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# STUDY OF HYDROGEN PEROXIDE ELECTROSYNTHESIS ON ELECTROCHEMICALY MODIFIED GRAPHITE USING A WJRDE

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**ABSTRACT.** The hydrogen peroxide electrosynthesis by partial reduction of oxygen represents an attractive alternative to the anthraquinone process. The result presented in this paper show that the two steps electro-activation of a graphite electrode, consisting in the oxidizing of the surface followed by the partial reduction of the active sites generated upon oxidation, induces an improvement of hydrogen peroxide electrosynthesis efficiency. Because the stability of the generated active sites is limited, a special programmable cyclic multi-step technique was used and the experimental parameters were optimized for a rectangular shape applied potential. In order to understand the electrosynthesis mechanism and to optimize the electro-activation potentials, cyclic hydrodynamic voltammetry studies were performed. For all the measurements, a wall-jet ring disk electrode was used.

**Keywords:** oxygen reduction, hydrogen peroxide electrosynthesis, electrochemical activation, graphite.

## INTRODUCTION

The hydrogen peroxide (HP) is an environmental friendly oxidizing agent with many applications in the pulp industry, organic and inorganic synthesis and waste water treatment [1, 2, 3, 4, 5]. It is worth to note the exceptional ability of HP for pollution control due to the fact that it is transformed into noncontaminant products such as water and oxygen. For example, HP can reduce the environmental impact caused by chlorine based oxidants. In wastewater treatment, HP can oxidize organic pollutants to $CO_2$, offering, in comparison to traditional biodegradation methods, several advantages in terms of treatment rate, cost and availability [3].

Presently, HP is produced mainly by the “anthraquinone process” (AqP). The electrochemical methods based on the two-electron reduction of oxygen offer some important advantages over the AqP, including higher purity, greater safety and also less separation steps, unwanted by-products and environmental concerns [2]. Considering this, the Hydrogen Peroxide Electrosynthesis by Partial Reduction of Oxygen (HPEPRO) has received increased attention during the last two decades as an alternative to the AqP process.

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The electrochemical reduction of oxygen on bulk carbon electrodes has been intensively studied because this material is electrocatalytically active for $O_2$ reduction in alkaline media [6,7,8]. Modified and unmodified carbonaceous materials are widely used for HPEPRO, a special attention being accorded to the graphite [7,8]. The native ability of carbonaceous materials to electrocatalyse the peroxide formation in alkaline solution was related to the high concentration of active centers on the surface of this electrode material. The chemical nature of active sites on graphite surfaces and how these affect electron transfer reactions have been the subject of many studies and suppositions [9,10,11,12,13 ].

In order to obtain increased electrocatalytical properties for HPERDO, the graphite surface can be modified through an electrochemical activation [11]. Unfortunately, this modification of the graphite surface also catalyzes the unwanted reaction corresponding to the subsequent reduction of the peroxide. This unwanted reaction lowers the selectivity of the graphite electrode for HPERDO and the efficiency of the electrosynthesis process.

In this work, the effect of graphite surface electroactivation upon HPEPRO efficiency was studied. In order to overcome the drawback of the electrochemical activation, a special programmable multi-step technique was elaborated.

## RESULTS AND DISCUSSION

Based on our previous researches [8], a similar experimental setup based on a wall-jet ring-disk electrode (WJRDE) was used, the main difference consisting of the replacement of the inox ring electrode with a Pt one. The evaluation of the hydrodynamic parameters of the new WJRDE (collection factor and the type of flow regime) was performed using a 2 mM $K_3[Fe(CN)_6]$ in 1 M KCl as supporting electrolyte. During all other measurements, for the detection of the generated $H_2O_2$, the ring was polarized at +0.5 V/RE.

In order to evaluate the effect of graphite surface electroactivation upon HPEPRO efficiency, a special programmable multi-step technique was elaborate. It consists of a cyclic three potential steps program. In the first step, in order to generate new activated sites, the graphite surface was oxidized at potentials between +1.0 and +1.5 V/RE. During the second step, the active centers formed in the first step were partially reduced at disk potentials between -0.6 and -0.8 V/RE. In the final step, the HPEPRO efficiency was evaluated at disk potentials between -0.2 and -0.3 V/RE. An example of the applied potential on the disk electrode and the corresponding currents recorded on disk and ring electrodes for 5 repeated experiments is presented in Figure 1.

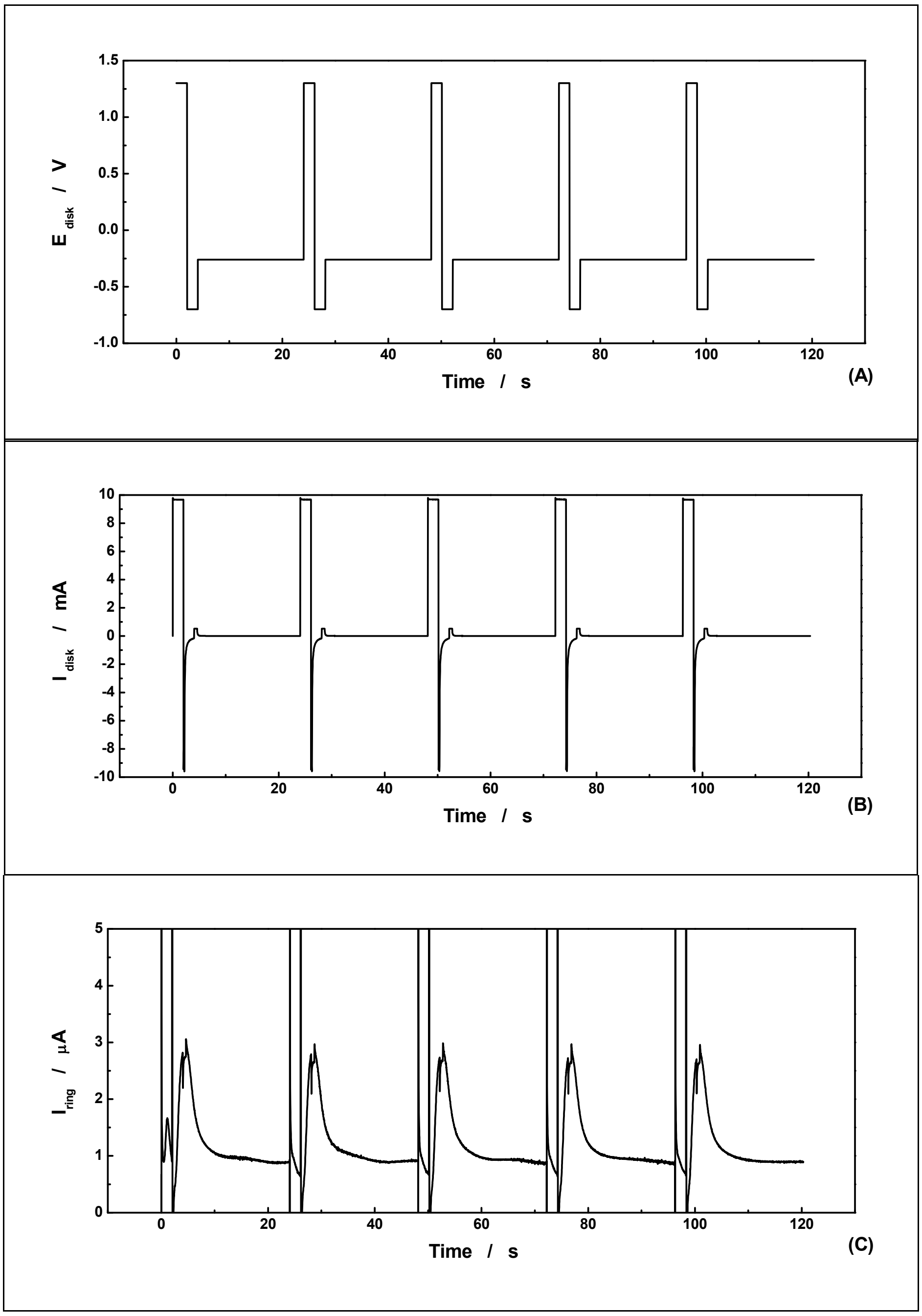

**Figure 1.** Applied potential on the disk (A) and the recorded currents on disk (B) and ring (C) for graphite oxidation at +1.3 V for 2 s, reduction at -0.7 V for 2 s and hydrogen peroxide generation at -0.26 V for 20 s (5 repeated experiments).

In the first step, activated sites are generated on the graphite surface, but they are in an oxidized form, incapable to electrocatalyse HPEPRO. We observed that the partial reduction of these active sites during the second step induces a significant improvement of hydrogen peroxide production.

The oxidative pre-treatment of the electrode surface, followed by partial reduction of the active sites allows the shift of the HPEPRO towards more positive values, which is an argument for the increase of the electrocatalytic properties of the modified graphite surface. We observed that the active sites in their partially reduced form, obtained by this original technique, are capable to generate hydrogen peroxide also through a pure chemical path. These active sites are, most probably, oxygen containing functional groups in their partially reduced form, very similar to the native functional groups of the graphite surface, considered responsible for the electrocatalytic properties of this material in the HPEPRO.

Based on the recorded currents on the ring electrode (see Figure 1.C), we concluded that the stability of the generated active sites is limited, requiring a periodic reactivation of the surface. For this reason, a special programmable multi-step technique was elaborated and employed. This technique allows the periodic reactivation of the graphite by cyclically repeating, in a programmed manner, the three potential steps described above.

The Figure 1.B and 1.C shows that the above described pre-treatment produces a net growth of the hydrogen peroxide yield during the third step, but the energy consumption during the first two steps is very large. This huge energy consumption is due to the large currents involved in (i) the oxidation and partial reduction of the graphite surface, (ii) the charge/discharge of the double layer capacitance, (iii) the adsorption / desorption of the reagents and products and also (iv) in the oxidation / reduction of the adsorbed electroactive species. From another point of view, the period of the three described steps plays also an important role in the energy consumption and the HPEPRO efficiency. Based on these information, a preliminary optimization study was performed using the described rectangular shape of the applied disk potential. The best result was obtained at the experimental parameters described in Figure 1.

In order to understand better the HPEPRO mechanism and to establish the optimum electro-activation potentials for the active sites' generation, we performed cyclic hydrodynamic voltammetry (CHV) studies, monitoring the produced HP on the ring electrode.

For the optimization of the oxidation potential (corresponding to the first step), the CHV measurements were performed starting from -0.8 V/RE and using different return potentials, the obtained results being presented in Figure 2.

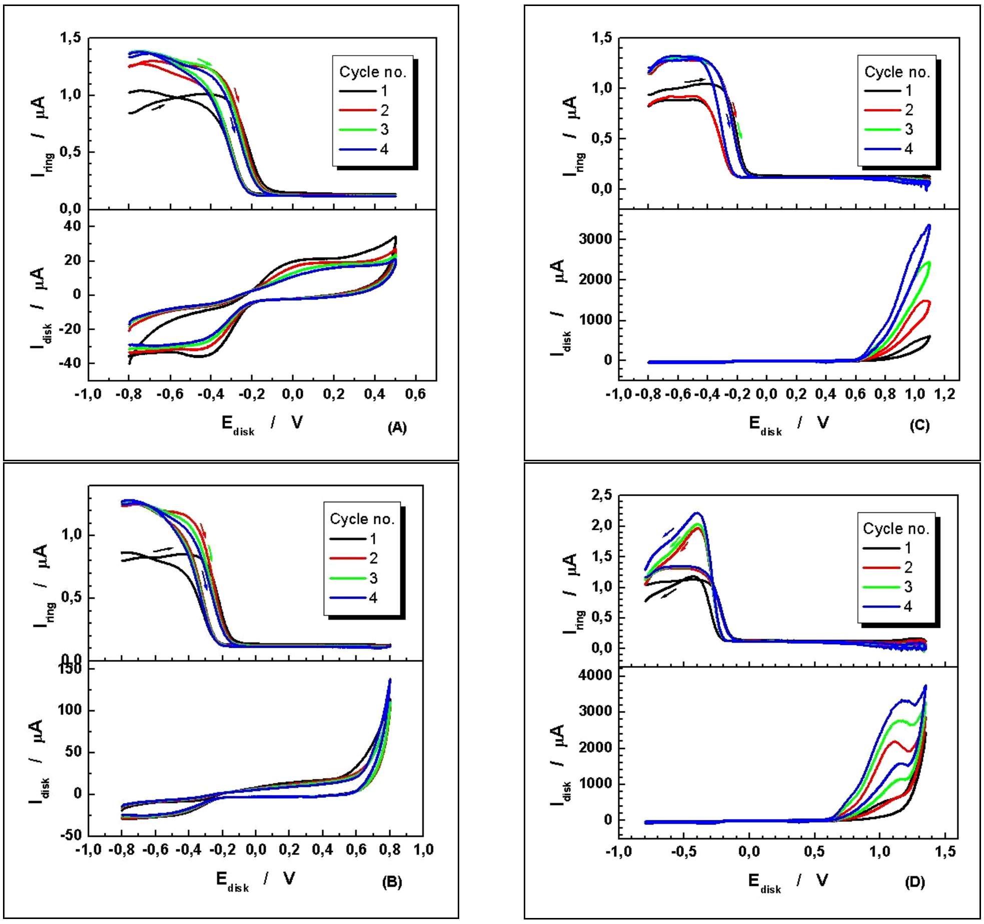

**Figure 2.** Influence of the oxidation potential upon HPERDO for cyclic hydrodynamic voltametry between - 0.8 V and + 0.5 V (A), + 0.8 V (B),+1.1 V (C), +1.35 V (D)

As it can be seen from Figure 2, the best results are obtained when the disk is oxidized at potential values between +0.5 and +0.8 V/RE. At higher oxidizing potentials (see Figure 2.C and 2.D), HPERDO is still improved, but the currents recorded on the disk are very large due to the oxygen evolution. This thing makes insignificant the obtained positive result (increased HP productivity) due to the high energy consumption.

In order to optimize the potential for the partial reduction of the active sites (corresponding to the second step), the CHV measurements were performed using the same return potential (+0.8 V/RE) and different starting potential values between -0.4 and -1.1 V/RE, the obtained results are presented in Figure 3.

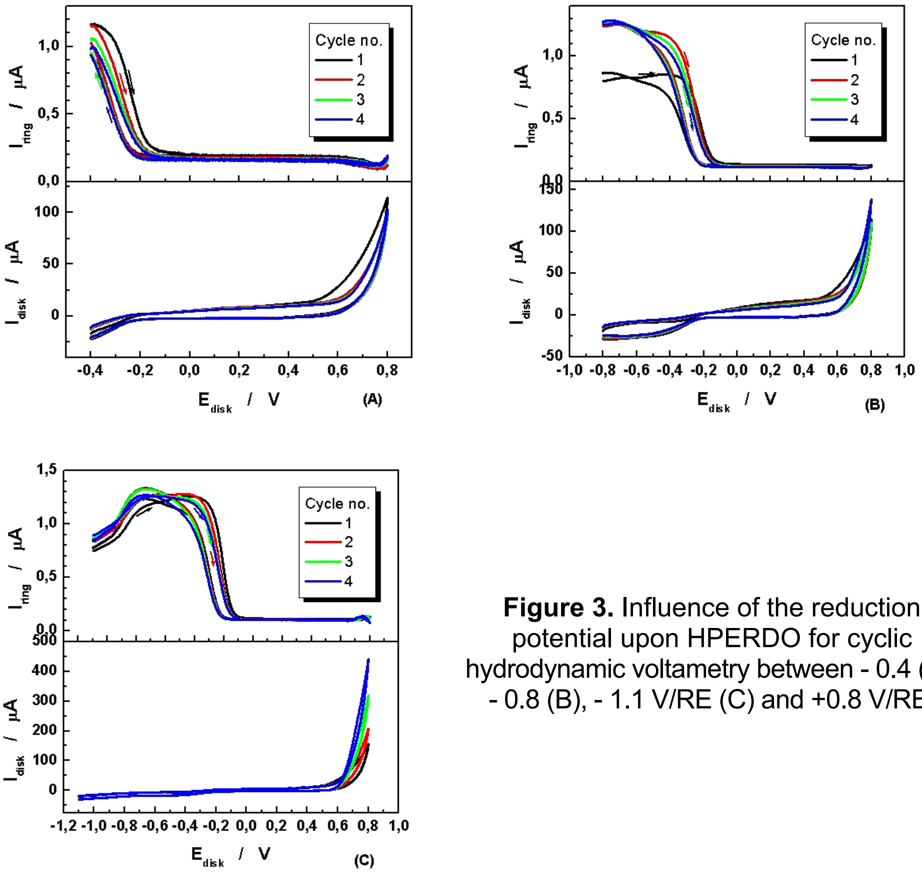

**Figure 3.** Influence of the reduction potential upon HPERDO for cyclic hydrodynamic voltametry between - 0.4 (A), - 0.8 (B), - 1.1 V/RE (C) and +0.8 V/RE.

Figure 3 shows that the applied potential for the partial reduction of the active sites generated by graphite surface oxidation is a key step for HPERDO and the optimum value is around -0.8 V/RE. For more positive potentials no effect can be observed and, for more negative potentials, the active centers are probably destroyed.

## CONCLUSIONS

Contrary to some previous results presented in the literature [11], our results show that the electrocatalytic activity of the graphite towards HPEPRO can be increased by electrochemical pre-treatment. The proposed electro-activation of the graphite electrode consists of two steps, involving the oxidation of the surface followed by the partial reduction of the species generated upon oxidation.

Due to the fact that the stability of the generated active sites is limited, a special programmable cyclic multi-step technique was designed and used. The experimental parameters were optimized for a rectangular shape applied potential, but the recorded energy consumption remains still high.

The promising results obtained require that further investigations should take place in order to minimize the energy consumption of the first two steps.

## EXPERIMENTAL SECTION

The electrochemical measurements were carried out in controlled hydrodynamic conditions, using a wall-jet ring-disc electrode (WJRDE). A disc (∅= 2.5 mm) of spectral graphite (Ringsdorff-Werke GmbH, Germany) was used as working electrode and the ring electrode (I.D. = 3 mm, O.D. = 3.5 mm) was made of Pt. The CE was a Pt wire and an Ag/AgCl/1M KCl system was used as reference electrode (RE). A peristaltic pump (Reglo Digital, Ismatec, Switzerland), a home-made wall-jet cell (WJC) [8] and a fully computer controlled home-made bipotentiostat were also used. Applications elaborated with the Labview 8.5 software were used to control the experimental parameters and data acquisition. The distance between the injector and disc electrode was fixed at 1 mm. The hydrodynamic regime - planar parallel flow was established using the method described in our previous paper [8]. The collecting efficiency (N) were evaluated using a 2 mM $K_3[Fe(CN)_6]$ solution in 1 M KCl as supporting electrolyte. For HPEPRO experiments, an air saturated ($[O_2]$ ~ 8 ppm) aqueous electrolyte, containing 1 M NaOH as supporting electrolyte, was pumped in the WJC at a volume flow rate of 1.42 mL/min.

### ACKNOWLEDGMENTS

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