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ORIGINAL PAPER

# Electrochemical and impedance spectroscopy studies of various diazonium salts on a glassy carbon electrode

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**Abstract** The derivatization of a glassy carbon electrode surface was achieved with and without electrochemical reduction of various diazonium salts in acetonitrile solutions. The surfaces were characterized, before and after their attachment, by cyclic voltammetry and electrochemical impedance spectroscopy to evidence the formation of a coating on the carbon surface. The results were indicative of the presence of substituted phenyl groups on the investigated surface. Also, the effects of diazonium thin films at the surface of a glassy carbon electrode, modification time, and salt concentration on their electrochemical responses in the presence of the $Fe(CN)_6^{3-/4-}$ probe were investigated. Electrochemical impedance measurements indicated that the kinetics of electron transfer is slowed down when the time and the concentration used to modify the glassy carbon electrode are increased. We therefore modified a glassy carbon surface via its derivatization with and without electrochemical reduction of various diazonium salts in acetonitrile solution.

**Keywords** Cyclic voltammetry · Charge transfer · Diazo compounds · Glassy carbon · Electrochemical impedance spectroscopy

## Introduction

During the past two decades, surface modification via the attachment of organic molecules and nanosized materials with specific end functionalities has been the subject of substantial research which is driven by a large number of technological applications in many different areas such as sensors, molecular electronics, electrocatalysis, and biomedical applications [1]. Methods leading to the formation of organic layers covalently bound to conductive surfaces are relatively scarce. Most of them use electrochemistry to induce the attachment [2–11]. In the electrochemical method, a solution-based radical is generated at the electrode (substrate) surface by reduction or oxidation of the modifier. The radical appears to couple to the surface via formation of a covalent bond. The most studied reaction is reduction of an aryldiazonium cation to yield an aryl radical which binds to the surface [12]. This modification process is very attractive because it avoids the use of oxidative conditions which can lead to the damaging oxidation of the carbon substrate [13] and also because it allows the presence of selected functional groups on the aryl groups. A specific substituent on the aryl group can be used to provide useful properties to the modified electrode and to elaborate more complex chemical structures that can have various applications [14, 15]. For example, this method has been used for covalent binding of enzymes and proteins and study of the voltammetric differentiation of dopamine and ascorbic acid [16]. Some results concerning the attachment of diazonium salts on glassy carbon and metals without electrochemical induction have been reported in recent papers [17, 18]. This spontaneous grafting has been also observed on silicium, gallium arsenide (GaAs), palladium [19], carbon black, and carbon nanotube surfaces [20, 21]. Compared with electrochemical grafting, this procedure provides a simpler and more versatile method for the elaboration of organic layers attached to the substrate. Its easy implementation is very attractive in the industrial field, as indicated by the large number of patents applications for the modification of carbon black and the production of inks.

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The aim of the present study was attachment of diazonium salts with different substituents on the phenyl group to a glassy carbon surface with and without electrochemical reduction in nonaqueous solution and investigation of $Fe(CN)_6^{3-/4-}$ behavior at the modified electrode surface. For this purpose, the following diazonium salts were chosen: 4-(trifluoromethyl)benzene diazonium tetrafluoroborate ($CF_3$-PD), 4-chlorobenzene diazonium tetrafluoroborate (Cl-PD), 4-nitrobenzene diazonium tetrafluoroborate ($NO_2$-PD), and 4-diazobenzenesulfonic acid ($SO_3H$-PD). The modified electrodes are referred to as GC-X where GC is the glassy carbon substrate and X is the substituent on the phenyl group. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques were used to detect the presence of the grafted molecular groups on the glassy carbon electrode.

## Results and discussion

### *Electrochemical response of the redox system on grafted electrodes with electrochemical induction*

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 and the concentration were varied. The reduction time was set at 10, 30, 90, and 270 s, the concentration both 1 and 5 mM, and the electrochemical modification potential was the cathodic peak potential, $E_p$, of each diazonium salt. The ferri/ferrocyanide couple in 0.1 M KCl aqueous solution presents a reversible system with $\Delta E_p = 0.081$ V on bare GC electrode. Figure 1 illustrates the responses of the ferri/ferrocyanide redox system on the modified glassy carbon electrodes at $E_p$ for 270 s.

The various diazonium layers on the glassy carbon electrode exhibit different blocking behavior for oxidation and reduction reactions of the $Fe(CN)_6^{3-/4-}$ redox system. For the same grafting conditions, the blocking effect is more important for the $NO_2$-modified electrode. The absence of the electrochemical response of the $Fe(CN)_6^{3-/4-}$ couple was first attributed to the hydrophobicity of the film and later to the change of GC electronic properties during reductive grafting leading to a decrease of the electron transfer rate [18]. Results from Fig. 2 and Table 1 show that the blocking effects increase (e.g., relative electroactivity, $I_{rel}$, decreases and surface coverage, $\theta$, increases) with increasing concentration and 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 [22].

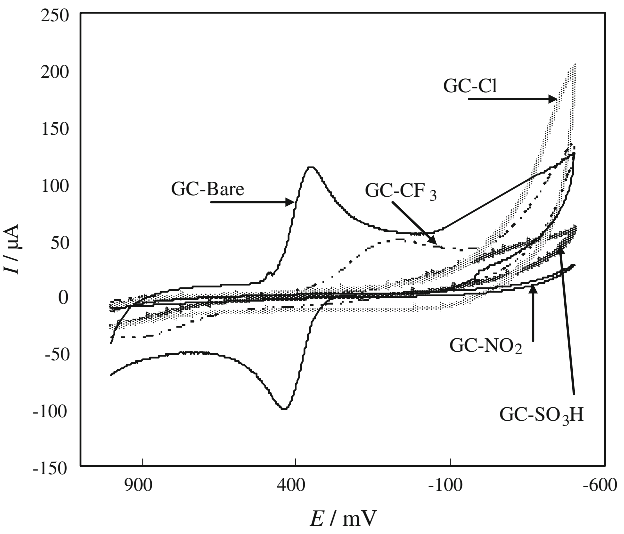

**Fig. 1** Responses of ferri/ferrocyanide on the modified glassy carbon electrodes at $E_p$ for 270 s

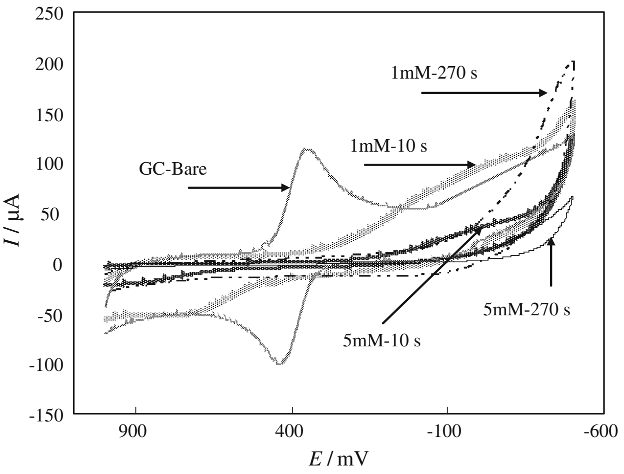

**Fig. 2** Responses of ferri/ferrocyanide on GC-$NO_2$ at different times and concentrations

Assessment on the blocking efficiency of the grafted layers on a glassy carbon electrode at various times was also evaluated by EIS in a 1 mM $Fe(CN)_6^{3-/4-}$ solution. Figure 3 presents the complex impedance plots for a bare electrode and (4-nitrophenyl)-modified glassy carbon electrodes in the presence of 1 mM $Fe(CN)_6^{3-/4-}$ at various reduction times. 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° (Fig. 3a).

The impedance plots for glassy carbon electrodes modified by electrochemical reduction of a (4-nitrophenyl) diazonium salt at $E_p$ at various times differ significantly from that of the bare electrode. The diameter of the semicircle increases with increasing electrolysis time (see Fig. 3b). The Warburg line is not observed for the modified

**Table 1** Relative electroactivity $I_{rel}$ (%) and surface coverage $\theta$ (%) obtained for aryl-modified glassy carbon electrodes at different concentrations of diazonium salts

| | $I_{rel}$ (%) | | | | $\theta$ (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | 10 s | 30 s | 90 s | 270 s | 10 s | 30 s | 90 s | 270 s |
| GC-$CF_3$ (1 mM) | 51.6 | 44.1 | 43.2 | 42.8 | 98.17 | 99.28 | 99.45 | 99.65 |
| GC-Cl (1 mM) | 50.1 | 40.0 | 38.1 | – | 98.66 | 99.68 | 99.74 | 99.82 |
| GC-$SO_3H$ (1 mM) | 43.5 | 31.1 | – | – | 99.40 | 99.82 | 99.84 | 99.86 |
| GC-$NO_2$ (1 mM) | – | – | – | – | 99.50 | 99.84 | 99.87 | 99.96 |
| GC-$CF_3$ (5 mM) | 49.2 | 43.0 | 39.7 | 36.7 | 99.11 | 99.50 | 99.72 | 99.78 |
| GC-Cl (5 mM) | – | – | – | – | 99.74 | 99.83 | 99.85 | 99.88 |
| GC-$SO_3H$ (5 mM) | – | – | – | – | 99.81 | 99.84 | 99.89 | 99.92 |
| GC-$NO_2$ (5 mM) | – | – | – | – | 99.87 | 99.90 | 99.94 | 99.98 |

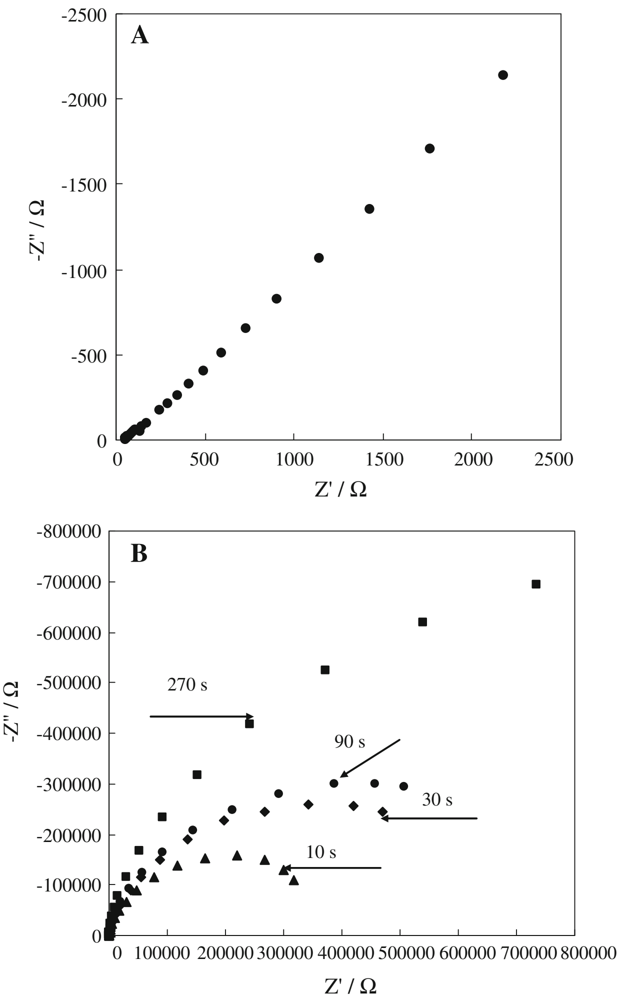

**Fig. 3** Complex impedance plots for a bare (**a**) and a modified glassy carbon electrode with 1 mM 4-nitrophenyl (GC-$NO_2$) (**b**) in the presence of 1 mM $Fe(CN)_6^{3-/4-}$ at various reduction times

electrodes. Qualitatively, the increase of the semicircle indicates that the electrode kinetics becomes slower as the glassy carbon 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. 4. They comprise the solution resistance, $R_s$, the charge transfer resistance, $R_{CT}$, the double layer capacitance, $C_{dl}$, capacitance of the coated layer, $C_c$, and resistance of the coated layer, $R_c$.

The impedance data were analyzed by using the electrical equivalent circuits and the results are shown in Table 2. The table shows that the charge transfer resistance increases dramatically following modification of the glassy carbon electrode from a value of 81 Ω for the bare electrode to $3.2 \times 10^5$ Ω after electrochemical modification for 270 s from a 5 mM (4-nitrophenyl)diazonium at $E_p$.

For the same 1 mM diazonium concentration, an increase of $R_{CT}$ was noticed when the electrolysis time increased from 10 to 270 s. A similar trend is observed in the other groups, although the amplitude of the difference in $R_{CT}$ values is different. The increase of $R_{CT}$ with the electrolysis time demonstrates that the film becomes more compact as the treatment time increases.

### *Electrochemical response of redox probe on grafted electrodes without electrochemical induction*

The characterization of the modified surface proceeded with the study of the barrier properties of chemically grafted layers by using $Fe(CN)_6^{3-/4-}$ as redox probe. The modification of the different diazonium layers without electrochemical induction was accomplished with the procedure described in the "Experimental" section, by immersing the sample in a 10 mM deaerated diazonium solution for 20 h. Samples were then analyzed by CV and EIS methods. After immersion, the reacted electrodes were transferred into a $Fe(CN)_6^{3-/4-}$ solution for electrochemical analysis. Figure 5 shows a representative set of cyclic

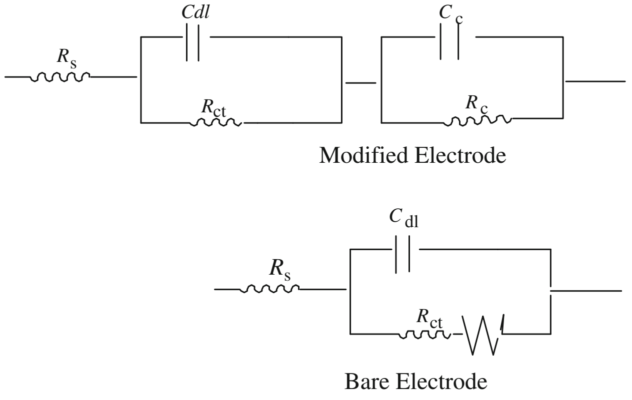

**Fig. 4** Equivalent circuits used for analysis of the electrochemical impedance data

voltammograms for various grafted layers on a glassy carbon electrode.

Differences in blocking properties were observed among the different diazonium salts used. This points to an influence of the substituent of the phenyl rings either on the formation of layer or on its resulting properties. The best results, in terms of blocking properties, were obtained with (4-nitrophenyl)diazonium salt. On the contrary, a weak modification of the electrochemical behavior of the probe is visible when the glassy carbon electrode is exposed to [4-(trifluoromethyl)phenyl]diazonium solution. Results obtained with glassy carbon electrodes chemically grafted are also compared with the glassy carbon electrode without electrochemical induction. Chemically grafted layers were efficient barriers to the $Fe(CN)_6^{3-/4-}$ probe in solution and they completely hinder the corresponding electron transfer processes. The Nyquist plots obtained for the modified electrodes are shown in Fig. 6.

A simplified representation allows the charge transfer resistance to be determined from the diameter of the semicircle. The charge transfer resistances of the various modified electrodes are shown in Table 3. Impedance data show that the charge transfer resistance increases dramatically with increasing semicircle diameter. Obviously, these data are consistent with the results obtained from CV measurements. The layers grafted with (4-nitrophenyl)-, (4-chlorophenyl)-, and [4-(trifluoromethyl)phenyl]diazonium salts are uncharged, so these layers are more hydrophilic than the (4-sulfophenyl)-derived layer. The difference between $R_{CT}$ of the modified electrodes in their neutral state is consistent with the existence of an influence of the hydrophobic character of the grafted layers and the intensity of their blocking effect. The $NO_2$-modified GC electrode exhibits a significant blocking effect (highest $R_{CT}$ value).

The layers obtained from spontaneous grafting will be of little use if one looks for a protective barrier (against diffusion of species, etc.), but they could find applications in systems where a very compact coverage of the surface is not necessary, such as attachment of enzymes to the surface. In this case an easier electron transfer to the surface would even be an advantage, for example, in the use of tethered redox probes as catalysts for redox enzymes.

In conclusion, the EIS measurements reveal that the layers obtained without electrochemical induction have a lower blocking effect toward the $Fe(CN)_6^{3-/4-}$ redox reaction. Also, these measurements show that the grafted layers did not afford a very compact coverage in comparison with electrochemical grafted layers. However these chemical layers could find applications in electroanalysis. Additionally, as grafting can be limited in some parts of a composite surface, this process could be interesting for further industrial applications.

## Experimental

### *Reagents*

Acetonitrile (ACN), tetrabutylammonium tetrafluoroborate ($TBABF_4$), potassium ferricyanide, potassium chloride, hydrochloric acid, *para*-substituted anilines used for diazonium salt synthesis, sodium nitrite, tetrafluoroboric acid, 4-nitrophenyldiazonium tetrafluoroborate, and 4-(trifluoromethyl)phenyldiazonium tetrafluoroborate were used as received from Fluka.

### *Synthesis of Cl-PD and $SO_3H$-PD*

The *para*-substituted aniline (17 mmol) was dissolved in 11.5 $cm^3$ of 50% w/w aqueous tetrafluoroboric acid

**Table 2** $R_{CT}$ (Ω) obtained values for aryl-modified glassy carbon electrodes at different concentrations of diazonium salts

| | 1 mM | | | | 5 mM | | | |
|---|---|---|---|---|---|---|---|---|
| | 10 s | 30 s | 90 s | 270 s | 10 s | 30 s | 90 s | 270 s |
| $GC-CF_3$ | $5.9 \times 10^3$ | $1.4 \times 10^4$ | $1.7 \times 10^4$ | $3.35 \times 10^4$ | $2.1 \times 10^4$ | $3.9 \times 10^4$ | $4.2 \times 10^4$ | $1.3 \times 10^5$ |
| GC-Cl | $8.1 \times 10^3$ | $3.1 \times 10^4$ | $3.8 \times 10^4$ | $6.1 \times 10^4$ | $4.2 \times 10^4$ | $6.6 \times 10^4$ | $7.0 \times 10^4$ | $2.5 \times 10^5$ |
| $GC-SO_3H$ | $1.1 \times 10^4$ | $3.5 \times 10^4$ | $5.6 \times 10^4$ | $8.1 \times 10^4$ | $5.8 \times 10^4$ | $7.0 \times 10^4$ | $8.1 \times 10^4$ | $2.8 \times 10^5$ |
| $GC-NO_2$ | $2.2 \times 10^4$ | $5.2 \times 10^4$ | $2.1 \times 10^5$ | $2.8 \times 10^5$ | $1.0 \times 10^5$ | $2.0 \times 10^5$ | $2.6 \times 10^5$ | $3.2 \times 10^5$ |

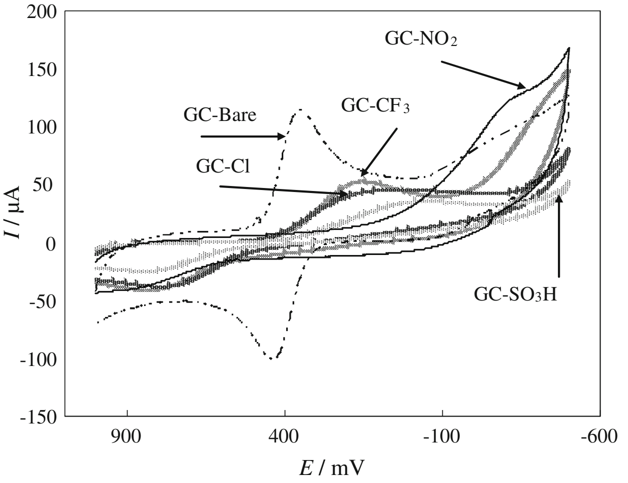

**Fig. 5** Responses of ferri/ferrocyanide on the modified glassy carbon electrodes after immersing in a 10 mM deaerated diazonium solution for 20 h

solution. After the solution was cooled to −3 °C, 2.4 g (34 mmol) of $NaNO_2$, dissolved in cold water, was slowly added to the mixture [23]. The solution was filtered and then cooled below −3 °C to favor crystallization and again filtered by suction, washed with ice water and cold ether, and finally dried under vacuum. The synthesized diazonium salts were kept in a desiccator at 3 °C, and the presence of diazonium functional group was verified by the observation of the characteristic absorption band at about 2,290 $\mathrm{cm}^{-1}$ in the IR spectra [24].

### *Electrode preparation and modification*

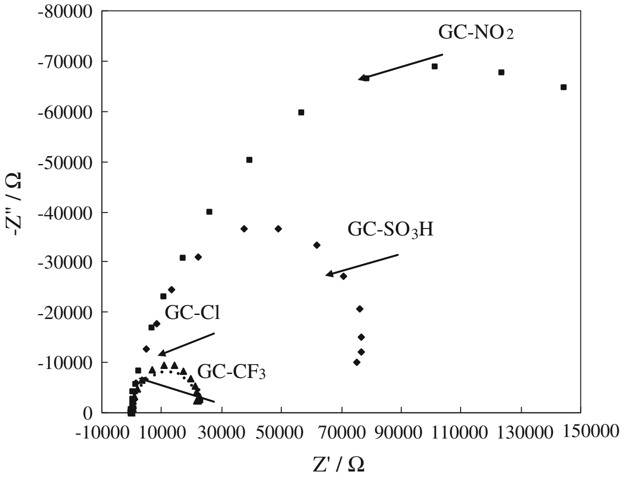

**Fig. 6** Complex impedance plots for various modified glassy carbon electrodes in the presence of 1 mM $\mathrm{Fe(CN)}_6^{3-/4-}$ after immersing in a 10 mM deaerated diazonium solution for 20 h

**Table 3** $\Delta E_\mathrm{p}$ (mV), $I_\mathrm{rel}$ (%), $\theta$ (%), and $R_\mathrm{CT}$ (Ω) values for aryl-modified glassy carbon electrodes without electrochemical induction

| | $\Delta E_\mathrm{p}^\mathrm{a}$ (mV) | $I_\mathrm{rel}$ (%) | $\theta$ (%) | $R_\mathrm{CT}$ (Ω) |
|---|---|---|---|---|
| GC-$CF_3$ | 672 | 44.1 | 99.20 | $1.5 \times 10^4$ |
| GC-Cl | 841 | 41.2 | 99.61 | $2.8 \times 10^4$ |
| GC-$SO_3H$ | 887 | 33.2 | 99.65 | $3.1 \times 10^4$ |
| GC-$NO_2$ | Not observable | – | 99.78 | $5.0 \times 10^4$ |

[a] $\Delta E_\mathrm{p}$ is the peak potential separation, i.e., $E_\mathrm{p}^\mathrm{a} - E_\mathrm{p}^\mathrm{c}$ (where a = anode, c = cathode)

The working electrode was a glassy carbon (GC) electrode and a platinum wire was utilized as counter electrode. All potentials were reported versus the reference electrode of Ag/AgCl (saturated KCl). The glassy carbon electrode surface was cleaned by polishing with 0.05-μm alumina slurry successively. After each polishing, the electrode was carefully washed with distilled water twice. Then, electrochemical modification of glassy carbon electrode was carried out in acetonitrile containing 0.1 M $TBABF_4$ and 1 or 5 mM diazonium salts for various times (10, 30, 90, and 270 s). For all films, the value of modification potential ($E_\mathrm{app}$) was determined from the respective diazonium salt voltammetric reduction peak potential ($E_\mathrm{p}^\mathrm{red}$). The spontaneous grafting consists in dipping cleaned electrodes in 10 mM diazonium salts in ACN solution over a period of 20 h. After immersion, substrates were rinsed with distilled water. The solution containing electroactive probe was ferricyanide/ferrocyanide (1 mM, 0.1 M KCl, adjusted at pH 7 with a 1 M KOH solution) for the various films. 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 $I_\mathrm{rel}$ is defined as:

$$I_\mathrm{rel}(\%) = I_\mathrm{pa}\ \text{with a film}/I_\mathrm{pa}\ \ \text{for a bare electrode} \times 100 \qquad (1)$$

where $I_\mathrm{pa}$ 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 [25]:

$$(1 - \theta) = R_\mathrm{CT}^\mathrm{o}/R_\mathrm{CT} \qquad (2)$$

where $\theta$ is the apparent electrode coverage, assuming that all currents are passed via bare spots on the electrode, and $R_\mathrm{CT}^\circ$ and $R_\mathrm{CT}$ represent the charge transfer resistance measured on a bare and on a modified glassy carbon electrode, respectively.

### *Instrumentation and procedure*

Electrochemical measurements were performed in a one-compartment cell with a three electrode configuration. Cyclic voltammetry (CV) was carried out with use of a potentiostat/galvanostat (EG&G Model 263 A, USA), with a PC and electrochemical setup that was controlled with M 270 software. Electrochemical impedance spectroscopy (EIS) was performed with a frequency response detector (EG&G Model 1025, USA), with a PC and electrochemical setup that was controlled with M 398 software. An ac voltage of 5 mV in amplitude using a frequency range from 50 MHz to 65 kHz was superimposed on the dc potential and applied to the studied electrodes. The dc potential was always set up at the formal potential of $Fe(CN)_6^{3-/4-}$. Experimental data of the electrochemical impedance plot were analyzed by using Boukamp software. The error for the all simulated quantities was less than 5%.

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