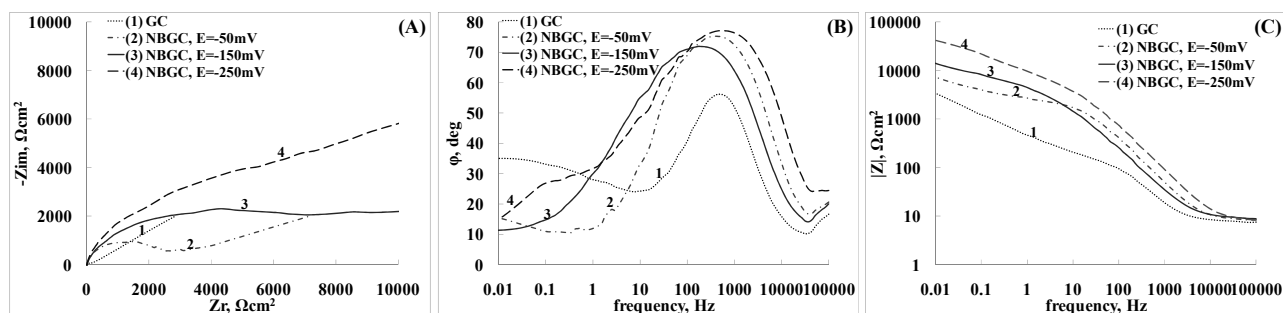


Fig. 6 – EIS plots in aqueous 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6 + 0.1\text{M NaCl}$  for NBGC electrodes obtained at various reduction potentials.

The impedance data were analyzed by Z-view impedance software by using the electrical equivalent circuits and the results are shown in Table 1. The table shows that the charge transfer resistance increases dramatically following modification of the GC electrode. It appears that the surface coverage of phenyl groups increases with electrolysis potential and at each potential

approaches a limiting coverage within 10 min. A similar trend is observed in the grafting of all aryl substituted groups. The increase of  $R_{CT}$  with the electrolysis time demonstrates that the film becomes more compact as the treatment time increases.

We performed also by EIS method a study of the influence of electrolysis potential on grafted

layer properties. The measurements were achieved after an electrolysis time of 1s at several applied potentials (chosen with respect of diazonium reduction potential at GC electrode). In Fig. 6 are presented the impedance plots for *NBGC* modified electrodes. The electrochemical impedance data depicted in Fig. 6 is consistent with the CV results and is characterized by an increase of the diameter of the semicircle as the grafting potential is made more negative.

A similar study was performed on *DMAGC* modified electrode. In contrast with the results obtained by CV where no significant changes were obtained, the results shown in Fig. 7 are characterized by an increase of the diameter of the semicircle obtained at high frequency as the grafting potential is made more negative. 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 and at the extreme negative potential value investigated for grafting ( $-700\text{ mV}$ ), the Nyquist plot shows a Warburg line at an angle of  $45^\circ$ . 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 diffusion of electroactive species. This is consistent with previous reports in the literature<sup>18</sup> showing that there can be also limits to the potential (in the negative sense) that can be used for film formation. Reduction of the aryl radical as an alternative reaction pathway to surface coupling can become favourable at sufficiently negative electrolysis potential.<sup>18</sup>

The influence of the concentration of the diazonium salt in the synthesis solution was also studied. Results presented in Fig. 8 for *NBGC* electrode show that the blocking effects increase with increasing concentration. This trend was observed for all grafted layers.

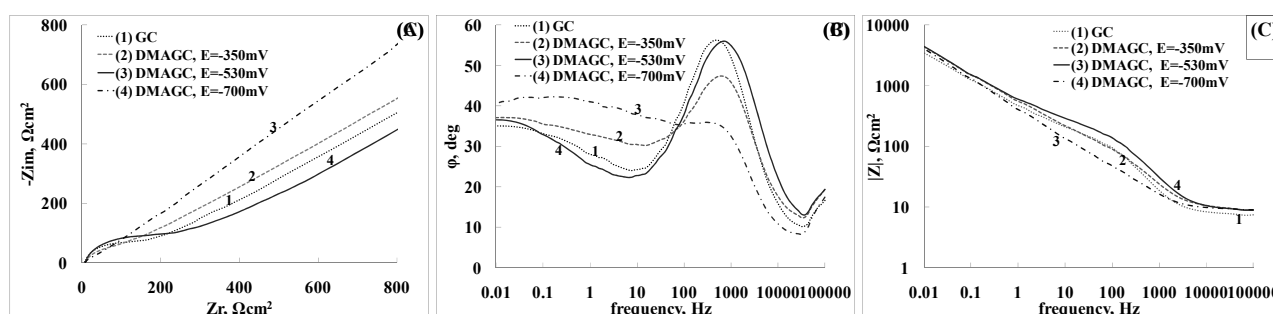


Fig. 7 – EIS plots in aqueous  $1\text{ mM K}_3\text{Fe}(\text{CN})_6 + 0.1\text{ M NaCl}$  for *DMAGC* electrodes obtained at various reduction potentials.

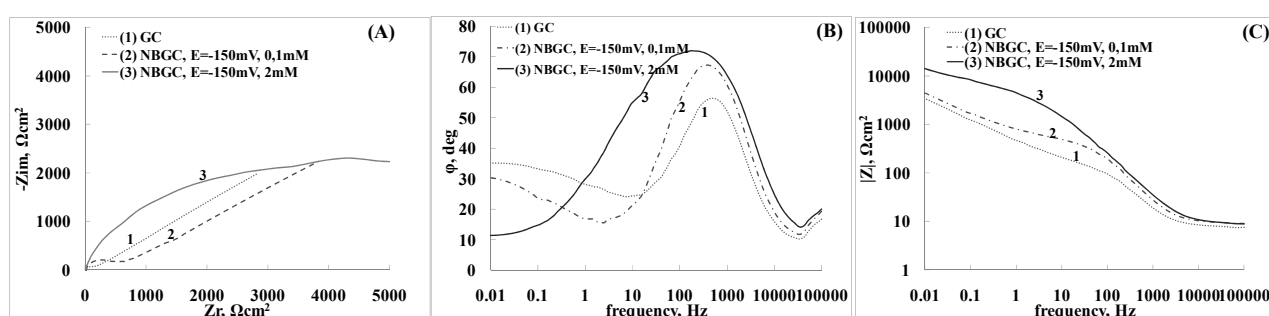


Fig. 8 – EIS plots in aqueous  $1\text{ mM K}_3\text{Fe}(\text{CN})_6 + 0.1\text{ M NaCl}$  for *NBGC* electrodes obtained at various diazonium salt concentrations in synthesis solution.

## 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, *DMADBF*<sub>4</sub> was more difficult to reduce than *NBDBF*<sub>4</sub> and *TDBF*<sub>4</sub>.

There were observed differences in blocking properties for the 4-nitrobenzene, *p*-tolyl and N,N-dimethylaniline groups: this points to an influence of the substituent of the phenyl rings on the formation of the layer and on its resulting properties. The best results, in terms of blocking properties, are obtained with 4-nitrobenzene groups. On the contrary, low modification of the electrochemical behaviour of the probe is visible when the GC electrode is exposed to DMABF<sub>4</sub> solutions.

Our results demonstrated that EIS is a more sensitive technique than CV to probe the modification of a thin grafted film.

The procedure applied in the case of studied compounds can be extended to the other diazonium salts including those that provide moieties conductive to further elaboration after attachment to the carbon surfaces. Also, these results should be very helpful in moving towards functionalization of carbon nanotubes and their use in sensors applications. This approach is currently being investigated in our laboratory.

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## REFERENCES

1. A. Laforgue, T. Addou and D. Belanger, *Langmuir*, **2005**, *21*, 6855-6865.
2. A. J. Downard, *Electroanalysis*, **2000**, *12*, 1085-1096.
3. P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson and J.M. Saveant, *J. Am. Chem. Soc.*, **1997**, *119*, 201-207.
4. A. Adenier, N. Barré, E. Cabet-Deliry, A. Chaussé, S. Griveau, F. Mercier, J. Pinson and C. Vautrin-UI, *Surface Science*, **2006**, *600*, 4801-4812.
5. C. Saby, B. Ortiz, G. Y. Champagne and D. Bélanger, *Langmuir*, **1997**, *13*, 6805-6813.
6. A. J. Downard and M. J. Prince, *Langmuir*, **2001**, *17*, 5581-5586.
7. J. K. Kariuki and M. T. McDermott, *Langmuir*, **2001**, *17*, 5947-5951.
8. J. Marwan, T. Addou and D. Belanger, *Chemistry of Materials*, **2005**, *17*, 2395-2403.
9. S. Liu, Z. Tang, Z. Shi, L. Niu, E. Wang and S. Dong, *Langmuir*, **1999**, *15*, 7268-7275.
10. J. L. Bahr and J.M. Tour, *J. Mater. Chem.*, **2002**, *12*, 1952-1958.
11. B. Ortiz, C. Saby, G. Y. Champagne and D. Belanger, *J. Electroanal. Chem.*, **1998**, *455*, 75-81.
12. P. Allongue, C. Henry de Villeneuve, G. Cherouvrier, R. Cortes and M.-C. Bernard, *J. Electroanal. Chem.*, **2003**, *550*, 161-174.
13. P. Hartig, T. Dittrich and J. Rappich, *J. Electroanal. Chem.*, **2002**, *524*, 120-126.
14. A. Adenier, M.-C. Bernard, M.M. Chehimi, E. Cabet-Deliry, B. Desbat, O. Fagebaume, J. Pinson and F. Podvorica, *J. Am. Chem. Soc.*, **2001**, *123*, 4541-4549.
15. A. Chausse, M. Chehimi, N. Karsi, J. Pinson, F. Podvorica and C. Vautrin-UI, *Chem. Mater.*, **2002**, *14*, 392-400.
16. M.-C. Bernard, A. Chausse, E. Cabet-Deliry, M.M. Chehimi, J. Pinson, F. Podvorica and C. Vautrin-UI, *Chem. Mater.*, **2003**, *15*, 3450-3462.
17. M. Delamar, R. Hitami, J. Pinson and J.M. Saveant, *J. Am. Chem. Soc.*, **1992**, *114*, 5883-5884.
18. A. J. Downard, *Langmuir*, **2000**, *16*, 9680-9682.