

*Full Paper*

## **The Phenomenon of Catalytic Wave in Surface Regenerative EC' Mechanism in Square-wave Voltammetry**

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**Abstract-** A peculiar feature of catalytic wave (or catalytic peak), appearing in voltammograms of a surface regenerative electrode mechanism (surface EC' mechanism), in which an irreversible reduction of substrate "Y" to its final form "Z" is mediated by an adsorbed redox couple Ox/Red, is studied theoretically under conditions of square-wave voltammetry. This phenomenon, also known under the term 'split-wave' in cyclic voltammetry, appears when the rate of electron transfer step at the electrode surface is fast and comparable to the rate of chemical regenerative reaction. The effect of the kinetics of chemical regenerative step to the features of simulated square-wave voltammograms is studied for systems featuring quasi reversible and fast electron transfer steps. We present a relevant set of theoretical data, while we focus on conditions under which the two peaks in square-wave voltammetry can be resolved. An experimental observation of this phenomenon, which occurs in a very limited kinetic region, provides a basis to propose a simple methodology for assessing the rate constant of catalytic reaction.

**Keywords-** Surface EC' mechanism; Catalytic wave; Kinetic of regenerative reaction; Protein-film voltammetry

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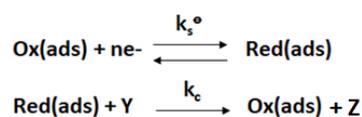
### **1. INTRODUCTION**

It is well known that many processes in everyday life require catalysts to accelerate the rate of mass/energy conversion in various systems. Consequently, there is a permanent search for simple electrochemical methods that will enable access to the kinetic parameters of various

catalytic processes. Although many enzymes are classified as specific catalysts with known functions, there are still efforts going on to evaluate their mechanism of action, and to get access to the kinetics of catalytic reactions of important classes of enzymes. The voltammetric techniques are, indeed, mostly explored electrochemical tools to investigate the activity of many redox enzymes [1]. Recent studies on enzymes electrochemistry with the help of the approach named “protein-film voltammetry” (PFV) have contributed to fundamental understanding of mechanism of action of important classes of redox enzymes [1-4]. Moreover, this methodology provides a platform for getting access to relevant kinetic parameters related to the enzyme’s activity [1,6]. In an optimal scenario, voltammetric techniques can be used to evaluate the magnitudes of catalytic rate constants, to afford information regarding the catalyst activity, and to help in the evaluation of the nature of catalytic mechanism. Although there are several methods reported to extract accurately and appropriately physical parameters of merit from voltammetric data [6-11], the features of so-called “electrochemical regenerative”, somewhere named “electrocatalytic mechanism” (or simply the “EC’ mechanism”), form the basis to assess enzyme’s activity and to get access to kinetics of enzyme-substrate reaction [1,6,12]. Traditionally, cyclic voltammetry (CV) is commonly used for mechanistic and kinetic characterization of enzyme-substrate interactions [1,6-9]. With the broader introduction of square-wave voltammetry [11,13], substantial progress in the field of kinetics of enzyme-substrate reactions has been recorded in the past two decades [11]. In this work, the phenomenon of catalytic post-wave of surface EC’ mechanism studied theoretically under conditions of square-wave voltammetry is explored as a simple and efficient approach to get access to the kinetics of regenerative chemical reaction.

## 2. MATHEMATICAL MODEL

In the current work, we consider theoretically a surface confined electrocatalytic (regenerative) electrode mechanism (surface EC’) under conditions of square-wave voltammetry (following reactions):



In the mathematical model, we suppose that all electrochemically active (Ox and Red) species are strongly adsorbed (“ads”) on the electrode surface, and there is no additional mass transfer going on via diffusion. We also assume that a uniform layer is formed by the immobilized species at working electrode surface, and no interactions exist between the redox adsorbates. In the reaction scheme (I), the symbol “Y” is assigned to an electrochemically inactive compound that is present in a large excess. Consequently, the concentration of substrate “Y” is virtually constant at the electrode surface in the course of voltammetric experiment, and the kinetics of chemical step in reaction mechanisms (I) is considered to be of

pseudo-first order. Moreover, substrate “Y” is supposed to react selectively with redox adsorbate “Red” in a chemically irreversible fashion, while being converted in electrochemically inactive form “Z”. The solution of the surface regenerative  $EC'$  mechanism under conditions in SWV is reported in [11,13-15]. The recurrent formula for calculating dimensionless currents  $\Psi$  of theoretical SW voltammograms of considered mechanism as a function of applied potential is given with equation (1).

$$\Psi_m := \frac{K \cdot e^{-\alpha \cdot \Phi_m} \left[ 1 - \frac{1 + e^{\Phi_m}}{K_{chem}} \cdot \sum_{j=1}^{m-1} (\Psi_j \cdot M_{m-j+1}) \right]}{1 + K \cdot e^{-\alpha \cdot \Phi_m} \cdot (1 + e^{\Phi_m}) \cdot \frac{M_1}{K_{chem}}} \quad (1)$$

The dimensionless current “ $\Psi$ ” is defined as  $\Psi = I / [(nFSf\Gamma^*)]$ . The meaning of the symbols in the last equation is as follows:  $I$  stays for the electric current,  $n$  is the number of electrons exchanged between working electrode and the redox adsorbates,  $F$  is the Faraday constant,  $S$  stays for the active area of working electrode,  $f$  is the SW frequency ( $f = 1/2t_p$ , where  $t_p$  is the duration of a single potential pulse in SWV), while  $\Gamma^*$  is the total surface concentration which equals the initial surface concentration of redox adsorbate Ox(ads).  $\Phi$  is a symbol of the dimensionless potential defined as  $\Phi = \frac{nF}{RT} (E - E^{s'})$ , where  $E^{s'}$  is the formal redox potential,  $\alpha$  is the electron transfer coefficient,  $R$  is universal gas constant, and  $T$  is a symbol for thermodynamic temperature.

Symbol  $K$  stays for the dimensionless rate parameter of electron transfer of the electrode reaction, and it is defined as  $K = k_s^0/f$ . This dimensionless electrode parameter  $K$  relates the magnitude of the standard rate constant of electron transfer  $k_s^0$  versus the applied SWV frequency. For the considered surface  $EC'$  catalytic mechanism, the dimensionless chemical kinetic parameter  $K_{chem}$  is defined as  $K_{chem} = k_c/f$ , where  $k_c$  is the first order rate constant of the regenerative (catalytic) chemical reaction. The last constant  $k_c$  is defined as:  $k_c = k_c' \times c(Y)$ , where  $k_c'$  is symbol of the real catalytic rate constant, while  $c(Y)$  is concentration of substrate Y that is present in excess in electrochemical cell. In equation (1),  $M$  is numerical integration factor defined as  $M = \exp[k_c(m/50)] - \exp[k_c(m-1)/50]$ . In last equation,  $m$  is the serial number of the time intervals. More details of the algorithms used in all models can be found in [11,13]. Commercially available software MATHCAD 14 has been used for calculating all theoretical SW voltammograms reported in this work.

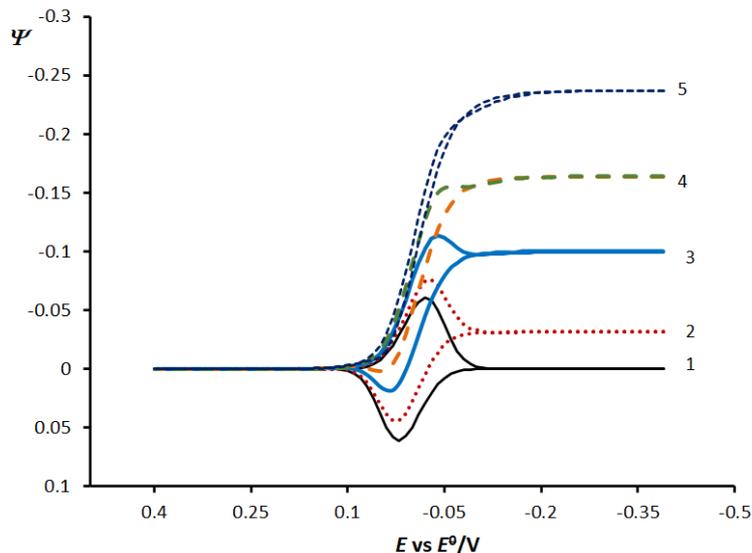
### 3. RESULTS AND DISCUSSION

In the last 40 years, cyclic voltammetry has proven a superior electrochemical tool of first choice for getting insight into mechanism of various electrochemical reactions coupled by

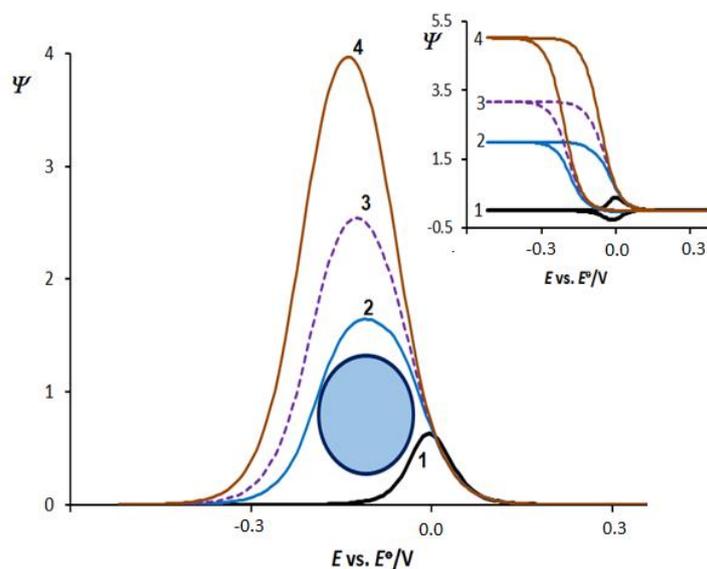
preceding, intermediary or follow up chemical steps [1,7-9,16]. Given the importance of electrochemical-catalytic (EC') mechanism, especially in evaluating the kinetics of enzyme-substrate interactions [1,7], it has been a challenge to get deeper insight into all relevant features of this electrode mechanism. Almost 40 years ago, Savéant and Su described various relevant features of cyclo-voltammetric responses of so-called "diffusional EC' catalytic mechanism" [17]. The cyclic voltammograms of simple one-electron and one-substrate electrocatalytic reactions (EC') evaluated by Savéant and Su [17] feature various forms depending on the magnitudes of dimensionless parameters  $K$  and  $K_{\text{chem}}$ . Authors of [17] classified the cyclic voltammograms according to their shape into nine so-called "kinetic zones", which are different regions that can be obtained at defined experimental conditions. Given the wide array in which the EC' zone diagram reported in [17] traverses (i.e., seven orders of magnitude along each axis), it is almost impossible task to define experimental conditions that will allow access to the entire range of voltammetric patterns obtained for a single substrate. Note that for the so-called "surface electrocatalytic" or "surface EC' mechanisms", there are no such diagrams developed in the literature under voltammetric conditions.

The surface EC' mechanism gained significant attention since it is adequate model to understand kinetics of enzyme-substrate interactions in the technique named "protein-film voltammetry" [1-7,11]. As elaborated in [8,17], the features of voltammetric patterns of a surface EC' mechanism are closely related to the magnitudes of chemical catalytic parameter and the time scale of voltammetric measurements. For the surface EC' mechanism, there are several theoretical works performed under voltammetric conditions, in which various aspects of this mechanism are comprehensively studied [11,13-15,18]. Shown in Figure 1 are representative cyclo-voltammetric patterns of a surface EC' mechanism, calculated as a function of the magnitude of dimensionless catalytic parameter  $K_{\text{chem}}$ . To get access to the rate of catalytic reaction, one commonly explores the features of so-called "S-shaped" [1,6-9] cyclo-voltammetric responses (Figure 1, curves 4-5). The "S-shaped" steady-state cyclic voltammograms imply that the forward and reverse scans trace very close to each other (curve 5 at Figure 1). This scenario in cyclic voltammetry happens when the concentration of the regenerative substance "Y" at the electrode surface equals to its bulk concentration [1,8,17]. In this region of so-called "total catalysis", the magnitude of the limiting current (measured at the upper plateau at the S-shaped cyclic voltammograms) is independent of the applied scan rate [8,17]. As reported in [1,8,17], under such circumstances, the limiting current is controlled only by the rate of regeneration of Ox via the chemical reaction between Red and Y. Hence, the dependence of the limiting current magnitudes is recorded as a function of  $c(\text{Y})$  can be explored for the determination of catalytic rate constant  $k_c$  [8,17]. The major concern of this approach is the fact that the "S" sigmoidal-like shaped cyclic voltammograms are quite difficult to be obtained experimentally [1,6]. In square-wave voltammetry, the voltammetric responses of surface EC' mechanism may be dependent on multiple variables including the catalyst and

substrate concentrations, magnitude of the rate constant of catalytic reaction, but also the parameters of the potential SW signal ( $f$ ,  $E_{sw}$ ,  $dE$ ).

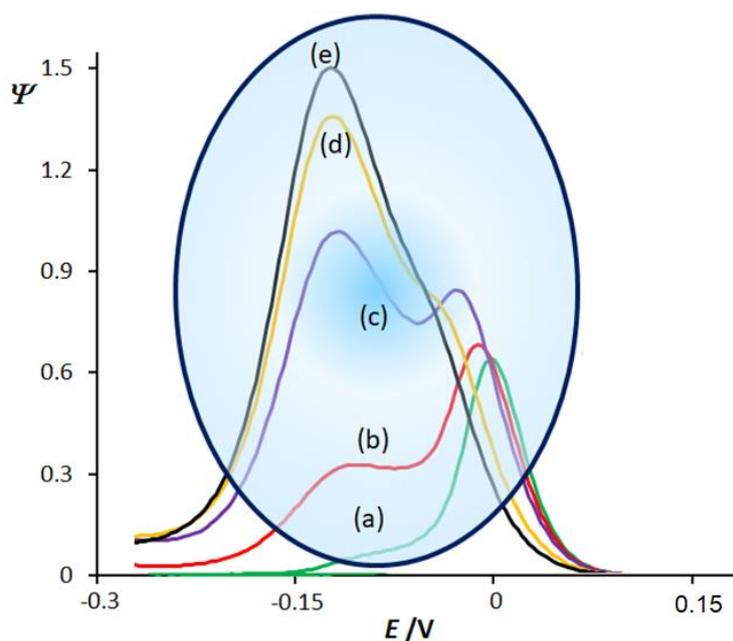


**Figure 1.** Cyclic voltammograms of a surface EC' mechanism calculated for magnitude of the dimensionless kinetic parameter  $K = 0.05$ , electron transfer coefficient  $\alpha = 0.5$ , number of electrons exchanged  $n = 1$ , potential step  $dE = 2$  mV, duration of potential step  $\tau = 0.01$ , and for magnitudes of the dimensionless chemical kinetic parameter  $K_{chem}$  of 0.00 (1); 0.08 (2); 0.45 (3); 0.65 (4) and 0.85 (5). Temperature in all experiments was set to 298 K.



**Figure 2.** Net square-wave voltammograms of a surface EC' mechanism calculated for magnitude of the dimensionless electrode kinetic parameter  $K = 0.3$ , electron transfer coefficient  $\alpha = 0.5$ , number of electrons exchanged  $n = 1$ , potential step  $dE = 1$  mV, square-wave amplitude  $E_{sw} = 50$  mV, temperature  $T = 298$  K, and for magnitudes of the dimensionless chemical kinetic parameter  $K_{chem}$  set to: 0.01 (1); 0.75 (2); 1.25 (3); and 2.50 (4). Shown in the inset are corresponding forward (reduction) and backward (reoxidation) currents.

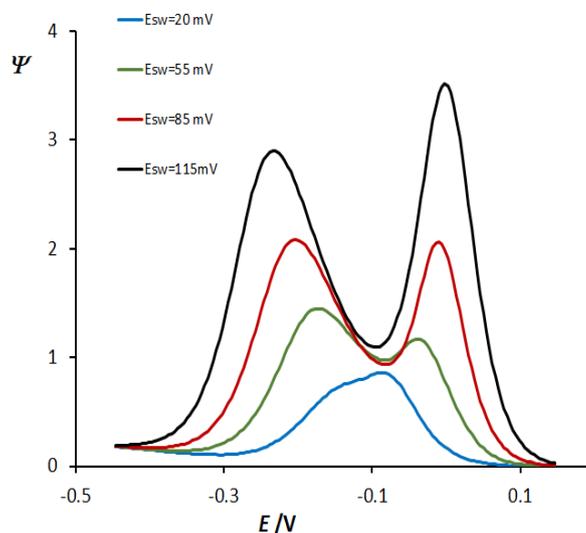
Theoretical patterns of the SWV responses, simulated at the value of dimensionless electrode kinetic parameter  $K = 0.3$ , and for several magnitudes of the dimensionless catalytic parameter,  $K_{\text{chem}}$  is given in Figure 2. Although an increased magnitude of  $K_{\text{chem}}$  (in regions of  $K_{\text{chem}} > 0.1$ ) causes the appearance of “S”-like shapes of the forward and backward current components (inset of Figure 2, curves 2-4), the net SWV responses get always a peak-like shape (Figure 2). As elaborated in [14], the reason for this feature is the measuring manner in SWV, and the effect of the square-wave amplitude that makes differences in magnitudes of forward and backward currents measured at the same potential.



**Figure 3.** Closer zoom of the net square-wave voltammograms of surface EC' mechanism belonging to the encircled region in Figure 2. Voltammograms are calculated for the magnitudes of the dimensionless chemical kinetic parameter  $K_{\text{chem}}$  of 0.08 (a); 0.32 (b); 0.45 (c); 0.62 (d) and 0.7 (e).

A very curious feature at the calculated SW voltammograms exists in region of  $0.3 < K_{\text{chem}} < 0.6$  (see Figure 3). This is an interim catalytic zone, in which comparable rates of electrode reaction of electron transfer and that of the regenerative chemical reaction exist. This scenario happens when the rate of the regenerative reaction is high enough to quickly turn the redox adsorbate Red to Ox. The competition between both reaction rates gives rise to two peaks: one quasi-reversible process due to the Ox-Red electrode transformation that appears at more positive potentials, and a catalytic wave that is due to the occurrence of electrocatalytic regenerative reaction appearing at more negative potentials. This phenomenon has been a subject of comprehensive studies of “diffusional” systems considered under conditions of cyclic voltammetry in following recent works [19-32]. The authors of [19-32] point out that the catalytic-wave feature is as a consequence of synchronization between the kinetics of

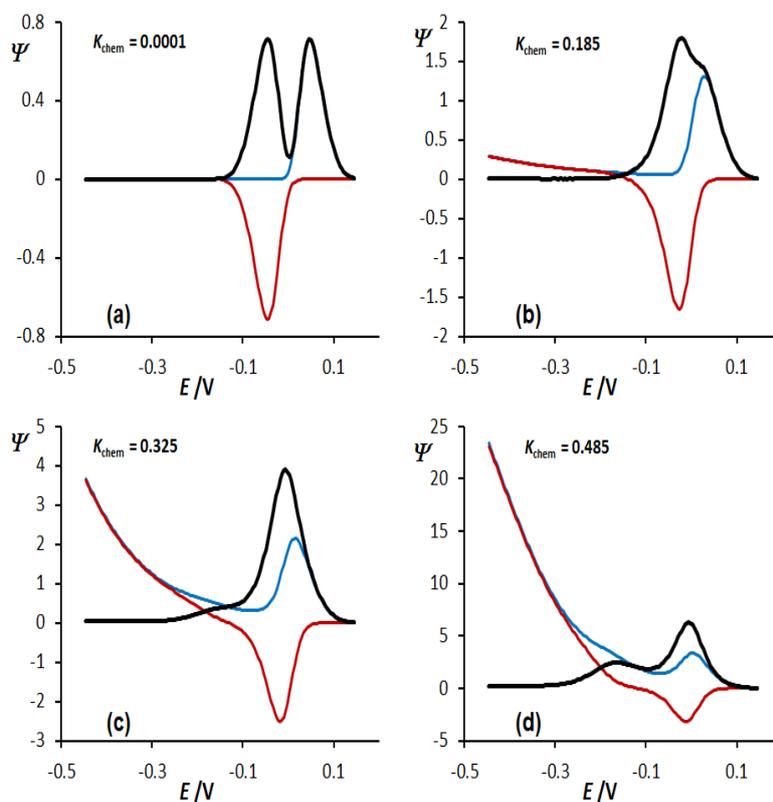
electron transfer step and the rate of chemical resupply of initial electroactive material in the current-measuring time frame of the applied potential. Evolution of both peaks in SWV depends strongly on the magnitude of square-wave amplitude, as it is portrayed in Figure 4.



**Figure 4.** Effect of the square-wave amplitude ( $E_{sw}$ ) to the features of simulated square-wave voltammograms of a surface EC' mechanism, calculated for  $K_{chem} = 0.4$ ,  $K = 0.25$  and  $dE = 0.5$  mV. Magnitudes of the square-wave amplitudes used in this set of calculations are given in the chart. Other simulation conditions were same as those reported for Figure 2.

An increase of the SW amplitude from 55 mV to 115 mV produces a separation between both peaks from 100 mV to 240 mV, respectively. In the same time, the ratio of the measured net SWV peak currents of the catalytic wave (at more negative potentials) vs. the net peak current of the process at more positive potentials changes from 1.25 (at  $E_{sw}$  of 55 mV) to 0.85 (at  $E_{sw}$  of 115 mV). These data imply that the square-wave amplitude is an important parameter that can be explored in the identification and characterization of the catalytic wave in SWV of an EC' mechanism. Indeed, it should be noted that the potential step  $dE$  also plays a significant role in the resolution and definition of both signals. A rather good separation between both peaks is obtained by using potential steps smaller than 1 mV, as it has been used for patterns presented at figure 4. It is also important to mention that the resolution between both peaks is also a function of the magnitude of the dimensionless kinetic parameter of electron transfer step  $K$ , as elaborated in [17]. This phenomenon at the considered surface EC' mechanism in SWV is observable if  $\log(K) > -1$ . For very fast electrode reactions, a specific feature of a surface redox mechanism is splitting of the net SW peak [13] (see Figure 5a). At surface EC' mechanism, if  $K_{chem} > 0.2$  (for  $K = 0.6$ ;  $E_{sw} = 85$  mV and  $dE = 1$  mV), the splitting phenomenon vanishes and only one voltammetric peak is observed (Figure 5b-c). However, if  $K_{chem} > 0.35$ , one witnesses the reappearance of the post-catalytic peak (Figure 5d), which is in accordance with the previous findings (see Figure 3). At magnitudes of  $K_{chem} > 0.6$ , the post-catalytic peak

merges with the large catalytic currents, and the situation of two resolved peaks is not observable any longer. These findings support the information that the phenomenon of defined catalytic peak exists only in a narrow zone of catalytic rate parameter i.e.,  $0.3 < K_{\text{chem}} < 0.6$ . Therefore, the experimental observance of post-catalytic peak in SWV might be explored to assess the magnitude of catalytic rate constant.



**Figure 5.** Scenario of *split square-wave voltammograms*: effect of the dimensionless catalytic parameter  $K_{\text{chem}}$  to the features of voltammograms of fast electrode reaction. Voltammograms were calculated for  $K = 0.6$ ,  $E_{\text{sw}} = 85$  mV and  $dE = 1$  mV. The values of  $K_{\text{chem}}$  used in this set of simulations are given in the charts. Forward (reduction) current compounds are assigned with blue color, while red color is associated with the backward (reoxidation) current components of the square-wave voltammograms. The net currents are assigned with black color. Other simulation conditions were the same as those reported for Figure 2.

#### 4. CONCLUSION

Although the feature of catalytic split-wave is experimentally observed in electrochemistry of many systems studied under conditions of cyclic and square-wave voltammetry (see for example references [19, 20, 32-35]), there has been a small gap in theoretical consideration of this phenomenon in SWV. In this work, the phenomenon of catalytic post-peak occurring in the square-wave voltammograms of the surface catalytic EC' mechanism has been studied

theoretically. The occurrence of two resolvable split square-wave voltametric peaks takes place in the zone of large and comparable kinetics of surface electrode reactions and that of the regenerative chemical step. At given circumstances, the resolution of both peaks in SWV depends on number of parameters, of which the square-wave amplitude, and the potential step have particular importance. Very small potential increments (preferably 0.5 mV or lower) and SW amplitudes between 50 mV and 100 mV ensure successful resolution of SW voltammograms in which both peaks are nicely separated. Application of very low frequencies under conditions of significant catalytic reaction commonly leads to vanishing of the splitting phenomenon, that can be made invisible due to the high intensity of the catalytic currents. Since the considered phenomenon of two peaks observed at this mechanism occurs in a very limited zone of the rate of catalytic reaction, we expect that the results presented in this work will help in kinetic experimental analyses of the surface catalytic mechanism studied under conditions of square-wave voltammetry.

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