

Stability of Substituted Phenyl Groups Electrochemically Grafted at Carbon Electrode Surface

Mathieu D'Amours and Daniel Bélanger*

Département de Chimie, Université du Québec à Montréal, Case Postale 8888, succursale Centre-Ville, Montréal, Québec, Canada H3C 3P8

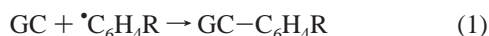
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The electrochemical reduction of an aryl diazonium tetrafluoroborate salt, dissolved in acetonitrile, at a carbon electrode surface allowed the grafting of aryl groups with the formation of a carbon–carbon bond. Groups such as 4-carboxyphenyl, 4-nitrophenyl, 4-diethylaniline (DEA), 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, was taken as an indication that a modification of the grafted layer occurred. Our results demonstrated that polarization at very positive (ca. 1.8 V) and negative (ca. –2 V) potentials is needed to observe an electrochemical response. Electrochemical impedance and X-ray photoelectron spectroscopies were 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. Interestingly, the XPS data indicate clearly that the grafted layer is not always completely removed at the extreme positive and negative potentials investigated. A mechanism was proposed to explain the transformation occurring during polarization of the modified electrode and involves desorption of the substituted aryl groups during the concomitant hydrogen, oxygen, or chlorine evolution and finally leaving close to a covalently bonded monolayer of the grafted species at the electrode surface.

Introduction

The activation of a carbon surface can generate surface functionalities that can change the chemical and physical properties of the electrode.^{1–7} Such activation can be carried out by thermal,^{1,3} electrochemical,^{1,2,4–7} and/or chemical^{1,2,4} processes in corrosive conditions but can only oxidize the surface and generate a limited range of oxygenated functionalities without selectivity and control of these groups. Recently, reductive processes were developed to prevent these shortcomings.^{8–12}

The electrochemical grafting of substituted aryl groups by reduction of the corresponding diazonium salt is an attractive way to modify carbon-based surfaces.^{8–13} It was introduced in the early 90s by Pinson and co-workers.⁸ 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 according to



This technique has the advantage of controlling the functionalization of the electrode surface by the selection of the R group in para position of the grafted molecule. Such modified carbon electrodes were characterized by a variety of electrochemical and spectroscopic techniques.^{8–12} While most of the initial studies suggested that monolayer formation was achieved,^{8–10,12}

recent studies have demonstrated that multilayer and aggregate formation is occurring in some experimental conditions.¹¹ The subsequent formation of multilayers and aggregates is thought to occur by reaction of an electrochemically generated phenyl radical with the phenyl group of the first layer.

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. 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 is to be contrasted with self-assembled monolayer (SAMs) on gold or silver based on long chain alkanethiols which could be either oxidatively or reductively desorbed despite strong sulfur–metal interaction.¹³ The desorption and instability at extreme potential limits of these SAMs have been previously studied in detail.^{14–17} On the other hand, the stability of an electrochemically grafted aryl group (from diazonium chemistry) has not been investigated so far. Accordingly, this paper reports the study of the stability of 4-diethylaniline, 4-nitrophenyl, 4-bromophenyl, and 4-carboxyphenyl groups when subjected to a range of negative and positive potential polarization that spans about 4 V.

Experimental Section

Reagents. Tetrabutylammonium tetrafluoroborate (NBu₄BF₄) (Aldrich) was dried by heating at 80 °C under vacuum for 24 h. Potassium ferricyanide, potassium ferrocyanide, potassium chloride, hexaammineruthenium (III) chloride, 4-diazo-*N,N*-diethyl aniline tetrafluoroborate, 4-nitrophenyl diazonium tet-

* Corresponding author. E-mail: belanger.daniel@uqam.ca. Tel: (514) 987-3000 (#3909). Fax: (514) 987-4054.

rafluoroborate, and 4-bromophenyl diazonium tetrafluoroborate were used as received from Aldrich.

Synthesis of 4-Carboxyphenyl Diazonium Tetrafluoroborate. 0.02 mol of p-aminobenzoic acid was dissolved in warm water, and this was followed by the addition of 3.6 mL of concentrated hydrochloric acid. After cooling to $-3\text{ }^{\circ}\text{C}$, 0.022 mol of NaNO_2 , dissolved in cold water, was added slowly to the mixture. The solution was filtered and 0.022 mol of NaBF_4 , dissolved in cold water, was added. The slurry was cooled below $-3\text{ }^{\circ}\text{C}$ to favor crystallization, filtered by suction, and washed with ice water and cold ether and finally dried under vacuum. The diazonium salt was kept in a desiccator at $3\text{ }^{\circ}\text{C}$ over phosphorus pentaoxide. NMR H^1 (DMSO): two doublets at 8.55 and 8.97 ppm.^{11,12} The diazonium function was detected by IR at about 2290 cm^{-1} .¹⁸

Electrode Preparation and Modification. Working electrodes made of glassy carbon electrodes (AIMCOR, Pittsburgh, Grade GC-10) were prepared from 3 mm diameter rods embodied into epoxy resin (Hysol, 56C). The electrical contact was made with silver epoxy (Dynaloy). Platinum gauze of ca. 1 cm^2 was used as counter electrode. All potentials were reported versus the reference electrode Ag/AgCl (saturated KCl). The glassy carbon electrode surface was cleaned by polishing with Buehler 1 and $0.05\text{ }\mu\text{m}$ alumina slurry (Tech-Met Canada). After each polishing the electrode was washed with Nanopure water by sonication and kept in water.⁹ Prior to electrodeposition, the electrode was sonicated in acetonitrile. Electrochemical modification of glassy carbon electrode was carried out in deaerated acetonitrile containing 5 mM of the diazonium salt and 0.1 M NBu_4BF_4 at -0.7 V for 240 s. The 4-*N,N*-diethylaniline groups were grafted in the same experimental conditions and also with a second method involving three scans from the open circuit potential (OCP) to -1 V at 50 mV/s and followed by a potentiostatic deposition at -1 V for 180 s.

The solutions containing the various electroactive probes were ruthenium hexamine (1 mM; KCl, 0.1 M, adjusted at pH 3 with HCl 0.1 M) to probe the DEA film and ferricyanide (5 mM; KCl 0.1 M, adjusted at pH 7 with NaOH 0.1 M) for the 4-bromophenyl and 4-nitrophenyl films. All solutions were deaerated with extra dry nitrogen during 15 min. Electrochemical impedance spectroscopy measurements were performed in 5 mM $\text{Fe}(\text{CN})_6^{3-}/5\text{ mM Fe}(\text{CN})_6^{4-}/0.1\text{ M KCl}$, adjusted at pH 7 with NaOH at OCP, and 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}/0.1\text{ M KCl}$, adjusted at pH 3 with HCl 0.1 M at OCP. The frequency range was 65 kHz to 0.1 Hz using a 10 mV sine-wave amplitude.

Instrumentation and Procedure. Electrochemical measurements were performed in a one-compartment cell using the three-electrode configuration. Cyclic voltammetry and chronoamperometry were carried out using either a potentiostat or galvanostat electrochemical interface SI1287 (Solartron Instruments) interfaced with a PC, and the electrochemical setups were controlled with DC Corrware (Scribner Associates, version 1.5c) software. Electrochemical impedance spectroscopy (EIS) experiments were performed with electrochemical interface SI1287 and a frequency response analyzer SI1255 (Solartron instruments) controlled by Zplot software (Scribner Associates, version 1.5b). The Zview software (Scribner Associates, version 1.5b) was used to analyze the impedance data.

X-ray photoelectron spectra (XPS) were obtained on glassy carbon plates (GLCP-10; The Electrosynthesis Co.) with a VG Escalab 220i-XL equipped with a hemispherical analyzer and an Al anode ($\text{K}\alpha$ X-rays at 1486.6 eV) used at 12–14 kV and 10–20 mA. The data were obtained at room temperature and typically, the operating pressure in the analysis chamber was

below 1×10^{-9} Torr. XPS survey and core level spectra were recorded for the as-deposited layers and also after the modified electrodes were subjected to selected positive and negative potentials. The core level spectra were used to evaluate the atomic concentrations of the species present at the glassy carbon electrode surface. The atomic concentrations (at. %) of each individual element were determined from the relative peak areas of the spectra and the corresponding sensitivity factors according to

$$\text{at. \%} = (A_i/s_i) / \sum (A_i/s_i)$$

where A_i is the area of the element i and s_i is the sensitivity factor for this element. For example, values of 1, 1.8, 2.93, and 2.84 were used for C1s, N1s, O1s, and Br3d, respectively.

FTIR measurements were performed with a Michelson series FTIR spectrometer (Bomem Hartmann & Braun) MB series and NMR measurements with a Gemini 300 MHz spectrometer (Varian Instruments).

Methodology. Following grafting of a film and rinsing, the electrode was polarized at a selected potential for 30 s in a pH 7 0.1 M KCl solution. The electrode was then characterized by cyclic voltammetry (CV), EIS (see below), and XPS (see above). The $\text{Fe}(\text{CN})_6^{3-/4-}$ or the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ redox systems was used to evaluate the film's 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 that observed 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 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 systems were also used to evaluate the integrity of the film by electrochemical impedance spectroscopy. 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.^{12a} The presence of defects in the film or its removal will be monitored by a sizable diminution of the R_{CT} of the Nyquist representation. If the grafted layer is completely removed, a R_{CT} similar to a bare electrode should be observed.

Results and Discussion

Cyclic Voltammetry and Electrochemical Impedance Spectroscopy. In an earlier study, we have shown that the electrochemical grafting of 4-carboxyphenyl groups at the surface of a glassy carbon electrode significantly inhibited the electron-transfer kinetics of redox species such as $\text{Fe}(\text{CN})_6^{3-}$.^{12a} The slower kinetics were explained by the electrostatic effects in the presence of negatively charged $\text{Fe}(\text{CN})_6^{3-}$ and dissociated COOH groups for solution pH higher than the pK_a of the COOH groups. 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 (ΔE_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.^{12a}

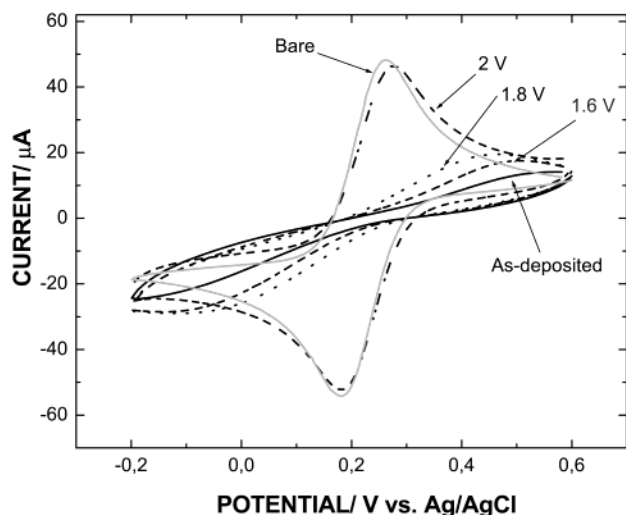


Figure 1. Cyclic voltammetry for a 4-carboxyphenyl modified glassy carbon electrode in aqueous 5 mM $\text{Fe}(\text{CN})_6^{3-}$ /0.1 M KCl pH 7 before (---) and after polarization at 1.6 (---), 1.8 (···), and 2.0 V (— · — · —) in 0.1 M KCl pH 7. The light gray CV identifies the bare glassy carbon electrode.

In the present work, cyclic voltammogram and complex impedance plots were measured in the presence of an appropriate redox couple ($\text{Fe}(\text{CN})_6^{3-/4-}$ or $\text{Ru}(\text{NH}_3)_6^{2+/3+}$) for the grafted electrode and after its polarization for various positive and negative potentials in aqueous 0.1 M KCl.

Figure 1 shows a representative set of cyclic voltammograms for such an experiment with a 4-carboxyphenyl modified electrode. In agreement with our previous studies, the electrochemical reaction of $\text{Fe}(\text{CN})_6^{3-}$ is significantly blocked by the grafted layer (---). The same is true for the modified electrode that was subjected to increasing positive polarization up to 1.4 V. However, when the anodic potential reached a value of 1.6 V (---) or 1.8 V (···), the CV displayed an increase of both the anodic and cathodic peak currents. A further increase of the anodic potential to 2.0 V (— · — · —) led to a CV that resembled that of a bare glassy carbon electrode (---), although the intensity of the peak currents remained slightly smaller and ΔE_p slightly larger.

The electrochemical impedance data depicted in Figure 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. At the extreme positive potential value investigated (2.0 V, curve — · — · —), the Nyquist plot shows a very small semicircle (diameter of about 100 Ω) and a low-frequency Warburg line at an angle of 45°, 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 V, indicating that similar diffusion phenomena are occurring at these electrodes and that the remainder of the grafted aryl groups does not 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 V also indicates that its roughness has not increased and that the surface of the electrode has not been damaged by oxidation.

The CV and electrochemical impedance data for a 4-carboxyphenyl modified electrode are summarized in Figure 3a. This figure depicts the ratio of the anodic peak current for the modified electrode after polarization at various potentials to that of a bare glassy carbon electrode and the variation of the charge-transfer resistance (R_{CT}) evaluated from the impedance data for

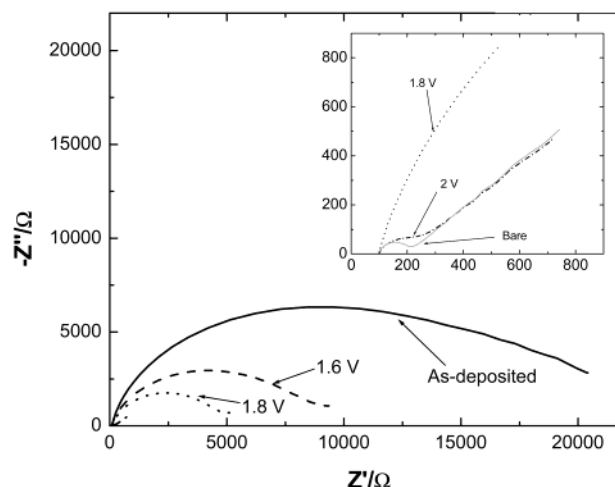


Figure 2. Electrochemical impedance spectroscopy plots for a 4-carboxyphenyl modified glassy carbon electrode in aqueous 5 mM $\text{Fe}(\text{CN})_6^{3-}$ /0.1 M KCl pH 7 before (—) and after polarization at 1.6 (---), 1.8 (···), and 2.0 V (— · — · —) in 0.1 M KCl pH 7. The light gray CV identifies the bare glassy carbon electrode.

a modified electrode subjected to various potentials. The expected inverse relationship between the CV and impedance data is clearly observed. A gradual decrease of R_{CT} and increase of the current of the CV are found when a potential of -1 V is reached. On the anodic side, a similar gradual variation is seen from 0 V up to about 1.8 V, and that is followed by an abrupt change of both parameters when the modified electrode is polarized at 2.0 V. Nonetheless, despite that a relatively good blocking behavior is maintained over a potential range of about 3.6 V, our results demonstrate that the permeability of the 4-carboxyphenyl layers is gradually increasing upon anodic and cathodic polarization and that the effect becomes more pronounced and abrupt at positive potentials.

For the 4-nitrophenyl, 4-bromophenyl, and DEA-modified electrodes, a similar trend is observed, although some differences can be clearly observed for the variation of R_{CT} and the CV current in comparison to the 4-carboxyphenyl electrode as illustrated in Figure 3 and in Table 1, which presents R_{CT} values for selected polarization potentials. First, the potential range for which the CV current remained barely detectable extends over 2.5, 4.6, and 5.5 V for the DEA, 4-nitrophenyl and 4-bromophenyl, respectively. The main difference between the DEA (Figure 3c) and the 4-carboxyphenyl (Figure 3a) modified electrode lies in the larger potential range where the CV current is not detectable for the former. Second, for the 4-nitrophenyl, DEA, and 4-bromophenyl modified electrodes polarized at negative potential values, a decrease of R_{CT} is occurring between -1 and -1.5 V prior to the onset of the CV current. For example, in the case of the 4-nitrophenyl modified electrode, a first decrease of R_{CT} is observed around -1.2 V, but that does not translate into an increase of the CV current yet (Figure 3b). 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. A similar observation has been made for SAMs where it was shown that ion penetration in the SAM could be activated when a critical potential was reached.¹⁷ On the other hand, it will be shown below that the potential induced modification of the 4-nitrophenyl layers on glassy carbon also generated a transformation of the nitro functional group. An abrupt change of R_{CT} and the CV current is also detected for polarization more negative than about -2.8 V. Third, a relatively good blocking

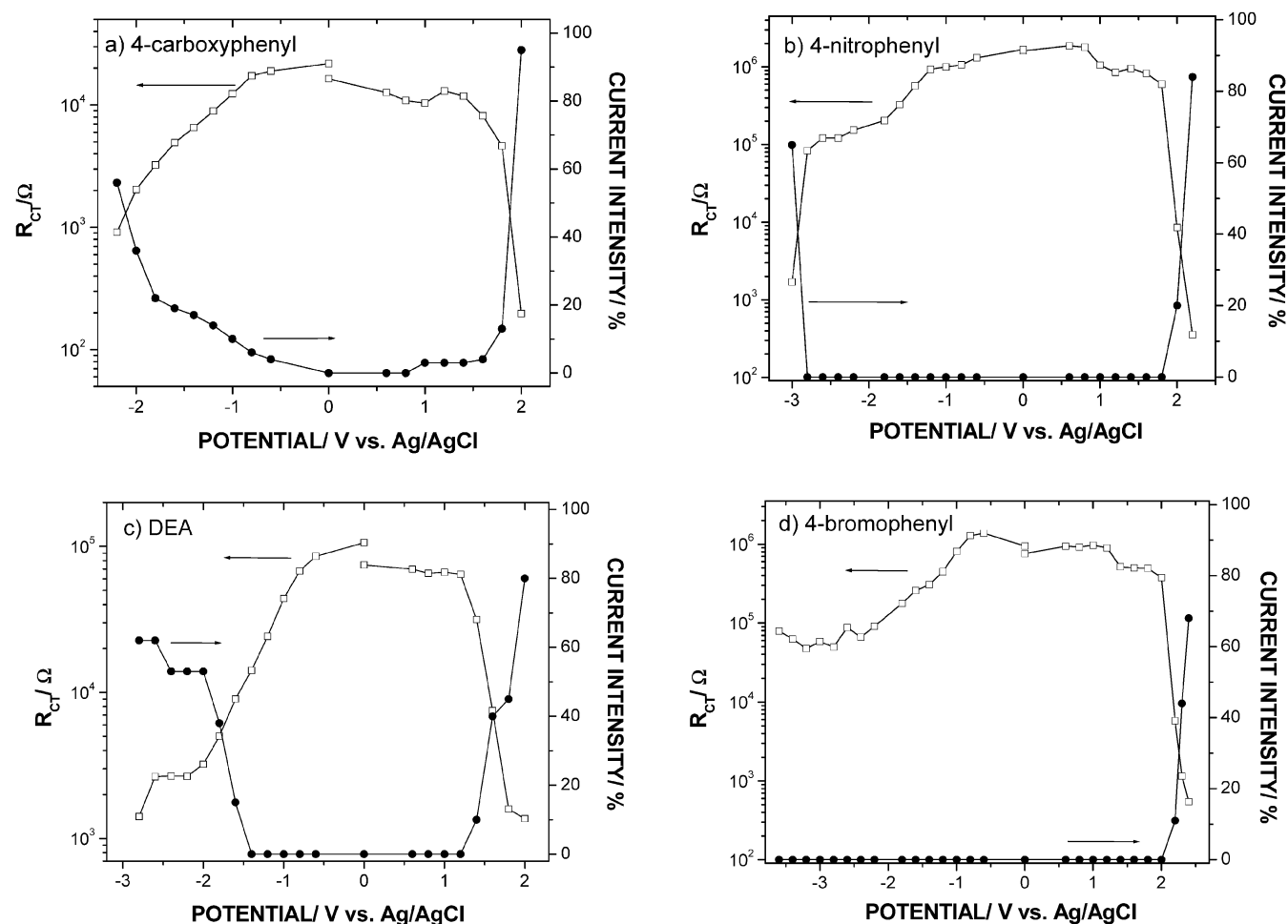


Figure 3. Variation of charge-transfer resistance (\square) and the current intensity (\bullet) as a function of the applied potential for: (a) 4-carboxyphenyl; (b) 4-nitrophenyl; (c) DEA, and (d) 4-bromophenyl modified glassy carbon electrode. See Methodology in the Experimental Section for details on the calculation of the current intensity.

TABLE 1: Atomic Composition of the Grafted Layers after Polarization at Various Potentials Correlated with Electrochemical Impedance Data

	atomic concentration (%)					N/C	R/C ^b	O/C	R_{CT} (Ω)	Γ^c (mol/cm ²)
	Cl1s	N1s ^a 400 eV	N1s ^a 406 eV	Br3d	O1s					
GC^d										
bare	87.5				12.5			0.14		
Nitro										
as-deposited	70.3	2.6	6.8		20.3	0.037	0.135	0.29	1.7×10^6	9.8×10^{-10}
1.8	73.4	4.7	5.3		16.6	0.064	0.135	0.23	6.0×10^5	9.8×10^{-10}
2.4	73.5	3.3	4.0		19.2	0.045	0.099	0.26	2.2×10^2	7.3×10^{-10}
-1.8	73.9	5.3	4.1		16.7	0.072	0.127	0.23	2.0×10^5	9.3×10^{-10}
-2.6	84.8	5.5	0		9.7	0.065	0.065	0.11	1.2×10^5	4.8×10^{-10}
Bromo										
as-deposited	79.1	2.0		9.0	9.9	0.026	0.140	0.13	7.6×10^5	10.2×10^{-10}
2.2 V	82.5	1.7		4.7	11.1	0.020	0.077	0.14	5.8×10^3	5.6×10^{-10}
2.4 V	83.8	0.9		1.5	13.8	0.011	0.030	0.17	5.4×10^2	2.2×10^{-10}
-1.6 V	78.4	2.0		7.9	11.8	0.032	0.135	0.15	2.6×10^5	9.2×10^{-10}
-2.6 V	92.2	0.9		0.5	6.4	0.012	0.018	0.07	8.8×10^4	1.1×10^{-10}
DEA										
as-deposited	75.1	8.2			16.7	0.110	0.110	0.22	8.5×10^4	8.0×10^{-10}
1.6 V	80.5	2.5			17.0	0.031	0.031	0.21	7.5×10^3	2.2×10^{-10}
2.6 V	83.3	0.9			15.9	0.011	0.011	0.19	6.3×10^2	0.77×10^{-10}
-1.6 V	81.1	7.2			11.7	0.089	0.089	0.14	9.0×10^3	6.5×10^{-10}
-2.6 V	85.4	5.3			9.3	0.062	0.062	0.11	2.7×10^3	4.6×10^{-10}

^a Contribution of the components at 400 and 406 eV, respectively. ^b R represents the atomic concentration of the substituent on the phenyl group and total nitrogen. ^c The surface concentration, Γ , was calculated by multiplying the R/C ratio by 7.3×10^{-9} mol/cm² [refs 9a, 21]. ^d Glassy carbon electrode.

behavior was still observed for the 4-bromophenyl groups for a polarization potential more negative than -3 V (Figure 3d) and the CV response remained almost negligible.

X-ray Photoelectron Spectroscopy, XPS. XPS was also used to characterize the modified electrode, and it will be shown below that it is a powerful tool to evaluate the change that

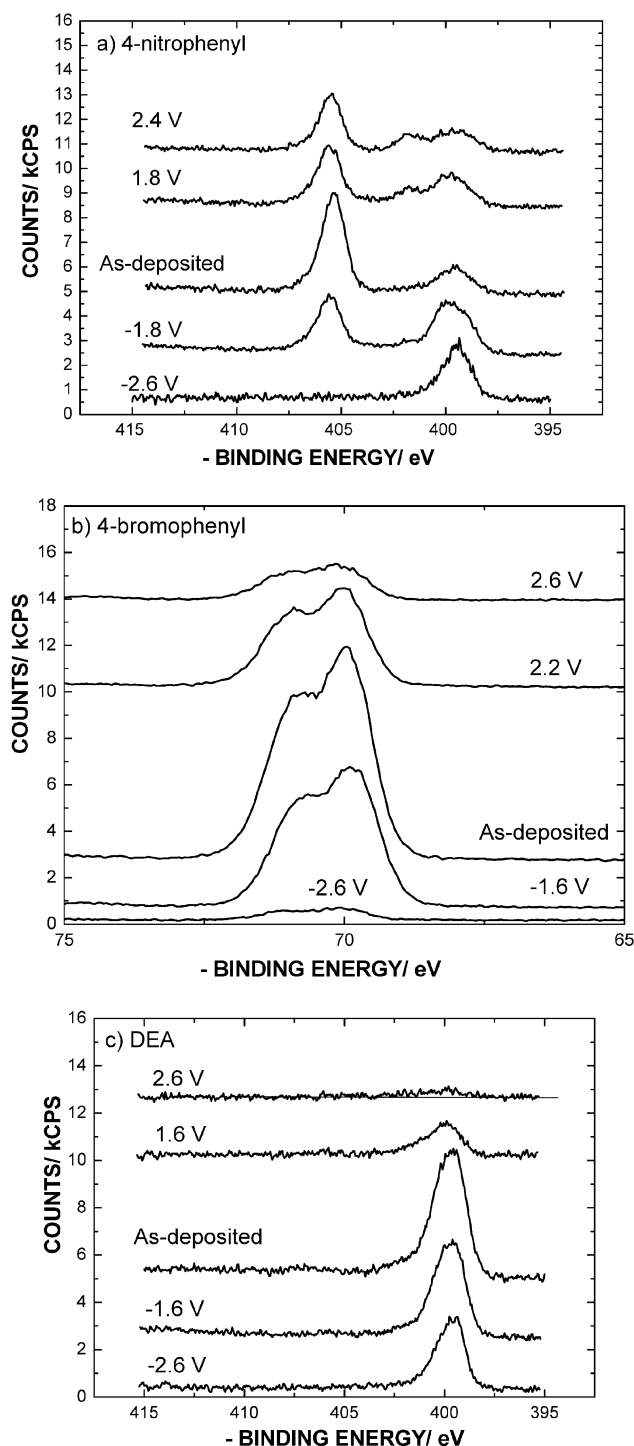


Figure 4. XPS core level spectra for various aryl-modified glassy carbon electrodes after polarization at various selected potentials in 0.1 M KCl: (a) N1s for 4-nitrophenyl; (b) Br3d for 4-bromophenyl, and (c) N1s for DEA. A straight line is drawn under the XPS spectrum of the DEA film polarized at 2.6 V to evidence the small but sizable signal.

occurred during the polarization of the modified electrode. In a first step, the change happening to the substituent of the phenyl groups will be investigated. Second, the loss of signal attributed to the grafted groups will be followed as a function of the applied potential. Selected core-level spectra for the 4-nitrophenyl-, 4-bromophenyl-, and DEA-modified electrodes are presented in Figure 4 and Table 1 summarizes relevant parameters that can be extracted from these XPS spectra.

The N1s core level spectra for the 4-nitrophenyl modified electrode, after polarization at selected potentials, are shown in Figure 4a. The as-deposited layer displays the characteristic peaks at 406 and 400 eV that are attributed to the nitrogen of the nitro groups and to the grafting of the diazonium, respectively.¹² More specifically, the signal at 400 eV, which is always observed for our diazonium modified electrodes, can be attributed to the reaction of solution diazonium salt with the already-grafted species to form an azo attachment to the electrode surface.^{12a} In a recent study, we have shown that mild reducing conditions do not completely reduce the nitro groups.^{12b} A similar conclusion can be also reached at intermediate potential such as -1.8 V (Figure 4a). The polarization of the 4-nitrophenyl modified electrode at -2.6 V led to the complete loss of the nitro peak at 406 eV and the growth of the peak at 400 eV (see also Table 1), which suggests that the nitro groups were electrochemically reduced to NH_2 in these experimental conditions.^{12b,19} Nevertheless, these results suggest that some substituted aryl groups are still present at the electrode surface despite the very negative potential applied to the modified electrode. The data of Figure 4a also show that polarization of the 4-nitrophenyl modified electrode at positive potentials led to a decrease of the nitro peak at 406 eV. The N1s peak at 401.7 eV for the 4-nitrophenyl film electrode polarized at 1.8 and 2.4 V may be attributed to the nitroso form generated by reduction of the nitro group.^{12b} Presumably, the precursor of the nitroso form is the hydroxylamine that is formed by the reduction of the nitro group during film grafting in the presence of trace amount of water in the electrolyte. The nitroso form is not detected by XPS for electrodes polarized at -1.8 and -2.6 V since its formation requires positive potential.

Figure 4b presents the Br3d core level spectra for the 4-bromophenyl modified electrodes upon polarization at selected negative potentials. The intensity of the Br3d core level spectra ($3d_{3/2}$ and $3d_{5/2}$ doublet at 70.7 and 70.0 eV) decreased as the potential was made more negative and a small but non negligible signal was still observed after a polarization of -2.6 V (see also Table 1). Interestingly, the variation of the N1s peak did not follow exactly that of the Br 3d peak (see Table 1). In one case (upon polarization at -2.6 V), the N atomic concentration even became larger than that of Br. The reduction of the bromobenzene groups should lead to their dehalogenation in nonaqueous media.²⁰ Indeed, Pinson et al. have shown that the electrochemical reduction of grafted 4-bromophenyl groups on HOPG is irreversible and generates bromide ions.^{8b} However, the dehalogenation of the 4-bromophenyl grafted groups in aqueous media is not complete since some bromine is always detected by XPS.

A slight decrease of the N1s signal is found in Figure 4c for the DEA-modified electrode for negative polarization whereas the decrease is much more significant for positive potentials. Thus, some residual signal (Br3d for 4-bromophenyl; N1s for DEA and 4-nitrophenyl; N1s for 4-carboxyphenyl (not shown)) was always observed for all modified electrodes even at very negative or positive potentials. These results demonstrate that a fraction of the grafted groups seems to be fairly robust even if the data of Figure 3 suggest poorer film integrity at positive polarization relative to negative polarization.

The atomic concentration of C, N, O, and Br of the surface of the glassy carbon electrode can be estimated by analysis of the XPS core level spectra and are included in Table 1 in addition to relevant ratios and the surface concentration of the grafted groups. The latter were calculated by multiplying the ratio of the total area under the N1s peak and the substituent

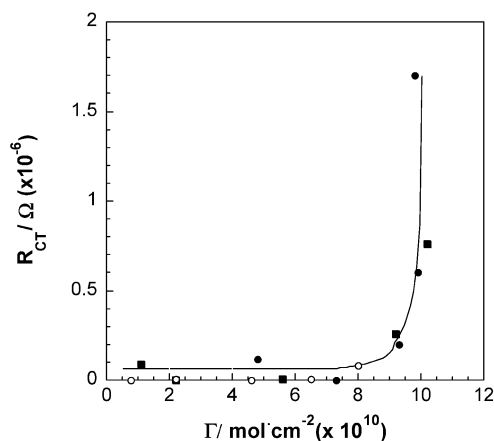


Figure 5. Plot of the charge-transfer resistance as a function of the surface coverage of grafted groups (4-nitrophenyl = ●; 4-bromophenyl = □; DEA = ○). See Table 1 for the data.

with respect to the C1s peak by a factor of 7.3×10^{-9} mol/cm 2 .^{9a,21} This factor represents the carbon atom surface density of basal plane graphite and was used as a rough approximation of the glassy carbon surface. Subsequently, a plot of all these R_{CT} values as a function of their respective surface coverage (Figure 5) revealed a dramatic increase of R_{CT} at about 10×10^{-10} mol/cm 2 . Interestingly, this surface coverage value corresponds roughly to that expected for monolayer coverage of grafted groups.^{8,9a} There is no obvious increase of the O/C ratio upon polarization at positive potential, and this observation suggests little oxidation of the carbon surface. On the other hand, the decrease of the O/C ratio for the 4-nitrophenyl, 4-bromophenyl, and DEA surface groups upon polarization at -2.6 V is probably due to the electrochemical reduction of some oxygenated surface groups initially present at the glassy carbon electrode surface.

General Discussion. The R_{CT} values for the 4-carboxyphenyl modified electrode subjected to the positive and negative potential limits investigated in this study were always larger than that observed for a bare glassy carbon electrode (Figure 2). In addition, the CV response was similar but the electron transfer kinetics were slightly faster at the bare electrode. Unfortunately, XPS is not useful to characterize surface grafted 4-carboxyphenyl groups that contain only carbon and oxygen in addition to the presence of some residual nitrogen.¹² The modified electrodes subjected to the most positive or negative polarizations in this study show electrochemical responses similar to those reported by other groups for as-grafted layers.^{9,11} On the other hand, these researchers found a much smaller blocking effect than that reported here for our as-deposited layers and elsewhere for as-grafted layers.^{10,12} Considering recent reports by Kariuki and McDermott¹¹ in which they demonstrated multilayer formation, these observations suggest that McCreery's procedure and experimental conditions⁹ yielded much thinner film (e.g., monolayer) than the one described here.

Thus, our data is consistent with the generation of a thick layer by our modification procedure. Then, a significant fraction of this thick layer is removed upon polarization as a result of hydrogen, oxygen, and/or chlorine evolution. This is supported by the observation of gas bubbles when the electrode potential reached a value sufficient to observe an increase of the CV response and a decrease of the R_{CT} values. It should be noted that oxidation of the surface carbon atom can also occur upon polarization at positive potential values,^{2,7} and this reaction could be also involved in the desorption process (vide infra). However, the invariance of the O/C ratio between the as-deposited

electrode and those subjected to positive polarizations suggests that carbon oxidation is not significant and that the organic films seem to suppress somewhat the oxidation of carbon.

The variation of the core level spectra for a characteristic element of the grafted groups was followed to investigate the effect of polarization. Both XPS and electrochemical data point to the presence of a small amount of residual substituted phenyl groups at the electrode surface, after polarization, which might be consistent with the presence of a monolayer or a submonolayer. It is noteworthy that even chlorine, which might be generated in our experimental conditions, cannot remove all the organic species that are grafted at the electrode surface. These remaining covalently bonded molecules are very robust and can withstand relatively extreme applied potentials. Others have shown that ultrasonication of the modified electrode cannot eliminate the grafted layer, which can be only removed by abrasion.^{8,21} On the other hand, the aryl groups that can be removed upon polarization are, most likely, not covalently bonded to the glassy carbon electrode and hence can be electrochemically removed. Accordingly, the electrochemical impedance data lend some support for this loss of material by R_{CT} diminution despite that the CV is not always as much affected.

Our results seem to suggest that the polymerization type reaction between the bound monolayer and the electrogenerated free radicals,¹² to yield a relatively thick layer of substituted phenyl species, appears unlikely unless cleavage of the carbon-carbon bond between two phenyl rings can occur during polarization of the modified electrode after the grafting procedure. However, we believe that the above grafting mechanism is operative for a few layers, although we do not have any evidence for that yet. The remainder of the film could be the result of the adsorption of reaction products coming from the electrogenerated aryl radical. These species could be a mixture of dimers and oligomers²² or coming from H-atom transfer from the solvent to aryl radicals.^{8b} Finally, it is worth mentioning that a film can be also generated at the surface of a gold electrode by electrochemical reduction of a diazonium salt in acetonitrile.²³ This confirms that passivation (blocking effect) of a glassy carbon electrode might involve other processes in addition to the covalent grafting step if one assumes that a gold-carbon bond cannot be formed by this procedure. However, Pinson et al. have recently shown that the electrochemical reduction of a diazonium salt on an iron electrode led to the attachment of the aryl groups to the iron surface.²⁴

It is interesting to compare the stability of these grafted layers with those formed by electrochemical oxidation of aryl acetates²⁵ and those of SAMs.¹⁴ Unlike the results presented in this study, electrochemical oxidation of grafted aryl groups, generated by anodic oxidation of aryl acetates, led to their removal from the glassy carbon electrode surface, as was indicated by cyclic voltammetry.²⁵ However, it should be noted that our CV data might also suggest that the grafted layers were completely removed but that XPS clearly revealed the presence of some grafted species. On the other hand, SAMs of sulfur-containing adsorbates were found to be stable over a more limited range of potential of about 1.2 V in aqueous media.¹⁴ Presumably, the SAMs were unstable in the potential range of hydrogen and oxygen evolution reactions. This has important consequence for electrochemical applications which will be limited to the potential range where the grafted layers or SAMs are stable, and accordingly the aryl-modified glassy carbon electrodes, which offer a wider potential range of stability, will presumably have a larger number of applications than SAMs on gold.

Conclusion

The stability measurements have shown that electrografted film of 4-carboxyphenyl, 4-nitrophenyl, DEA, and 4-bromophenyl at a glassy carbon electrode can be used in a potential window of 3.6, 4.6, 2.6, and 5.6 V, respectively, despite that 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 electrografting process, presumably leaving a thinner film (submonolayer) at the electrode surface. Our results demonstrated that electrochemical impedance spectroscopy is a more sensitive technique than CV to probe the modification of a thin grafted film. The resulting electrode could be useful to perform further chemistry with the residual grafted groups and immobilize other molecules. This approach is currently being investigated in our laboratory.

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