

## Stability of Substituted 4-Bromophenyl and 4-Nitrophenyl Groups Electrochemically Grafted at Carbon Electrode Surface

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The electrochemical reduction of an aryl diazonium tetrafluoroborate salt, dissolved in acetonitrile, at a carbon electrode surface allowed the grafting of aryl groups with the formation of a carbon-carbon bond. Groups such as 4-nitrophenyl and 4-bromophenyl were grafted at a glassy carbon electrode surface. The stability of these grafted groups, present at the glassy carbon electrode surface, was studied at various electrode potentials in aqueous media. In appropriate experimental conditions, the as-grafted groups severely inhibit the cyclic voltammetry response of selected redox probes. Thus, the reappearance and/or increase of an electrochemical response, after polarization, were taken as an indication that a modification of the grafted layer occurred. The results of this work demonstrated that polarization at very positive (*ca.* 1.8 V) and negative (*ca.* -2 V) potential is needed to observe and electrochemical response. Electrochemical impedance spectroscopy was also used to investigate the stability of the grafted layers. The impedance data usually tracks fairly well the cyclic voltammetry results, although the former appears to be more sensitive to changes that are occurring upon polarization of the modified electrode.

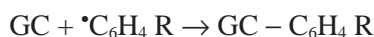
**Key Words:** Modified glassy carbon, Cyclic voltammetry, Impedance spectroscopy, Polarization potential.

### INTRODUCTION

Modification of the carbon surface is an important objective in electrochemistry and material science<sup>1</sup>. Much attention has been paid to covalently modified electrodes on which some functional groups such as carboxyl and amino groups are grafted for catalytic, analytical and biotechnological applications<sup>2-5</sup>.

The electrochemical grafting of substituted aryl groups by reduction of the corresponding diazonium salt is an attractive way to modify carbon-

based surfaces<sup>6-17</sup>. Electrochemical grafting of a monolayer of substituted aryl groups is 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 according to



After modification, it is essential to know the electrochemical stability of the films as well as the specific reactions caused by the reduction or the oxidation of the functional group<sup>17</sup>. In principle, the grafted group should be stable against desorption due to the presence of a covalent bond between the electrode surface and the organic group. This paper reports the study of the stability of 4-bromophenyl and 4-nitrophenyl groups when subjected to a range of negative and positive potential polarization that spans about 3.5 V.

## EXPERIMENTAL

Tetrabutylammonium tetrafluoroborate ( $\text{NBu}_4\text{BF}_4$ ) (Fluka), potassium ferricyanide, potassium chloride, hexaammineruthenium(III) chloride, 4-bromobenzenediazonium tetrafluoroborate and 4-nitrobenzenediazonium tetrafluoroborate (Fluka) were reagent grade and were used as received. Solutions were prepared fresh daily and degassed with ultra pure (99.99%) nitrogen gas for 10 min before use.

**Electrochemical measurements:** Electrochemical measurements were performed using a computer-controlled potentiostat-galvanostat (model 263A; EG&G instrument). A three electrode electrochemical cell was used with Ag/AgCl/KCl (sat) as reference electrode, Pt wire as a counter electrode and glassy carbon (Metrohm) as the working electrode.

**Modification procedure:** Prior to the modification, glassy carbon electrode was polished with 0.3  $\mu\text{M}$   $\alpha\text{-Al}_2\text{O}_3$  powders and rinsed with distilled water. The electrochemical modification of the glassy carbon electrode was performed from an acetonitrile solutions containing 5 mM 4-bromobenzenediazonium or 5 mM 4-nitrobenzenediazonium tetrafluoroborate salts in 0.1 M  $\text{Bu}_4\text{NBF}_4$  and applying potential between -0.7 to 1.4 V during 10 cycles. After the modification, the electrode was rinsed thoroughly with distilled water.

**Electrochemical impedance spectroscopy:** Electrochemical impedance spectroscopy (EIS) experiments were performed with frequency response detector (Model 1025; EG&G instrument), controlled by M 398 software. The Boukamp equivalent circuit software (copy right B.A. Boukamp, version 4.55) was used to analyze the impedance data.

**Methodology:**

After grafting of a film and rinsing the electrode was polarized at a selected potential for 360 s in 0.1 M KCl solution. The electrode was then characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The 5 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  in 1 M KCl redox system 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 or its removal will be evidenced by the apparition of sizable current that may reach at a bare electrode if the grafted layer is completely removed. If the film was still present, another more positive (or negative) potential was applied and the resulting electrode was analyzed again by CV and EIS until potential limits of about -3.5 V and 2.5 V were reached. In this study, the results are presented as a function of the potential at which the modified electrode was polarized, as the percentage of current intensity:

$$\text{Current Intensity (\%)} = \frac{\text{Intensity of the cathodic peak with a film}}{\text{Intensity of the cathodic peak for a bare electrode}} \times 100$$

The redox system as well as electrochemical impedance spectroscopy was used to evaluate the integrity of the film. A compact and blocking film will inhibit the redox reaction of the redox probe and will cause an increase of the charge-transfer resistance ( $R_{\text{CT}}$ ) of the impedance data<sup>18</sup>. The presence of defects in the film or its removal will be monitored by a sizable diminution of the  $R_{\text{CT}}$  of the Nyquist representation. If the grafted layer is completely removed, a  $R_{\text{CT}}$  similar to a bare electrode should be observed.

**RESULTS AND DISCUSSION**

Electrochemical grafting of 4-bromophenyl and 4-nitrophenyl groups at the surface of a glassy carbon electrode significantly inhibited the electron-transfer kinetics of redox species<sup>14</sup> such as  $\text{Fe}(\text{CN})_6^{3-/4-}$ . The slower kinetics and/or blocking effect of the grafted layer for the  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox system 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 voltammogram and also by an increase of the diameter of the semicircle of a Nyquist plot<sup>14</sup>.

In present work, cyclic voltammogram and complex impedance plot were measured in the presence of an appropriate redox couple  $\text{Fe}(\text{CN})_6^{3-/4-}$  for the grafted electrode and after its polarization for various positive and negative potentials in aqueous 0.1 M KCl. Fig. 1 shows a representative set of cyclic voltammograms for such an experiment with a 4-bromophenyl modified electrode. The electrochemical reaction of  $\text{Fe}(\text{CN})_6^{3-/4-}$  is significantly blocked by the grafted layer.

The same is true for the modified electrode (b) that was subjected to increasing positive polarization up to 1.4 V. However, when the anodic potential reached a value of 1.6 V (c) or 1.8 V (d), the CV displayed an increase of both the anodic and cathodic peak currents. A further increase of the anodic potential to 2.5V (e) led to a CV that resembled with bare glassy carbon electrode (a), although the intensity of the peak currents remained slightly smaller and  $\Delta E_p$  slightly larger. The electrochemical impedance data depicted in Fig. 2 is consistent with the CV results and is characterized by a decrease of the diameter of the semicircle as the anodic potential is made more positive.

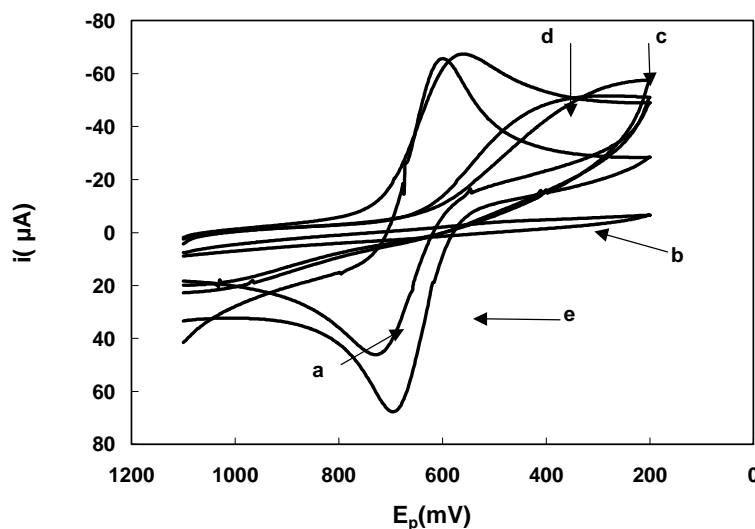


Fig. 1. Cyclic voltammetry for 4-bromophenyl modified glassy carbon electrode in aqueous 5 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  in 1 M KCl solution before and after polarization at 1.6, 1.8 and 2.5 V

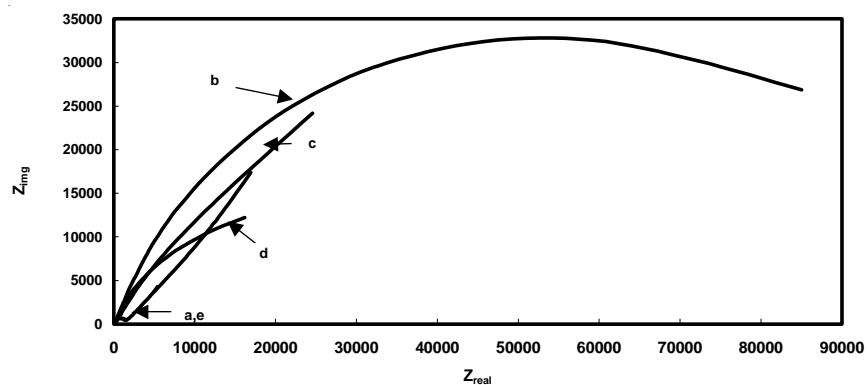


Fig. 2. Electrochemical impedance spectroscopy plot for a 4-bromophenyl modified glassy carbon electrode in aqueous 5 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  in 1 M KCl solution before and after polarization at 1.6, 1.8 and 2.5 V

At the extreme positive potential value investigated (2.5 V, curve e in Fig. 2), the Nyquist plot shows a very small semicircle (diameter of about  $2.86 \times 10^{-2}$ ) and a low frequency Warburg line at an angle of  $45^\circ$ , which is similar to that observed for a bare glassy carbon electrode. Interestingly, the Warburg diffusion line is similar for both the bare and the modified electrode subjected to a potential of 2.5 V, indicating that similar diffusion phenomena are occurring at these electrodes and that the remainder of the grafted aryl groups doesn't appear to hinder the diffusion of electroactive species. The fact that the Nyquist plot is nearly the same for the bare electrode and the electrode depassivated at 2.5 V. This phenomenon also indicates that its roughness has not increased and that the surface of the electrode has not been damaged by oxidation. The electrochemical impedance data for 4-bromophenyl modified electrode are summarized in Fig. 3.

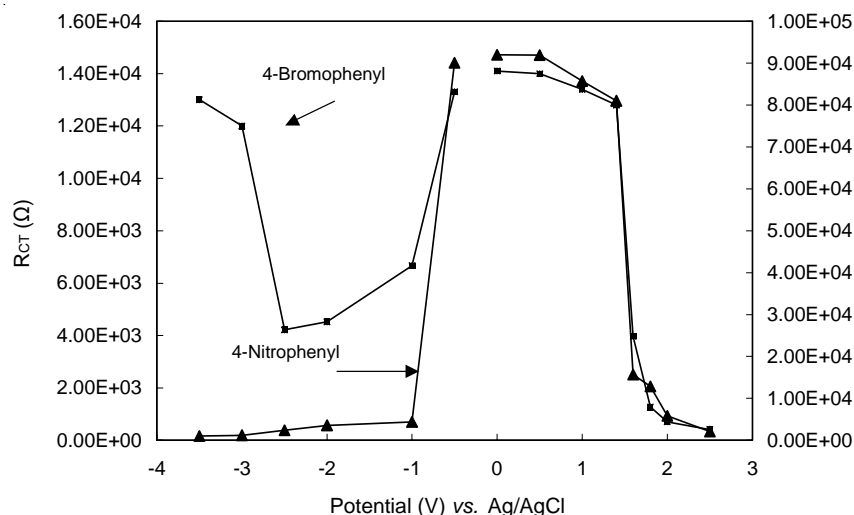


Fig. 3. Variation of charge-transfer resistance as a function of the applied potential for 4-bromophenyl and 4-nitrophenyl modified glassy carbon electrode

Fig. 3 depicts the variation of the charge transfer resistance ( $R_{CT}$ ) evaluated from the impedance data for a modified electrode subjected to various potentials. A gradual decrease of  $R_{CT}$  is found when a potential of -0.5 V is reached and that is followed by an abrupt change when the modified electrode is polarized at -1 V.

On the anodic side, a similar gradual variation is seen from 0 V up to 1.4 V which followed by an abrupt change when the modified electrode is polarized at 2.5 V. Our results demonstrate that the permeability of the 4-bromophenyl layers is gradually increasing upon anodic polarization and that the effect become more pronounced and an abrupt at positive potentials. For the 4-nitrophenyl a similar trend is observed, although some differences can be clearly observed for the variation of  $R_{CT}$  and CV current

in comparison to the 4-bromophenyl electrode as shown in Fig. 3, which presents  $R_{CT}$  values for selected polarization potentials. First, for the 4-nitrophenyl and 4-bromophenyl modified electrode polarized at negative potential values. A decrease of  $R_{CT}$  is occurring between (-0.5) and (-1) V prior to the onset of the CV current. Also, a first decrease of  $R_{CT}$  is observed around -1.2 V, but that does not translate into an increase of the CV current as shown in Fig. 4.

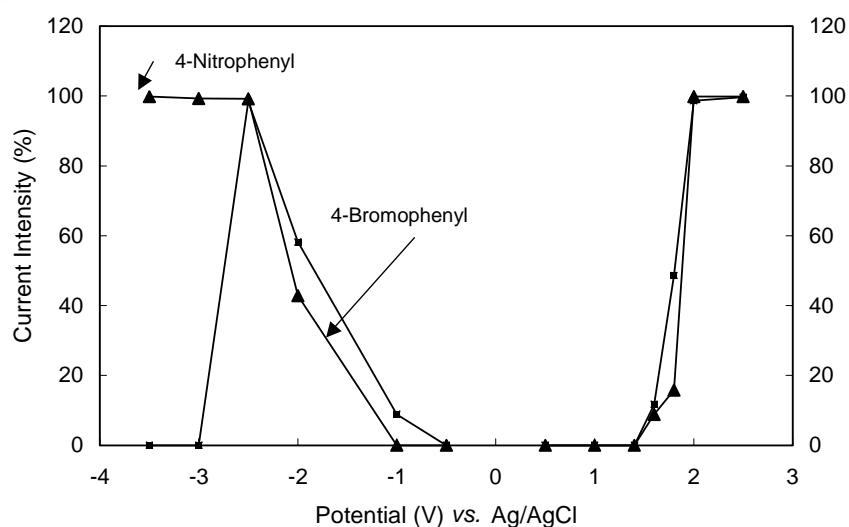


Fig. 4. Variation of current intensity as a function of the applied potential for 4-bromophenyl and 4-nitrophenyl modified glassy carbon electrode

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. A relatively good blocking behaviour was still observed for the 4-bromophenyl groups for a polarization potential more negative than (-2.5) V (Fig. 3) and the CV response remained almost negligible.

### Conclusion

The stability measurements showed that the electro grafted film of 4-bromophenyl at a glassy carbon can be used in a potential range between 1.2 to -0.7 V, despite of some modification of the grafted film can occur within this potential range. Electrochemical polarization of the aryl-modified electrode can remove aggregates generated during the electrochemical electro grafting process, presumably leaving a thinner film at the electrode surface. The results of this work demonstrated that electrochemical impedance spectroscopy is a more sensitive technique than CV to probe the modification of a thin film grafted film.

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