

Electrochemical Activity of Modified Glassy Carbon Electrodes with Covalent Bonds Towards Molecular Oxygen Reduction

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The formation of covalent bonds on glassy carbon electrodes (GCEs) by producing oxidized functional groups (-COOH, -OH, -CHO, etc.) and using molecules such as 4-aminopyridine (4-AP), isonicotinic acid (IA) and 4-aminobenzoic acid (PABA) is proposed in this work with the aim of forming stable bonds. These modifications are done by using bulk electrolysis at an anodic fixed potential and by the Kolbe's reaction. Then, these modified systems are probed towards dioxygen reduction and it is seen that the oxidized GCE is the most active system, while the GCE modified with PABA possesses the lowest activity towards the reduction of O₂. By doing kinetic studies it was possible to calculate the transferred electrons and the Tafel slope for the most active system. In this sense, this reaction implies 2 transferred electrons and the Tafel slope has a value of 68 mV·decade⁻¹ in the oxidized GCE. Finally, AFM studies were done in order to get information about the morphological behavior of these systems in which each one presents different roughness (R_q values).

Keywords: Carbon electrodes, covalent modified electrodes, molecular oxygen reduction, Kolbe's reaction.

1. INTRODUCTION

Carbon-based electrodes, such as GCE, have great advantages in electrochemical analysis due to their broad potential window, low background current, rich surface chemistry, low economic cost and appropriateness for various sensing and detection applications [1]. However, electron transfer rates that are seen at these electrodes are usually slower than on noble metal electrodes [2, 3, 4]. In this sense, the electrochemical activity on GCEs can be increased towards some analytes once their surfaces are submitted to an anodic oxidation, since new oxidized functional groups are formed after this procedure [5,16]. Also, short, plane and aromatic molecules such as 4-aminopyridine, isonicotinic

acid and 4-aminobenzoic acid can be used in order to obtain new covalent modifications through different methods like via aminopyridil cation radical [6,7] and via Kolbe's reaction (figure 1). This last reaction consists of the oxidative decarboxylation of a carboxylic acids or carboxylates with the formation of dimers and carbon dioxide [8]. In this way, atoms from these molecules will covalently bond with atoms from the GCE in order to gain more stability, which is gained by forming a full electron shell and by sharing their outer most (valence) electrons. These bonds are largely composed of carbon atoms linked by single, double, or triple bonds, but other elements are also unified into molecules by covalent bonds either as linking atoms or as part of peripheral groups [9]. Therefore, this reaction constitutes one of the most relevant methods of modification in electrosynthesis to form of a wide variety of organic compounds, derived from a radical chemistry [10].

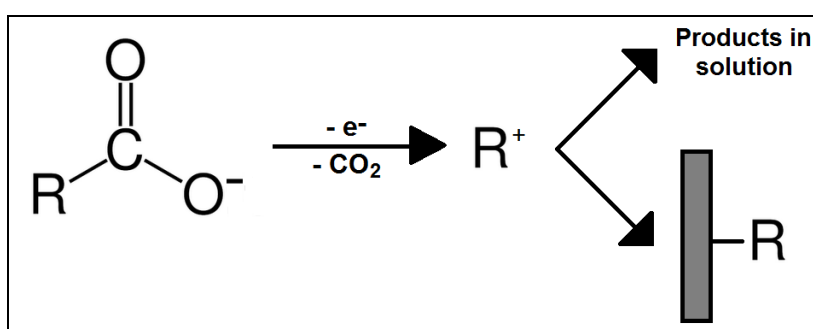


Figure 1. Mechanism of Kolbe's reaction

Electrochemically assisted covalent modification of carbon surfaces is a relatively recent development in modified electrode research. Pinson et al. in 1990 [11,12] was the first to describe electrochemical generation of a covalent bond between a carbon surface and a modifier which was based on the oxidation of diamines giving amine radicals. Then, two years later, they showed that reduction of aryl diazonium salts at carbon electrodes also form a covalent bond between carbon and an aryl radical [13]. Nowadays, possible applications of covalently modified carbon surfaces are being studied, which the design of catalytic carbon surfaces to improve the efficiency of these systems is still an important challenge. Also, covalently modified electrodes can be used to explain morphological effects on electron transfer at different electrodes, specially carbon electrodes [14,15].

In this work, four different modifications are proposed in order to form covalent bonds on a GCE surface: oxidation of GCE, GCE + 4-AP, GCE + IA and GCE + PABA, and are compared with the bare electrode in terms of electroactivity towards dioxygen reduction so as in terms of morphological characteristics.

2. EXPERIMENTAL

2.1. Reagents

Tetrabutylammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$), potassium chloride (KCl), potassium ferricyanide ($K_3[\text{Fe}(\text{CN})_6]$), 4-aminopyridine (4-AP), isonicotinic acid (IA), 4-aminobenzoic acid

(PABA) and sodium hydroxide (NaOH) were analytical grade reagents purchased from Sigma Aldrich. Deionized water was obtained from a Millipore-Q-system. Argon (99.99% pure) gas was purchased from AGA-Chile. Ethanol, triethylamine and acetonitrile were purchased from Sigma Aldrich.

2.2. Equipment

Cyclic voltammetry studies were performed on a CHI instrument 750D potentiostat galvanostat.

The conventional three-electrode system consisted of a glassy carbon working electrode (GCE), Ag/AgCl (sat.KCl) reference electrode, and a platinum wire-counter electrode.

AFM studies were done by using an Innova® Atomic Force Microscope (AFM). Tapping mode was employed in all samples.

2.3. Preparation of modified electrodes

The glassy carbon electrode was polished to a mirror finish on a felt pad using alumina slurries (3 mm). Then, it is put on an ultrasonic system in order to remove the excess of alumina for 60 seconds and by cycling the potential between -0.8 V and 0.7 V in a solution of NaOH 0.1 M (Ar atmosphere), the electrode response was stabilized.

With the aim of obtain modified electrodes with covalent bonds, four different systems were probed: oxidized GCE, GCE + 4-AP, GCE + IA and GCE + PABA. The first modification was done by applying a fixed anodic potential (+1.6 V) until the system reached an amount of charge of 0.1 C (300 s approximately). After this procedure, a voltammetric profile of the modified GCE was obtained at the same conditions described for the non-modified system and it was compared.

To get the GCE modified with 4-AP, a solution of 4-AP $1 \text{ mmol}\cdot\text{L}^{-1}$ was prepared in ethanol using $0.2 \text{ mol}\cdot\text{L}^{-1}$ of n-Bu₄NPF₆ as support electrolyte. The GCE was submerged in the solution and an anodic potential was applied to the system (+1.8 V during 180 s). Then, the electrode was washed in ethanol and the modification was probed by cycling the potential in a solution of K₃[Fe(CN)₆] $1 \text{ mmol}\cdot\text{L}^{-1}$ using KCl as support electrolyte ($0.1 \text{ mol}\cdot\text{L}^{-1}$). Finally, it was compared to the bare GCE at the same conditions.

As third and fourth modification, IA and PABA were used to modify the GCE by carrying out the Kolbe's reaction. In a first stage, a solution of each carboxylic acid was prepared using ethanol as dissolvent ($8 \text{ mmol}\cdot\text{L}^{-1}$) plus 0.7 mL of triethylamine in order to get the respective carboxylates. Then, an aliquot was taken as so as to prepare a solution of each carboxylate ($4 \text{ mmol}\cdot\text{L}^{-1}$) using $0.2 \text{ mol}\cdot\text{L}^{-1}$ of n-Bu₄NPF₆ as support electrolyte. The GCE was submerged in the carboxylate solution and 10 cycles were done between -0.6 V to 1.6 V, homogenizing after 2 cycles with Ar. The system was sonicated during 10 minutes in acetonitrile and then, both systems were probed using the couple redox Fe(II)/Fe(III) as described for 4-AP.

Finally, all the modified electrodes were probed in a NaOH 0.1 solution saturated in dioxygen (during 20 minutes before each measurement) by cycling the potential between 0.2 V and -0.9 V.

3. RESULTS AND DISCUSSION

3.1. Generation of covalent bonds on a GCE surface

3.1.1. Oxidized GCE

With the aim of corroborate the surface modification after anodic oxidation, a cyclic voltammogram is reproduced and the voltammetric profile shows a different response versus the bare GCE (non-shown). New cathodic current peaks are observed and are attributed to the reduction of oxidized groups on the electrode surface since the measurements are done in Ar atmosphere. Another way to check the modification out implies the corroboration of the amount of charge after applying a fixed potential of 1.6 V until the system reaches a constant charge of 0.1 C.

3.1.2. Modification through aminopyridil cation radical method

Once the modification procedure is done, the system is probed towards the redox couple Fe(II)/Fe(III) and compared to the bare GCE response. In figure 2 is possible to observe how the redox couple response is annulated, which means that the surface has been successfully modified since pyridil group is non-active towards the redox couple.

The immobilization of the aminopyridil group on the GCE surface is mediated by the electro-oxidation of the electrode. In this case, the amine group of 4-AP is oxidized in order to form a cation radical, while the nitrogen from the pyridine group has no modification during the anodic procedure [6,7].

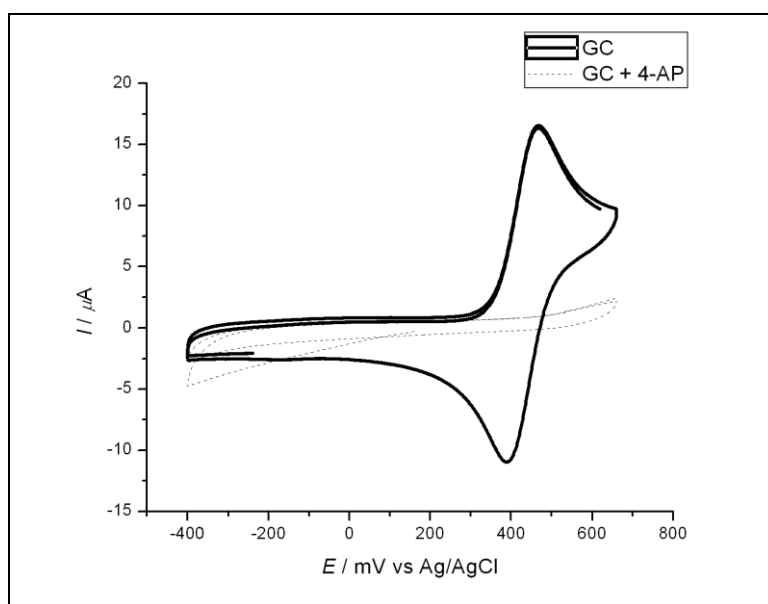


Figure 2. Voltammetric profile corresponding to the redox couple $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{2-}$ $1 \text{ mmol}\cdot\text{L}^{-1}$ in $\text{KCl } 0.1 \text{ mol}\cdot\text{L}^{-1}$ of a bare GCE (solid line) and a modified GCE with 4-aminopyridine (4-AP) (dashed line). Scan rate, $\nu=100 \text{ mV}\cdot\text{s}^{-1}$

3.1.3. Modification through carboxylates using Kolbe's reaction

Figures 3a and 3b show the voltammetric responses of the carboxylates electro-oxidation that were formed from isonicotinic acid (IA) and 4 – aminobenzoic acid (PABA). The response inhibition is observed on the voltammetric profiles for both cases but it is more significant on modification with PABA.

The diminution effect on the peak currents is evidence of a modified electrode surface. In both cases, the formation of radicals is present through a decarboxylation process (CO_2 liberation). These radicals are submitted to oxidation in order to obtain carbocations, which are very reactive and capable to react with the dissolvent to form products like acetamides or benzylic carboxylates and acylamides or aliphatic carboxylates (figure 1). Also, these species may react with the carbon atoms (sp^2) that are present on the electrode surface (benzylic or alkylaromatic carboxylates).

In this way, while carbon atoms react with the carboxylates, covalent bonds are formed between these molecules and the chemical species of the electrode [8-10], leaving the piridinic and amine groups towards the bulk solution and which are going to be new active sites on the electrode.

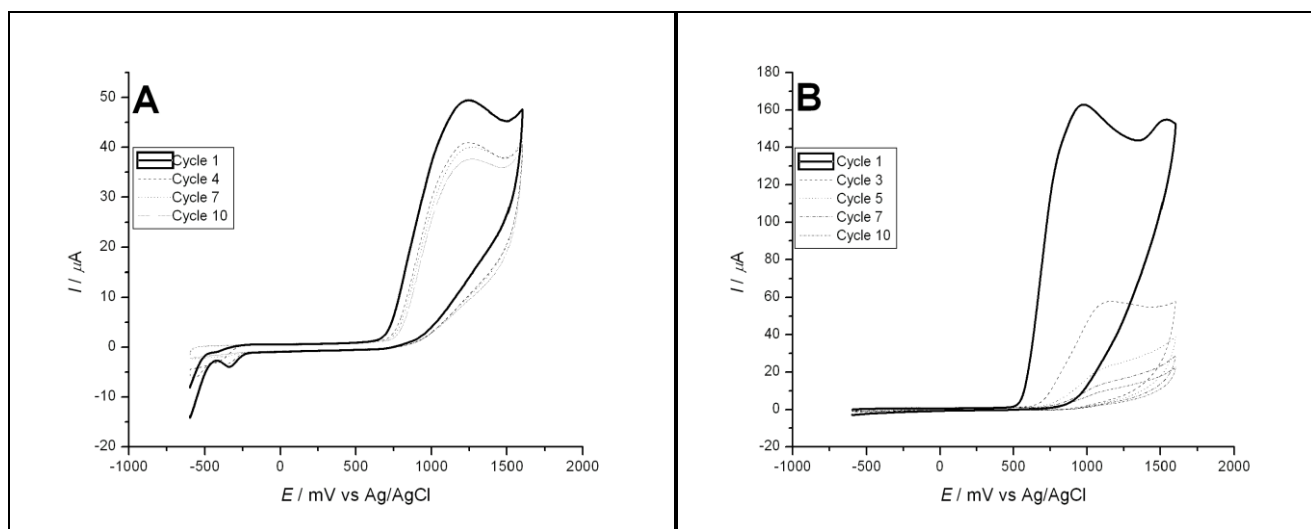


Figure 3. Voltammetric response of carboxylates oxidation: **A**) isonicotinic acid (IA), **B**) 4 – aminobenzoic acid (PABA). Concentration of carboxylates: $4 \text{ mmol}\cdot\text{L}^{-1}$ in $\text{CH}_3\text{CN} + \text{n-Bu}_4\text{NPF}_6$ $0.2 \text{ mol}\cdot\text{L}^{-1}$. Scan rate, $\nu = 100 \text{ mV}\cdot\text{s}^{-1}$.

After the modification procedure, the existence of these new molecules on the systems are corroborated by analyzing the response of the redox couple Fe(II)/Fe(III) (figure 4) as probe reaction. In both cases, there is an annulation of the response of this redox couple, similar to what happens by using the cation radical method with 4 – AP.

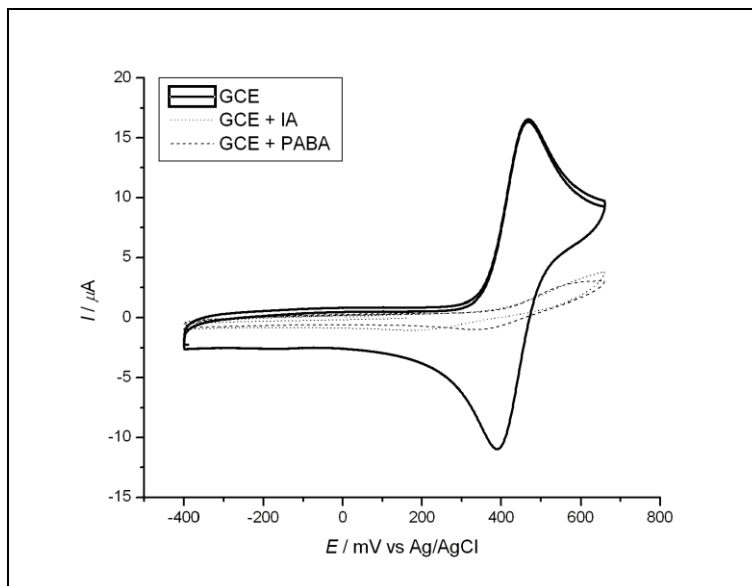


Figure 4. Voltammetric profile corresponding to the redox couple $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{2-}$ $1 \text{ mmol}\cdot\text{L}^{-1}$ in $\text{KCl } 0.1 \text{ mol}\cdot\text{L}^{-1}$ of a bare GCE (solid line) and modified GCEs with carboxylates: isonicotinic acid (IA) (dashed lines), 4 – aminobenzoic acid (PABA) (dotted line). Scan rate, $\nu=100 \text{ mV}\cdot\text{s}^{-1}$.

3.2. Electroactivity of modified electrodes towards dioxygen reduction

In order to compare all the generated systems, figure 5 shows the different responses of the modified electrodes with covalent bonds towards dioxygen reduction. In this figure is possible to observe that the oxidized GCE is the most active system in comparison to the rest ones.

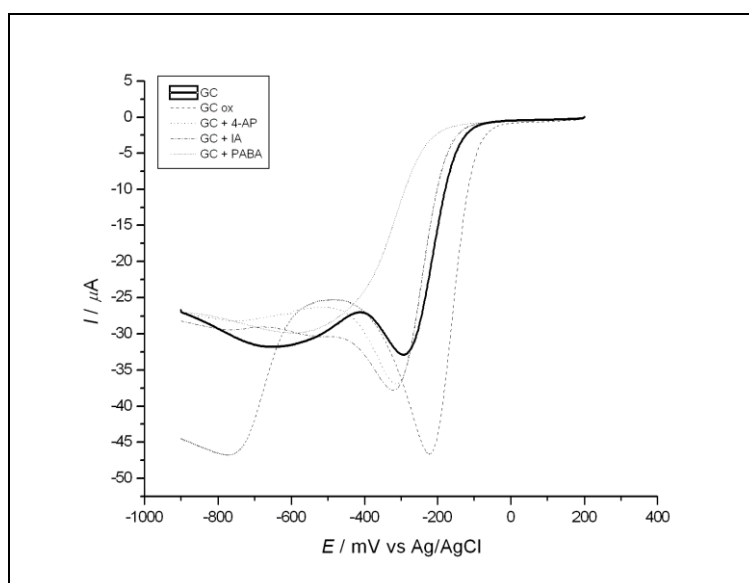


Figure 5. Voltammetric response of different generated systems towards dioxygen reduction: oxidized GCE (solid line), GCE + 4 – AP (dashed line), GCE + IA (dotted line), GCE + PABA (dot-dashed line), in $\text{NaOH } 0.1 \text{ mol}\cdot\text{L}^{-1}$. Scan rate, $\nu=100 \text{ mV}\cdot\text{s}^{-1}$.

The oxidized functional groups on the surface promote a catalysis phenomenon since the potential peak is reduced and the peak current is increased. Parallel to this, a new reduction peak appears at more negative potentials, which might be attributed to the reduction of oxidized groups or to the dioxygen reduction through 2 steps.

Also, it is possible to observe that the modified electrode with IA has a similar response to the one modified with 4 – AP towards dioxygen reduction. This phenomenon was expected since, in these both cases, the molecular fraction that is exposed to the bulk solution corresponds to the pyridine. Parallel to this, when the GCE is modified with PABA, the molecular fraction that is exposed corresponds to an amine group, which has a different response towards dioxygen reduction. In this last case, it is possible to observe that there is a passivation or blocking effect in comparison to the bare GCE and gives evidence that these groups are non-active towards dioxygen.

3.3. Kinetic studies

Kinetic analysis of oxidized GCE was done since it is the best system towards O₂ reduction. By making a plot between the logarithm of the current peak ($\log I_p$) versus the logarithm of the scan rate ($\log v$), it is possible to obtain information concerning to the system control (figure 6). As it is shown, the slope value corresponds to 0.45 (≈ 0.5), which points out to a diffusion – controlled process consistent with a high rate – constant catalytic system [16].

In order to corroborate this information, a plot between the current peak (I_p) versus the square root of the scan rate was done. A good relationship was obtained ($R^2 = 0.998$) and with the slope value ($149.49 \times 10^{-6} \text{A}(\text{Vs}^{-1})^{-1/2}$) was possible to calculate the number of transferred electrons (n) by using the Randles – Sevcik equation (equation 1) [17,18], where α is the electron transfer coefficient, n_a the number of electrons in the rate – determining step of the reaction, D_o ($2 \times 10^{-5} \text{cm}^2 \cdot \text{s}^{-1}$) [19] the diffusion coefficient of the electroactive species, C_o the concentration of dioxygen in the solution and A the electrode area (0.07cm^2). In this case, C_o corresponds to $11 \text{mg} \cdot \text{L}^{-1}$ ($3.438 \times 10^{-7} \text{mol} \cdot \text{cm}^{-3}$) considering room pressure and temperature, 0.94 atm and 10 °C, respectively.

$$I_p = (2.99 \times 10^5)n [(1-\alpha)n_a]^{1/2} C_o A D_o^{1/2} v^{1/2} \quad (1)$$

With the aim of calculate $(1 - \alpha)n_a$ that must be known, an approximation based upon its dependence on the difference of potentials ($E_p - E_{p/2}$) was used (equation 2). Then, $(1 - \alpha)n_a$ is 3.06 and implies that $n \approx 2$.

$$(1 - \alpha)n_a = \frac{0.0477 V}{(E_p - E_{p/2})} \quad (2)$$

This result agrees with literature about dioxygen reduction in an alkaline solution [20], where 3 equivalents of OH⁻ will be produced at the end of the reaction as main product.

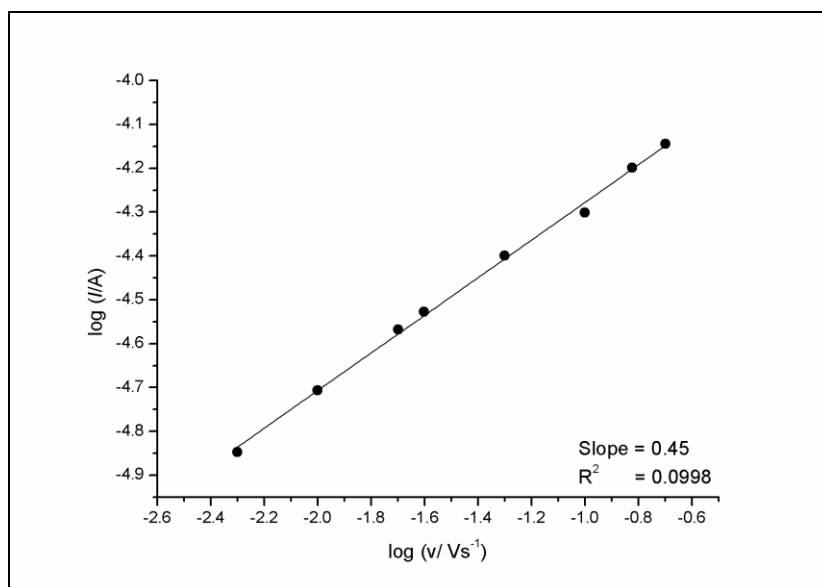


Figure 6. Plot of $\log I_p$ versus $\log v$ for oxidized GCE in NaOH $0.1 \text{ mol}\cdot\text{L}^{-1}$ saturated in dioxygen. Scan rate: $0.005 \text{ V}\cdot\text{s}^{-1} - 0.200 \text{ V}\cdot\text{s}^{-1}$

Additionally, Tafel slope was calculated so as to get information about the rate – determining step of dioxygen reduction reaction.

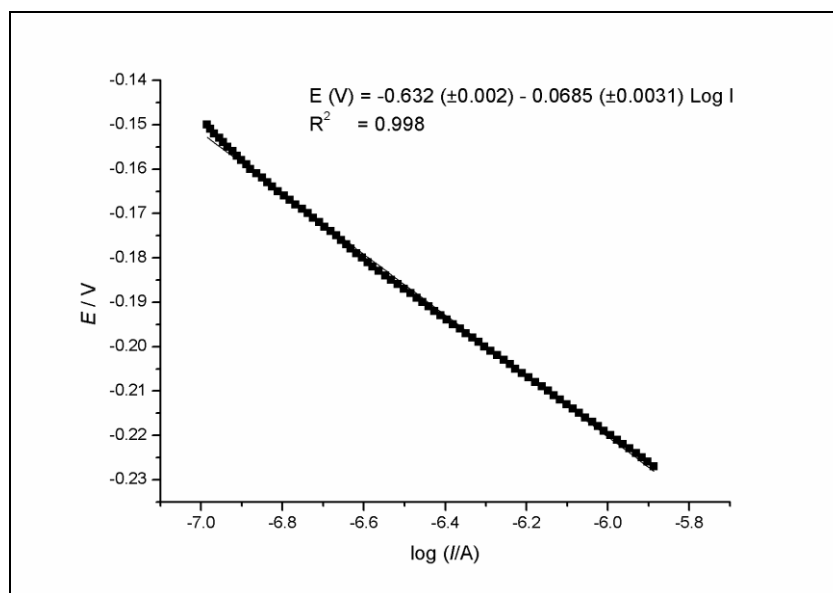


Figure 7. Plot of E versus $\log I$ (Tafel plot) for oxidized GCE in NaOH $0.1 \text{ mol}\cdot\text{L}^{-1}$ saturated in dioxygen. Scan rate: $0.005 \text{ V}\cdot\text{s}^{-1}$.

Figure 7 shows the Tafel plot with the corresponding slope value ($68 \text{ mV}\cdot\text{decade}^{-1}$), which means that there is a fast electron transfer (\bar{E}) previous to a slow chemical step (\bar{C}) [21]. Usually, a Tafel slope of $60 \text{ mV}\cdot\text{decade}^{-1}$ is observed at potentials higher than approximately 0.8 V and that of

120 mV·decade⁻¹ is observed at potentials lower than 0.8 V [22-24], so this result is interesting since it is not following the tendency of Tafel slopes values described before for O₂ reduction. This situation can be understood by knowing in which condition the adsorption of dioxygen is on the electrode surface (Temkin or Langmurian condition) [25-27]. In this sense, the mechanism would be as following:

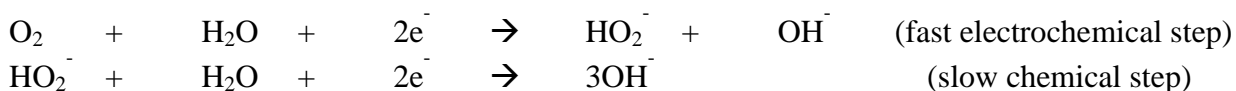


Table I shows kinetic parameters calculated for the rest of the modified systems. As it is seen, the Tafel slopes values vary in comparison to the oxidized system. Differences in Tafel slopes demonstrate that the mechanism of dioxygen electroreduction is different even if all of them reduce this molecule via 2 electrons.

Table I. Kinetic parameters for modified systems with covalent bonds.

Electrode	Tafel slope (mV·decade ⁻¹)	Transferred electrons
GCE + 4-AP	80	2
GCE + IA	73	2
GCE + PABA	100	2

3.4. Morphological studies

Figure 8 shows the morphological studies of the modified electrodes by using AFM as technique. As it is observed, there are differences between the modified surfaces and the bare GCE, which clearly shows some lines that are characteristic of the cleaning process with alumina (figure 8a). After any modification, none of these lines are appreciated on the GC surfaces.

Oxidized GCE shows a different morphology in comparison to the bare GCE, since new oxidized groups (-COOH, -OH, -CHO, etc.) are formed on the surface (figure 8b). Then, GCE modified with 4-AP, IA and PABA are also different (figures 8c, 8d and 8e, respectively), but in this last case the modified surface seems more plain than the rest.

Table II shows R_q values in order to get information about the surface roughness. As it is possible to observe, GCE + 4-AP is the most rough surface and GCE + PABA shows the lowest value between the modified electrodes.

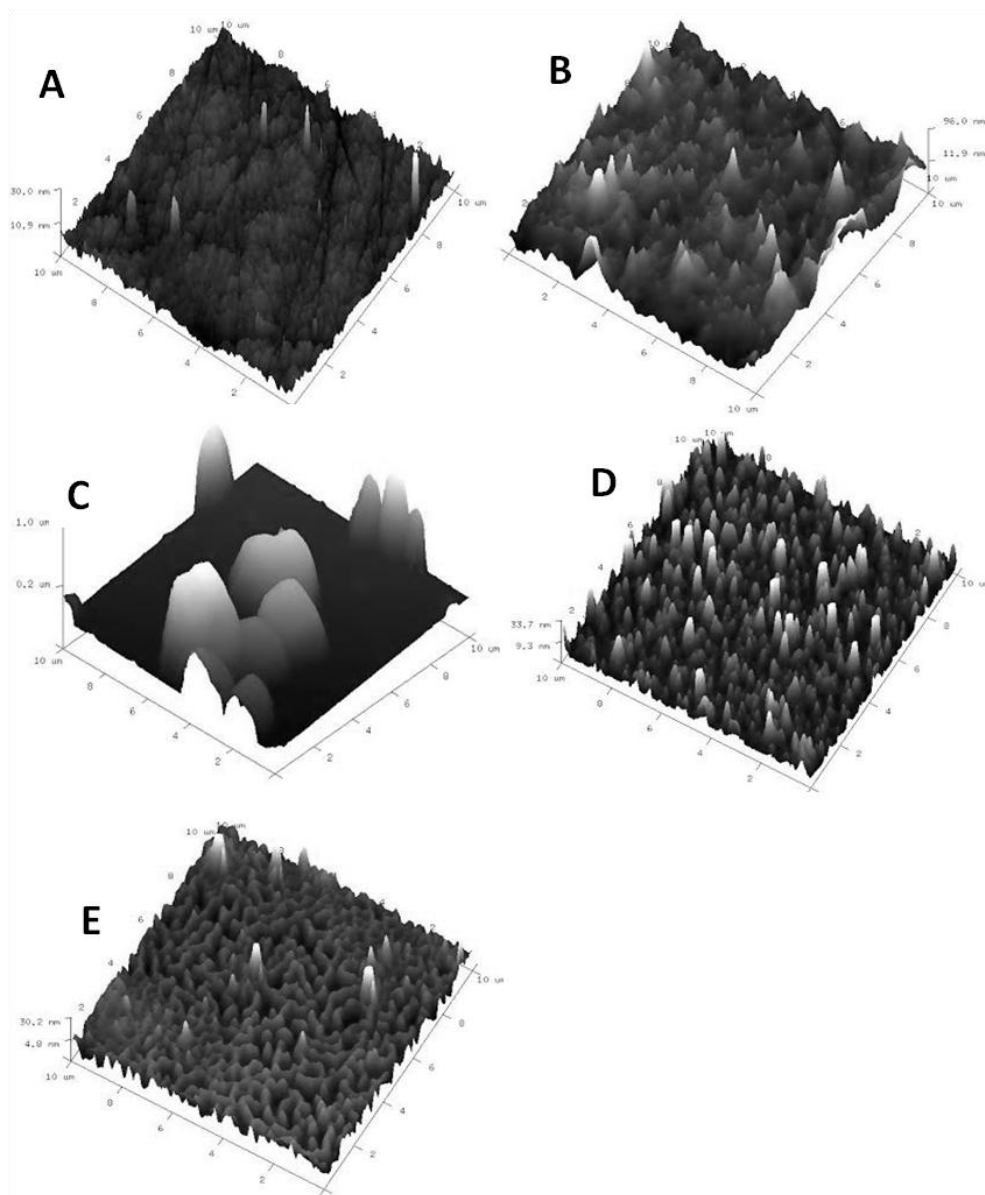


Figure 8. AFM images of bare GCE **A)** and modified GCEs with covalent bonds: **B)** oxidized GCE, **C)** 4 – AP, **D)** IA, **E)** PABA.

Table II. R_q values corresponding to the bare GCE and modified GCEs with covalent bonds

Electrode	Image R_q (nm)
Bare GCE	2.35
Oxidized GCE	19.6
GCE + 4-AP	278
GCE + IA	7.43
GCE + PABA	6.89

The last situation may be explained based on the chemical nature of PABA, which while it is carbocation on the oxidation process, this molecule reacts easily with others acting as an electrophile [28] and then forming a dimer on the surface (figure 9). This phenomenon can explain the low reactivity towards dioxygen reduction.

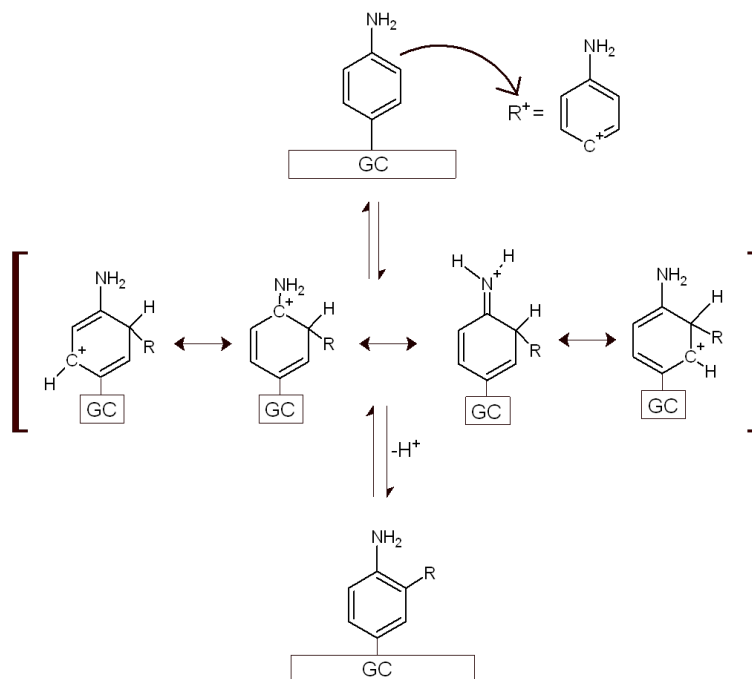


Figure 9. Electrophilic aromatic substitution of 4-aminobenzoic acid on a GCE, that explains through the resonance model the amine group donor property, and its condition of being ortho/para director.

4. CONCLUSIONS

Covalent bonds were successfully generated on GCEs by producing oxidized functional groups and by using molecules such as 4-aminopyridine, isonicotinic acid and 4-aminobenzoic acid. Each modification has a different response towards dioxygen reduction, which GCE + PABA contain the lowest activity in comparison to the rest ones. This last behavior is due to the chemical nature of PABA that can react very easily by electrophilic aromatic substitution ($S_{E}Ar$), so it can form a dimer or a polymer on the electrodic surface. Because of this condition, a blocking effect is observed on the electroactivity towards O_2 reduction.

Parallel to this, oxidized GCE is the most active system, which can reduce O_2 at lower potentials and with a higher response in terms of current. This system reduces O_2 via 2 electrons, and Tafel slope value ($\approx 60 \text{ mV} \cdot \text{decade}^{-1}$) supposes a fast electron transfer (\ddot{E}) previous to a slow chemical step (\bar{C}), producing 3 equivalents of OH^- at the end of the reaction.

Finally, AFM studies demonstrate morphological changes between every modified system in comparison to the bare GCE. Also, R_q values show differences in terms of roughness, which bare GCE (cleaned electrode) has the lower value since no modification is done on its surface.

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