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Theoretical Contribution Towards Understanding Specific Behaviour of “Simple” Protein-film Reactions in Square-wave Voltammetry

Rubin Gulaboski*^[a]

Abstract: Surface reactions of uniformly adsorbed redox molecules at working electrode surface are seen as adequate models to studying chemical reactivity of many lipophilic enzymes. When considered under pulse voltammetric techniques, these systems show several uncommon features, whose origin is still not completely clear. The phenomena of “quasireversible maximum”, “splitting” of the net peak in square-wave voltammetry, and the very steep descent of Faradaic currents of simple surface redox reactions exhibiting fast electron transfer are just some of the features that make these systems quite interesting for further elaborations. In this work, we present a set of theoretical calculations under conditions of square-wave voltammetry in order to try to explain some of aforementioned phenomena. The major goal of our work is to get insight to some voltammetric and chrono-amperometric features of two considered surface reactions, i.e. (1) the “simple” surface redox reaction, and (2) surface redox reaction coupled to follow-up irreversible chemical reaction of electrochemically generated redox species (or surface ECirr). We focus on the role of created Red(ads)

(here in the reduction pulses only) to the current components of calculated square-wave voltammograms exhibiting fast electrode reaction. We show that the irreversible chemical removal of electrochemically generated Red(ads) species, created in the potential pulses where half-reaction of reduction $\text{Ox(ads)} + \text{ne} \rightarrow \text{Red(ads)}$ is “defined” to take place, causes significant increase of all square-wave current components. The results presented in this work show how complex the chrono-amperometric features of surface redox reactions under pulse voltammetric conditions might be. In addition, we point out that both half reactions of a given simple surface redox process can occur, at both, “only reduction” and “only oxidation” potential pulses in square-wave voltammetry. This, in turn, contributes to the occurrence of many phenomena observed in simple protein-film voltammetry reactions. The effects of chemical reaction rate to the features of calculated square-wave voltammograms of surface ECirr systems with fast electrode reaction are reported for the first time in this work.

Keywords: Protein-film voltammetry • square-wave voltammetry • surface ECirr reaction • split SW peaks

1 Introduction

Voltammetry of adsorbed redox active substances forming a monolayer film on working electrode surface is applied for more than 40 years. Over the last three decades plenty of relevant theoretical models have been developed to describe the redox features of various surface electrode processes under different voltammetric conditions [1–19]. The surface redox reactions are commonly considered as adequate models of “protein-film voltammetry”, which is an efficient methodology capable of getting insight into chemistry of many lipophilic redox enzymes [20–29]. Therefore, we use the terms of both “simple surface” and “simple protein-film” reactions as synonyms in this work. Among voltammetric techniques applied, the square-wave voltammetry (shortly SWV) is particularly appealing for getting mechanistic, kinetic, and thermodynamic information of many surface electrode reactions [1,2,4]. Although there is a strong theoretical basis for exploring the SWV to studying protein-film (surface) reactions [1,5–9,11,12,14–19,23,25–27], still many intriguing aspects of these systems need to be identified. For example, the net-

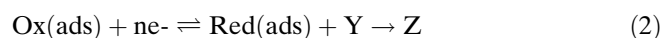
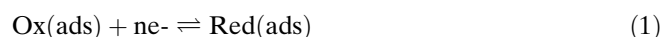
peak currents of “most simple” surface electrode reaction in SWV show maximal values for moderate rates of electron transfer between working electrode and the redox adsorbates. After reaching a maximum, by further increase of the rate of electrode reaction, the Faradaic currents of SW voltammograms fall rapidly near to zero value. In addition, a phenomenon of splitting the net SW peak might occur. This happens at protein-film reactions exhibiting very fast electron transfer [1,5]. For a fast simple protein-film reaction described with redox scheme: $\text{Ox(ads)} + \text{ne} \leftrightarrow \text{Red(ads)}$, defined in conditions of “split SW peaks”, there are few more remarkable phenomena reported in the literature [1,5,7,11,15]. In such conditions, the reduction peak shifts towards more positive values, while opposite holds for the oxidation peak of SW voltammograms by increasing the rate of electron transfer

[a] R. Gulaboski
Faculty of Medical Sciences, Goce Delcev University, Stip,
Macedonia
E-mail: rubin.gulaboski@ugd.edu.mk

[1,5]. Hints about the origins of these features of a simple surface redox reaction in SWV are mainly given in [1,5]. As the rate of electron transfer increases, the time required to convert Ox(ads) to Red(ads) at a given potential decreases. When the current-measuring period at given potential step is longer than the time required for conversion of Ox(ads) to Red(ads), then the peak currents will approach to zero. This happens, because a very small amount of Ox(ads) remains to be converted to Red(ads) at the end of the pulses, where current is being measured in SWV. However, one should bear in mind that at all the potentials where the reduction step is considered to take place (i.e. the half-reaction $\text{Ox(ads)} + \text{ne}^- \rightarrow \text{Red(ads)}$), occurrence of re-oxidation of electrochemically created Red(ads) to Ox(ads) is also thermodynamically possible. This competitive half-reaction might especially happen in significant extent at potentials that are nearby the standard redox potential of Ox(ads)/Red(ads). We made in this work set of theoretical calculations of simple surface (i.e. simple protein-film) redox reactions, and of simple surface redox reaction coupled to irreversible follow-up chemical step (i.e. surface ECirr mechanism), both exhibiting fast electrode reactions. The aim is to investigate some of the voltammetric and chrono-amperometric features of the two considered surface confined systems in SWV. Also, we like to take insight into the role of created Red(ads) (here in the reduction pulses only) to the all current components of calculated square-wave voltammograms. We believe that the approach described in this work will get us step closer to better understanding some of specific features of fast simple protein-film reactions under pulse voltammetric conditions.

2 Theoretical Models

We consider in this work theoretically some of the SWV features of two surface reactions of redox active adsorbates, described by following reaction schemes:



Reaction (1) is a “simple” surface redox reaction, while reaction (2) is a surface redox reaction coupled with irreversible chemical reaction of the product Red(ads) (or surface ECirr). In both cases, we consider that Ox(ads) and Red(ads) are firmly adsorbed on the working electrode surface, forming a redox active monolayer film, and there is no mass transfer taking place by diffusion. By “Y” (in mechanism 2) we assign a given (non-electroactive) substance present in electrochemical cell that selectively and irreversibly converts chemically Red(ads) to electro-inactive substance “Z”. Also, we assume that no interactions occur between the redox adsorbates. Y is an electrochemically inactive compound that is present as dissolved in large excess in electrochemical cell. Therefore, its concentration is supposed to be constant during

the voltammetric experiments. Consequently, the chemical step in mechanism (2) will be of pseudo-first order.

In the mathematical model, following initial and boundary conditions apply to both redox mechanisms:

$$t = 0; \Gamma(\text{Ox}) = \Gamma_{\text{löschen}}^*(\text{Ox}); \Gamma(\text{Red}) = 0$$

(holds for both mechanisms 1 and 2)

$$t > 0; \Gamma(\text{Ox}) + \Gamma(\text{Red}) = \Gamma^*(\text{Ox})$$

(holds true for mechanism 1)

for $t > 0$, the following conditions apply for mechanism (1) and (2):

$$d\Gamma(\text{Ox})/dt = -I/(nFS)$$

(holds for both mechanisms 1 and 2)

$$d\Gamma(\text{Red})/dt = -I/(nFS) \quad (\text{holds for mechanism 1})$$

$$d\Gamma(\text{Red})/dt = I/(nFS) - k_c\Gamma(\text{Red})$$

(holds for mechanism 2)

At the electrode surface, the Butler-Volmer formalism defines the current as a function of surface concentrations of redox adsorbates Ox and Red, the kinetics of electron transfer rate and the applied potential:

$$I/(nFS) = k_s \exp(-\alpha\Phi) [\Gamma(\text{Ox}) - \exp(\Phi)\Gamma(\text{Red})]$$

By I we assign the current, n is the number of electrons exchanged, S is the electrode surface area, α is the electron transfer coefficient, $\Gamma(\text{Ox})$ and $\Gamma(\text{Red})$ are the surface concentrations of Ox and Red, respectively. Φ is the dimensionless potential defines as $\Phi = nF(E - E_{\text{löschen}}^{\text{Ox(ads)/Red(ads)}})/RT$, where F is Faraday constant, R is a universal gas constant, T is thermodynamic temperature, and $E_{\text{löschen}}^{\text{Ox(ads)/Red(ads)}}$ is the standard redox potential of Ox(ads)/Red(ads) redox couple. The solutions of both reaction mechanisms under SWV conditions are known in the literature, and can be found in [1,26]. The recurrent formulas for calculating the dimensionless currents Ψ Leerzeichen (Ψ is normalized as $\Psi = I/[nFS\Gamma^*(\text{Ox})]$) of the square-wave voltammograms as a function of applied potential for both reactions are given with:

$$\Psi_m := \frac{\lambda \cdot e^{-\alpha \cdot \Phi_m} - \lambda \cdot e^{-\alpha \cdot \Phi_m} \cdot \frac{(1 + e^{\Phi_m})^{m-1}}{50} \cdot \sum_{i=1}^{m-1} \Psi_i}{1 + \frac{\lambda \cdot e^{-\alpha \cdot \Phi_m} \cdot (1 + e^{\Phi_m})}{50}}$$

Recurrent formula simple surface redox reaction in square-wave voltammetry (mechanism 1)

$$\Psi(\text{ECirr})_m := \frac{\lambda \cdot e^{-\alpha \cdot \Phi_m} - \frac{\lambda}{50} \cdot e^{-\alpha \cdot \Phi_m} \cdot \sum_{i=1}^{m-1} \Psi(\text{ECirr})_i - \lambda K^{-1} \cdot e^{\Phi_m \cdot (1-\alpha)} \cdot \sum_{i=1}^{m-1} (\Psi(\text{ECirr})_i \cdot M_{m-i+1})}{1 + \frac{\lambda}{50} \cdot e^{-\alpha \cdot \Phi_m} + \lambda K^{-1} \cdot e^{\Phi_m \cdot (1-\alpha)} \cdot M_1}$$

Recurrent formula for a surface redox reaction coupled with irreversible chemical reaction

(ECirr) in square-wave voltammetry for (mechanism 2)

The recurrent equations for both mechanisms are evaluated by numerical integration method, with assumption that the electrode reactions obey the Butler-Volmer kinetic formalism [1]. In both mathematical models, it is assumed that only the oxidized adsorbates Ox(ads) are present at the beginning of the experiment. All calculations have been performed with help of MATHCAD 16-schen14 package.

The dimensionless SW voltammograms of both redox mechanisms depend on potential signal parameters (amplitude E_{sw} , potential step dE), as well as on electron transfer coefficient α , and the dimensionless kinetic parameter λ . λ is directly related to the rate of heterogeneous electron transfer of the electrode reaction. This dimensionless kinetic parameter is defined as $\lambda = k_e/f$, where k_e Leerzeichen(s^{-1}) is the heterogeneous standard rate constant of electron transfer, while f is the SW frequency ($f=1/\tau$, where τ is the duration of each potential SW pulse). In all simulations, the SW frequency f was set to 10 Hz, SW amplitude was $E_{sw}=50$ mV, while the potential step dE was 4 mV. Additionally, calculated SW voltammograms of surface ECirr mechanism depend on dimensionless chemical parameter K , defined as $K = k_c/f$, where k_c is the standard chemical rate constant (s^{-1}). The dimensionless kinetic parameter K reflects the rate of irreversible chemical reaction to the features of calculated voltammograms, related to the time-frame of current measurements in SWV. All voltammograms are simulated starting from positive and running the potential towards negative values. The standard redox potential of Ox(ads)/Red(ads) couple was set to 0.0 V. Detailed overview about algorithms used in both mechanisms can be found in [1,26,27].

3 Results and Discussions

3.1 Simple Surface Redox Reactions

Major goal of this work is to approach the origin of some of the specific features of simple surface (or simple protein-film) reactions in square-wave voltammetry reported in the literature [1–5]. Shown in Figure 1 is a set of calculated square-wave voltammograms of a simple surface redox reaction featuring different kinetics of the electrode reaction.

By varying the rate of electron transfer step (via modifying the value of dimensionless kinetic parameter λ), several remarkable features at calculated voltammograms can be identified. Initially, by increasing the value of λ from 0.1 to 0.7, an increase of all voltammetric peak current components-forward, backward and the net (voltammograms (a) and (b) on the top in Figure 1) is observed. In the same region of λ values, another remarkable feature is shifting of the forward (reduction) peak towards more positive potentials, and the backward (oxidation) peak toward more negative potentials. By further increase of λ between 1 and 5, a significant decrease of all current components of simulated voltammograms is detected, which eventually results in “splitting” of the net SW voltammetric output to two peaks (see voltammograms (c) and (d) in Figure 1). The potential separation between the split SW net peaks increases by increasing of kinetics of electron transfer rate [1,5]. At very large values of λ , (roughly for $\lambda >$ of 35) the current of all forward, backward and net components falls almost to zero. Issues that we intend to resolve in described situations are: 1) why the voltammetric peak current is passing through maximum by increasing λ and falling to zero at large values of λ ; 2) Why reduction peak shifts to more positive potential values (i.e. reduction becomes much easier), and oxidation shifts to more negative potentials (or, oxidation becomes much easier process) by increasing kinetic parameter λ ; 3) what is the role of the electrochemically generated Red(ads) species in the processes taking place in reductive potential pulses?

In Figure 2 we show a single SW potential pulse, while we focus on processes going on at two defined segments in the “reduction” part of potential pulse only.

The potential segment assigned with “A” (between points 1 and 2) is the so-called “dead time” or “no-current measuring” potential sector. The second sector “B” (between points “2” and “3”) is located at the end of the reduction potential pulse. As we know, sector “B” is the potential segment where current is measured in square-wave voltammetry. The significant diminishment of the capacitance current against the Faradaic current measured in SWV is a main reason to sampling the current in a tinny time sector at the end of the SW potential pulses [1,3]. Before taking a closer insight into the processes going on at single reduction potential SW pulse in both sectors “A” and “B”, we should bear in mind four very important facts at this redox mechanism: 1) The sum of the surface concentrations of electroactive species Ox(ads) and Red(ads) at any time of every potential pulse equals the initial surface concentration of Γ^* Leerzeichen(Ox), or Γ Leerzeichen(Ox) + Γ Leerzeichen(Red) = Γ^* (Ox) (Γ is

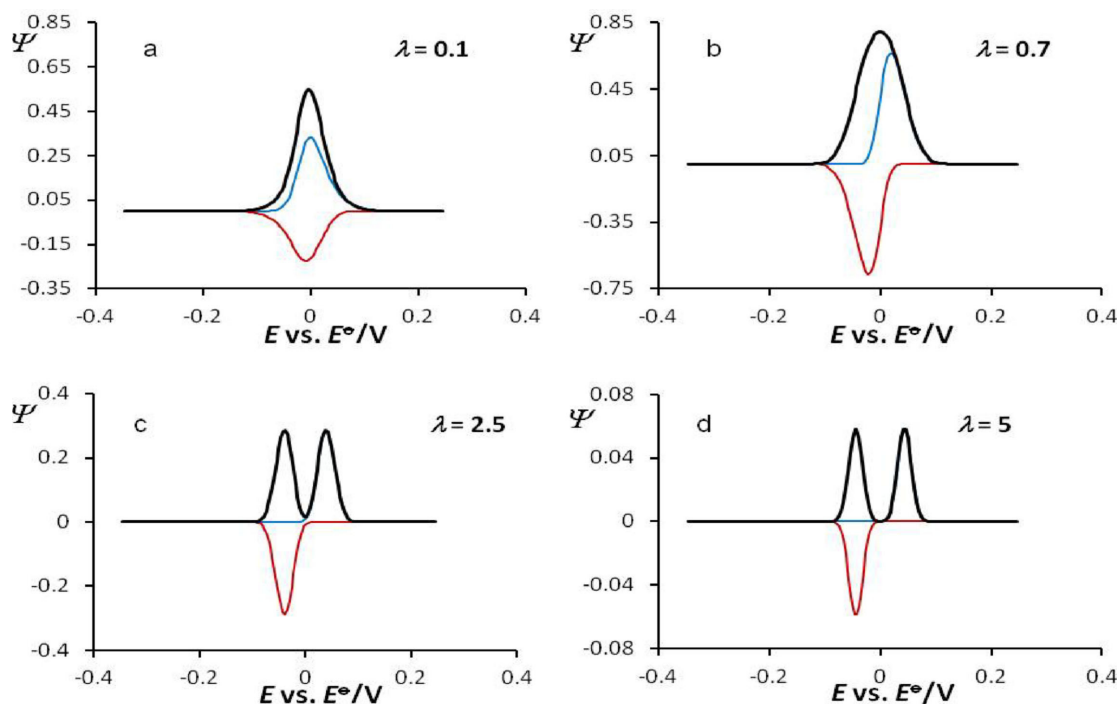


Fig. 1. *Simple surface redox reaction*: Simulated square-wave voltammograms showing the reduction (blue line), oxidation (red line) and net (black line) currents as a function of dimensionless kinetic parameter of electrode reaction λ . The other simulation parameters were: electron transfer parameter $\alpha=0.5$; SW frequency $f=10$ Hz; potential step $dE=4$ mV; square-wave amplitude $E_{sw}=50$ mV; number of exchanged electrons $n=2$; temperature of $T=298$ K, and standard redox potential of redox couple $E^{\circ}_{Ox/Red}=0.0$ V. In all simulations, the starting potential was set to $+0.3$ V and the final potential was -0.3 V vs. $E^{\circ}_{Ox/Red}$.

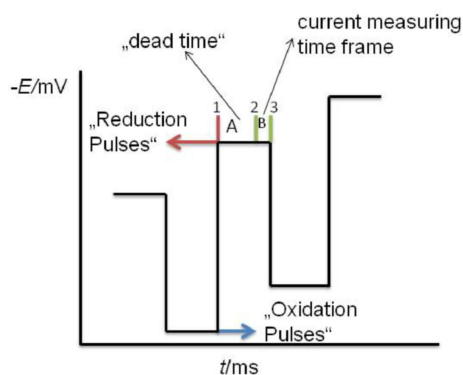


Fig. 2. Schematic representation of two time-regions in given "reduction" segment of potential pulse in square-wave voltammetry. The current in SWV is measured in sector "B".

a symbol of surface concentration); 2) Reduction of Ox(ads) to Red(ads) gives a positive current (as it is defined in our model here), while the oxidation of Red(ads) to Ox(ads) gives a negative current; 3) At every "reduction" potential pulse, both half reactions can occur (same holds true for the "oxidation" pulses, too); 4) At given "reduction" potential pulses that are located nearby the standard redox potential of the couple Ox(ads)/Red(ads), the kinetics of the reaction $\text{Red(ads)} - ne \rightarrow \text{Ox(ads)}$ can be also quite significant. Since the half-reaction $\text{Ox(ads)} + ne \rightarrow \text{Red(ads)}$ takes place not only in

potential segment "B", but also in segment "A" of "reduction" pulses, significant amount of Ox(ads) can be converted to Red(ads) even in the initial times of many reduction potential pulses. Because a large amount of Red(ads) can be built up during this "dead time" in sector "A", it is worth to investigate the amount of Red(ads) created during a single "reduction" potential pulse at different times, and to evaluate the role of created Red(ads) in the forward (reduction in this case) SW currents. For achieving this, we performed a set of "chrono-amperometric simulations", while we calculated the voltammetric outputs at different times of defined reduction SW pulses. We divided every single reduction potential pulse to 25 time segments (each lasting 1 ms) in order to inspect some chrono-amperometric features of considered simple surface redox reaction.

In Figure 3 we present a set of calculated square-wave voltammograms recorded at different time periods of potential pulses, simulated for k_s of 50 s^{-1} . Although the features of these SW voltammograms resemble to those in Figure 1, there is one very important difference.

At very beginning of measuring time of the pulse (Figure 3, SW voltammogram (a) calculated for $\tau=1$ ms), calculated voltammograms feature very high peak currents. By further increase of time at which the current is being sampled at single potential pulses, the peak currents of all SWV components drop dramatically (voltammograms (b) and (c) in Figure 3). Eventually, splitting is

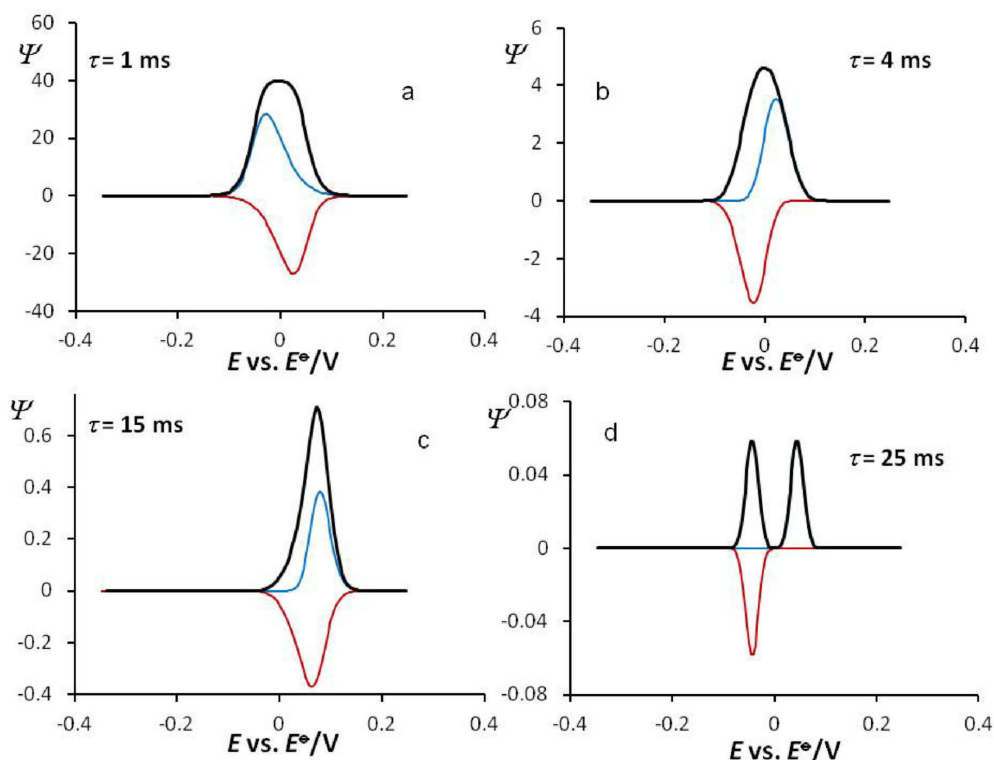


Fig. 3. Simple surface redox reaction: Theoretical square-wave voltammograms calculated at different times of potential pulses. Standard rate constant of electron transfer is $k_s = 50 \text{ s}^{-1}$. All other parameters were the same as those in Figure 1.

achieved of the net SWV component, when current is measured at the end of the potential pulses (for $\tau > 22$ ms voltammogram (d) in Figure 3). Oppositely from voltammograms shown in Figure 1, the currents measured in this manner drop permanently by increasing the time at which voltammograms are calculated. In Figure 4A we present a set of forward (reduction) SW currents, measured in chrono-amperometric manner at several SW potential pulses, as a function of measuring time τ . Note that the pulses #43 and #50 are quite relevant, since they are located nearby the standard redox potential of couple Ox(ads)/Red(ads) (which is set to 0.0 V in all simulations). Remarkably, the forward currents measured at pulses #43 and #50 show a very sharp exponential descent, dropping to very low (near zero) values at end of potential pulses. From the calculated values of the forward currents shown in Figure 4A, and by using the corresponding Butler-Volmer equation, we can calculate the ratio of $\Gamma(\text{Red})/\Gamma^* \text{Leerzeichen}(\text{Ox})$ as a function of measuring time τ at given potential reduction pulses. For this, we use the following substitution $\Gamma \text{Leerzeichen}(\text{Ox}) = \Gamma^* \text{Leerzeichen}(\text{Ox}) - \Gamma \text{Leerzeichen}(\text{Red})$ in the modified Butler-Volmer equation.

From the two relevant curves presented in Figure 4B (evaluated for the 43rd and 50th SW pulses, in reduction segment only), we can see that the surface concentration of electrochemically created species $\Gamma \text{Leerzeichen}(\text{Red})$ is quite high and it very quickly approaches values of the initial concentration of $\Gamma^* \text{Leerzeichen}(\text{Ox})$. This is a

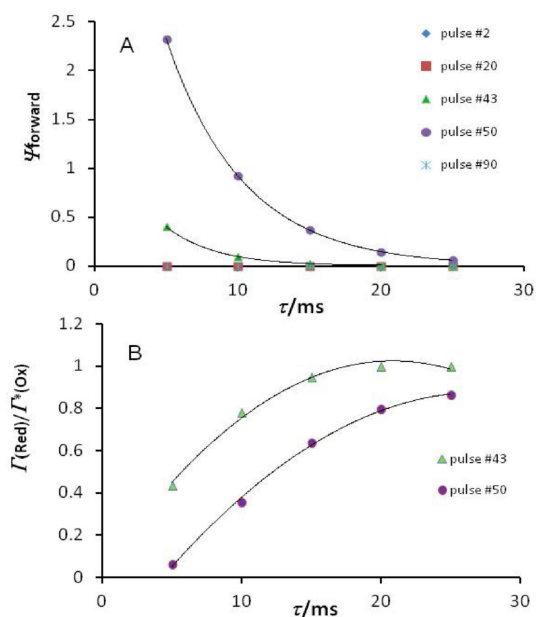


Fig. 4. Simple surface redox reaction: A. Dependence of the peak currents of forward (reduction) peaks as a function of the measuring time at given reduction potential pulses. B. Dependence of the ratio $\Gamma \text{Leerzeichen}(\text{Red})/\Gamma^* \text{Leerzeichen}(\text{Ox})$ as a function of the measuring time at given reduction potential pulses. Standard rate constant of electron transfer was $k_s = 50 \text{ s}^{-1}$ while the other parameters were the same as those in Figure 1.

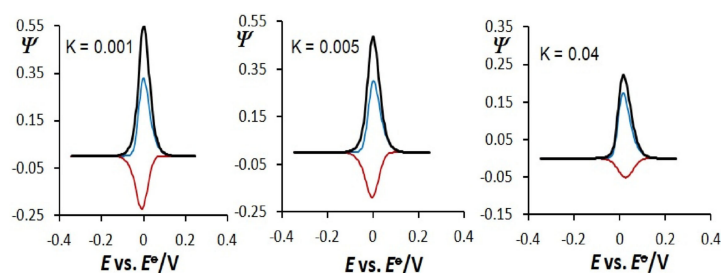


Fig. 5. Surface ECirr reaction: Effect of the dimensionless chemical kinetic parameter K to the features of the SW voltammograms of surface ECirr reaction calculated for $k_s = 1 \text{ s}^{-1}$. All other parameters were the same as those in Figure 1.

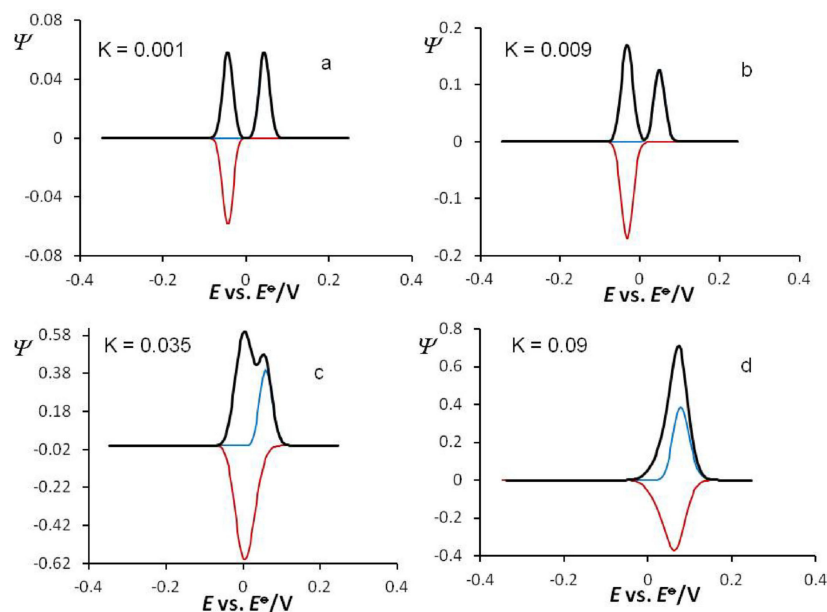


Fig. 6. Surface ECirr reaction: Effect of the dimensionless chemical kinetic parameter K to the SW voltammograms featuring fast electron transfer simulated for $\lambda = 5$ (situation of split SW peaks). All other parameters were the same as those in Figure 1.

rather significant fact implying that electrochemically generated Red(ads) species might have important role in SW voltammetric features of “simple” surface redox reaction. Especially important are the so-called “reductive” potential segments of the pulses, where it is supposed that electrochemically generated Red(ads) species should not have electrochemical activity.

3.2 Surface ECirr Redox Reaction

The major idea of this work is to get relevant information about possible influence of Red(ads) species (electrochemically generated at the “reductive” potential pulses) to the features of SW voltammograms of simple surface redox reactions. We are specifically focused on the effects that Red(ads) show to the SW voltammograms, due to their possible redox transformation at the very same potential pulses where they get electrochemically generated (reductive part of the pulses in this work). To get relevant hints about this, we considered theoretically some of the SWV features of a surface redox reaction

coupled to irreversible chemical transformation of Red(ads) i.e. the surface ECirr reaction mechanism. Since at surface ECirr mechanism only the electrochemically created Red(ads) species can react with the chemical agent Y, one intuitively expects that chemical reaction rate should affect the backward (oxidation) components of calculated SW voltammograms only [1, 3, 26]. However, for the reaction mechanism (2) in SWV, this is true (to some extent) only for surface electrode reactions featuring slow or moderate electron transfer (see voltammograms in Figure 5).

When electrode kinetics of surface ECirr reaction is fast, then a quite interesting phenomenon is observed by increasing the kinetics of follow-up irreversible chemical step. Shown in Figure 6 is the influence of the rate of chemical kinetic parameter K to calculated SW voltammograms featuring fast electron transfer. We consider in Figure 6 a situation of “split SW net peaks” as a starting point.

Remarkably, an increase of dimensionless chemical parameter K is followed by a simultaneous increase of

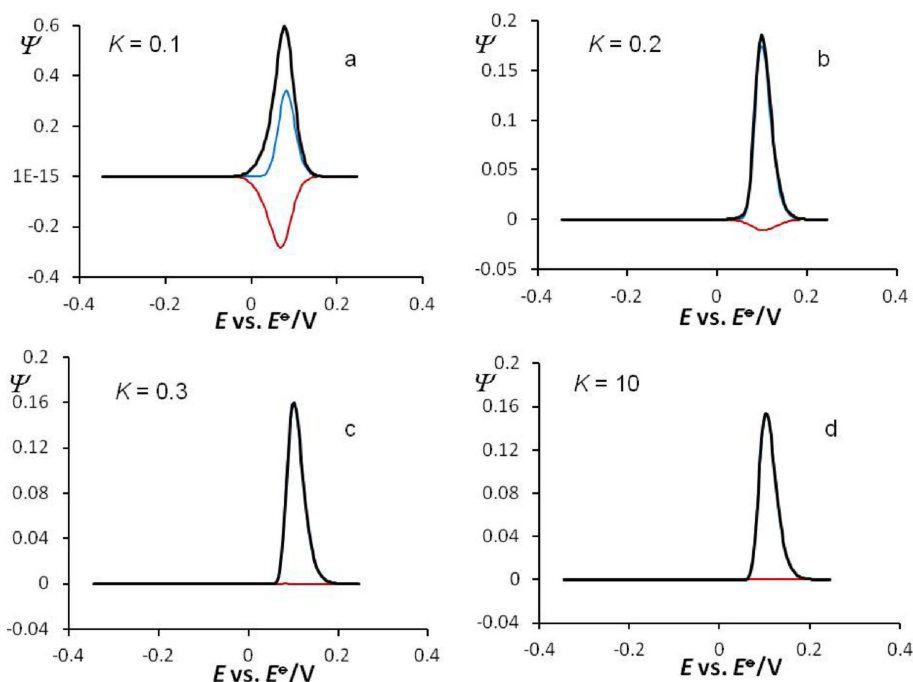


Fig. 7. Surface ECirr reaction: Effect of the dimensionless chemical kinetic parameter K to the SW voltammograms featuring fast electron transfer simulated for $\lambda = 5$. These SW voltammograms are continuation of those presented in Figure 6 but calculated for several high rates of the chemical reaction. All other parameters were the same as those in Figure 1.

both forward and backward current components of calculated SW voltammograms (Figure 6). Furthermore, by increasing the value of K from 0.001 to 0.035 (this is a section of moderate rate of chemical reaction), more pronounced increase is seen by backwards current component (see forward and backward currents in Figure 6b and 6c, respectively). This effect is completely in disagreement to the features of diffusional ECirr reaction [1–4]. As we know, every increase of chemical rate parameter K should speed up conversion of Red(ads) to electroinactive product Z. Consequently, the unusual effect of rising of both SW forward and backward current components by increasing of chemical rate kinetics in Figure 6 must be linked to the irreversible removal of Red(ads) out of the electrode reaction. In addition, by increasing of value of chemical parameter K , the oxidative (backward) peak starts shifting toward more positive potentials, while the position of forward (reduction) peak remains almost the same (Figure 6). Eventually, the phenomenon of split SW peaks vanishes for K values bigger than 0.05, and a single reversible-like voltammogram is observed (see voltammogram (d) calculated for $K = 0.09$ in Figure 6). The further increase of the rate of chemical reaction leads to SW voltammetric outputs that are intuitively expected for an ECirr mechanism (Figure 7). SWV voltammograms calculated for $K > 0.2$ are constant and independent on K (voltammograms (c) and (d) in Figure 7).

Figure 8 portrays the effect of chemical parameter K to the forward (reduction) and backward (oxidation) peak currents, calculated for two values of λ . Obviously, an

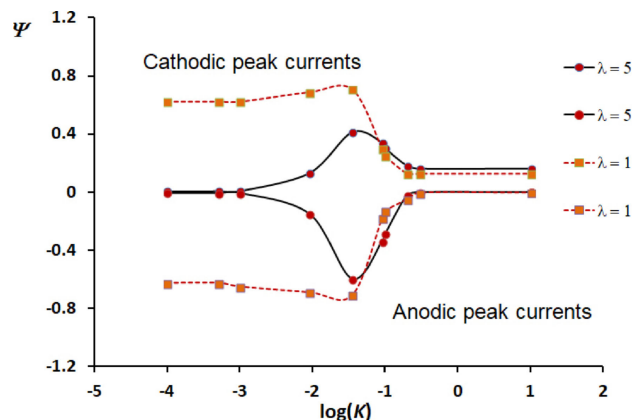


Fig. 8. Surface ECirr reaction: Plot of cathodic and anodic peak currents of calculated SW voltammograms as a function of logarithm of chemical parameter K . Curves are calculated for two different values of λ .

increase of K produces a nicely pronounced maximum by both SW peak current components, in situations when λ falls into the region of fast electron transfer (see curves calculated for $\lambda = 5$ in Figure 8).

Shown in Figure 9A are chronoamperometric curves of forward currents of a surface ECirr redox reaction featuring fast electrode kinetics. Calculations are performed under identical conditions as those in Figure 4, and for a moderate rate of chemical reaction ($K = 0.09$).

The descent of forward currents with time (Figure 9A) is not very steep by the surface ECirr reaction as it is at

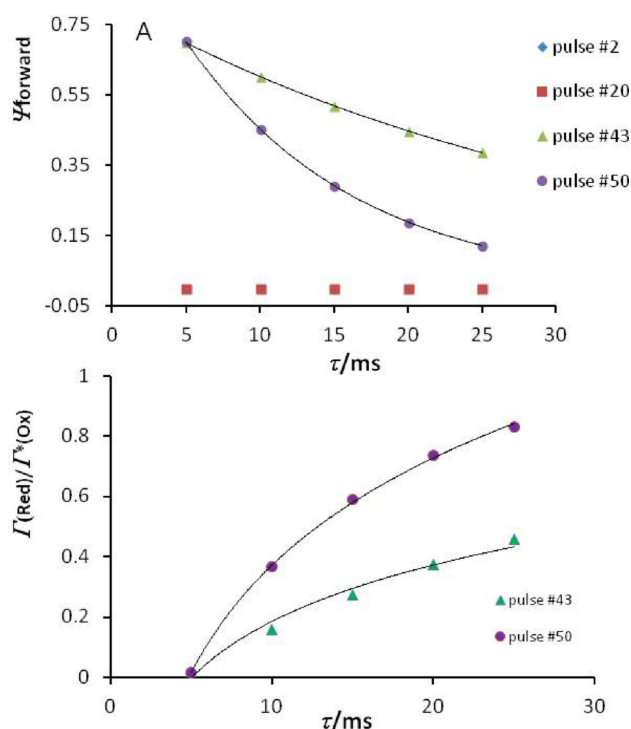


Fig. 9. Surface ECirr reaction: A. Dependence of peak currents of forward (reduction) peaks as a function of the measuring time at given reduction potential pulses. B. Dependence of the ratio $\Gamma_{\text{Leerzeichen(RED)}}/\Gamma^*_{\text{Leerzeichen(OX)}}$ as a function of measuring time at given reduction potential pulses. Standard rate constant of electrode reaction was $k_s = 50 \text{ s}^{-1}$, while the dimensionless chemical parameter was set to $K = 0.09$. Other parameters were the same as those in Figure 1.

simple surface redox reaction (Figure 4A). At this stage, it is also worth to compare the features of curves of reduction currents measured at the end of 43rd and 50th potential segment of Figure 9A and Figure 4A. Remarkably, in case of a surface ECirr reaction, the forward (reduction) currents, measured at the end of potential reduction signal, are one to two orders of magnitudes higher than the corresponding ones of simple surface reaction. In addition, the ratio $\Gamma_{\text{Leerzeichen(RED)}}/\Gamma^*_{\text{Leerzeichen(OX)}}$ by a surface ECirr mechanism, calculated as a function of measuring time τ at the defined potential reduction pulses, is much smaller (as expected) than corresponding one by simple surface reaction (compare curves at Figure 9B with those at Figure 4B). The facts presented in Figures 6 and 8 reveal that Red(ads) species created during “dead time” of potential reduction pulses play important role in observed unusual features of fast simple surface redox reaction when studied under SW voltammetric conditions.

4 Conclusions

As the kinetics of electrode reaction increases, several specific voltammetric features of so-called “simple” surface redox reactions studied with square-wave voltamme-

try have been reported so far [1,3,5,26,27]. The phenomenon of quick current descent of surface reactions exhibiting fast electrode kinetics is ascribed to a small amount of corresponding redox adsorbates remaining as “electroactive” in current-measuring time window of potential pulses in SWV [1,5]. In addition, an increase of the rate of electrode reaction at these systems causes shifting of reduction peak towards more positive values and of the oxidation peak towards more negative values. This phenomenon eventually results with splitting of the SW net voltammetric peak [1,5]. We consider in this work the role of electrochemically created redox adsorbates to the occurrence of aforementioned phenomena. Note that these effects do not exist by simple diffusional redox reactions [1,3,4]. The SWV is a pulse technique designed to measure currents of electrode reaction in a tinny time segment at the end of potential pulses. However, chronoamperometric features of fast simple surface redox reactions in SWV are quite specific. Since entire electroactive material (Ox(ads)+Red(ads)) by “simple” surface redox reactions remains firmly adsorbed at the electrode surface during the electrochemical experiment, there is a thermodynamic condition for both half-reactions to take place simultaneously. This can happen even at given potential pulses that are considered as only “reduction” or only “oxidation” in SWV. Considering an initial reduction process $\text{Ox(ads)} + ne^- \rightarrow \text{Red(ads)}$ going on at the “reduction” potential pulses in SWV, for example, it is assumed that only process of reduction of Ox(ads) to Red(ads) takes place at these potential pulses. However, we have shown that significant amount of reduced form (Red(ads)) can be electrochemically generated in the “dead time” of those “reduction” potential SW pulses. Depending on potential applied, the Red(ads) species (generated electrochemically in the “dead time” of reduction potential SW pulses) can undergo re-oxidation in the remaining time-frame at the very same “reduction” pulses where they got created. However, their re-oxidation in the measuring time-frame of “reduction” potential SW pulses would produce a current with opposite sign than the current “defined” to be measured at those potential pulses. Correspondingly, this effect should give a smaller total current detected in the current-measuring time-frame at given SW pulse. This phenomenon might be one reason for getting lower currents in SWV at simple surface reactions exhibiting high rates of electrode reaction [1,5]. To get more insights into these effects, we performed several sets of chrono-amperometric calculations. Additionally, we considered some relevant voltammetric features of surface ECirr redox reaction exhibiting fast electrode kinetics rate. With several sets of theoretical results, we show that an irreversible removal of Red(ads) species from the redox system can contribute to significant increasing of all SWV current components compared to those of a simple surface redox reaction. This effect happens when the kinetics of irreversible chemical reaction is about one to two order of magnitude smaller than the rate of electrode reaction. Moreover, the irreversible

removal of Red(ads) species at surface ECirr featuring fast electrode step, contributes to eventual disappearance of the split SW peaks phenomenon (see voltammogram (d) in Figure 6 and voltammograms in Figure 7). The fact that irreversible removal of Red(ads) species from SW “reduction potential pulses” contributes to an increase (and not decrease) of all current components of SW voltammograms featuring fast electrode kinetics implies pivotal role of Red(ads) species in specific behaviour of surface redox reactions [1,5]. From thermodynamic point of view, eventual significant re-oxidation of Red(ads) species, created in the dead-time of “reduction pulses”, would contribute to disturbance of Ox(ads)/Red(ads) equilibrium in the current-measuring time sector of a given reduction potential pulse. Thermodynamics teaches that every disturbance of equilibrium conditions requires additional energy to re-establish the equilibrium [4]. A consequence of such an event will be portrayed in shifting of peak potentials of both forward and backward peaks, and eventual appearance of the “split SW net peak” phenomenon [1,3–5]. These effects do not appear in simple diffusional reactions. This is because the mass transfer by diffusion of created Red species gets them away from electrode surface, thus hindering their significant re-oxidation in the very same reduction potential pulses where they got generated. The definitions of “only reduction” and “only oxidation” potential pulses does not hold true for surface redox reactions in square-wave voltammetry. Indeed, at these systems, there are thermodynamic conditions for both half-reactions to take place significantly at given “only reduction” and “only oxidation” SW potential pulse. This is probably a major reason for all specific features observed by “simple” surface redox reactions when studied with pulse voltammetric techniques [1]. In our further work, we are going to present in more details the features of fast surface ECirr redox reaction in cyclic stair-case voltammetry. With approach presented in this work, we hope to improve our understanding of some of specific features of surface redox reactions when studied in pulse voltammetric techniques.

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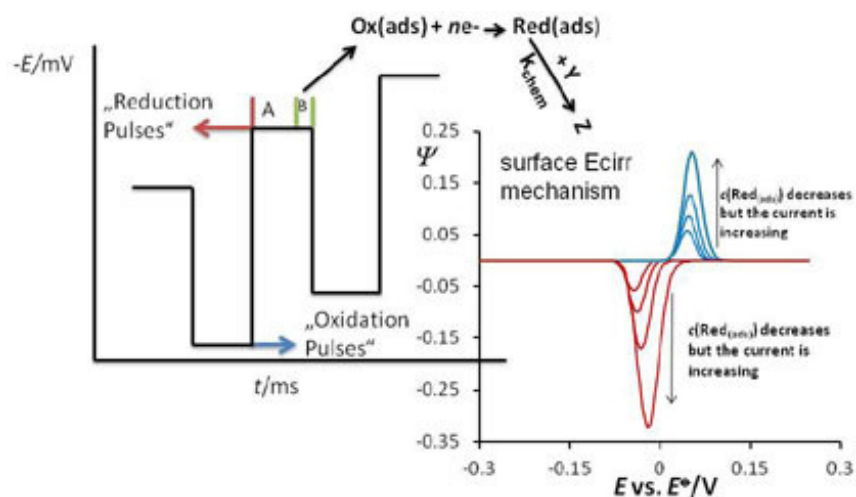
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R. Gulaboski*

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Theoretical Contribution Towards Understanding Specific Behaviour of “Simple” Protein-film Reactions in Square-wave Voltammetry