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GRAPHITE ELECTRODE ELECTROACTIVATED BY POTENTIOSTATIC MULTI-SEQUENCE TECHNIQUES FOR HYDROGEN PEROXIDE ELECTROSYNTHESIS

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ABSTRACT. Studies concerning the hydrogen peroxide electrosynthesis carried out by cyclic hydrodynamic voltammetry (CHV), revealed that graphite anodisation followed by a sequence of surface partial reduction has a positive effect upon the HPE efficiency. In order to improve the promising results obtained by CHV a set of original multi-sequences techniques for repetitive potentiostatic graphite electroactivation for HPE efficiency improvement was designed. The new electroactivation protocols were tested in hydrodynamic controlled conditions using a Pt-graphite wall-jet ring disk electrode. The potentiostatic measurements using different shapes of the applied signal allowed us to identify the possible processes involved in the electroactivation and production sequences. Experimental optimisation of the original potentiostatic electroactivation technique of the graphite cathode was carried out leading to a decrease of the electrical energy consumption.

Keywords: *hydrogen peroxide electrosynthesis, graphite electroactivation, wall-jet ring disk electrode, multi-sequence technique*

INTRODUCTION

The use of hydrogen peroxide, a “green” reagent, is continuously increasing in many technological processes (bleaching, wastewater treatment etc.) [1]. The exceptional ability of this compound to reduce or eliminate pollution makes it safe for the environment because it is transformed into noncontaminant products such as water and oxygen [2].

Hydrogen peroxide electrosynthesis (HPE) by partial reduction of oxygen (PRO) has received much attention over recent decades [3 – 6]. HPE allows to electrogenerate on site this valuable chemical using only water, atmospheric oxygen and electricity.

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Modified and unmodified carbonaceous materials are widely used for HPE, a special attention being paid to graphite [7 - 11] due to increased HPE efficiency on this material. The reactivity of carbon electrodes is essentially influenced by the material microstructure, the cleanliness of the electrode surface as well as by the type and the number of the functional groups existing on the electrode surface. All these parameters depend considerably on the type of the used carbon material and the applied pretreatments. The presence of native functional groups such as carboxyl, phenolic hydroxyl, quinine-type carbonyl on the carbon surface explains the special ability of carbon materials to reduce oxygen to hydrogen peroxide since they are involved in the reduction mechanism [12]. A major drawback for HPE on carbon electrodes is the slow kinetics of the reaction. An increased number of functional groups or active centres can be related to an enhancement of the electrocatalytic effect for these electrode materials.

Consequently, different pretreatment procedures, including electrochemical ones, were investigated and numerous studies attempted to establish the effect of carbon electrodes pretreatment upon oxygen reduction reaction [12-16]. The electrochemical pretreatments involve the application of relatively large negative or positive potentials to the working electrode. The amplitude and duration of the applied potentials varied largely, many researchers recommending the use of potential cycling or alternating current wave forms [12, 17-21]. These studies generally concluded that the performance of carbon electrodes can be improved by electrochemical pretreatment which introduces new functional groups on the electrode surface or modifies the nature of the native active centres [12], increasing the number of the oxygen functional groups [17] especially of quinoid type functional groups [15, 19].

Unfortunately, the simple oxidized carbon electrodes catalyze the total oxygen reduction or the subsequent reduction of hydrogen peroxide, affecting the HPE process efficiency [15]. To overcome these impediments, in the present paper, we describe a set of original multi-sequences techniques used for graphite electroactivation with the aim of enhancing the HPE efficiency.

RESULTS AND DISCUSSION

1. Preliminary studies by cyclic hydrodynamic voltammetry

Paliteiro et al. [15] point out that after anodisation the graphite electrodes become more active for the complete reduction of oxygen, without an increase in HPE efficiency. Contrarily to this observation, during our preliminary studies [16] concerning the graphite electroactivation by cyclic hydrodynamic voltammetry (CHV) on ring-disk electrode, we noticed an interesting phenomenon: when the graphite electrode was polarised to relatively large negative potential values after a preliminary oxidation at positive potential values, an enhancement in the current detected on the ring electrode (I_r) could be registered. An example, including 4 successive voltammograms (without polishing the electrode surface between measurements) and also I_r (that indicates the H_2O_2 electrosynthetized on the disk), is presented in Figure 1.

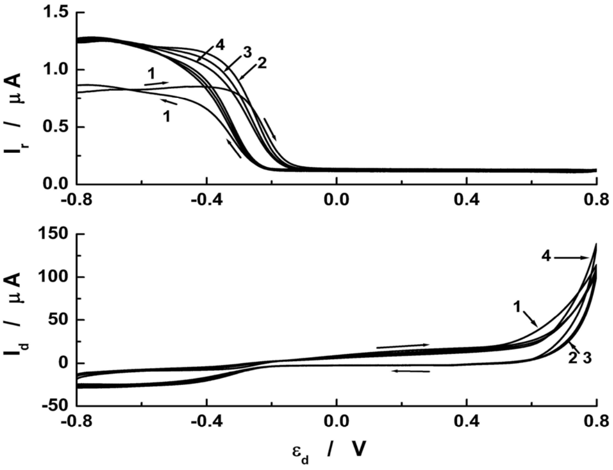

Figure 1. The correlation between the disk applied potential (ε_d) and the currents recorded by CHV on disk (I_d) and ring (I_r) for 4 consecutives cycles between -0.8 V and +0.8 V. The numbers on the figures represent the cycle number. Experimental conditions: v = 10 mV/s; volumetric flow rate (V_f = 1.42 mL/min

As one can see, at disk potentials higher than +0.6 V, the corresponding recorded current on the disk electrode (I_d) greatly increased due to the oxygen evolution and the intense oxidation of the graphite surface. For the cathodic scans, I_r clearly increases after the first cycle (corresponding to a fresh, unmodified graphite surface). In spite of HEP enhancement, this kind of electroactivation implied high energy consumption because of the large currents involved. This enhancement in HPE could be explained by the fact that during the oxidation new active centres are generated on the graphite surface. Unfortunately, these freshly generated active centres are not able to catalyse HPE because, more probably, they are in an oxidised form. Contrarily, after a short time polarisation of the oxidised electrode at more negative potential values (near the value corresponding to the total oxygen reduction), we observed that H_2O_2 production increased. We supposed that the process taking place at these negative potentials (that we called partial reduction) transforms the newly generated oxidised active centres in partially reduced ones, more suitable for the HPE process.

In order to better understand the previous described behaviour and to improve the electrocatalytic properties of graphite for HPE, we carried out similar tests concerning the graphite electroactivation using CHV between several values of oxidation (+0.5, +0.8, +1.1 and +1.35 V) and partial reduction (-0.4, -0.8 and -1.1 V) potentials. Based strictly on comparative observations of I_r and I_d values, we conclude that the best results concerning the HPE efficiency increase were obtained when the graphite electrode was subjected to oxidation potential values between +0.5 V and +0.8 V and the partial reduction that followed the anodisation took place at -0.8 V. Another important finding was that the partial reduction potential value has a great importance and this sequence represents a key factor for the HPE efficiency increase. Accordingly, enhancements of HPE process could not be observed when the partial reduction potential was considerably different from -0.8 V. We explain this phenomenon by the fact that, at more positive values, the applied potentials were not negative enough for a proper electroreduction of the active centres. Contrarily, the active centres generated during anodisation were totally reduced or destroyed at potential values more negative than -0.8 V. Even though this manner of graphite electroactivation shows a promising HPE enhancement effect, unfortunately, it is time consuming and, consequently, inefficient for larger scale applications. Another approach using an original multi-step technique is further described.

2. Potentiostatic electroactivation using rectangular multi-step signal

The new proposed multi-impulse potentiostatic technique consists in a rapid switch between the potential values corresponding to the graphite electroactivation and HPE. Concretely, a programmed rectangular multi-step signal (RMSS), consisting of three specific potential values, was applied on the disk electrode. These values correspond to three processes: anodisation (1), partial reduction (2) and actual HPE (3), also named production sequence (PS). The anodisation sequence (AS) and the partial reduction sequence (PRS) were provided for the graphite electroactivation while the third one was used to evaluate the effect of this electroactivation on the HPE process efficiency.

During the AS a positive potential was applied to the disk electrode for a short time period with the purpose to generate active centres on the graphite surface in their oxidized form. To partially reduce the newly generated active centres, a negative potential value was applied during the PRS, for a similar period. Finally, a less negative potential value was applied in the PS for a longer period of time and the HPE efficiency was evaluated based on I_r evolution. The partially reduced active centres presented a poor stability and for this reason I_r decreased over a rather short period of time (≈ 10 seconds). Taking this into account we considered that the electroactivation process needs to be periodically repeated, including all the potential sequences described above. We performed this type of experiments and as an example, in Figure 2 we present the results obtained using a RMSS for five consecutive cycles, at three different oxidation potential values.

Comparing the presented I_r values with those obtained in a steady-state potentiostatic HPE experiment (I_r around 1.1 µA), it can be noticed a great increase of H_2O_2 production immediately after each electroactivation phase. Unfortunately, the recorded I_d values attain very high values during the AS and PRS. As a consequence, even if the HPE is enhanced in the PS, this increase becomes insignificant because of the huge energy consumption during the electroactivation sequences.

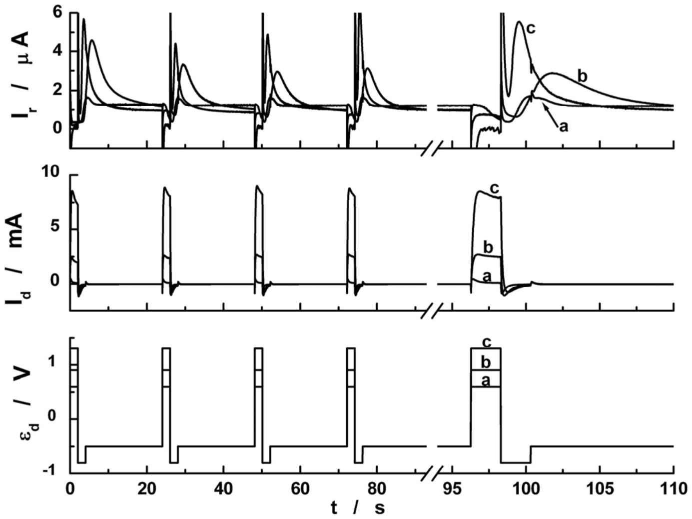

Figure 2. The influence of the disk applied potential (ε_d) on the currents recorded on disk (I_d) and ring (I_r) for different values of the oxidation potential: a) +0.6 V; b) +0.9 V; c) +1.3 V. Experimental conditions: volumetric flow rate (V_f) = 1.42 mL/min.; $t_{AS} = t_{PRS}$ = 2 s; t_{PS} = 20 s; ε_{PRS} = -0.8 V; ε_{PS} = -0.5 V

In the attempt to enhance the HEP process and to reduce the energy consumption, we perform several measurements using the RMSS in different experimental conditions: potentials ranged between +0.5 and +2.0 V for anodisation, -0.4 and -1.0 V for partial reduction and -0.6 and -0.1 V for peroxide PS and steps duration from 0.5 to 10 s for activation and from 20 to 200 s for PS.

Unfortunately, the very high currents recorded during the activation steps allowed us to make only relative comparisons between the effects of the different sets of experimental conditions, without a real possibility to evaluate the current efficiency (CE) or the specific energy consumption (SEC). Consequently, we appreciate that the best results were obtained for potentials of +1.1 V for anodisation, -0.8 V for partial reduction and -0.5 V for the PS, respectively. Concerning the steps duration, the best results were achieved at 2 s for AS and PRS and at 20 s for the PS.

The measurements based on the RMSS also confirmed that the PRS is essential in the graphite electroactivation process because the enhancement of HPE efficiency was not observed when this step was skipped. Based on previous observed phenomena, in Table 1 we summarize the possible processes which we consider that can explain the large currents recorded on the disk in the electroactivation steps and also, the HEP improvement.

Table 1. Possible processes involved in the sequences of graphite electroactivation and peroxide production and their effect on HEP efficiency

Sequence	Processes	Eq.	PEUH[a]
AS	graphite $\rightarrow C_{ox}* + n^{b} e^-$	(1)	+
	$4 HO^- \rightarrow O_2 + 2 H_2O + 4 e^-$	(2)	+
	$C_{DL, PS} \rightarrow C_{DL, AS} + n e^-$	(3)	-
	$C_{red}* \rightarrow C_{ox}* + n e^-$	(4)	-
	$HO_2^- + HO^- \rightarrow O_2 + H_2O + 2 e^-$	(5)	-
PRS	$C_{ox}* + n e^- \rightarrow C_{red}*$	(6)	+
	$C_{DL, AS} + n e^- \rightarrow C_{DL, PRS}$	(7)	-
	$C_{red}* + n e^- \rightarrow$ graphite	(8)	-
	$O_2 + 2 H_2O + 4 e^- \rightarrow 4 HO^-$	(9)	-
	$HO_2^- + H_2O + 2 e^- \rightarrow 3 HO^-$	(10)	-
	$H_2O + 2 e^- \rightarrow H_2 + 2 HO^-$	(11)	-
PS	$O_2 + H_2O + 2 e^- \rightarrow HO_2^- + HO^-$	(12)	+
	$C_{red}* + O_2 + H_2O \rightarrow HO_2^- + HO^- + C_{ox}*$	(13)	+
	$C_{DL, PRS} \rightarrow C_{DL, PS} + n e^-$	(14)	-

[a] The process effect upon HPE efficiency: (+) positive; (-) negative

[b] n represents an indefinite number of electrons

First of all, due to the rectangular shape of the polarisation signal, the extremely large values of I_d at the beginning of each step can be attributed to the charging and discharging processes of the electrical double layer for each sequence: anodisation ($C_{DL, AS}$) partial reduction ($C_{DL, PRS)}$ and production ($C_{DL, PS}$), symbolised by the equations 3, 7 and 14.

A great amount from the recorded current during AS can be associated with the graphite anodisation, requesting important amount of energy to generate the active centres in their oxidized form (**$C_{ox}*$**), this being an important and mandatory process for the graphite electroactivation (Eq. 1) and favourable to our goal. Moreover, at higher positive potential values, the oxygen evolution reaction (Eq. 2) had a significant contribution to the large current observed. This process can increase the oxygen availability near and on the graphite surface, counterbalancing the low oxygen solubility in electrolyte and inducing a positive effect upon HPE. In parallel to the favourable processes, during the AS, the partially reduced active centres (**C_{red}***) could be oxidized (Eq. 4), loosing their electrocatalytic ability and also increasing the current consumption. Finally, the oxidation of generated hydrogen peroxide (Eq. 5) decreased HPE efficiency.

During PRS, we consider that the most favourable process for HPE enhancement consists in the partial reduction (Eq. 6) of the active centres generated upon anodisation (**C_{ox}***), these partially reduced active centres being able to catalyse the H_2O_2 synthesis (Eq.12). The side processes that took place during PRS were: the total reduction of the partially reduced active centres (Eq. 8), the total reduction of oxygen (Eq. 9), the subsequent oxidation of generated hydrogen peroxide (Eq. 10) and hydrogen evolution at excessive negative potential values (Eq. 11).

In the PS, carried out at less negative potentials than during PRS, the most important processes are the HPE (Eq. 12) and the peroxide synthesis (Eq. 13) catalysed by the partially reduced active centres generated is the previous sequences (AS and PRS), both processes having a positive effect upon HPE improvement. The latter process, described in Eq. 13, seems to be a pure chemical one, fact proved by several experiments carried out at disk potential around -0.25 V, when we record a significant I_r even if I_d is almost zero. Both processes described in Eq. 12 and 13 use the initial dissolved oxygen as well as the supplementary O_2 generated during AS (Eq. 2), the last one inducing a significant increase in peroxide production.

Based on the above described experimental results and processes from Table 1, we conclude that, comparing to the unmodified carbonaceous materials, the electroactivated graphite using RMSS is more efficient for HPE. Moreover, the described *in-situ* electroactivation technique can be conducted continuously, without periodical external electrode treatment such as mechanical, thermal or chemical modification, reducing the maintenance time and the required costs. Unfortunately, the great amount of electric energy employed in the electroactivation sequences cause a modest improvement of HPE. As a consequence, we decided to modify the shape of the disk applied signal in order to reduce the global energy consumption.

3. Potentiostatic electroactivation using multi-sequence signal of sweeps and plateaus

As resulting from the previous results, the extremely large values for I_d recorded when a cyclic RMSS was used have two main reasons: (i) the charging and discharging of the double layer and (ii) the undesired redox processes of some active centres and the products obtained in the previous sequence. It is worth to mention that these products (like H_2O_2 and O_2) can be adsorbed on the electrode surface and remain in the proximity of the electrode, further decreasing HPE efficiency. In order to reduce the mentioned disadvantages, we decided to change the shape of the applied signal, replacing the step potential changes between the desired potential values with linear sweeps, obtaining a new multi-sequence signal of sweeps and plateaus (MSSSP). It consists in a PS carried out at a constant potential value, followed by three sweeps used to reach the extreme potential values for anodisation, partial reduction and, finally, to return to the PS specific value. We replaced the RMSS with MSSSP considering that the current due to the charging and discharging of the double layer capacitance will be significantly decreased and the interest products could be transported further from the interface, diminishing their undesirable transformation. Moreover, this shape of the applied signal can better exploit the C_{red}*, diminishing their oxidation current during the AS.

A first set of measurements using MSSSP was carried out using ramps with low scan rates (10 mV/s) and, comparing to the experiments based on RMSS, the newly obtained results revealed a small decrease of the I_d during the electroactivation sequences and, also, an increase of HPE efficiency. Based on these promising results, we started a first optimisation study concerning the potential values for AS and PRS. In order to validate the results obtained by CHV, a PS of 20 s was added before each AS, at the potential value equal to the extreme potential value for PRS. The optimisation criterion was represented by the amount of electrogenerated peroxide during the 4th PRS normalised in respect to the value calculated for the first PRS, corresponding to the unmodified graphite. The relative amounts of H_2O_2 were calculated for several sets of extreme potential values for oxidation and partial reduction, all being presented in Table 2.

Table 2. The relative amount of electrogenerated peroxide during the 4th PRS for different values of extreme potentials for anodisation and partial reduction

Partial reduction minimum potential (V)	Anodisation maximum potential (V)			
	+0.5	+0.8	+1.1	+1.35
-0.4	0.59	0.66	1.19	0.92
-0.5	0.74	0.89	1.32	1.20
-0.6	0.85	0.88	1.31	1.12

As one can see, the optimal extreme values found were +1.1 V for the anodic process and -0.8 V for the partial reduction of the active centres. At low scan rates, the electroactivation process takes a relatively long time that causes very large electric energy consumption and for this reason we started a new set of optimisation experiments concerning the scan rates, values of 50, 100 and 200 mV/s were investigated. In order to increase the relevance of the findings, the duration of the experiments was extended up to 30 cycles/experiment, being comparable to long industrial approach. As an example, Figure 3 presents the results of the experiment where the best enhanced of HPE efficiency was observed when a scan rate of 100 mV/s was used for reaching the electroactivation potential values.

The experiments carried out at high scan rate revealed that the I_d values diminished, but remained still too large for an efficient and economical HPE process. As an example, from the data presented in Fig. 3, the amount of electrical charge used for electroactivation was around 100 times larger than that employed for HPE.

All the experiments described above allowed us to conclude that the new potentiostatic technique for graphite electroactivation, implying anodisation followed by partial reduction, has a positive effect for HPE, increasing the amount of H_2O_2 obtained during the production sequences. This electrical energy consumption was maximal for the RMSS experiments. In the case of MSSSP the energy consumption decreased when low scan rates were used, but the minimal value was obtained during the measurements using MSSSP with high scan rates.

Several other optimisation studies were carried out concerning the PS potential and duration and also the combination of different scan rates for the electroactivation sequences, all of them confirming the optimal values of -0.5 V for the PS potential and of 100 mV/s for the scan rate.

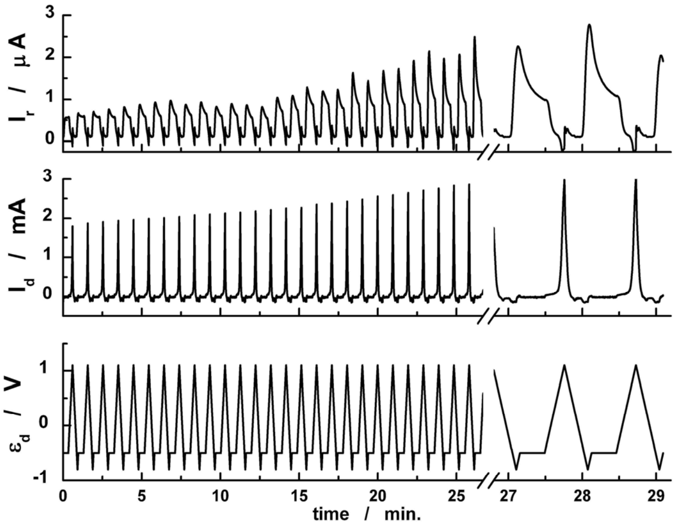

Figure 3. The correlation between the disk applied potential (ε_d) and the currents recorded on disk (I_d) and ring (I_r) for 30 cycles at high scan rate (100 mV/s) between the electro-activation and production sequences. Experimental conditions: volumetric flow rate (V_f) = 1.42 mL/min.; t_{PS} = 20 s; $\varepsilon_{AS, MAX}$ = +1.1 V;$\varepsilon_{PRS, MIN}$ = -0.8 V; ε_{PS} = -0.5 V

CONCLUSIONS

In order to increase the HPE efficiency on a graphite electrode, we developed a new electroactivation protocol consisting in the initial surface oxidation followed by a partial reduction. In this way, new active centres are generated on the graphite surface, but their stability is limited, requiring repeated electroactivation.

Consequently, a multi-sequence technique was proposed and tested in potentiostatic conditions. Based on the potentiostatic experiments, we conclude that, using this manner of graphite pretreatment, an enhancement in peroxide production could be obtained, the partial reduction of the newly generated active centres playing a key role in the process. The potentiostatic measurements allowed us to identify the possible processes involved in the electroactivation and production sequences. Because high current values were recorded on the disk electrode during electroactivation the multi-sequence electroactivation technique was applied using different signal shapes.

The energy consumption decreased for MSSSP signal carried out at low scan rates and the minimal value was obtained for the measurements using MSSSP with high scan rates.

EXPERIMENTAL SECTION

$K_4[Fe(CN)_6]$ and NaOH (purchased from Merck) were of analytical grade and were used as received. 1 M NaOH aqueous solution was used as supporting electrolyte for establishing the hydrodynamic condition and HPE investigation, respectively. All solutions were prepared with double distilled water (Double D Still, JENCONS, England).

The electrochemical measurements performed at room temperature (25 ± 1 ^{o}C) were carried out in controlled hydrodynamic conditions, using a wall-jet ring-disk electrode (WJRDE). The working electrode was a disk ($\varnothing$= 2.5 mm) of spectral graphite (Ringsdorff-Werke GmbH, Germany) and the ring electrode (I.D. = 3 mm, O.D. = 3.4 mm) was made of Pt. The counter electrode was a Pt wire. An Ag/AgCl/1 M KCl system was used as reference electrode (RE) and *all potential values presented are referred to this electrode*. A peristaltic pump (Reglo Analog, Ismatec, Switzerland), a wall-jet type cell (WJC) [22] and a fully computer controlled home-made bipotentiostat were also used. Applications elaborated using Labview software were exploited to control the experimental parameters and for data acquisition and treatment. Before each set of experiments, the WJRDE surface was polished on waterproof emery paper of 800 and 1200 grit (Struers, Denmark) and, subsequently, it was intensively washed with double distilled water.

Within measurements of hydrodynamic voltammetry with linear scan of the flow rate [23], the distance between the injector and disk electrode was fixed at 1 mm in order to achieve a planar parallel flow hydrodynamic regime in the WJC. The collecting efficiency (N) was evaluated using a 10 mM $K_4[Fe(CN)_6]$ solution in 1 M NaOH as supporting electrolyte and a value of 0.11 was obtained. N represents the ratio between the absolute values of the currents recorded on the ring and on the disk electrode. The current recorded on the disk electrode is due to $K_4[Fe(CN)_6]$ oxidation process, while the current on the ring is recorded when a fraction of $K_3[Fe(CN)_6]$ generated during the oxidation process on the disk is reduced to $K_4[Fe(CN)_6]$. For HPE experiments, an air saturated ($[O_2]$ ~ 8 ppm) aqueous solution of the supporting electrolyte, was pumped in the WJC at a volume flow rate of 1.42 mL/min. To evaluate the amount of hydrogen peroxide generated on the disk, the ring electrode was polarised at a constant potential value of +0.5 V, corresponding to the mass transport controlled domain for the H_2O_2 oxidation and an optimal signal to background ratio. Significant oxidation currents are usually recorded in strong alkaline media for Pt electrodes even at relatively low positive potential values (> +0.5 V) [24]. For this reason, we applied an oxidative pretreatment on the ring electrode in order to minimize the background recorded currents. This pretreatment consisted in oxidizing the ring at +0.8 V for 10 seconds and, afterwards, the applied potential was maintained at +0.5 V until a stable current value of +0.4 μA was recorded. Consequently, this background value was subtracted from all recorded ring currents.

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