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**”BABEŞ-BOLYAI” UNIVERSITY OF CLUJ NAPOCA**  
**FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING**

**HYDROGEN PEROXIDE ELECTROSYNTHESIS ON  
CATHODIC MATERIALS ACTIVATED BY  
ELECTROCHEMICAL TECHNIQUES**

*PhD Thesis Abstract*

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## Table of Contents

<b>INTRODUCTION</b>	<b>1</b>
<b>PART I</b>	
<b>LITERATURE DATA</b>	
<b>1. IMPORTANCE OF HYDROGEN PEROXIDE AND GENERAL SYNTHESIS METHODS</b>	<b>3</b>
<b>1.1. Hydrogen peroxide – depolluting agent</b>	<b>3</b>
<b>1.2. Methods for hydrogen peroxide synthesis</b>	<b>4</b>
<b>2. HYDROGEN PEROXIDE ELECTROSYNTHESIS BY CATHODIC REDUCTION OF THE OXYGEN</b>	<b>9</b>
<b>2.1. Electrode Materials</b>	<b>9</b>
2.1.1. Carbon and modified carbon electrodes	9
2.1.1.1. <i>Carbon electrodes modified with quinones</i>	10
2.1.1.2. <i>Carbon electrodes modified with conducting polymers</i>	15
2.1.1.3. <i>Carbon electrodes modified with metal complexes with organic macrocycles</i>	17
2.1.1.4. <i>Modified carbon electrodes subjected to ultrasounds</i>	18
2.1.2. Other types of electrode materials	19
<b>2.2. Mediated electrocatalytic oxygen reduction</b>	<b>22</b>
<b>2.3. Electrogenerated hydrogen peroxide applications</b>	<b>22</b>
2.3.1. Advanced oxidation processes (Fenton, electro-Fenton, photo/UV electro-Fenton)	23
2.3.2. Electrogenerated hydrogen peroxide for organic synthesis	24
<b>2.4. Enhancement of hydrogen peroxide electrosynthesis efficiency</b>	<b>27</b>
<b>2.5. Conclusions of the literature review</b>	<b>29</b>
<b>Annex I</b>	<b>32</b>
<b>PART II</b>	
<b>PERSONAL CONTRIBUTIONS</b>	
<b>3. ELECTROCHEMICAL METHODS, APPARATUS AND REAGENTS</b>	<b>38</b>
<b>3.1. Electrochemical methods</b>	<b>38</b>

3.1.1. Voltammetry	38
3.1.2. Hydrodynamic voltammetry	39
<b>3.2. Apparatus</b>	<b>42</b>
<b>3.3. Software</b>	<b>44</b>
<b>3.4. Reagents</b>	<b>45</b>
<b>4. POTENTIOSTATIC GRAPHITE ELECTROACTIVATION</b>	<b>46</b>
<b>4.1. Studies by cyclic hydrodynamic voltammetry</b>	<b>46</b>
4.1.1. Optimization of graphite anodizing potentials	48
4.1.2. Optimization of graphite partial reduction potentials	52
<b>4.2. Multi-impulse tests using rectangular signals</b>	<b>53</b>
4.2.1. Optimization of the parameters from the anodizing sequence	54
4.2.2. Optimization of the parameters from the partial reduction sequence	56
<b>4.3. Multi-impulse tests of ramps and plateaus applied signals</b>	<b>60</b>
4.3.1. Ramps carried out with low scan rates	61
4.3.2. Ramps carried out with high scan rates	66
4.3.3. Other attempts using ramps and plateaus applied signals	71
4.3.3.1. <i>The application of extended durations in different sequences</i>	71
4.3.3.2. <i>The use of low scan rates during different sequences</i>	74
<b>4.4. Concluding remarks for the potentiostatic graphite electroactivation</b>	<b>76</b>
<b>5. GALVANOSTATIC GRAPHITE ELECTROACTIVATION</b>	<b>78</b>
<b>5.1. Galvanostatic electroactivation using symmetrical linear scan</b>	<b>80</b>
<b>5.2. Tests using rectangular asymmetric current profiles</b>	<b>84</b>
5.2.1. Optimization of the parameters from the galvanostatic electroactivation sequences	84
5.2.2. Optimization of production sequence duration	85
<b>5.3. Galvanostatic autoadaptive graphite electroactivation</b>	<b>87</b>
<b>5.4. Optimization of the HPE process using the autoadaptive galvanostatic graphite electroactivation</b>	<b>92</b>
<b>5.5. Concluding remarks for the galvanostatic graphite electroactivation</b>	<b>94</b>
<b>6. FLOW SHEET FOR A PILOT PLANT FOR HPE BASED ON THE LABORATORY RESEARCH</b>	<b>98</b>
<b>7. GENERAL CONCLUSIONS</b>	<b>101</b>
<b>References</b>	<b>105</b>

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

#### List of symbols

$C_{DL}$	Double-layer capacitance (F)
$C_{ox}^*$	Active centres in oxidized form
$C_{red}^*$	Partially reduced active centres
I	Current (A)
N	Collecting efficiency
t	Time or duration (s)
v	Scan rate ( $V s^{-1}$ or $\mu A s^{-1}$ )
$V_f$	Volumetric flow rate ( $mL min^{-1}$ )
$\epsilon$	Electrode potential (V)

#### Subscripts

AS	Anodization sequence
d	Disk
MAX	Maximum
MIN	Minimum
PROG	Programmed
PRS	Partial reduction sequence
PS	Production sequence
r	Ring

#### Abbreviations

AqP	Anthraquinone process
AS	Anodization sequence
CE	Current efficiency
CHV	Cyclic hydrodynamic voltammetry
HPE	Hydrogen peroxide electrosynthesis
PRO	Partial reduction of oxygen
PRS	Partial reduction sequence
PS	Production sequence
RE	Reference electrode

## **Introduction**

The increased industrial activity caused severe pollution in the environment with dramatic consequences upon the atmosphere, water and soil. Consequently, a continuous interest arises for developing researches that offer solutions for an efficient removal of the pollutants [1].

An alternative for wastewater treatment could be the use of electrochemical technologies, which have the advantage of being versatile, compatible with the environment and cost efficient [1]. By using these technologies, it is possible to destroy or to modify some refractory organic compounds, as well as to lower the toxicity and to remove pigments and colorants by partially oxidizing the organic compounds [2].

For this purpose it is possible to electrogenerate the chemical oxidant (chlorine, hypochlorite or hydrogen peroxide) which reacts with the pollutants [2]. Among these chemicals, hydrogen peroxide has the unique property of decomposing to water and oxygen and thus, it does not generate other substances that are polluting or incompatible with the environment [3]. Hydrogen peroxide has numerous applications which include its use in: “green” organic chemistry for highly selective oxidation processes and epoxidation; pulp and paper bleaching; almost all industrial fields, with emphasis on the chemical industry and environmental protection [4-43].

## **Literature Data**

Due to the numerous applications of hydrogen peroxide, an enhanced interest for the electrosynthesis of this valuable chemical is noticed. The electrosynthesis process constitutes an alternative to the actual almost exclusive  $\text{H}_2\text{O}_2$  production practice, which is the anthraquinone process. This process requires important energy consumption and generates waste.

Hydrogen peroxide electrosynthesis by cathodic reduction of the oxygen has to overcome difficulties such as: the low solubility of the oxygen, the subsequent reduction of the electrosynthesized hydrogen peroxide and the slow reaction rate.

The electrocatalytic system (the electrode material and the electrolyte) is important for obtaining an enhanced reaction rate and selectivity for hydrogen peroxide synthesis. The electrode material influences significantly the hydrogen peroxide electrosynthesis (HPE) process. The electrode surface modification by using different chemical and electrochemical methods can be used in order to enhance its electrocatalytic ability.

Even though, at the moment, a generally accepted mechanism for the oxygen reduction does not exist [44-46], it is generally accepted that a fast reduction involving 4 electrons can take place without generating intermediary products (hydrogen peroxide) or a slow bielectronic reduction can occur, generating  $H_2O_2$ .

Among the cathodic electrode materials, carbon [47] has an important role due to the special native abilities for the hydrogen peroxide electrosynthesis. These properties of carbon materials refer to the presence of functional oxygen containing groups on the electrode surface which get involved in the 2 electron reduction of the oxygen.

Many researchers agree [48-64] that the most important role in oxygen reduction to peroxide can be attributed to the quinone type functionalities present on the surface of carbon electrodes. For this reason, the attempt to modify the carbon electrodes with quinone functionalities is a procedure commonly used in order to enhance the catalytic properties of the carbon electrodes and the best results are obtained for phenantrenquinone [65-69].

Conducting polymers [70,71] can serve as basis for electrocatalyst's application on carbon with a very efficient dispersion of the catalyst.

Gold is another electrode material that has good selectivity for hydrogen peroxide electrosynthesis. Using ultrasounds seems to improve the efficiency of the electrosynthesis process [40-43].

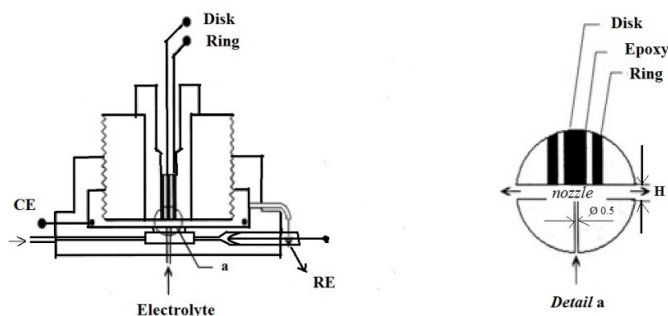
Given the complexity of the processes involved in the oxygen reduction, the further studies should better explain the oxygen interaction with different electrode materials in order to optimize the process. A special attention should be paid to the study of carbon or modified carbon materials that have special abilities for  $H_2O_2$  electrosynthesis and are also cheap and abundant.

## Original contributions

### 3. ELECTROCHEMICAL METHODS, APPARATUS AND REAGENTS

The electrochemical methods used were cyclic voltammetry and hydrodynamic voltammetry on the disk electrode in the WJRDE (wall-jet ring-disk electrode) system.

The electrochemical measurements were carried out using a wall-jet ring-disk electrode (WJRDE) system that has a four-electrode configuration (**Figure 1.**): the disk electrode that is also the working electrode, concentric to the disk electrode is the ring electrode kept at a fix potential during the measurements, the counter electrode and the reference electrode. The electrolyte is introduced perpendicularly and axially to the disk electrode surface in the fix disk-ring assembly.



**Figure 1.** Wall-jet cell system equipped with a ring-disk electrode

The polarization of the working electrode is carried out following a previously established programme, while the ring electrode is polarized at constant potential value in order to detect the hydrogen peroxide produced on the graphite disk electrode

### 4. POTENTIOSTATIC GRAPHITE ELECTROACTIVATION

The research aimed to improve the electrocatalytic capacity of a graphite electrode for the hydrogen peroxide electrosynthesis (HPE) process by the partial reduction of the oxygen (PRO). The new electrode material was obtained by activation through the electrochemical modification of a pyrolytic graphite electrode.

#### **4.1. Studies by cyclic hydrodynamic voltammetry**

Literature data [60] points out that, after anodization, the graphite electrodes become more active for the complete reduction of oxygen, without an increase in HPE efficiency. The result of the graphite anodization consists, in the first step, in an enhanced hydrogen peroxide production, but the subsequent peroxide reduction reaction is also electrocatalyzed by the anodized graphite. As a consequence, by simply anodizing the graphite this becomes more active for the total reduction of the oxygen to water.

The first tests were carried out in order to try a possible graphite electroactivation using cyclic hydrodynamic voltammetry (CHV) between several values of anodic and cathodic potential values [72, 73].

During these tests it was noticed that if the graphite electrode was initially oxidized at positive potential values and afterwards was subsequently reduced at cathodic potential values, an important enhancement in the ring current value could be registered when the disk electrode was polarized at the less negative potential values, where the partial reduction of oxygen (PRO) took place.

This could be explained by the fact that, during the anodic treatment, active centres were generated in their oxidized form (e.g. organic radicals or quinone functionalities) which became partially reduced when they were subjected to negative potential values. These new active centres, in their partially reduced form, are responsible for the enhancement of the HPE process. It was noticed also that the partial reduction of the active centres constitutes a key step in the graphite electroactivation process, confirmed by the fact that the above mentioned enhancement in the ring current value could not be observed when the graphite was only anodized (no partial reduction).

These first tests of CHV constituted a fundamental study and only qualitative considerations were made. Even though this manner of graphite electroactivation shows a promising HPE enhancement effect, unfortunately, the technique is time consuming and, consequently, inefficient for larger scale applications. For these reasons, another approach was tried during the research: the idea to apply a new multi-step technique for the graphite electroactivation.

#### **4.2. Multi-impulse tests using rectangular signal**

The new proposed multi-impulse potentiostatic technique [74, 75] consists in a rapid switch between the potential values corresponding to the graphite electroactivation



and HPE. Concretely, a programmed rectangular multi-step signal, consisting of three specific potential values corresponding to the processes: anodization (1), partial reduction (2) and, actual HPE (3), also named production sequence (PS), was applied on the disk electrode.

For this purpose, a Labview application has been developed which allowed the application of the desired signal on the disk electrode. The screenshot of the software application can be seen in **Figure 2**, where the experimental parameters variation domains and their online evolution can be seen. The specific screenshot (**Figure 2**) was made for the case where the disk electrode is activated through the multi-impulse potentiostatic technique.

The enhancement of the HPE efficiency using the multi-impulse electro-activation technique could be observed when a rectangular shape potential signal was applied on the disk electrode. This signal is constituted by three distinct potential steps, described as follows:

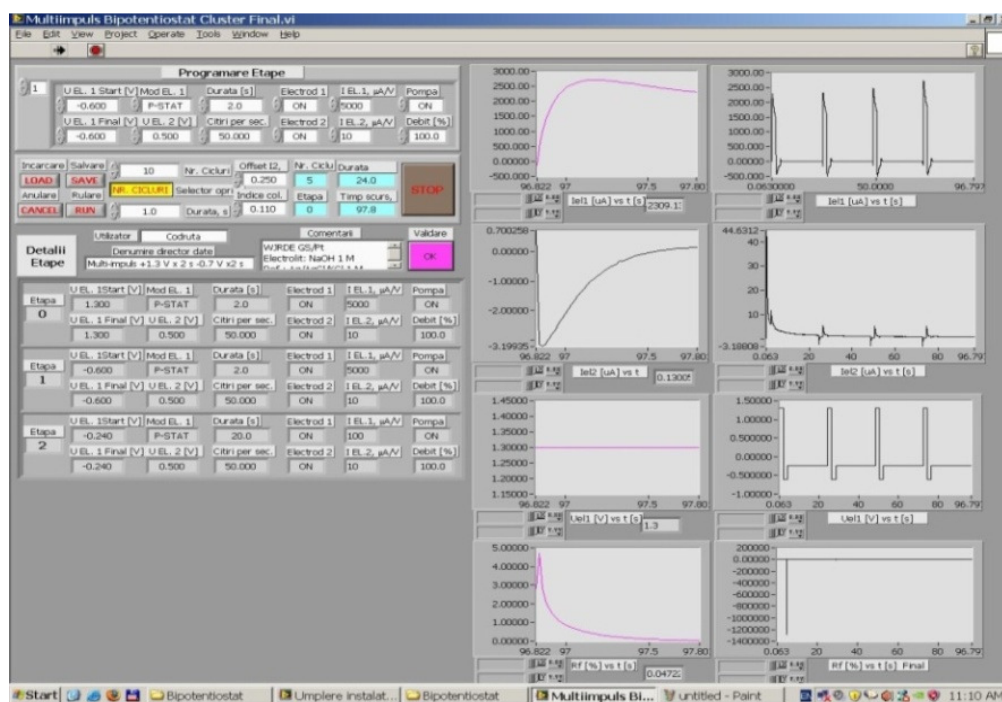
**I. Anodization Sequence** – the graphite electrode is polarized at positive potential values, during a certain time interval, in order to generate active centres in their oxidized form on the electrode surface.

**II. Partial Reduction Sequence** – when the potential is switched and maintained for a short time period to negative values in order to partially reduce the active centres generated in the first sequence.

**III. Hydrogen peroxide electrosynthesis sequence** – the potential is switched and maintained to less negative potential values compared to the values used for the partial reduction of the active centres. During this sequence the effect of the graphite electroactivation upon the enhancement of the HPE process can be evaluated based on the current values registered on the ring electrode.

The practical way to perform the graphite electroactivation consisted in potentiostatic experiments in order to optimize the parameters for each sequence. In **Figure 3** is shown the optimization of the anodization potential for three different potential values.

Considering the current values registered on the ring electrode during these experiments it was noticed that the stability of the generated active centres is limited, requiring a periodic reactivation of the electrode surface. The multi-impulse technique allows such a periodic activation of the graphite surface by repeating, in a programmed manner, the three potential step sequences which were described previously.



**Figure 2.** Screenshot of the experimental parameters variation domains and their real time evolution

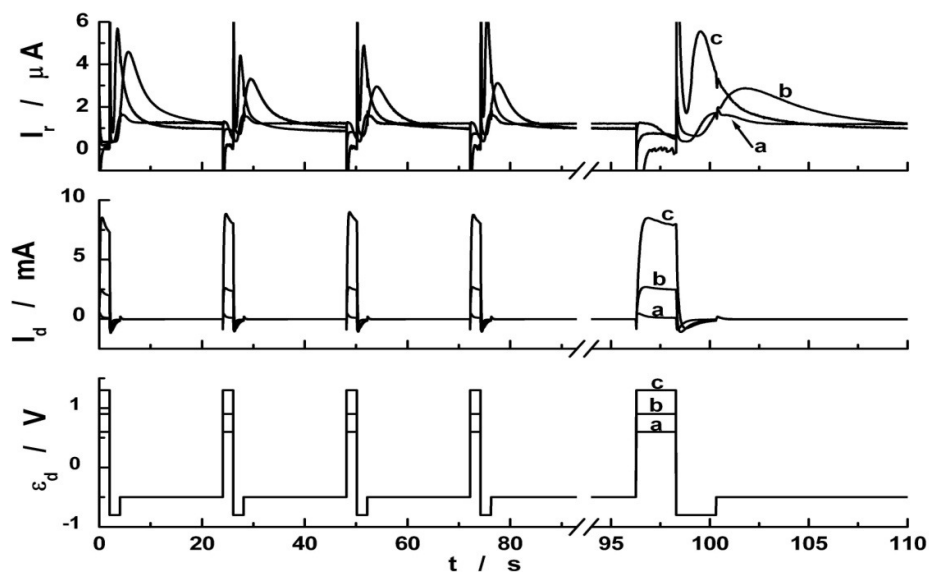
As a result of the optimization of the graphite electroactivation parameters, by using the multi-impulse technique, we could appreciate that this type of electroactivation results in an enhancement of the HPE efficiency. By increasing the anodization potential value, the efficiency of the HPE process increased, but no optimal value could be established at this point. Moreover, a time interval of 2 second for the anodization process generated the best results.

When the cathodic potential values used for the partial reduction of the active centres became more negative, the efficiency of the HPE process decreased. For a time interval of 2 seconds during the anodization sequence, the optimal time interval for the partial reduction is also 2 seconds.

The high amplitude currents registered on the disk electrode during the electroactivation sequences make the observed positive effect very small when we take into account the costs implied by the electroactivation.

In this context an attempt was made in order to explain the huge currents registered on the disk during the electroactivation sequences. The processes that can possibly contribute to

the high current value on the disk electrode for each electroactivation sequence are reviewed in **Table 1**.



**Figure 3.** The influence of the disk applied potential ( $\epsilon_d$ ) on the currents recorded on the disk ( $I_d$ ) and ring ( $I_r$ ), during five consecutive cycles, for different values of the oxidation potential: a) +0.6 V; b) +0.9 V; c) +1.3 V. Experimental conditions:  $V_f = 1.42$  mL/min.;  $t_{AS} = t_{PRS} = 2$  s;  $t_{PS} = 20$  s;  $\epsilon_{PRS} = -0.8$  V;  $\epsilon_{PS} = -0.26$  V.

Firstly, due to the rectangular shape of the signal the high current at the beginning of each sequence can be attributed to the double layer charging/discharging processes symbolized by equations 3, 7 and 14.

A large part of the current registered during anodization sequence can be associated with this process that requires a high energy consumption in order to generate the active centres in their oxidized form ( $(C_{ox}^*)$ , Ec. 1).

Supplementary, at high positive potentials oxygen evolution (Ec. 2) has a significant contribution to the high current observed. Also, during the anodization sequence, the active centres partially reduced ( $(C_{red}^*)$ ) can be oxidized (Ec. 4) and they lose the electrocatalytic ability. Also their oxidation increases the energy consumption.

The oxidation of the hydrogen peroxide electrogenerated is another unfavourable process that can undergo during anodization (Ec. 5), diminishing the HPE process efficiency as well.

We considered that the most favourable process for an efficient HPE during the partial reduction sequence consists in the partial reduction (Ec. 6) of the active centres

generated during anodization ( $C_{ox}^*$ ). These new active centres, partially reduced, are able to electrocatalyze the synthesis of hydrogen peroxide (Ec. 12).

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

Sequence	Processes	Equation	PEUH <sup>a</sup>
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)	-
	$C_{red}^* + n e^- \rightarrow \text{graphite}$	(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)	-

<sup>a</sup> The process effect upon HPE efficiency: (+) positive; (-) negative

<sup>b</sup> n represents an indefinite number of electrons

The unfavourable processes that can take place during this sequence are: the total reduction of the partially reduced active centres (Ec. 8), the total reduction of the oxygen (Ec. 9), the subsequent reduction of the generated hydrogen peroxide (Ec. 10) and hydrogen evolution at excessive negative potential values on the disk electrode (Ec. 11).

The most important processes that take place during the production sequence at less negative potential values than for the partial reduction are: HPE (Ec. 12) and hydrogen peroxide synthesis (Ec. 13). Both processes are catalyzed by the partially reduced active centres generated during the previous sequences (anodization and partial reduction) and have a positive effect upon HPE efficiency.

Taking into account the promising results, the researches continued in the attempt to reduce the excessive current values registered on the disk electrode during the electroactivation sequences. For this purpose we tried an optimization of the signal shape by eliminating the sudden variations of the potential values applied to the disk electrode.

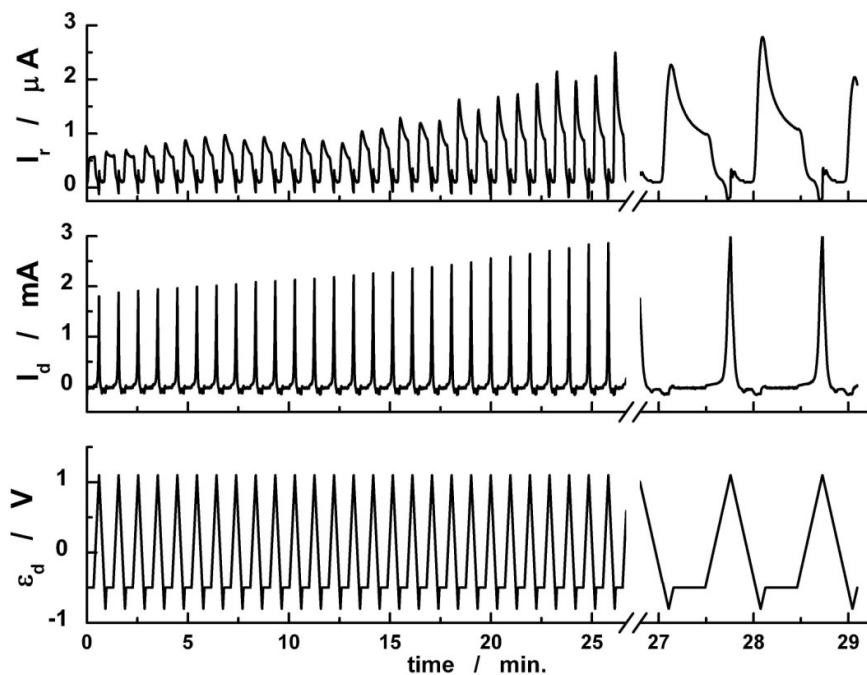
### 4.3. Multi-impulse tests of ramps and plateaus applied signals

In the new technique the switch between potential values during the electroactivation sequences was replaced with linear ramps for reaching the electroactivation potential values and a plateau during HPE [76, 77].

In an attempt to reduce the high currents registered on the disk as a result of the double layer capacity charging/discharging processes, ramps obtained by applying low scan rates (10 mV/s), between the potential values applied for electroactivation, were used.

For the new ramps and plateaus applied signals, even though the currents are smaller than in the case of the rectangular signal shape, the current values are still very high during electroactivation.

Similar to the CHV tests, the extended time needed for the electroactivation sequences, when low scan rates were used, is energetically inefficient and impossible to scale-up for an industrial application. A possible solution could consist in reaching the electroactivation potential values by applying high scan rates.



**Figure 4.** The correlation between the disk applied potential ( $\epsilon_d$ ) and the currents recorded on disk ( $I_d$ ) and ring ( $I_r$ ) for 30 cycles at high scan rate (100 mV/s) between the electroactivation and production sequences. Experimental conditions:  $V_f = 1.42$  mL/min.;  $t_{PS} = 20$  s;  $\epsilon_{AS, MAX} = +1.1$  V;  $\epsilon_{PRS, MIN} = -0.8$  V;  $\epsilon_{PS} = -0.5$  V.

As can be seen in **Figure 4**, when high scan rates were employed, the current values on the disk increased with every cycle. The ring currents had a positive trend, which

was confirmed by the values obtained when integrating the ring currents generated in the production sequence of each cycle. According to these values, the optimal scan rate value was 100 mV/s.

Unfortunately, the problem of the high disk currents was not adequately resolved even when using high scan rates during the electroactivation sequences

## **5. GALVANOSTATIC GRAPHITE ELECTROACTIVATION**

Considering that the potentiostatic electroactivation of the graphite implies large energy consumption for all the signals applied to the disk electrode, a new approach consisting in galvanostatic activation of the graphite was used [78].

### **5.1. Galvanostatic electroactivation using symmetrical linear scan**

Taking into account the fact that the main deficiency of the potentiostatic electroactivation is the excessive electrical energy needed for the activation sequences, the idea of applying periodic current inversions to the graphite electrode emerged.

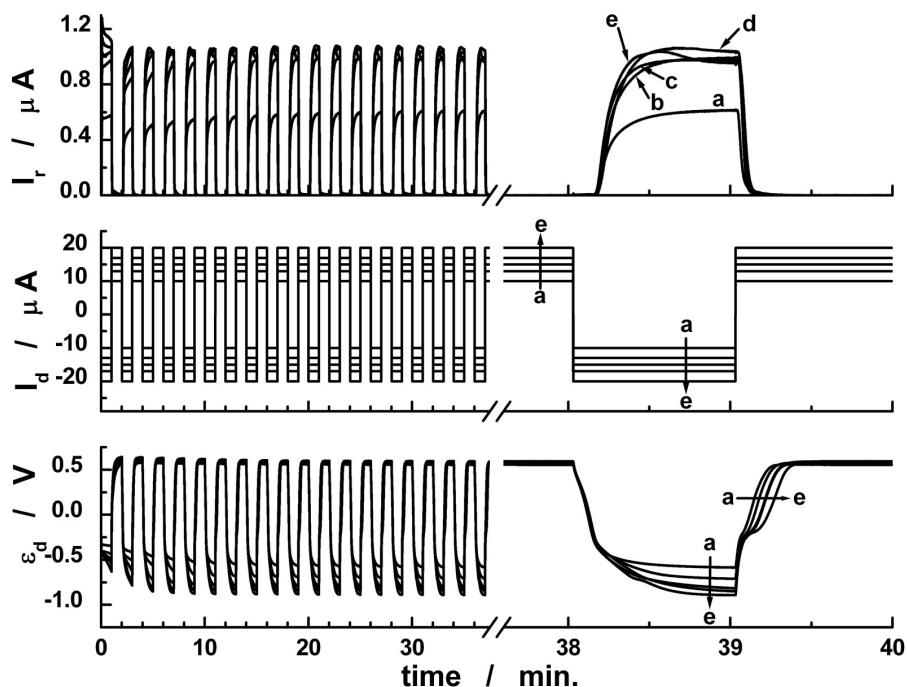
In this way, one can hope that, when on one electrode the anodization process is carried out, simultaneously, on the other electrode, the partial reduction of the active centres generated upon anodization takes place and, afterwards, the HPE process. Subsequently, when switching the polarities of the electrodes, the processes would interchange, allowing a periodic reactivation of the graphite electrode without wasting energy.

In order to test the above idea, the current was varied through the graphite electrode, in a cyclic manner, between symmetrical (positive and negative) values, in the same WJRDE system. This allowed us to observe the evolution of the disk potential values and the scanning effect upon the current on the ring ( $I_r$ ).

The disk potential values that were registered at the disk electrode interface had a slow evolution and consequently, it was concluded that a rectangular current profile could be applied without the risk of sudden and extreme potential jumps.

For the next set of experiments, a symmetrical rectangular current profile was applied to the disk electrode consisting in switching every 60 s between symmetrical positive and negative current values of  $\pm 10 \mu\text{A}$ ,  $\pm 13 \mu\text{A}$ ,  $\pm 15 \mu\text{A}$ ,  $\pm 17 \mu\text{A}$  and  $\pm 20 \mu\text{A}$ , a number of 20 consecutive cycles being recorded for each experiment. The comparative responses concerning the evolution of the disk potential as well as of  $I_r$  are presented in **Figure 5**.

The main purpose of the research using symmetrical signals (galvanostatic, triangular or rectangular) was to evaluate the possibility to scale up this application to industrial level.



**Figure 5.** The influence of the disk applied current ( $I_d$ ) on the recorded disk potential ( $\epsilon_d$ ) and ring current ( $I_r$ ) for 20 cycles at different symmetric  $I_d$  values of: a)  $\pm 10 \mu\text{A}$ ; b)  $\pm 13 \mu\text{A}$ ; c)  $\pm 15 \mu\text{A}$ ; d)  $\pm 17 \mu\text{A}$ ; e)  $\pm 20 \mu\text{A}$ . Experimental conditions:  $V_f = 1.42 \text{ mL/min.}$ ;  $t_{AS} = t_{PRS\&PS} = 60 \text{ s.}$

The industrial application would consist in an electrochemical reactor with two compartments equipped with identical electrodes, placed in a symmetric arrangement. In this industrial application the polarities of the electrodes would be switched periodically, allowing the reactivation of the graphite electrode without wasting energy.

The results of the tests carried out were promising, yet some technical problems need to be solved in order to evacuate the electrolyte from the cathodic compartment before switching the electrodes' polarity.

## 5.2. Tests using rectangular asymmetric current profiles

An alternative to the industrial application proposed above, could consist in a two compartment electrochemical reactor where the graphite electrode is used as cathode and is electroactivated periodically in galvanostatic mode.

A new type of experiments was designed in order to evaluate the efficiency of this industrial application. For these measurements, we used the same WJRDE system and the applied current was controlled using a rectangular asymmetric signal. This signal included the three current steps, corresponding to the already described processes for the potentiostatic electroactivation experiments: anodization, partial reduction and hydrogen peroxide production.

As a result of these experiments it was found that the optimal solution for graphite galvanostatic electroactivation consisted in anodizing the disk electrode at +100  $\mu\text{A}$  for 2 seconds and partial reduction at -100  $\mu\text{A}$  for 1.5 seconds. By comparing the evolution of the currents on the ring electrode during the experiments for the optimization of the production sequence, the best results were obtained for a 60 seconds HPE time interval.

From another point of view, it is worth to mention that the amount of electrical energy used during the electroactivation sequences had reasonable values, representing around 30 % from the global energy consumption. Moreover, an increase of the HPE efficiency of approx. 35 %, compared to the unmodified graphite electrode, was evaluated.

### **5.3. Galvanostatic autoadaptive graphite electroactivation**

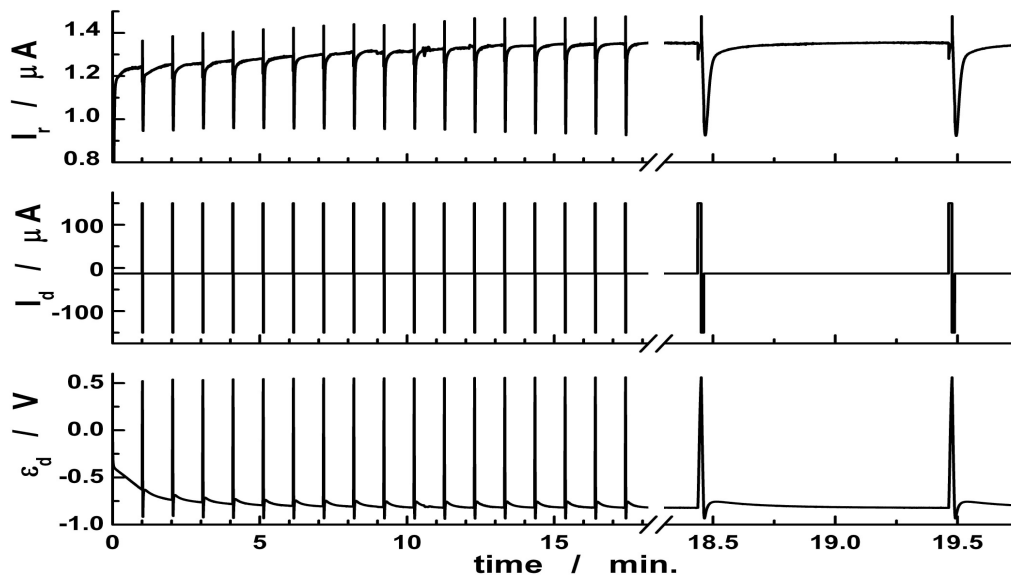
Based on the previous results, we concluded that the galvanostatic electroactivation of the graphite using an asymmetrical rectangular signal did not allow a rigorous control, for an extended period of time, of the disk potential values reached during the electroactivation sequences: anodization, partial reduction and hydrogen peroxide production. This is caused by the continuous modification of the electrode surface and, consequently, the electroactivation parameters must be continuously re-adjusted [79].

Since the initially designed Labview application allowed us to set only fixed sequence duration, it was modified in order to allow an autoadaptive control of the electroactivation and HPE processes.

Based on this new set of measurements, we concluded that the best limitative potential values were +0.5 V for the anodization and -0.8 V for the partial reduction sequences, respectively. In **Figure 6**, a progressive enhancement of the HPE efficiency can be observed.

It is worth mentioning that, comparing to the asymmetric galvanostatic experiments, the graphite electroactivation with the autoadaptive technique allowed the reduction of electrical energy used during electroactivation, the new evaluated value representing around 20 % from the global energy consumption.





**Figure 6** The evolution of the disk potential ( $\epsilon_d$ ), disk applied current ( $I_d$ ) and ring current ( $I_r$ ) for 20 cycles of galvanostatic autoadaptive electroactivation. Experimental conditions:  $V_f = 1.42$  mL/min.;  $\epsilon_{AS, PROG} = +0.5$  V;  $\epsilon_{PRS, PROG} = -0.8$  V;  $t_{PS} = 60$  s;  $I_{d, AS} = +150$   $\mu$ A;  $I_{d, PRS} = -150$   $\mu$ A;  $I_{d, PS} = -13$   $\mu$ A.

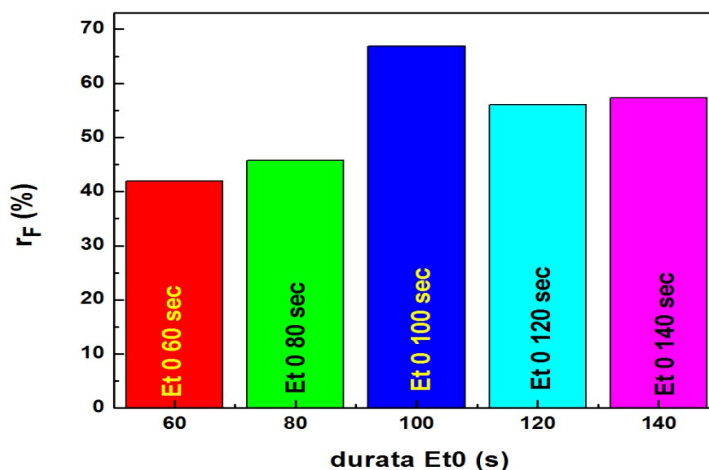
#### 5.4. Optimization of HPE process using the autoadaptive galvanostatic graphite electroactivation

Considering the favourable results, the research continued in order to optimize the positive effect of the autoadaptive galvanostatic electroactivation. Concretely, long duration experiments were carried out for optimizing the production duration (60, 80, 100, 120 and 140 seconds respectively) during 100 cycles for each experiment.

The experiments were designed in this manner in order to obtain information regarding the extended galvanostatic exploitation of the graphite. For these experiments the best limitative potential values already determined (+0.5 V for the anodization and -0.8 V for the partial reduction) were used. The results of these experiments are presented in **Figure 7**.

## 6. FLOW SHEET FOR A PILOT PLANT FOR HPE BASED ON THE LABORATORY RESEARCH

Based on the thesis results, a technological plan for HPE was proposed. This contains an electrochemical reactor with two buffer reservoirs: one for the NaOH 1 M electrolyte solution, which initially feeds the plant and one used for the recirculation of the solution that contains hydrogen peroxide.



**Figure 7** The current efficiency (CE) for HPE production sequence optimization experiments (60, 80, 100, 120 and 140 seconds) using the graphite autoadaptive galvanostatic electroactivation

The electrochemical reactor is compartmented by a cation exchange membrane and the electrodes used (the anode and cathode) are made of graphite and have the same surface area. The reactor is galvanostatically operated, by applying the autoadaptive technique for a periodic electroactivation of the cathode.

## 7. GENERAL CONCLUSIONS

The main personal contributions to the thesis are:

An investigation technique for the oxygen reduction reaction, based on the WJRDE system, was designed. Using this technique, several experimental protocols based on potentiostatic and galvanostatic control were elaborated in order to investigate the electrode processes.

The software elaborated specially for these studies allows the facile programming of the experimental parameters. It also facilitates the optimization process of these parameters when the proposed new multi-impulse technique is employed.

### *The potentiostatic experiments showed:*

- ✓ When anodizing the graphite electrode, new active centres are generated on the graphite surface

✓ The active centres (most probably of quinonic type) are in an oxidized form, unable to electrocatalyze the hydrogen peroxide electrosynthesis.

✓ By partially reducing the active centres, an important enhancement of hydrogen peroxide production is obtained.

✓ The active centres partially reduced are capable to generate  $H_2O_2$  also by a pure chemical mechanism, fact confirmed by the detection of hydrogen peroxide on the ring electrode when the disk current is almost zero.

✓ The stability of the active centres generated is limited and requires a periodic reactivation of the electrode surface.

✓ Even if the described graphite activation determines an enhancement in the hydrogen peroxide production, the energy consumption during the electroactivation sequences is very large and it needs to be diminished.

✓ In order to diminish the energy consumption different signals (ramps and plateaus carried out with different scan rates) were applied to the graphite electrode;

✓ When ramps obtained by using low scan rates are employed (2 – 10 mV/s) the energy consumption is still large;

✓ By applying high scan rates (100 mV/s) the energy consumption diminishes slightly.

***The galvanostatic experiments showed:***

✓ In this type of electroactivation it is possible to control the potential values by choosing the appropriate current densities applied on the graphite disk;

✓ The HPE in galvanostatic mode results in a gradual deactivation of the graphite electrode, as a consequence the electroactivation appears as a necessity;

✓ The galvanostatic electroactivation using symmetrical linear scan experiments showed:

➤ the potentials registered at the disk electrode interface have a slow evolution;

➤ it is possible to apply a rectangular current profile without the risk to register extreme and sudden potential jumps;

✓ The galvanostatic electroactivation experiments using rectangular current profiles showed:

➤ it is possible to control the potential values by appropriately choosing the charge quantity consumed

✓ The evaluation of HPE process efficiency in galvanostatic mode by applying a three sequence rectangular signal (for anodization, partial reduction and H<sub>2</sub>O<sub>2</sub> production) showed:

- the optimal anodization current is +100 μA applied on the disk for 2 seconds;
- the optimal partial reduction current is -100 μA applied on the disk for 1.5 seconds;
- an optimal production sequence of 60 seconds was determined;
- the electrical energy used for electroactivation is about 30% from the global energy consumption;
- the HPE process efficiency when the galvanostatic technique is employed is 35% higher than for the unactivated graphite electrode;
  - using a rectangular polarizing current for fixed time intervals unfavourable potential values (too negative) can be reached;
  - to avoid this, the initial Labview application was modified in order to allow an autoadaptive control of the electroactivation sequences and the HPE process;

✓ The autoadaptive control of the electroactivation and of the HPE process allowed the optimization of the limiting potential values: +0,5 V for the anodization process and -0,8 V for the partial reduction process when a progressive enhancement of the HPE process is obtained;

✓ When the autoadaptive technique was used, a further reduction of the electric energy used for electroactivation is registered, the new value representing about 20% from the global energy consumption;

✓ The experiments for the optimization of the production sequence during 100 cycles showed that the maximal efficiency of the HPE process is obtained for duration of production of 100 seconds.

✓ Based on the thesis results a technological plan for HPE was proposed.

✓ Compared to the optimal parameters determined from the lab scale experiments, using a WJRDE system, the pilot plant described above could be operated using improved parameters by using turbulent flow conditions that could intensify the mass transport to the electrodes.

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