

## Direct 4-Electron Reduction of Molecular Oxygen to Water Mediated by Cu-10-(4-aminophenyl)-5,15-dimesitylcorrole-modified Electrodes

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At pH 3 and 7, a glassy carbon electrode modified by deposition of a physio-adsorbed Cu-10-(4-aminophenyl)-5,15-dimesitylcorrole reduces molecular oxygen to water through a 4-electron direct transference. In the case of a glassy carbon electrode modified by electropolymerizing the same corrole on the surface, the reduction occurs by two parallel ways giving peroxide and water simultaneously. However at pH 7 this electrode gives peroxide as the unique product. This indicates that the way of modifying the electrode affects the product of reduction of oxygen. At pH 12, both modified electrodes catalyze the reduction to peroxide. It is noticeable that a Cu-azamacrocyclic reduces oxygen to water. At all the studied pH values, the modified electrodes are unstable and lose activity after a first cycle in the presence of oxygen.

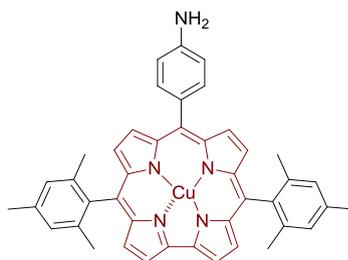
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**Keywords:** Oxygen to Water Reduction, Cu-Corrole, Modified Electrodes, Electrocatalysis, Reduction and Oxidation of Peroxide.

## 1. INTRODUCTION

The catalytic reduction of oxygen to water, a 4-electron transfer, has been the subject of intense research, in particular because of its importance in the oxygen/hydrogen fuel-cell process, metal-air batteries and electrochemical sensors [1,2]. Metallated macrocycles are of interest for the electrocatalysis of  $O_2$  reduction because they mimic the active sites of enzymes for this reaction (*e.g.*, quinol and cytochrome *c* oxidases) [3] and might be used as electrode materials in technological devices [1,2]. Porphyrins and phthalocyanines have been studied extensively as catalysts to promote direct  $4e^- O_2$  reduction [4-13]. On the other hand, corroles – porphyrin analogues containing three methine bridges and one direct pyrrole-pyrrole linkage– have begun to be explored as similar catalysts as well, partly due to the increased availability by one-step synthetic pathways [14-23]. Despite the obvious similarities between these two classes of tetrapyrrolic macrocycles, there are some fundamental differences as well. First, unlike dianionic porphyrins, corrole ligands are typically trianionic and form a completely different set of metal complexes, which are formally high-valent relative to stable metalloporphyrins [24-31]. Moreover, the smaller cavity of the corrole ring facilitates stabilization of metals in high oxidation states. Another major difference has to do with the inherently lower symmetry of the corrole macrocycle ( $C_{2v}$ ) compared with porphyrins ( $D_{4h}$ ). Most corroles are planar, while porphyrins are routinely ruffled or saddled. The missing *meso* carbon atom makes corroles more resistant to nonplanar distortions [32].

Very recently, Kadish *et al.* [33] have studied the catalytic activity of a *meso*-substituted cobalt (III) corrole coated on an edge-plane pyrolytic graphite electrode for the electroreduction of  $O_2$  in 1.0 M  $HClO_4$ . The authors concluded that cobalt corroles containing electron-withdrawing substituents are better catalysts than those having electron-donating groups on the three *meso*-phenyl rings. Collman and co-workers [34] used a rotating disk electrode to study  $O_2$  electroreduction with metallocorroles. They observed that catalysis begins at potentials that are 0.5–0.7 V more positive than the expected potential of the M (III/II) couple based on studies in non-aqueous solutions. The path of  $O_2$  reduction depends on the nature of the central metal ion. Cobalt corroles promote  $O_2$  reduction to  $H_2O_2$ , whereas iron corroles catalyze  $O_2$  reduction via parallel two- and four-electron pathways, with predominate four-electron reaction [34].



**Figure 1.** Structure of the studied Cu complex of 10-(4-aminophenyl)-5,15-dimesitylcorrole.

At our knowledge no works have been made so far considering copper corroles as potential catalysts for oxygen electroreduction due to the poor results obtained with their porphyrin analogues.

In this paper, we report catalysis studies toward O<sub>2</sub> reduction for glassy carbon electrodes modified with a Cu-10-(4-aminophenyl)-5,15-dimesitylcorrole (see Fig. 1). The aim of the work was to determine and compare the catalytic effect of dried-drop modified electrodes and electrodes modified by electropolymerization using an amine-functionalized Cu-corrole material.

## 2. EXPERIMENTAL

### 2.1. Corrole synthesis

*Cu-10-(4-aminophenyl)-5,15-dimesitylcorrole.* The first step involves the 2+1 condensation of mesityldipyrrromethane and 4-nitrobenzaldehyde to afford the nitro-functionalized corrole [35,36]. To 450 mL of CH<sub>2</sub>Cl<sub>2</sub>, degassed by purging with Ar for 15 min, BF<sub>3</sub>·OEt<sub>2</sub> (6 μL, 0.043 eq.) was added, followed by the immediate addition of mesityldipyrrromethane (300 mg, 1.13 mmol, 1 equiv) and *p*-nitrobenzaldehyde (171 mg, 1.13 mmol, 1 equiv), and the mixture was stirred at room temperature for 1 h. Subsequently, *p*-chloranil (833 mg, 3.39 mmol, 3 equiv) was added and the solution was heated at reflux temperature for 1 h. The solvent was evaporated and, after purification by column chromatography (silica, eluent CH<sub>2</sub>Cl<sub>2</sub>), 10-(4-nitrophenyl)-5,15-dimesitylcorrole was obtained (60 mg, 16%). Every step of this procedure was carried out under an inert atmosphere (Ar) and protected from light.

This corrole was then reduced using the procedure described by Zhang *et al.* (using SnCl<sub>2</sub>/HCl in EtOH) [35] to obtain 10-(4-aminophenyl)-5,15-dimesitylcorrole: To a solution of 10-(4-nitrophenyl)-5,15-dimesitylcorrole (237 mg, 0.36 mmol) in ethanol (50 mL), SnCl<sub>2</sub>·2H<sub>2</sub>O (922 mg, 4.1 mmol) was added. Subsequently, 27 mL of HCl (37%) was added slowly to the solution and the reaction mixture was stirred in an open flask at 70 °C and protected from light for 6 h. Afterwards, the solution was cooled down to room temperature and ice was added. NH<sub>4</sub>OH was added until neutral pH and the solution was extracted with ethyl acetate (3 x 50 mL). The combined organic phases were washed with brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent was evaporated.

The crude amino-functionalized corrole was immediately metallated (without prior purification) to obtain the desired Cu-corrole: To the crude free base corrole in THF (25 mL), Cu(OAc)<sub>2</sub> (130 mg, 0.72 mmol) was added and the mixture was stirred for 15 min under an Ar atmosphere and protected from light. After evaporation of the solvent and purification by column chromatography (silica, eluent CH<sub>2</sub>Cl<sub>2</sub>), the desired corrole was obtained. Yield 81%; UV/Vis (DMF): λ<sub>max</sub> (ε, M<sup>-1</sup> · cm<sup>-1</sup>) 394 (3921), 433 (3345), 537 (778), 632 (466) nm; MS (ESI) calcd for C<sub>42</sub>H<sub>36</sub>CuN<sub>5</sub> 685.2, found *m/z* 685.5; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.95 (s<sub>br</sub>, 2H, H<sub>β</sub>), 7.55 (d, <sup>3</sup>J = 7.3, 2H, Ph), 7.40 (s<sub>br</sub>, 2H, H<sub>β</sub>), 7.24 (s<sub>br</sub>, 2H, H<sub>β</sub>), 7.20 (s<sub>br</sub>, 2H, H<sub>β</sub>), 7.03 (m, 6H, Ph + H<sub>β</sub>), 6.38 (s<sub>br</sub>, 2H, NH), 2.42 (s, 6H, Me), 2.07 (s, 12H, Me); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.0, 147.2, 144.4, 143.7, 138.3, 137.6, 134-132 (br, CH<sub>β</sub>), 130.8 (CH), 128.2 (CH), 121.1 (CH), 114.4 (CH).

## 2.2. Electrochemical measurements

In all experiments pro analysis or higher purity chemicals were used. Before each experiment the working electrode (glassy carbon, GC) was polished with alumina slurry (particle size 0.3  $\mu\text{m}$ ) on soft leather and afterwards washed with deionized water. Before all the experiments, solutions were purged with high-purity nitrogen. This atmosphere was maintained over the solution during the measurements, except when  $\text{O}_2$  was bubbled (99.995% AGA). For electrochemical studies in aqueous media 0.1 M NaCl solutions were used. pH 3 was adjusted with a solution of concentrated HCl and pH 12 was adjusted with a solution of concentrated NaOH. The electrolyte for organic solutions was 0.1 M tetrabutylammonium perchlorate (TBAP) and the solvent was dimethylformamide (DMF).

All electrochemical measurements were carried out in a conventional three-compartment electrochemical cell. The glassy carbon modified electrode and a Pt foil were used as the working and counter electrode, respectively. All quoted potentials are referred to an Ag/AgCl (KCl saturated) electrode. For the rotating-ring-disk-electrode (RRDE) experiments, a platinum ring-glassy carbon disk-working electrode was used. The collection efficiency of the RRDE ( $N$ ) was determined using a standard redox couple,  $\text{Fe}(\text{CN})_6^{3-/4-}$  in 1.0 M KCl solution. The experimental collection efficiency factor was found to be 0.23. The potential of the disk ( $E_D$ ) was scanned from +0.6 V to -0.2 V vs. Ag/AgCl at a scan rate of 10  $\text{mVs}^{-1}$ . The potential of the ring ( $E_R$ ) was fixed at 1.1 V and the current-potential voltammograms were recorded during scanning at different rotation rates (100, 400, 900, 2500 and 3500 rpm). Spectroelectrochemical measurements were carried out using a platinum grid electrode as the working electrode and the corrole was dissolved in a solution of 0.1 M TBAP-DMF. Time of stabilizing the potential (electrolysis) before each experiment was 30 minutes.

## 2.3. Equipment

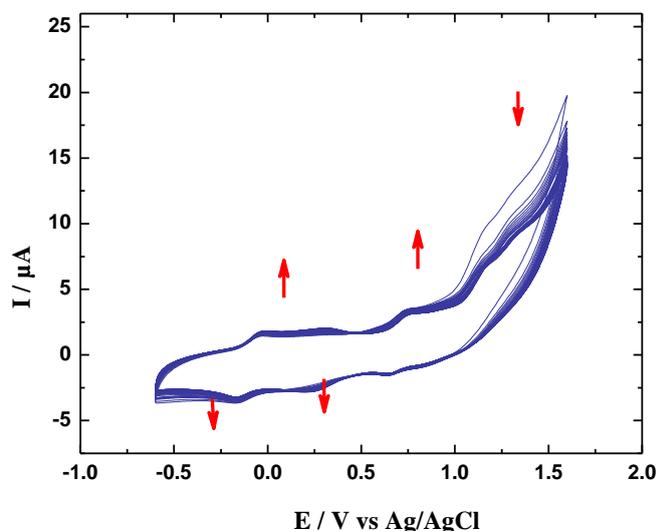
Cyclic voltammetry and rotating disk experiments were carried out using a CH-Instrument Scanning Electrochemical Microscope (Bipotentiostat) model CHI900B, a CH-Instrument Electrochemical Analyser model CHI604C and a Modulated Speed Rotator (MSR) model AFMSRCE from Pine Instruments. Spectroelectrochemistry measurements were conducted in a quartz cell of 1 mm path length in a spectrophotometer SPECORD Analyticjena S100 coupled to a Voltalab potentiostat PGZ100 model from Radiometer.

## 2.4. Modified electrode preparation

1. Dried-drop electrode (DDE) preparation: One drop of a 1 mM corrole in DMF solution was deposited on the glassy carbon surface and then dried in a heater at 80  $^\circ\text{C}$  during 30 minutes.

2. Polymer modified electrode (PE) preparation: The electropolymerization of the corrole was performed on the glassy carbon electrode by successive potential scans between -0.6 and 1.6 V at 100  $\text{mVs}^{-1}$  in a solution containing 1 mM of the corrole in DMF and 0.1 M TBAP. At the positive limit, oxidation of the amino groups sets out and the film starts growing, producing a current increase as the

number of cycles increases (Fig. 2). After 100 cycles the electrode was removed from the electrochemical cell, washed with distilled water and dried in a heater at 80 °C during 30 minutes.



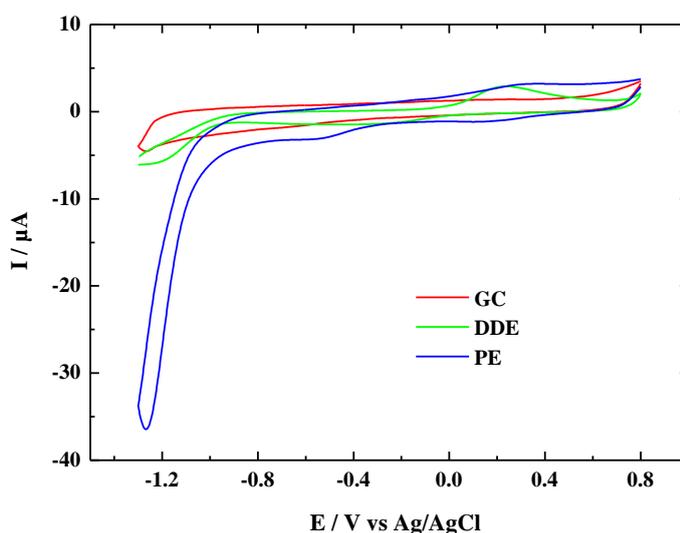
**Figure 2.** Cyclic voltammograms recorded during the electropolymerization of Cu-10-(4-aminophenyl)-5,15-dimesitylcorrole (0.1 mM of corrole in DMF and 0.1 M TBAP, 100 cycles at a scan rate of 100 mVs<sup>-1</sup>).

### 3. RESULTS AND DISCUSSION

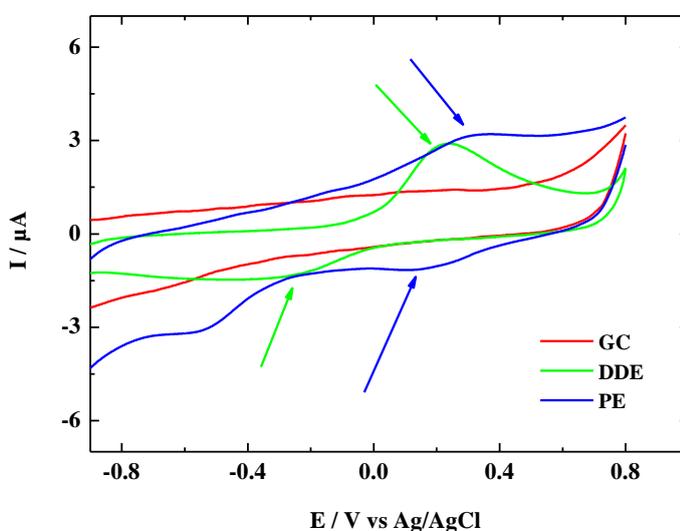
The free base mono-amino-functionalized AB<sub>2</sub>-corrole, 10-(4-aminophenyl)-5,15-dimesitylcorrole, has previously been prepared by Zhang *et al.* [35] The first step involves the 2+1 condensation of mesityldipyrromethane [36] and 4-nitrobenzaldehyde to afford the nitro-functionalized corrole [36-38], which is then reduced to the aminocorrole using SnCl<sub>2</sub>/HCl in EtOH. However, we have prepared the nitro-functionalized corrole using the conditions optimized for the synthesis of *meso*-pyrimidinylcorroles [39-41], and we were able to isolate the desired corrole in an acceptable 16% yield (vs 21% on applying the conditions as reported by Gryko *et al.* [37]). Reduction of the nitro group to obtain 10-(4-aminophenyl)-5,15-dimesitylcorrole was first carried out using the procedure described by Zhang *et al.* [35] However, since the observed yield was rather low (and some starting material remained), a few changes have been made to this method according to the procedure described by Collman *et al.* for the reduction of 5,10,15-tris(*o*-nitrophenyl)corrole [42]. The crude amino-functionalized corrole was immediately metallated (without prior purification) to obtain the desired Cu-corrole in a nice 81% overall yield (Fig. 1).

Figure 3 shows the voltammetric responses of the DDE and PE electrodes in aqueous solution at pH 3 (GC = glassy carbon). In both cases, the couple Cu(III)/(II) seems to appear (indicated by arrows) and some irreversible behavior is present (Fig. 3B). It is well-known that in the case of copper corroles, the ligand is non-innocent [32,43-47]. Copper corroles are inherently saddled, even in the

case of sterically hindered corroles. This distortion is due to copper metal-ligand orbital interactions. The ground state of copper in the corrolato ligand is solvent and substitution dependent. In this sense it is not correct to describe the metal couple simply as Cu(III)/Cu(II), but rather as  $[\text{Cu(II)} \dots \text{L}^+]/\text{Cu(II)}$ . The ligand is non-innocent due to attractive interactions of the Cu  $3d_{x^2-y^2}$  and b1 corrolato HOMO orbitals. The difference in the potential of the anodic and the cathodic peak then corresponds to the chemical difference between the oxidized and the reduced species [32,43-47]. In any case,  $\Delta E_p$  is similar to the values reported in literature [46,48]. Also, it is necessary to consider that in this case the corrole is not dissolved in an organic solution but it is adsorbed on the surface and put in an aqueous electrolyte solution.



A

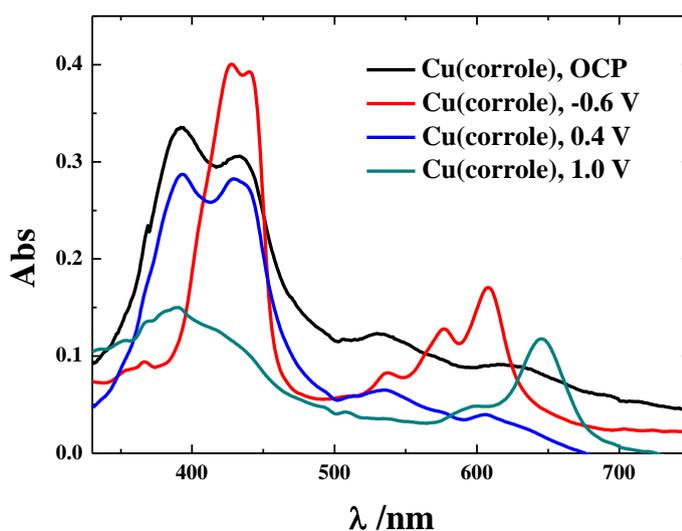


B

**Figure 3.** A) Cyclic voltammograms of modified electrodes in aqueous solution at pH 3 (red: GC, green: DDE, blue: PE (scan rate:  $0.1 \text{ Vs}^{-1}$ ,  $\text{N}_2$ ). B) Zoomed area of Figure 3A.

From Figure 3, it is interesting to note that the reaction of the evolution of hydrogen (discharge of current at negative potentials) is only catalyzed by the PE, and the DDE has the same behavior as bare glassy carbon toward the reaction. This is the first indication of the major influence of the way of modification of the electrode on the electrochemical characteristics of the modified surface. This behavior has been observed before for porphyrins [49].

Figure 4 shows the spectroelectrochemical response of the Cu-corrole (dissolved in DMF) at open circuit potential (OCP), at -0.6 V, when Cu is reduced, at 0.4 V, when Cu is oxidized and at 1.0 V, where the electropolymerization begins. It is rather surprising to observe two maxima for the Soret Band. In most cases, a sharp Soret Band appears that is dependent on the solvent and the *meso* substituents. However, some wide and ill-defined Soret Bands have been reported before, as in the case of a copper corrole xanthene complex [50-52].



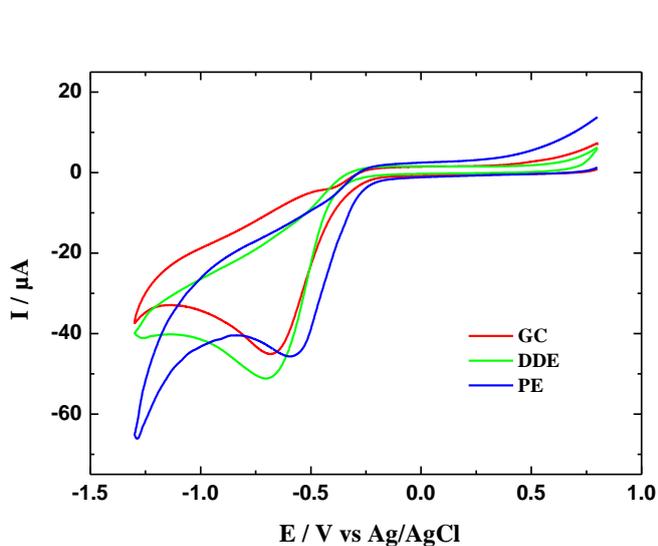
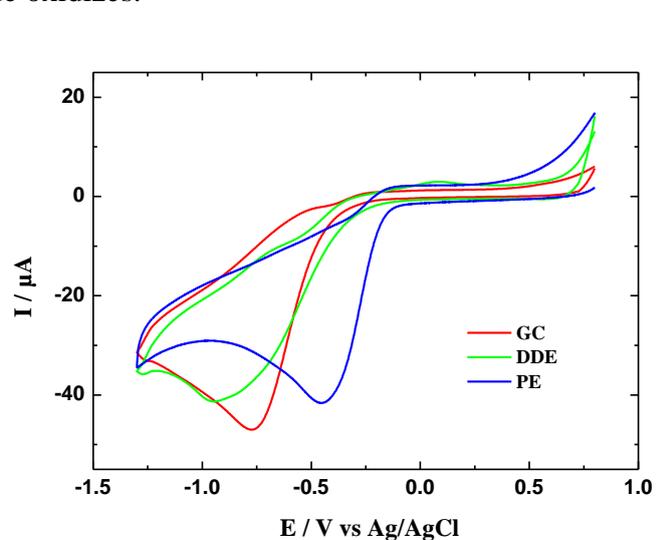
**Figure 4.** Spectroelectrochemical response of the Cu-corrole dissolved in DMF/TBAP at different applied potentials under a  $N_2$  atmosphere.

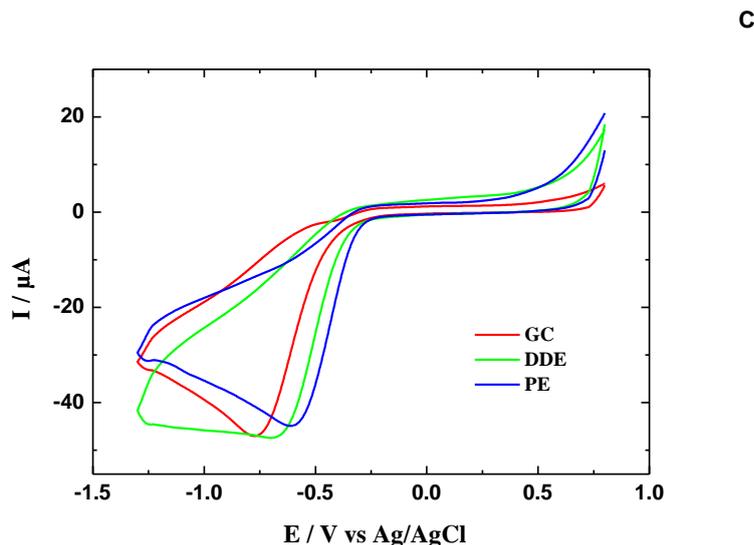
It can be seen from Figure 4 that the profiles corresponding to open circuit potential and 0.4 V are similar, indicating that in both cases Cu is in its quasi-Cu(III) state. When Cu is reduced (-0.6 V), a drastic change in the UV-visible spectrum is observed, indicating a change in the symmetry of the complex. When Cu has a pure 2+ oxidation state, it enhances its size and the orbital interaction probably diminishes due to the different electronic density on the d orbitals of the copper metal. This interaction is responsible for the strong saddled distortion [32]. In this case, it is not surprising to see a very strong change between the spectra of the reduced and the oxidized species. Also, a very notable change occurs when the corrole is oxidized at 1.0 V. At this potential oxidation of the amino groups begins and the polymerization can initiate. Normally, polymerization occurs after the formation of the amino radical cation that attacks the “ortho” position of a neutral molecule. The radical dimer attacks another neutral molecule until an insoluble oligomer is formed, which deposits on the electrode. In the case of the corrole under investigation, steric hindrance can block the growth of the polymer. In that

case, the polymer would not be formed but only dimers are probably obtained. In any case, the symmetry of the species changes and the  $\pi$  electronic cloud is drastically modified by the enhanced conjugation.

Figure 5 shows the voltammetric response of the modified electrodes toward the reduction of oxygen at pH 3 (A), 7 (B) and 12 (C). As in the case of the evolution of hydrogen, at pH 3, PE electrocatalyzes the reaction shifting the potential to more positive values. DDE has a behavior more similar to that shown by the glassy carbon electrode. However, small shifts in the potential of the foot of the reduction wave are observed. At pH 7 and 12, the two modified electrodes and the bare glassy carbon show a more similar behavior. There are also small shifts in the potential where the reduction wave begins for the modified electrodes.

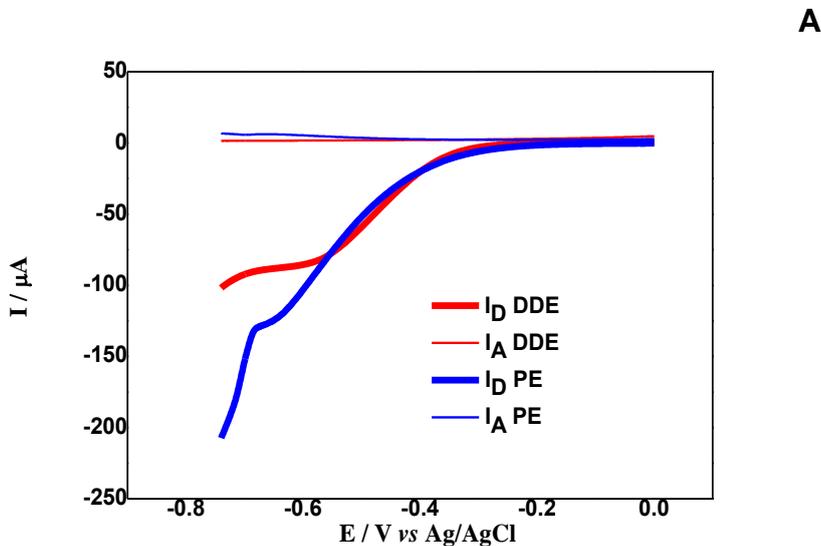
In spite of the low catalytic response of DDE at pH 3 and the low catalytic response of the modified electrodes at pH 7 and 12, some experiments were performed to determine the product of the reduction of oxygen. For both electrodes, experiments with a ring-disk electrode were done. In each case, the ring is platinum and the disk glassy carbon. The applied potential for the ring is 1.2 V vs. Ag/AgCl, where peroxide oxidizes.

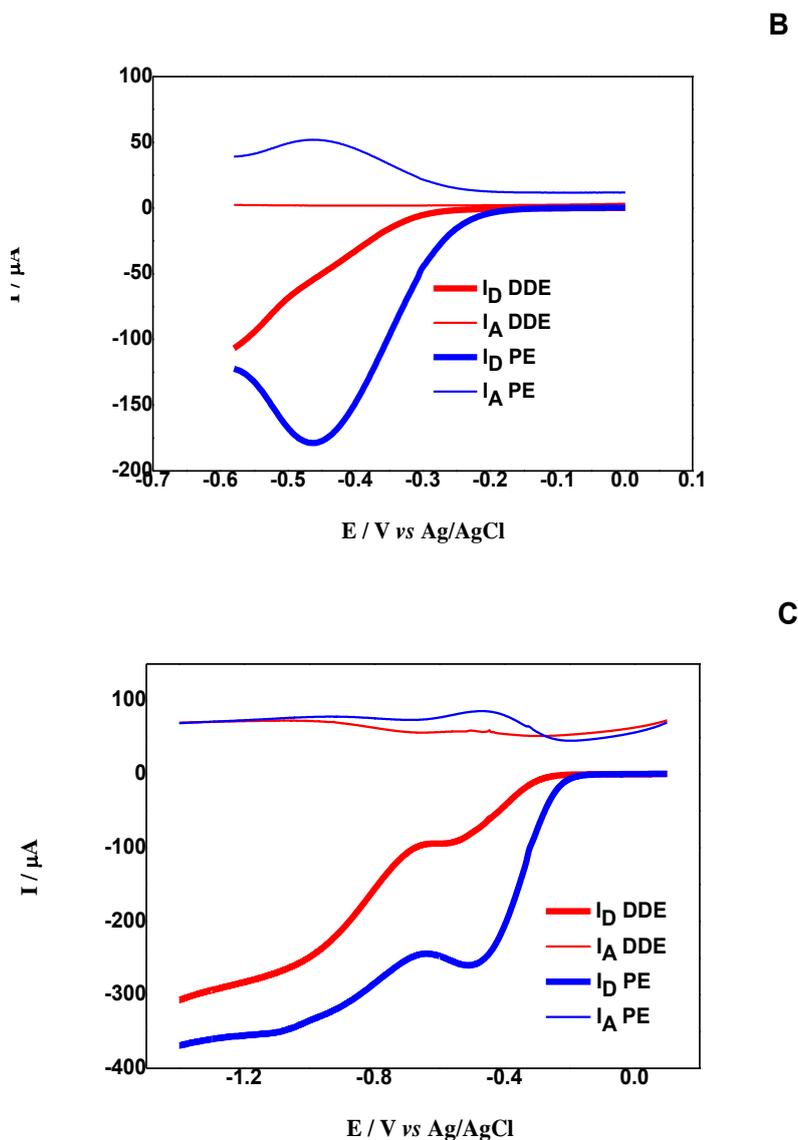




**Figure 5.** Voltammetric response of the modified electrodes toward the reduction of oxygen: A) pH 3, B) pH 7 and C) pH 12 (red: GC, green: DDE, blue: PE; scan rate: 0.1 Vs<sup>-1</sup>).

Figure 6 shows the response of the modified ring-disk electrode when the glassy carbon disk is modified by the Cu-corrole. It is interesting to observe that neither at pH 7, nor at pH 3, there is current in the ring in the case of the DDE, demonstrating that the DDE electrocatalyzes the reduction of O<sub>2</sub> directly to water. It is surprising that only the DDE catalyzes the reduction through 4 electrons. In the case of PE, little intensity of the current for the disk is obtained, showing that probably there are two parallel reactions at pH 3. One of these is a reduction with two electrons to peroxide and the second one is the direct reduction to water. The second way of reducing oxygen is the most important way of reduction because the current observed in the ring is very low in intensity. At pH 7, PE only catalyzes the reduction to peroxide (Fig. 6B) and DDE catalyzes the reaction to water. At pH 12, both electrodes give peroxide as the final product of the reduction (Fig. 6C).





**Figure 6.** Catalysis of  $\text{O}_2$  reduction at a ring–disk (Pt–GC) electrode in aqueous solution: A) pH 3, B) pH 7 and C) pH 12 (rotation rate: 800 rpm; scan rate:  $5 \text{ mVs}^{-1}$ ; red bold line: DDE disk current, red thin line: DDE ring current, blue bold line: PE disk current, blue thin line: PE ring current).

On the other hand, using equation 1, the number of transferred electrons can be calculated.

$$n = 4 \cdot I_D / (I_D + I_R/N) \quad \text{Eq.1}$$

where

$n$  = transferred electrons

$I_D$  = disk current at fixed potential

$I_R$  = ring current at the same fixed potential

$N$  = collection factor.

According to this equation, Table 1 shows the calculated transferred electrons.

**Table 1.** Calculated transferred electrons for the corrole-modified electrodes at pH 3, 7 and 12.

pH	Modified electrode	Calculated transferred electrons
3	DDE	3.8
3	PE	3.5
7	DDE	3.4
7	PE	1.8
12	DDE	1.1
12	PE	1.4

It can be seen from Table 1 that the number of electrons in the case of DDE at pH 3 and 7, where the product is water, is not 4. Also, when the product is peroxide, the calculated number of electrons is not 2. This discrepancy can be explained by the fact that both modified electrodes are extremely unstable. In fact, both modified electrodes at the 3 different pH values are capable to electrocatalyze the oxidation and the reduction of peroxide (not shown) during ten cycles or more. However, during the reduction of oxygen, when the product is peroxide, they lose their capacity to reduce peroxide instantly and this is the reason for detecting peroxide in the ring electrode. For that reason we are sure that a 4-electron direct transference takes place for the DDE electrode at pH 3 and 7. A mechanism of  $2e + 2e$  (via peroxide) is not possible with these systems because they lose their capacity to reduce peroxide. The reason for the peculiar instability is not known for now. We suppose that oxygen reacts generating water and peroxide and the liberation of these products is related with the destruction of the catalyst active sites.

#### 4. CONCLUSIONS

At our knowledge this is the first report about the reduction of molecular oxygen to water electrocatalyzed by a Cu-azamacrocyclic. In fact, Cu-10-(4-aminophenyl)-5,15-dimesitylcorrole-modified electrodes can reduce oxygen *via* 4 electrons to give water at pH 3 and 7 when the modifying is due to the adsorption of a solution containing the corrole. At pH 12, only peroxide is obtained. When the modification takes place by electropolymerizing the solution containing the corrole the behavior is different. At pH 3 this electrode gives water and peroxide in parallel ways. At pH 7 and 12 this modified electrode gives peroxide as the unique product. Both modified electrodes are extremely unstable and lost its activity after the first reduction cycle in the presence of molecular oxygen.

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