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# Studies on the Electrocatalytic Reduction of Hydrogen Peroxide on a Glassy Carbon Electrode Modified With a Ruthenium Oxide Hexacyanoferrate Film

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The electrocatalytic reduction of hydrogen peroxide on a glassy carbon (GC) electrode modified with a ruthenium oxide hexacyanoferrate (RuOHCF) was investigated using rotating disc electrode (RDE) voltammetry aiming to improve the performance of the sensor for hydrogen peroxide detection. The influence of parameters such as rotation speed, film thickness and hydrogen peroxide concentration indicated that the rate of the cross-chemical reaction between Ru(II) centres immobilized into the film and hydrogen peroxide controls the overall process. The kinetic regime could be classified as LS*k* mechanism, according to the diagnostic table proposed by Albery and Hillman, and the kinetic constant of the mediated process was found to be 706 $mol^{-1}$ $cm^3$ $s^{-1}$. In the LS*k* case the reaction layer is located at a finite layer close to the modifier layer/solution interface

**Keywords:** Albery-Hillman´s diagnostic table, modified electrode, rotating disc electrode, electrocatalysis, hydrogen peroxide.

## 1. INTRODUCTION

Amperometric sensors for hydrogen peroxide present several applications, such as in environmental, pharmaceutical, medicine, food samples and as disinfectant and bleaching agent in various industrial and household products [1-3]. Their advantages are based on low detection limits, large dynamic concentration range, good selectivity, rapid response time and inherent miniaturization and portability. However, these features depend on the use of mediators capable of recognizing the analyte in complex samples. Several chemical compounds have been attached onto the electrode to minimize the energy required in the electrochemical reduction of hydrogen peroxide [4-12]. Recently,

we have reported the development of a glassy carbon electrode coated with an electrodeposited film of ruthenium(III) oxide hexacyanoferrate (RuOHCF) for the determination of 2´-deoxyguanosine [13], ascorbate [14, 15] and hydrogen peroxide [16]. At surfaces containing this chemical modifier, hydrogen peroxide is electrocatalytically reduced at 0.0 V, allowing amperometric determinations with a low limit of detection (1.7 μmol $L^{-1}$) [17] and good selectivity. To our knowledge, until now, there is no detailed study on the mechanism of the electrocatalytic reduction of $H_2O_2$ on RuOHCF films. Hence, in the present work the kinetics of the reaction involving hydrogen peroxide and immobilized Ru (II) centers was investigated by using rotating disc electrode (RDE) voltammetry. Data were analyzed with the model developed by Albery and Hillman [18, 19], which allows a full characterization of the electrocatalytic process based on the limiting current dependence upon rotation speed, film thickness and substrate concentration.

## 2. EXPERIMENTAL SECTION

### *2.1. Chemicals, materials and samples*

All solid reagents were of analytical grade and were used without further purification. The solutions were prepared by dissolving the reagents in deionized water processed through a water purification system (Nanopure Infinity, Barnstead). Potassium ferricyanide, potassium chloride, potassium permanganate, hydrogen peroxide, sulfuric acid and ferric chloride were obtained from Merck (Darmstadt, Germany) and ruthenium (III) chloride was obtained from Alfa Aesar (Massachusetts, USA). Hydrogen peroxide solutions were daily prepared from a 30% m/m stock solution and standardized as reported in the literature [20].

### *2.2. Electrodes and instrumentation*

An Autolab PGSTAT 30 (Eco Chemie) bipotentiostat with data acquisition software made available by the manufacturer (GPES 4.8 version) was used for electrochemical measurements. A homemade Ag/AgCl (saturated KCl) and a platinum wire were used as reference and counter electrodes, respectively. Voltammetry with a glassy carbon rotating disc electrode (RDE) was carried out using an analytical rotator (AFMSRX, Pine Instrument Company) connected to the potentiostat. Atomic force microscope images were obtained with a 5500 Atomic Force Microscope (AFM) (N9410S). Experiments were carried out using a 1 $cm^2$ glassy carbon plate (Alfa Aesar, Massachusetts, USA).

### *2.3. Modification of the Electrode Surface*

The surface of the GC electrode was polished with alumina suspension (1 μm, Alfa Aesar, Massachusetts, USA) on a microcloth polishing pad, rinsed with water and sonicated for five minutes in distilled water. The electrodeposition of the ruthenium oxide hexacyanoferrate film onto the surface

of the glassy carbon electrode was performed by repetitive sweeping at the potential limits of -0.5 and 1.3 V at 100 mV $s^{-1}$ in a solution containing 0.5 mol $L^{-1}$ KCl + 0.05 mol $L^{-1}$ HCl + 1mmol $L^{-1}$ $K_3Fe(CN)_6$ + 1 mmol $L^{-1}$ $RuCl_3$. The stability of the modified electrode was verified by recording cyclic voltammograms with the modified electrode in a supporting electrolyte solution containing 0.5 mol $L^{-1}$ KCl + 0.05 mol $L^{-1}$ HCl at the same potential limits.

## 3. RESULTS AND DISCUSSION

### *3.1. Electrochemical behavior of the RuOHCF modified electrode*

AFM was used to confirm the electrodeposition of the RuOHCF film. Fig.1 depicts 3D views of AFM images obtained for a freshly polished bare glassy carbon electrode before and after the film deposition.

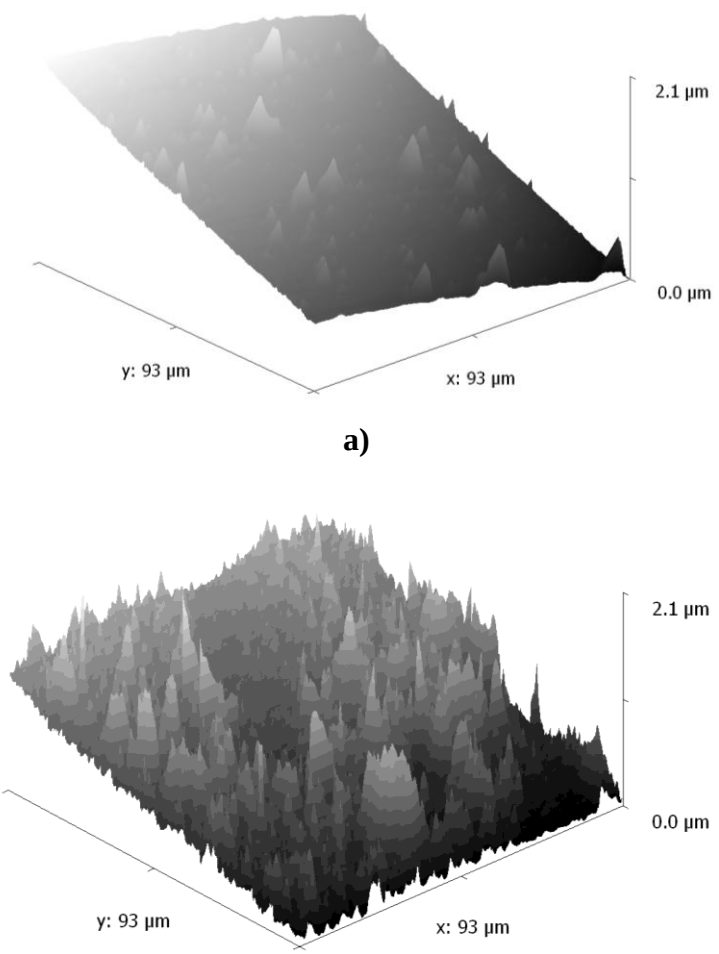



**Figure 1.** AFM-images of the glassy carbon surface before (A) and after (B) electrodeposition of a RuOHCF film ($\Gamma = 9.16\times10^{-9}$ mol $cm^{-2}$).

At the conditions described in the Experimental section for the film deposition [13, 21], an extremely rough surface is obtained as a consequence of the growth of an insoluble material with a heterogeneous morphology, and the surface area is largely increased (average maximum height of the roughness 0.052 and 0.485 µm, respectively, for a bare and a modified electrode).

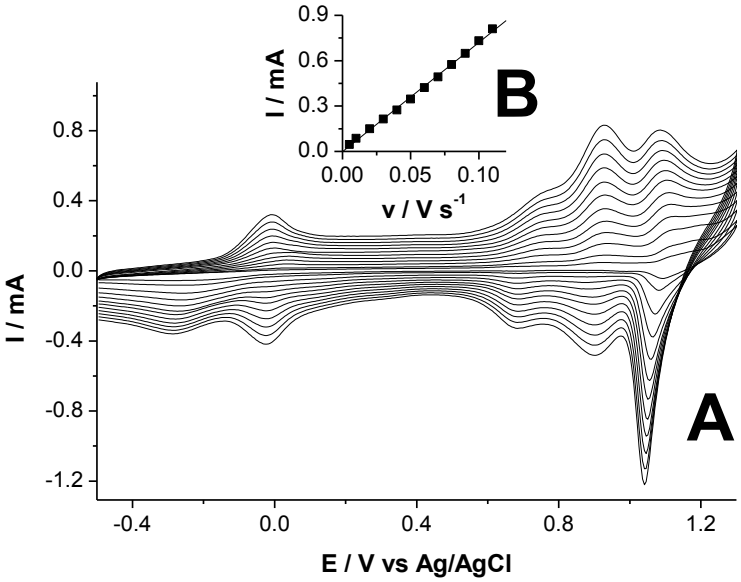



**Figure 2**. Cyclic voltammograms recorded in a solution containing 0.5 mol $L^{-1}$ KCl and 0.05 mol $L^{-1}$ HCl using a RuOHCF modified electrode ($\Gamma = 9.16\times10^{-9}$ mol $cm^{-2}$) at different scan rates (A). Linear relationship between peak current values (measured at 0.93 V) and scan rate (B).

The effect of the scan rate on the electrochemical behavior of the RuOHCF modified electrode was studied as shown in Fig. 2. A linear correlation between current (measured at 0.93 V) corresponding to the Ru(III)/Ru(IV) couple and scan rate indicates that the flow of electrons inside the film is fast. Fig 2 B shows a linear relationship between peak current and scan rate, contrary to what is expected when the process is controlled by diffusion of an electroactive species in solution. Such behavior is typical for modified electrodes that exhibit reversible redox process [22].

### *3.2. Electrocatalytic reduction of hydrogen peroxide*

The electrocatalytic activity of the modified electrode towards the cathodic reduction of hydrogen peroxide is presented in Fig. 3. After the addition of hydrogen peroxide, a significant current enhancement is seen at around 0.0 V with a simultaneous decrease in the corresponding anodic peak. This observation is a clear evidence of electrocatalysis, attributable to the reaction of electrogenerated Ru(II) centers with diffusing hydrogen peroxide according to the following equation:

$$2KRu^{II}[Fe^{II}(CN)_6] + H_2O_2 + 2H^+ \rightleftharpoons 2Ru^{III}[Fe^{II}(CN)_6] + 2K^+ + 2H_2O \qquad (1)$$

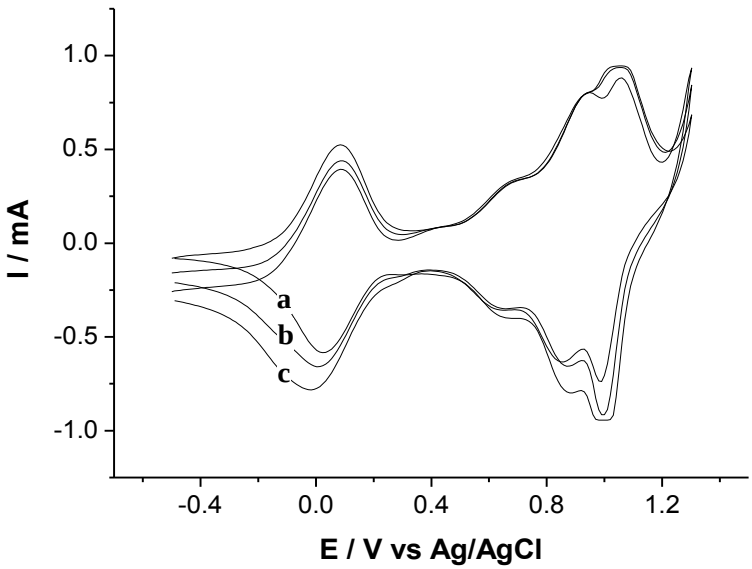



**Figure 3.** Cyclic voltammograms recorded in a solution containing 0.5 mol L KCl + 0.05 mol $L^{-1}$ HCl before (a) and after (b,c) addition of hydrogen peroxide (final concentration 2.45 (b) and 4.82 (c) mmol $L^{-1}$) by using a RuOHCF modified electrode ($\Gamma$=9.16×$10^{-9}$ mol $cm^{-2}$). Scan rate = 25 mV $s^{-1}$

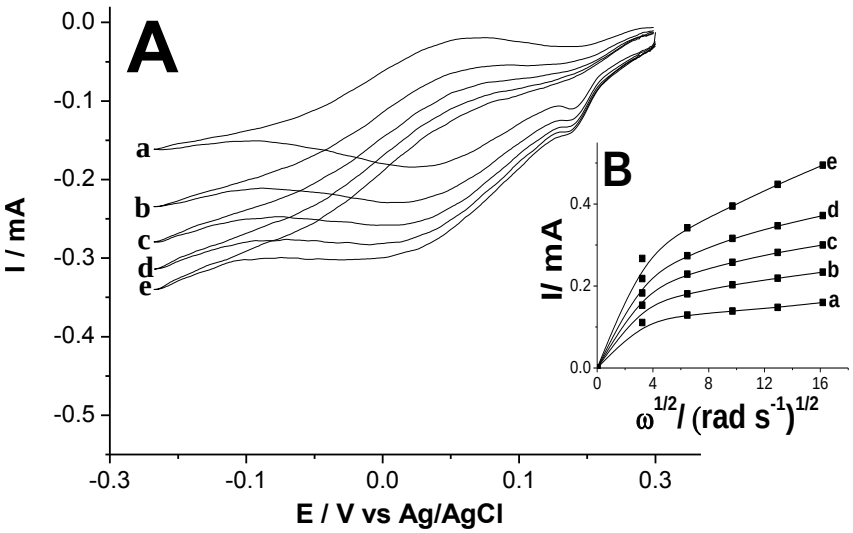



**Figure 4.** Cyclic voltammograms (A) recorded in a solution containing 2.45 mmol $L^{-1}$ $H_2O_2$ + 0.5 mol $L^{-1}$ KCl + 0.05 mol $L^{-1}$ HCl using a RuOHCF modified electrode ($\Gamma$ = 9.16×$10^{-9}$ mol $cm^{-2}$) at different rotation speeds: 100 rpm (a), 400 rpm (b), 900 rpm (c), 1600 rpm (d) and 2500 rpm (e). Scan rate: 20 mV $s^{-1}$. Levich plots (B) for the reduction of hydrogen peroxide at different concentrations: 1.00 (a), 1.82 (b), 2.45 (c), 3.43(d) and 4.82 mmol $L^{-1}$ (e) using a RuOHCF modified electrode.

In order to investigate in more details the electrocatalytic process, modified electrodes were used in rotating disc electrode voltammetric experiments. Data were obtained with different rotation speeds, film thickness and hydrogen peroxide concentration to obtain information on the possible rate-

determining step as well as on the location of the reaction zone. Fig. 4A shows voltammograms recorded at different rotation speeds with a RuOHCF modified electrode ($\Gamma = 9.16\times10^{-9}$ mol cm$^{-2}$) in supporting electrolyte solution containing hydrogen peroxide at a fixed concentration. Enhanced limiting currents in voltammograms recorded at increased mass transport conditions are observed. Similar RDE voltammetric experiments were carried out by varying the concentration of hydrogen peroxide. The Levich plots shown in Fig. 4B demonstrate that at relatively high rotation rates the electrode response to hydrogen peroxide is no longer only limited by diffusion, but also by the kinetics of the reaction between catalytic sites of the film and the substrate.

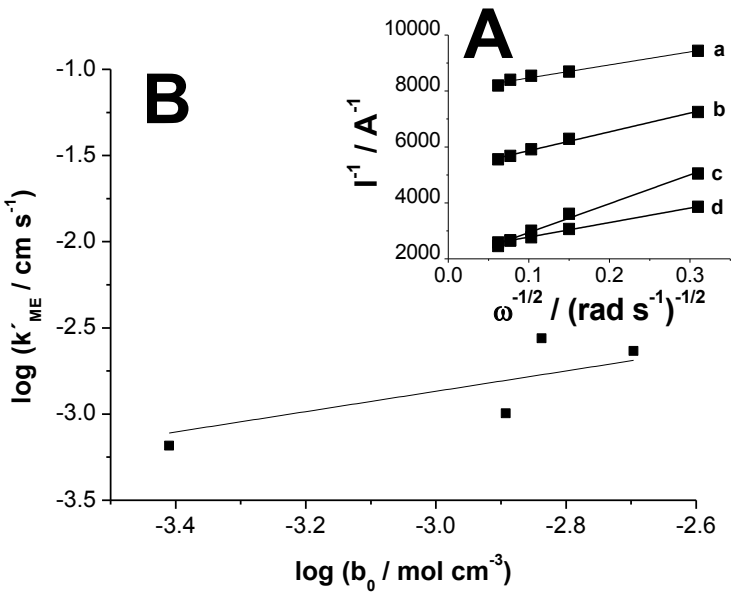



**Figure 5.** Koutecky´–Levich (A) plots for reduction of hydrogen peroxide in a solution containing 1.00 mmol L$^{-1}$ $H_2O_2$ + 0.5 mol L$^{-1}$ KCl + 0.05 mol L$^{-1}$ HCl using a RuOHCF modified electrode with different $\Gamma$ values: $1.54\times10^{-9}$ mol cm$^{-2}$ (a), $9.16\times10^{-9}$ mol cm$^{-2}$ (b), $1.04\times10^{-8}$ mol cm$^{-2}$ (c) and $1.44\times10^{-8}$ mol cm$^{-2}$ (d). Dependence of log k´$_{ME}$ vs log $b_0$ (B).

Information on the limiting dynamic steps was achieved by minimizing the influence of mass-transport of hydrogen peroxide to the film surface. This is typically done using the limiting current at an infinite rotation rate via a Koutecký-Levich plot. At this condition, charge transport, substrate diffusion within the film and the cross-chemical reaction may determine the value of 1/I at $\omega^{-1/2} = 0$. Accordingly, Fig. 5A shows Koutecký-Levich plots for four RuOHCF modified electrodes containing different film amounts (from 1.54 x $10^{-9}$ to 1.04 x $10^{-8}$ mol cm$^{-2}$). The kinetic limitation of the electrode process is confirmed by considering the intercept values at $\omega^{-1/2} = 0$ of all linear plots, which are positive. The intercept corresponds to infinite rotation rate with negligible concentration polarization in the electrolyte solution and can be used to get information on the mediated reaction. As intercept values are inversely proportional to the concentration of the diffusing substrate, current is not limited by charge diffusion within the film layer and the reaction rate is controlled by transport of hydrogen peroxide within the film and/or by the cross-exchange reaction. For such an electrodic system the

characteristic current may be determined by the Koutecký-Levich analysis by using the relationship:

$$\frac{1}{I_{\lim}} = \frac{1}{nFAc_s}\left[\frac{1}{Lev\omega^{1/2}} + \frac{1}{k'_{ME}}\right] \qquad (2)$$

$$Lev = 0.62D^{2/3}\nu^{-1/6} \qquad (3)$$

where A is the area of the electrode, $c_s$ is the substrate concentration at the bulk solution, ω is the rotation speed in rad $s^{-1}$ and $k'_{ME}$ is the heterogeneous rate constant of the electrochemical process. Lev is the Levich constant and is given by equation 3 [23, 24], where D is the diffusion coefficient of the substrate in the electrolyte and ν is the kinematic viscosity. $k'_{ME}$ was determined using the values of the intercept at $\omega^{-1/2} = 0$ (Figure 5A), n = 2 for the reduction process of hydrogen peroxide and the Equation 2 for each experimental condition.

By taking into account the calculated $k'_{ME}$ values, it is possible to apply the diagnostic procedure [24] reported by Albery and Hillman [18, 19, 24, 25] to elucidate the kinetics of the overall process. As limiting current is dependent on rotation rate and Koutecký-Levich plots are linear (Fig. 4 and 5) , it is necessary to calculate the value of the Levich constant, Lev, from the gradient of the linear Koutecký-Levich plots (Fig. 5A) and compare the result with the one obtained by using a bare electrode. The mean value of the Lev constant was found to be (8 ± 2) x $10^{-4}$ cm $s^{-1/2}$, in good agreement with the value obtained for the Lev constant (8.9 x $10^{-4}$ cm $s^{-1/2}$), which was calculated by using the equation 3 (diffusion coefficient of hydrogen peroxide in solution = 1.71 x $10^{-5}$ $cm^2$ $s^{-1}$ [26, 27] and ν = 0.01 $cm^2$ $s^{-1}$). Since both Lev values agreed, there were only four possible cases to consider: Sk´, LSk, Lk and $LEt_y$. In order to decide which case applies, the order of $k'_{ME}$ versus $b_o$ (concentration of electrocatalytic sites into the film, calculated as described in a previous work [21]) was analyzed in a log-log plot (Figure 5B). The slope of the straight line was found to be 0.59 (~0.5), which suggests an LSk case taking into account the diagnostic scheme proposed by Albery and Hillman [24]. According to this model, the reaction takes place at a finite layer close to the film/solution interface.

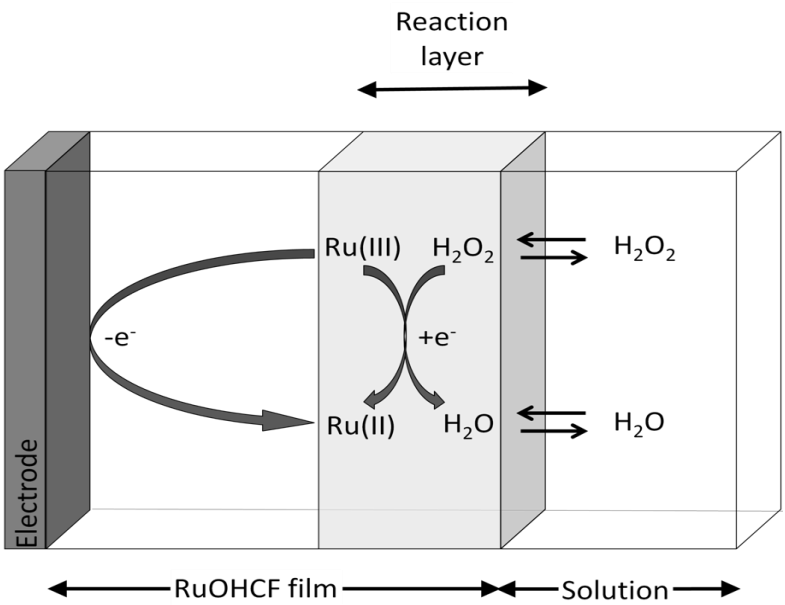
The rate constant of the mediated process (*k*) in the LSk case can be determined according to the following equation:

$$k'_{ME} = \kappa\,(k\, b_0\, D_Y)^{1/2} \qquad (4)$$

where $b_0$ is the concentration of electrocatalytic sites into the film (1.09×$10^{-3}$ mol $cm^{-3}$) [21], $D_Y$ is diffusion coefficient of hydrogen peroxide in the modifier layer (an approximation to the value obtained in biofilms at 25 °C was used (7 x $10^{-6}$ $cm^2$ $s^{-1}$) [28]), and κ is the partition coefficient of the substrate between the film and the solution (usually use a value of 1). With the $k'_{ME}$ value from Figure 5A (curve d) (2.3 x $10^{-3}$ cm $s^{-1}$) and the equation 5, the rate constant (*k*) was calculated as 693 $mol^{-1}$

$cm^3$ $s^{-1}$ (for a surface excess of 1.44 x $10^{-8}$ mol $cm^2$), which indicates a low electrocatalytic efficiency when compared with other metal-hexacyanoferrates such as SnHCF [29] and NdHCF [30].

The reaction zone is close to the film/solution interface for an electrodic process following the LSk case. Accordingly, it is expected that the flow of charge ($D_{ct}b_o/L$) is much higher than the flow of species resulting from the kinetic step ($k\Gamma c_s$). By calculating theses two parameters using $D_{ct}$, L and $b_o$ values previously reported [21], $D_{ct}b_o/L$ and $k\Gamma c_s$ were found to be 5 x$10^{-9}$ and 1 x $10^{-11}$ mol $cm^{-2}$ $s^{-1}$, respectively. As $D_{ct}b_o/L >> k\Gamma c_s$, the assumption that the reaction is located in the film/solution interface is confirmed, in agreement with the LSk mechanism. Considering the results obtained in this work, a possible mechanistic proposal for the process involving the electrocatalytic reduction of hydrogen peroxide at RuOHCF modified platforms is illustrated in the Scheme 1.




**Scheme 1.**

## 4. CONCLUSIONS

RDE studies indicated that the rate of cross-chemical reaction between Ru(II) centers immobilized into the film and hydrogen peroxide controls the limiting current and the value of the rate constant was found to be 706 $mol^{-1}$ $cm^3$ $s^{-1}$. The kinetic regime may be classified as an LSk mechanism, according to the Albery and Hillman model. In the LSk case the reaction takes place at a finite layer close to the film/solution interface, indicating that diffusion into the film does not consist of one of the limiting steps of the overall process.

## 5. ACKNOWLEDGEMENTS

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## Appendix

Acronyms used in the manuscript:

$b_0$ = Concentration of catalytic centers at the modify layer, $mol\ cm^{-3}$

A = Geometric area, $cm^2$

L = Coating thickness, *cm*

κ = Partition coefficient of the substrate between film and solution, *dimensionless*

$D_y$ = Diffusion coefficient of the substrate into the film, $cm^2\ s^{-1}$

$D_{ct}$ = Diffusion coefficient of charge transport in the film, $cm^2\ s^{-1}$

D = Diffusion coefficient of the substrate in the solution, $cm^2\ s^{-1}$

The notation used to describe the Albery-Hillman models defines the location of the reaction into the film: L, throughout the layer; LE, near the electrode interface; LS, near the electrolyte interface; LRZ, reaction zone in the middle of the layer and S, at the electrolyte layer. The subscribed notation indicates whether kinetics (*k*) or mass-transport ($t_y$ *or* $t_e$ (transport of reactant or electrons, respectively) controls the overall process.

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