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Mathematical Modeling of Electrode Processes – Potential Dependent Transfer Coefficient in Electrochemical Kinetics

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This chapter is dedicated to professor Zbigniew Galus, who consistently applied mathematical approach to electrochemical kinetics and to memory of professor Bogdan Jakuszewski who was succeeded in both theoretical and experimental electrochemistry.

1. Introduction

The connection between experimental results and mathematical modeling of electrode processes may become an inspiration for new results and deeper understanding of the nature of electrochemical processes and its kinetic description. Sometimes experiment is preceded by a theory, sometimes it is the other way round. To avoid over discovering of phenomena, uncertainties and even mistakes, a responsible validation of model results is required. The analysis of complex, multi-electron electrode processes with chemical step(s) provides the respective examples.

2. Elementary and apparent kinetic parameters in modeling of electrode processes

In chemical kinetics, elementary (one step) and complex (multi-step) processes are described. Exactly the same situation is observed in electrochemical kinetics where electron transfer steps and chemical steps are often coupled in various sequences. Therefore, electrochemical kinetics uses two kinds of kinetic parameters: elementary describing each single step of kinetic sequence and general (apparent, observed) relating to or describing the complex mechanism as a whole.

Consequently, there is a need of showing similarities, dissimilarities and relations between the two approaches to avoid possible confusion. The following significant problems are to be discussed here:

- The distinction among apparent and elementary kinetic parameters (Sanecki & Skitał, 2002a; Skitał & Sanecki, 2009).
- The accuracy of electrochemical kinetic parameters determination by the estimation method (Sanecki et al., 2003, 2006b).

- The analysis of complex current responses (Sanecki & Lechowicz, 1997; Sanecki & Kaczmarski, 1999; Sanecki & Skitał, 2002a; Sanecki et al., 2003; 2006a, 2006b, 2010; Skitał et al., 2010).
- The relationship between apparent and elementary kinetic parameters (Sanecki & Skitał, 2002a; Skitał & Sanecki, 2009) and its consequences.

Most of electrochemical processes are complex and electrodics deal with multicharge transfer reactions as well as with multicomponent systems not considered here (Bard & Faulkner, 2001; Sanecki & Skitał, 2002b). The extraction of elementary kinetic parameters from experimental responses of multicharge reactions always requires an appropriate kinetic model, even if its application is not clearly given. Even a single formula used for calculation of kinetic parameters is a model. Therefore, a need of appraisal of assumptions basing every kind of model is evident. If the formulae available in electrochemistry textbooks and monographs are not adequate for considered mechanism, a respective rigorous mathematical model of kinetic case is required. If the applied model is appropriate to considered experimental data, the physical sense of obtained kinetic parameters is clear and the ones are reliable for further discussion. We will show further that the simple model is not appropriate for processes with chemical step unless the chemical step is extremely fast or slow and a simplification is justified.

The difference between elementary and apparent kinetic parameters denotes their physical sense: (1)– elementary ones describe single step i (e.g. k_i i α_i), general ones (*apparent*, *observed*) (e.g. k_{app} i α_{app}) describe a sequence of steps (mechanism) as a whole i.e. electrochemical and chemical steps together, as well as the way they were obtained: (2)– elementary ones are obtained by estimation with the use of complex current response, apparent usually with the use of simplified model (formula) in relation to the same response. The use of elementary parameters method is a consequence of the fact that mechanism is described as a sequence of elementary steps. General and apparent kinetic parameters are useful when application of an analytical or estimation method to complex systems is not possible. An example of apparent kinetic parameters approach is the conception of general transfer coefficient e.g. applied to interpretation of Tafel plots of complex multi-electron processes (Bockris & Reddy, 1970). Similar discussion of apparent and elementary kinetic parameters can be found in monograph by Brenet and Traore (Brenet & Traore, 1971).

Acquisition of rigorous mathematical model of considered process is fundamental for any discussion of quantitative type. The actual numerical possibilities and availability of respective software are quite enough to solve practically each of mechanisms met in practice. The respective numerical procedure of nonlinear curve fitting, called multi-parameter estimation (MPE) is in general followed with validation of obtained kinetic parameters. The criterion of optimization is a minimization the difference between experimental and theoretical response by least squares method. In electrodics MPE operates on a set of CV responses for various scan rates (and eventually on responses for various concentrations). It is a fundamental rule in electrochemistry simulations. The respective fits should be optimized for different scan rates even if there is a possibility to determine it on single curve only. The considered set of CV curves for different scan rates should be covered by the only one set of kinetic parameters (Speiser, 1996a, 1996b). The power of CV is determined by the possibility to study the electrochemical system by using different time scales by changing potential scan rate (Speiser, 1985).

The form of $i=f(E)$ and $c=f(E)$ responses corresponding to a sum of steps as well as for individual intermediate species can be predicted for almost each of mechanisms, which is the important advantage of modeling. Another one is a possibility of simple moving from elementary to general kinetic parameters. For now, however, it has not been possible to complete it inversely. The limitation of the number of estimated parameters, even if series of kinetic runs are used, is a disadvantage of MPE method. The credibility of MPE method decreases with the number of them and confidence intervals become wider simultaneously. It is however a general problem which denotes all complex systems and is a result of their complexity and not of a calculation method. MPE is a global method i.e. it operates on whole original, non processed responses (please note a comment given with equations (5)–(8)).

The electrochemical responses are in most cases complex and reflect the influence of various factors (e.g. chemical, electron transfer, adsorption steps) on its shape. Therefore, a model should include all of them. Respective electrochemical current response or concentration response is a function of many variables and it is easy to show the influence of a single kinetic parameter on its shape. In other words, an electrochemical response is directly a superposition of one-electron current responses and indirectly of chemical kinetic parameters. This chapter contains a number of respective examples, which visualize the part of complex relationships between relevant kinetic parameters and the resulting electrochemical response, namely Fig. 2–8, 9, 11–14, 15D.

3. The accuracy of electrochemical kinetic parameters determination by estimation method

For consecutive reaction steps there is a problem with the ability of a calculation procedure to extract kinetic parameters of the second kinetic step when the overall not naturally resolved current response is rate limited by the first step. In the early fifties of the last century Schwemer and Frost (Frost & Schwemer, 1952; Schwemer & Frost, 1951) and Frost and Pearson (Frost & Pearson, 1961) first solved the problem of two consecutive second order reactions in chemical kinetics. The attention was focused on the accuracy of k_1 and k_2 determination (e.g. error values k_1 ±2–4%, k_2 ±5–10% were reported (Kuritsyn et al., 1974). Analogous problems exist in electrochemical kinetics. In the first approach, in voltammetry for ECE process, the errors of kinetic parameters for the first and second one-electron steps are determined during estimation routine procedure applied to experimental response. The statistical treatment is incorporated into an algorithm. There are two other ways: (a) applying an estimation procedure to theoretical (simulated) CV curves to obtain the kinetic parameters with the best possible accuracy for the system; (b) applying an estimation procedure to the same simulated CV curves altered by the addition of noise, a non perfect zero base line, and a slight ohmic drop in order to imitate experimental errors of real voltammetric curves. The ways (a) and (b) serve only for the purpose of modeling studies. In practice, the kinetic parameters are determined entirely with the use of experimental voltammograms. The method of validation based on theoretical (synthetic) responses is seldom applied but is worth recommendation. In particular, the fact that accuracy of the evaluated parameters depends on the k_2/k_1 ratio will be shown. This means that not only the system with the rate limited by the first electron transfer is considered, i.e. the case when $k_2>k_1$, but also that the whole spectrum of k_2/k_1 ratios is taken into account for the ECE reaction scheme.

Three approaches are possible for calculating confidence intervals of the estimated parameters. Firstly, a numerical method used for the estimation and fitting procedure is applied to a single experimental curve and the statistical treatment is incorporated into an algorithm (not accessible for user). This is a non-linear regression problem solved by the least squares method (Bieniasz & Speiser, 1998a, 1998b; Lavagnini et al., 1989; Scharbert & Speiser, 1989; Seber & Wild, 1989; Speiser, 1985). For example, refs. (Bieniasz & Speiser, 1998b; Lavagnini et al., 1989) discuss in details the error space of kinetic parameters obtained during a single estimation procedure. In the second approach, the errors are determined on the basis of repeated experiments as reported by Jäger and Rudolph (Jäger & Rudolph, 1997). The population of kinetic parameters obtained by estimation provide the mean value, median, standard deviation, confidence intervals, etc. In the third approach, the estimations are repeated for theoretical responses with different starting points; it turns out that for some kinetic parameters, the calculated values (e.g. k_1) are identical or almost identical (with errors that have no physically important meaning), for others (e.g. k_2) they are not identical and for some cases they differ even by an order of magnitude. The confidence intervals for the populations of particular kinetic parameter (k_1, k_2, etc.) become available. The third approach and the reproducibility of kinetic parameters k_1, α_1, k_2, α_2 by comparing input parameters with output ones evaluated according to procedures (a) is presented here. An example of first and second step kinetic parameters validation is presented in Fig. 1, respectively.

To summarize: after numerical fitting procedure (estimation) applied to experimental response, it is worth to repeat the procedure with the use of obtained theoretical data which imitate the experimental response. After that, both (derived from experimental and theoretical responses) error spaces of kinetic parameters should be critically compared (Sanecki et al., 2003). Generally, a precise determination of second stage kinetic parameters in a consecutive process is impossible if their magnitude is much higher than that in the first stage even if the errors of the kinetic parameters are evaluated from ideal theoretical CV curves. It means that such a result is an inner feature of the investigated system alone and not a result of any calculation procedure which is not able to change it.

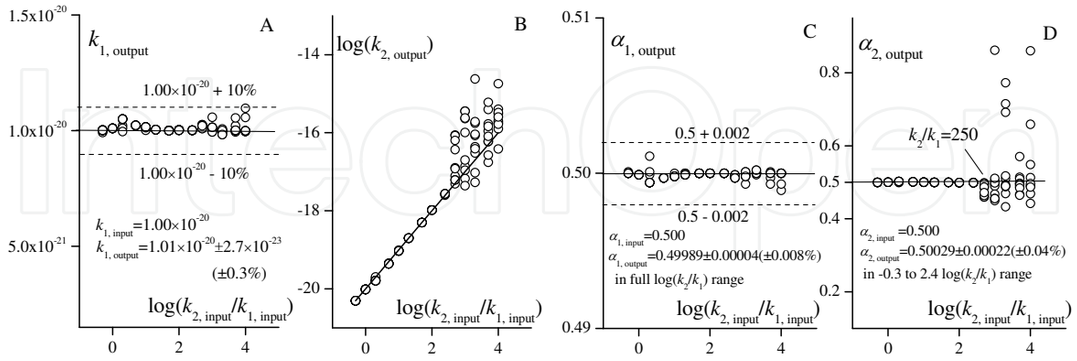


Fig. 1. Visualization of reproducibility of input kinetic parameters for theoretical CV curves of ECE reaction mechanism (1)-(3), point 5.1. Note that the rate constants are expressed on the saturated calomel electrode scale which results in unexpectedly small values of k_1 and k_2 (see also ref. (Sanecki et al., 2003)). [Reprinted from *J. Electroanal. Chem.*, Vol. 546, Sanecki, P., Amatore, C. & Skitał, P., The problem of the accuracy ..., 109-121, Copyright (2003), with permission from Elsevier.]

4. The list of applied kinetic models and description of numerical procedures

The problems formulated in this chapter were solved using *ESTYM_PDE* program. The *ESTYM_PDE* program has been designed to solve and estimate parameters of partial differential equations (PDE) describing one-dimensional mass and heat transfer coupled with chemical reaction. One of the program options enables solution of electrochemical reaction models. The numerical algorithm is based on an implementation of the method of orthogonal collocation on finite elements (OCFE) (Berninger et al., 1991; Gardini et al., 1985; Kaczmarski, 1996; Kaczmarski et al., 1997; Ma & Guiochon, 1991; Villadsen & Michelsen, 1978; Yu & Wang, 1989). After discretization of the space derivatives due to the method of OCFE, the obtained set of ordinary differential equations is solved with the backward differentiation formulae, implemented in the *VODE* procedure (Brown et al., n.d.). To estimate model parameters one of the best and fastest algorithms based on the least square fitting as proposed by Marquardt (Marquardt, 1963) in the version modified by Fletcher (Fletcher, n.d.) was used. The calculations of confidence level of estimated parameters were performed according to the method described in (Seber & Wild, 1989).

In the recovery process or estimation of model parameters, the set of differential equation must be solved many times as required by the least-squares algorithm. A single solution of the actual electrochemical reaction model takes 1-15 s (calculation of a single CV curve). The full estimation procedure, however, takes 0.5-2 hours. The time of estimation depends on the choice of initial values of estimated parameters and on the accuracy imposed for ODE solver. The highest applied accuracy of calculations was 1×10^{-15}. The accuracy is related to that of solving ordinary differential equations with VODE procedure and to absolute accuracy of the estimation of parameters. The last one was adjusted to be six orders of magnitude lower than expected value of an estimated parameter. The relative accuracy used in VODE was 1×10^{-13} and absolute accuracy was 1×10^{-15}. The Levenberg-Marquard procedure was applied as described in report (Fletcher, n.d.; Marquardt, 1963) without any changes. The same was for VODE procedure. All calculations were performed using the extended precision.

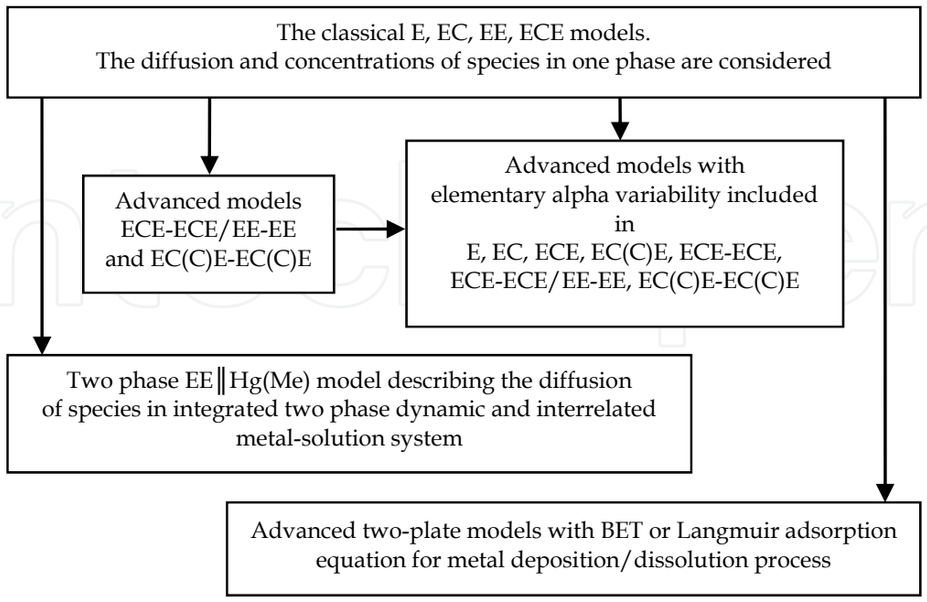
The algorithm applied for solving PDE's in *ESTYM_PDE* was also used in other programs for modelling adsorption chromatography processes (Kaczmarski et al., 1997, 2001; Kim et al., 2005, 2006a, 2006b). Other algorithms to estimate parameters of PDE are being used as well. Among them are *ELSIM* and *DigiSim*® programs in which a Simplex method and Levenberg-Marquard algorithm are applied, respectively. Simulation packages are described in papers (Bott et al., 1996; Bott , 2000; Feldberg, 1969) (*DigiSim*®) and (Bieniasz, 1997; Bieniasz & Britz, 2004) (*ELSIM*). The applied theory of electrochemical simulations is described in refs. (Bard & Faulkner, 2001; Bieniasz & Britz, 2004; Bieniasz & Rabitz, 2006; Britz, 2005; Feldberg, 1969; Gosser, 1993; Speiser, 1996a). The *ESTYM_PDE* program, similarly to other analogous programs available, provides the possibility of calculating concentration versus both space parameter and time for various geometries of the electrode.

To test a simulation software, Speiser (Speiser, 1996a) proposed to use ECE/DISP1 sequence (Amatore & Saveant, 1977). In paper (Sanecki et al., 2003), there is a comparison of available *Simulators* gathered by Speiser on the ground of the test (Table 1 and 2 and p.11 in (Speiser, 1996a)). We extended both of Speiser's tables by means of including our data for the example with the use of *ESTYM_PDE.* It is clear that all programs give practically the same results. The correctness of our calculations was also confirmed by the comparison of *ESTYM_PDE* with *DigiSim*® program. The results of calculations obtained for representative examples were exactly the same (Sanecki & Skitał, 2008).

Various examples of solving electrochemical problems by means of *ESTYM_PDE* software were described in our papers (Sanecki, 2001; Sanecki & Kaczmarski, 1999; Sanecki & Skitał, 2002a, 2007a, 2007b, 2008; Sanecki et al., 2003, 2006a, 2006b, 2010; Skitał & Sanecki, 2009; Skitał et al., 2010). The mathematical kinetic models of investigated mechanisms are presented in Table 1 with relevant references in which the models were applied with or without inclusion of the alpha variability parameter. Consecutively, the Scheme 1 illustrates the mutual interdependence of models.

Mechanism (model)	Reference
E_r	(Sanecki & Skitał, 2008)
E	(Sanecki & Skitał, 2008)
E_rC	(Sanecki & Skitał, 2007a, 2008)
E_rE_r	(Sanecki et al., 2006a)
$E_rE_r \Vert Hg(Me)$	(Sanecki et al., 2006a)
ECE	(Sanecki, 2001; Sanecki & Kaczmarski, 1999; Sanecki & Skitał, 2002a, 2007b, 2008; Sanecki et al., 2003; Skitał & Sanecki, 2009)
E_rCE_rC	(Sanecki & Skitał, 2008)
EC(C)E	(Sanecki & Skitał, 2007b)
ECE-ECE	(Sanecki, 2001; Sanecki & Kaczmarski, 1999; Sanecki & Skitał, 2007a, 2008)
ECE-EC(C)E	(Sanecki & Skitał, 2007b)
E_rCE_rC-E_rCE_rC	(Sanecki & Skitał, 2008)
E_rCE-ECE/E_rE-EE	(Sanecki et al., 2006b)
EE two-plate model with BET or Langmuir adsorption equation	(Sanecki et al., 2010; Skitał et al., 2010)

Table 1. Kinetic models prepared and/or applied to electrode processes.



Scheme 1. Kinetic models prepared and/or applied to electrode processes and their mutual interdependence.

The MPE method is now widely applied in the determination of kinetic parameters of different dynamic processes e.g. for chromatography data with the use of respective mathematical model (Kaczmarski, 2007; Kim et al., 2005, 2006a).

5. The ECE process in cyclic voltammetry. The relationships between elementary and apparent kinetic parameters

Even textbook reaction mechanisms are not immune to changes.
Bernd Speiser

5.1 Stepwise - concerted mechanism competition and complex α_{app} plots

The reduction process going through two one-electron steps with chemical reaction between them is typical for a large number of processes in both organic and inorganic electrochemistry and is still of current interest e.g. (Andrieux et al., 1992; 1993, 1994, 1997; Antonello & Maran, 1997, 1998, 1999; Antonello et al., 2001, 2002a, 2002b; Costentin et al., 2009; Daasbjerg, 1999; Jaworski & Leszczyński, 1999; Najjar et al., 2007; Pause et al., 1999, 2001; Savéant, 1987, 1992, 1993; Severin et al., 1993; Speiser, 1996a; Workentin et al., 1995).

$$RX + e \overset{k_1, a_1}{=} RX^{\bullet -} \tag{1}$$

$$RX^{\bullet -} \xrightarrow{k_f} R^{\bullet} + X^{-} \tag{2}$$

$$R^{\bullet} + e \overset{k_2, a_2}{=} R^{-} \tag{3}$$

$$RX + e \overset{k_{concerted}}{=} R^{\bullet} + X^{-} \tag{4}$$

The first set (1)-(3) constitutes an ECE (stepwise, sequential) mechanism. The equation (4) describes the *concerted* mechanism that may or may not be followed by a second electron transfer (3).

Berzins and Delahay (Berzins & Delahay, 1953) were probably the first ones who successfully applied the modeling method to unravel contentious kinetic problem. Nicholson and Shain (Nicholson & Shain, 1964, 1965a) were the first ones to describe the full mathematical model of ECE process followed with its experimental verification (Nicholson & Shain, 1965b). The determination of elementary kinetic parameters from complex CV current responses and the analysis of the competition between stepwise and concerted mechanism presented in this chapter were realized by applying the ECE process mathematical model, identical with the one described by Nicholson and Shain.

During investigation on elementary transfer coefficient (ETC) variability (sub chapters 6 and 7), we came across a series of results in which α variability and its nonlinear complex plots together with stepwise-concerted mechanism transition were reported e.g. papers quoted here in place before eq. (1)-(4). We recognized the respective parameter as the apparent α since its value was generally calculated with the use of formulae (5) or (6) (Matsuda & Ayabe, 1955) as well as by the convolution method (7)-(8) (Bard & Faulkner, 2001; Galus,

1994; Speiser, 1996a). Both of the models were derived for processes without chemical step and therefore applying the dependences (5) and (6) for ECE process has no appropriate physical basis. Consequently, kinetic parameters, plots and conclusions, obtained for the applied model cannot have clear physical sense (unless the chemical step is extremely slow or extremely fast and the process becomes E or EE, respectively).

$$E_{p/2} - E_p = \Delta E_{p/2} = \frac{1.857 \cdot R \cdot T}{(\alpha \cdot F)} \tag{5}$$

(two selected characteristic points of CV curve are taken into consideration)

$$\frac{\partial E_p}{(\partial \log v)} = \frac{1.15 \cdot R \cdot T}{(\alpha \cdot F)} \tag{6}$$

(several selected characteristic points of CV curve are taken into consideration)

$$I(t) = \frac{1}{\pi^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \tag{7}$$

$$\ln k_{app}(E) = \ln D_0^{1/2} - \ln \frac{\left[I_{lim} - I(t)\right]}{i(t)} \tag{8}$$

where I_{lim} is the limiting current of convoluted (semiintegrated) curve; the CV curve as a whole is taken into consideration).

The stepwise-concerted competition problem was solved (Sanecki & Skitał, 2002a; Skitał & Sanecki, 2009) by respective simulations presented shortly here. To compare the stepwise and concerted mechanisms on the basis of both elementary and apparent kinetic parameters approach, a procedure reverse to that known from the literature was applied. The well-known procedure involves recording of CV experimental curves from which α_{app} values are calculated using peak width formula (5) or (6) or (7,8) method. The resulting $\alpha_{app}=f(E,v)$ dependences are used to conclude about possible mechanism transition.

In our approach, CV theoretical responses for the whole spectrum of well defined mechanisms from purely stepwise (low k_f value) to purely concerted (high k_f value), are generated. Then, just like for experimental curves, α_{app} values and $\alpha_{app}=f(E,v)$ patterns are determined as specific for the implemented mechanism. The procedure and its results are shown in Fig. 2 and Fig. 3, respectively.

Fig. 3A illustrates that the range of sharp peaks cannot be interpreted as a mechanism transition symptom since it remains in pure stepwise area. The order of magnitude of k_f necessary to reach concerted area, determined from $I_p v^{-0.5}=f(v)$ dependence (Fig. 3 B,C), (see also (Sanecki & Skitał, 2002a)), is $>10^9$ s^{-1}. The results confirm that α_{app} values obtained from peak width (5) or dE_p/dv dependence (6) for ECE process do not judge stepwise/concerted alternative hypothesis. Simultaneously, it turned out that non linear α_{app} patterns of type as presented in Fig. 3A are characteristic for ECE processes within very pure stepwise mechanism.

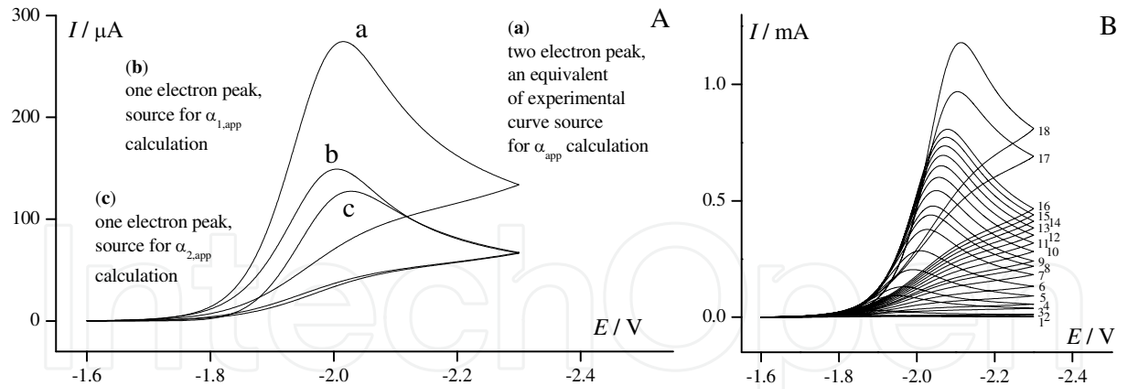


Fig. 2. (A) The theoretical CV responses obtained for the sequence of elementary steps given by eqs. (1) ÷ (3). (a): two-electron peak; (b): one-electron peak of step (1); (c): the same as (b) for step (3). (B) A series of two-electron peaks at various scan rates: 0.01, 0.1, 1, 2, 5, 10, 18, 25, 30, 40, 50, 60, 70, 80, 90, 100, 300, 500 V/s, increasing from the bottom to the top. [Reprinted from *Comput. Chem.*, Vol. 26, Sanecki, P. & Skitał P., The cyclic voltammetry simulation of ..., 297-311, Copyright (2002), with permission from Elsevier.]

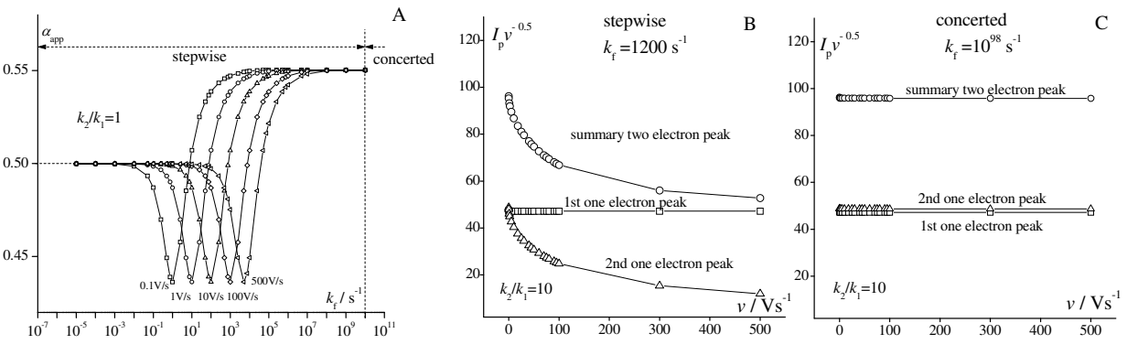


Fig. 3. The simulations of the sequence of (1) ÷ (3) steps. (A) The dependence of α_{app} on k_f at different scan rates. Input parameters: α_1=α_2=0.5. The output parameters were calculated from eq. (5). (B), (C). The relationship $i_p\, v^{-0.5}$ vs v as a diagnostic criterion. [Reprinted from *Comput. Chem.*, Vol. 26, Sanecki, P. & Skitał P., The cyclic voltammetry simulation of ..., 297-311, Copyright (2002), with permission from Elsevier.]

5.2 The analysis of complex current responses and α_{app} plots obtained as a result of convolution method

The result of application of convolution method to CV current responses is expected to be a linear type ln$k$=f(E) dependence. An α value can be determined from its slope (Bard & Faulkner, 2001). For ECE process, however, the line obtained from parent two-electron ECE peak is curved (the degree of its curvature depends on k_2/k_1 ratio and k_f value) and straight line approximation leads only to general, apparent parameters of no clear physical sense (Skitał & Sanecki, 2009). Moreover, the pseudo-linear plots clearly demonstrate involvement of two different steps of two-electron process (Fig. 4). Since linear regression is not sufficient here, the results of the convolution of two-electron ECE curves under discussion call for detailed mathematical procedure to evaluate kinetic parameters of individual steps. The simulation data (Fig. 4A) indicate that convolution method can be applied only to some

boundary cases of ECE mechanisms as E or EE type with k_f from 10^9 value to $k_f=10^{98}$ as infinity, similarly as in Fig. 3 data.

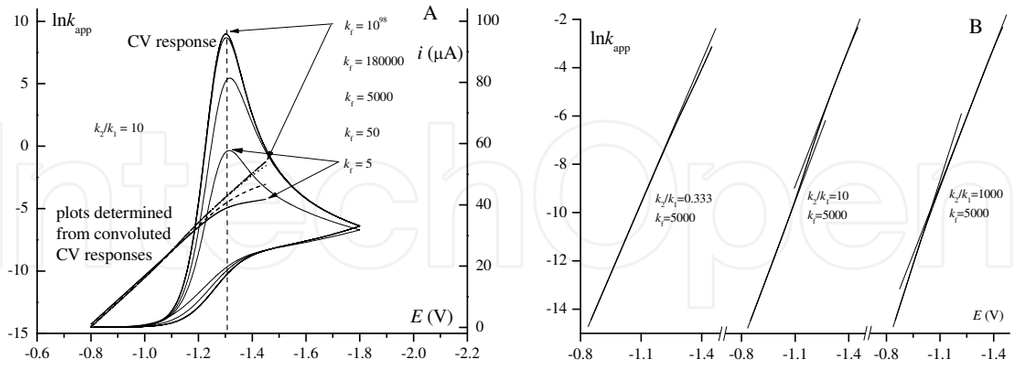


Fig. 4. (A) The influence of k_f on the shape of CV responses and lnk_{app}=$f(E)$ dependences for simulated ECE mechanism. The interdependence between input CV curves and convolution results is shown. The length of non-linear curve fragment increases when k_f increases (from the bottom to the top). The rate constants k_{app} were calculated by convolution method (eq. (7) and (8)). (B) The influence of k_2/k_1 ratio on the shape of lnk_{app}=$f(E)$ dependence obtained from convoluted CV responses for simulated ECE mechanism. Parameters of CV curves are as follows: k_1=0.03 cm s^{-1}, α_1=α_2=0.5, v= 1 Vs^{-1}. The k_2/k_1 and k_f values are presented on the plot. Note the increase of complexity of structure from the left to the right. For values of parameters and details see original paper (Skitał & Sanecki, 2009). [Reprinted from *Polish J. Chem.*, Vol. 83, Skitał P. & Sanecki P., The ECE Process in Cyclic Voltammetry. ..., 1127–1138, Copyright (2009), with permission from Polish Chemical Society.]

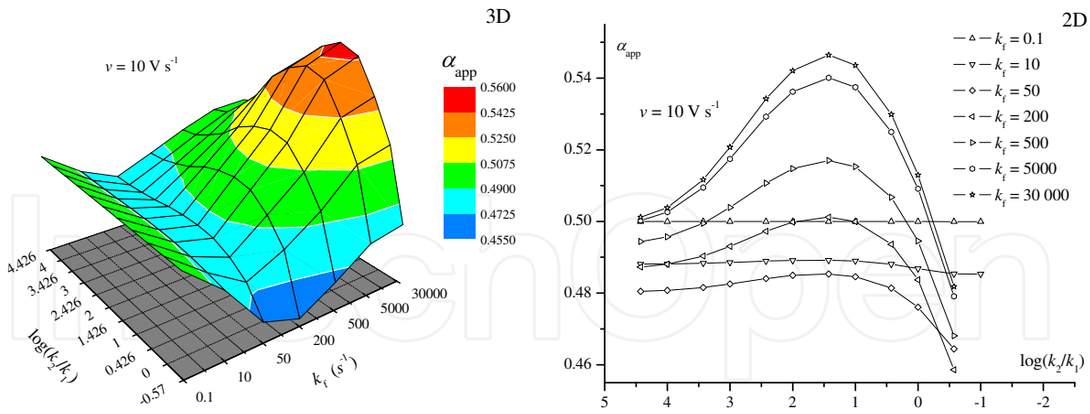


Fig. 5. The result of modeling of ECE process in cyclic voltammetry. An example of 3D plot: general parameter α_{app}, determined by convolution method, as a function of log(k_2/k_1) and k_f on 3D and 2D plots. Scan rate 10 V/s, k_1=0.03 cm s^{-1}; the values of kinetic parameters are in original paper (Skitał & Sanecki, 2009). For k_f value less than 0.1 s^{-1} (not included), where process can be simplified to E one, the respective 3D plot is flat. The 2D plot can be obtained by cutting the 3D one with a respective plane. [Reprinted from *Polish J. Chem.*, Vol. 83, Skitał P. & Sanecki P., The ECE Process in Cyclic Voltammetry. ..., 1127–1138, Copyright (2009), with permission from Polish Chemical Society.]

The fact of revealing of the complex structure of the considered ECE system in the form of broken linear or bent $\ln k=f(E)$ dependences (Fig. 4) makes the application of convolution method suitable only for coarse calculation of kinetic parameters or as precursor of estimation method. The results, in the form of α_{app} vs. k_f and k_2/k_1 plot presented in Fig. 5., indicate that the convolution method (7)-(8) applied leads to nonlinear α_{app} plots similar to these determined by means of eq. (5) and (6) and described in paper (Sanecki & Skitał, 2002a). The changes in α_{app} value and non-linear α_{app} patterns are present in stepwise mechanism zone and not in the range of its eventual change to concerted one.

Bent linear dependence $\ln k$ vs. E from Fig. 4B is not surprising. It is well-known that such a processed electrochemical responses in form of bent straight lines reveal the complexity of the original response of consecutive process (Ružić, 1970, 1974). It means that system requires another kinetic model with elementary kinetic parameters. Similar situation can be found for some normal pulse polarography data (Sanecki & Lechowicz, 1997), some overlapped voltammetric data (Rusling, 1983) and in our simulation results (Fig. 4, 5).

The Fig. 5 data indicate, that linear, non-linear and various complex α_{app} plots of 2D type are only a special cases of 3D dependences. The dependences α_{app} on k_f as well as α_{app} on k_2/k_1 presented by us in (Sanecki & Skitał, 2002a) can be considered as the members of the same category.

In the light of presented facts, it is clear that variation of α_{app}, visualized by 2D and 3D plots is only an intriguing picture with no consequence for electrode kinetics since no change of mechanism was proven. As discussed earlier, the only cause of such plots origin is the fact, that paradigm of eqs. (5)-(6) as well as (7)-(8) (Bard & Faulkner, 2001; Greef et al., 1985) does not contain any chemical step.

In the process of modeling applied here (CV curves in Figs. 2, 4), no linear variability of ETC was either assumed or introduced into the model (α_i=0.5=const) i.e. normal Butler–Volmer's kinetics was applied. Therefore, the output α_{app} dependences (Figs. 3, 4 and 5) cannot contain α_{el} variability (Sanecki & Skitał, 2002a).

Conclusions

1. Stepwise and concerted processes are the limiting cases of ECE mechanisms with different chemical k_f constant (Sanecki & Skitał, 2002a; Sanecki & Skitał, 2007b).
2. For concerted mechanism it is possible to avoid the unclear defined $k_{concerted}$ constant (neither electrochemical nor chemical) in eq. (4) when kinetic description of ECE process with elementary kinetic parameters is applied.
3. The categories of nonlinear and complex α_{app} plots, as well as curved or bent $\ln k_{app}=f(E)$ dependences as the result of application of EE or E or convolution kinetic model for ECE process, are a symptom of influence of chemical reaction on current response and not a change of mechanism. The observed non linear α_{app} variability and complex α_{app} plots are in accordance with Butler-Volmerian kinetics and are not a result of elementary α potential dependence.

6. The application of EC, ECE and ECE-ECE models with potential dependent transfer coefficient to selected electrode processes

The classical Butler-Volmer electrochemical kinetics with a priori assumed invariability of α ($\partial\alpha/\partial E$=0) provides approach which adequately describes the majority of observed

electrode processes. The problem of α variability appears in some special cases of kinetic analysis e.g. during investigation of multi-stage electron transfer separated by a large potential interval, for series of substituted compounds with the same reactive group as well as for experimental long distance current-potential dependences of quasi-reversible processes (Corrigan & Evans, 1980; Matsuda & Tamamushi, 1979; Sanecki, 2001; Sanecki & Kaczmarski, 1999; Sanecki & Skitał, 2007b). The first case of the type was described by Pierce and Geiger as *alpha kinetic discrimination* (Pierce & Geiger, 1992). Currently, extended and still growing application of variety of solid electrodes (McDermott et al., 1992), including chemically modified and semiconductor electrodes, makes the problem of diversification and variability of transfer coefficient much more important than ever before.

The significance of the discussed problem is confirmed by simple calculations, based on relevant literature data (Angell & Dickinson, 1972; Garreau et al., 1979; Savéant & Tessier, 1982; Savéant & Tessier et al., 1977), which leads to the conclusion that ETC variability effect is usually 5-10 times stronger than the double layer correction effect (see also Sanecki & Skitał, 2007a).

Transfer coefficient is one of the fundamental concepts in electrode kinetics. The extensive theoretical support, including all modern theories of charge transfer, predicts the potential variability of ETC (Dogonadze, 1971; Hush, 1958; Levich, 1966; Marcus, 1956; Marcus, 1960; Marcus, 1977). The variation of ETC for reduction and oxidation processes of individual compounds and ions has been systematically investigated by Savéant's group, Corrigan and Evans and others (Angell & Dickinson, 1972; Bindra et al., 1975; Corrigan & Evans, 1980; Dogonadze, 1971; Frumkin, 1932; Garreau et al., 1979; Hush, 1958; Levich, 1966; Marcus, 1956; Marcus, 1960; Marcus, 1977; Matsuda & Tamamushi, 1979; McDermott et al., 1992; Nagy et al., 1988; Parsons & Passeron, 1966; Rifi & Covitz, 1974; Samec & Weber, 1973; Sanecki, 1986; Savéant & Tessier, 1975; Savéant & Tessier, 1982; Tyma & Weaver, 1980). The studies have been focused on the experimental detection of the ETC variability. The research goal has been achieved with minimal further continuation. In refs. (Angell & Dickinson, 1972; Bindra et al., 1975; Corrigan & Evans, 1980; Garreau et al., 1979; Matsuda & Tamamushi, 1979; McDermott et al., 1992; Nagy et al., 1988; Parsons & Passeron, 1966; Samec & Weber, 1973; Savéant & Tessier, 1975; Savéant & Tessier, 1982; Tyma & Weaver, 1980) one can easily find or calculate the $\partial\alpha/\partial E \neq 0$ values for the one electron processes and for resolved two electron reduction (Sanecki, 2001; Sanecki & Kaczmarski, 1999). The investigation of a problem of the potential dependent α has been continued by several authors (Chidsey, 1991; Finklea, 2001a, 2001b; Finklea & Haddox, 2001; Finklea et al., 2001; Haddox & Finklea, 2003; Miller, 1995; Smalley et al., 1995). What is more, well known analogy of α and β to α_B and β_B of the BrØnsted parameters (Albery, 1975; Frumkin, 1932; Rifi & Covitz, 1974), the ETC has also been interpreted as a Hammett-type reaction constant ρ (Sanecki, 1986). This interpretation, due to similarity of the homogenous and heterogeneous kinetics, allows the more flexible approach to the ETC value and is easy to understand by non electrochemists (Rifi & Covitz, 1974).

At present, the majority of electrochemists do not apply the ETC variability or consider it meaningless. Therefore, there is a need to indicate the special cases in which the effect may be of importance (Sanecki & Skitał, 2007a, 2007b). Our choice of respective experimental cases was focused on the following four examples (points 6.1-6.4). In turn, point 6.5 is devoted to comparison of IR_u drop and $\partial\alpha/\partial E$ parameter influence on CV responses.

6.1 Repetition of the important literature example of the observed elementary α variability case

Corrigan and Evans (Corrigan & Evans, 1980) showed that inclusion of α variability in form of $\partial\alpha/\partial E$ parameter into kinetic model of one-electron quasireversible reduction process of 2-nitro-2-methylpropane Eq. (9):

$$t\text{-BuNO}_2 + \mathrm{e}^- \xrightarrow{k_1,\alpha_1} t\text{-BuNO}_2^{\bullet -} \xrightarrow{k_{ch}} t\text{-Bu}^{\bullet} + \mathrm{NO}_2^- \tag{9}$$

leads to better fit between experimental and theoretical responses.

We obtained the result similar to that but for more extended scan rate range on GC and Hg electrodes in DMF solution, where the effect turned out to be more distinct. Our results are presented in Table 2 and in Fig. 6 ($\partial\alpha/\partial E$ =0 and $\partial\alpha/\partial E \neq 0$ for comparison) where the value $\partial\alpha/\partial E$ = 0.42 V^{-1} was obtained as kinetic parameter by estimation for both electrodes.

The data shown in Table 2 indicate that our results, including the obtained $\partial\alpha/\partial E$ values, are in full agreement with the results obtained by Corrigan and Evans. In the light of presented facts the need of introducing α variability into kinetic model of the considered system is clear (Fig. 6). The better fit obtained for model with $\partial\alpha/\partial E$ included is confirmed by statistical data (Sanecki & Skitał, 2007a).

	(Corrigan & Evans, 1980)		(Sanecki & Skitał, 2007a)	
	Hg	Pt	GCE	Hg
$\partial\alpha/\partial E$, V^{-1}	0.37± 0.03	0.40	0.42±0.02	0.42±0.03
scan rate range	10-100 Vs^{-1}		0.1-100 Vs^{-1}	
medium	AN, TBAP	AN, TEAP	DMF, 0.3 M TBAP	
kinetic model	E		EC	

Table 2. CV reduction of 2-methyl-2-nitropropane. The comparison of our α variability results with analogical data published by Corrigan and Evans. [The Table reproduced by permission of The Electrochemical Society.]

6.2 Comparison of two ECE-ECE reduction steps with large potential difference (reduction of 1,3-benzenedisulfonyl difluoride)

A comparison of two identical reduction processes located at different potentials may be considered as a classical model for determination of α variability. The approach was first presented by Pearce and Geiger (Pierce & Geiger,1992). In turn, the α variability was determined by the comparison of two $-SO_2F$ group reduction on Hg electrode (Sanecki & Kaczmarski, 1999) ($\Delta\alpha$ method – the two different values of α were optimized by estimation). At present, the same system was investigated using the GCE electrode.

The results (Fig. 7) indicate that for electroreduction of 1,3-benzenedisulfonyl difluoride (1,3-BDF), the ECE kinetic model without α variability is not possible. There is a significant difference between the α's for both reduction stages i.e. between α_1 and α_3 as well as between α_2 and α_4 (note also the difference in a shape of the peaks). Fig. 7, the left column plots indicate that a model without $\Delta\alpha$ variability provides crossing experimental and theoretical plots. Both

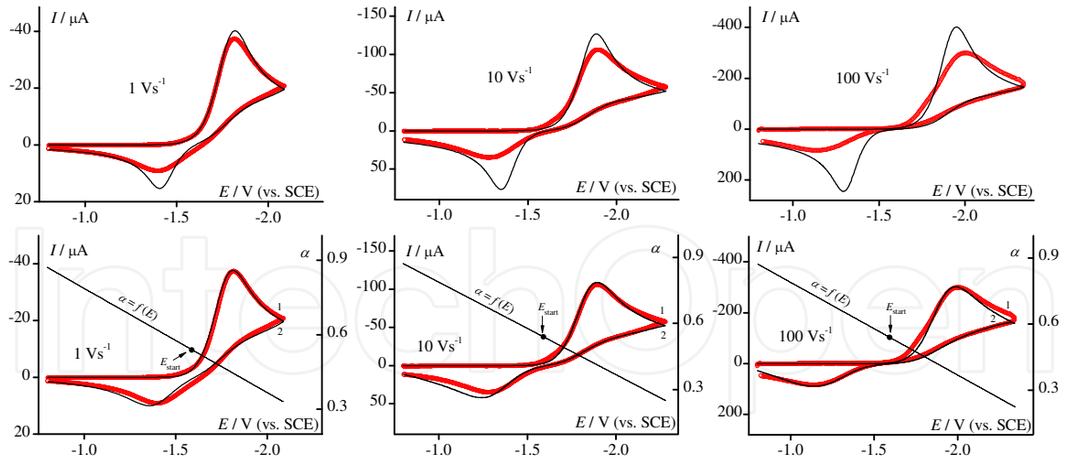


Fig. 6. CV reduction of 2-methyl-2-nitropropane. The comparison of two EC models: without (top row) and with (bottom row) α variability included. For parameters and details see original paper (Sanecki & Skitał, 2007a). [Reproduced by permission of The Electrochemical Society.]

of the approaches, i.e. introducing of different α values ($\Delta\alpha$ variability) and continuous α variability ($\partial\alpha/\partial E$), gave very similar results. The small potential difference and respective confidence intervals do not allow determination of the difference between α's within each of the two considered reduction stages (two-electron reduction of SO_2F). Moreover, the comparison of various electron transfers steps: anion radical creating (1) and radical reducing (2) is not appropriate for α variability determination.

The results and comparison of the two applied methods of α variability determination are presented in Table 3.

The method of α variability determination	**GC electrode** (Sanecki & Skitał, 2007a)	**Hg electrode** (Sanecki & Skitał, 2007a)	**Hg electrode** (Sanecki & Kaczmarski, 1999)
Estimation of the different α values	ΔE_p=0.705 V $\partial\alpha/\partial E$ = 0.20 ± 0.07	ΔE_p=0.749 V $\partial\alpha/\partial E$ = 0.51 ± 0.09	$\partial\alpha/\partial E$ = 0.44 ± 0.04
Estimation of the $\partial\alpha/\partial$E parameter	$\partial\alpha/\partial$E = 0.20 ± 0.03 V^{-1}	$\partial\alpha/\partial E$ = 0.41 ± 0.07	

Table 3. The comparison of α variability values for the electroreduction of 1,3-BDF. [The Table reproduced by permission of The Electrochemical Society.]

6.3 Comparison of two reduction steps within ECE process with a small potential difference. Reduction of *p*-toluenesulfonyl fluoride

The comparison of experimental CV responses for ECE reduction of *p*-toluenesulfonyl fluoride (TSF) (dissociative electron transfer process) with respective $\Delta\alpha$ variability model and variable α with $\partial\alpha/\partial E$ parameter included model is presented in paper (Sanecki & Skitał, 2007a). Due to small potential difference between the steps (56 mV at v=1 Vs^{-1}), where the steps are not naturally resolved, the difference between models with α variability

included and not included is insignificant here. Moreover, the two ways of α variability introduction lead to almost the same dependences which suggests that the models are equivalent (Sanecki & Skitał, 2007a).

6.4 Comparison of the *p*-toluenesulfonyl fluoride and benzenesulfonyl fluoride reductions. The substituent effect

When the two consecutive steps of two-electron process are not naturally split and $k_2<k_1$ or $k_2\approx k_1$, it is possible to determine the elementary transfer coefficients with satisfactory accuracy. For such cases the difference of peak potentials is seen on calculated elementary steps parameters (Sanecki & Skitał, 2007a). When $k_2>k_1$, the respective confidence intervals for second electrochemical step are wider than those for the first one in case of 1,3-BDF electroreduction (Fig. 7).

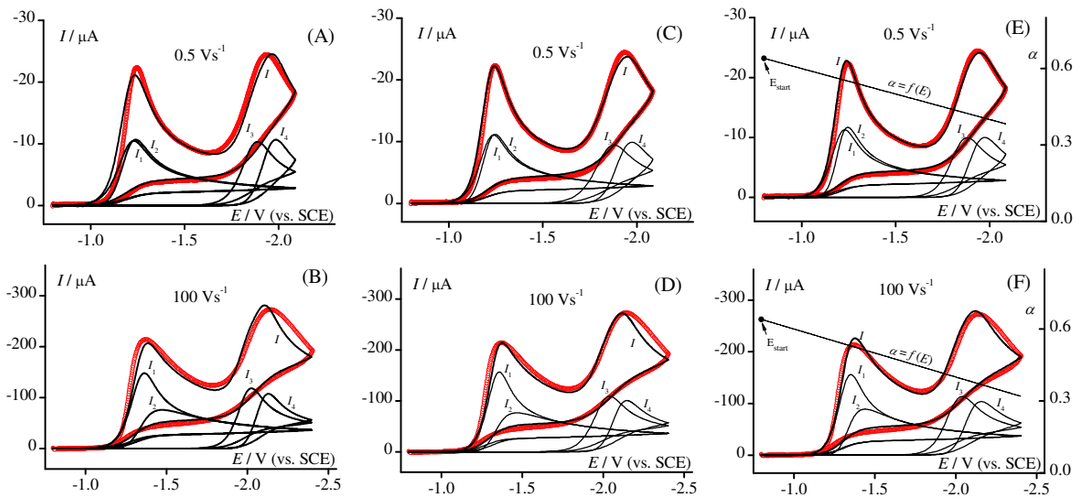


Fig. 7. Comparison of experimental (red points) and theoretically obtained curves (black lines) of the CV electroreduction of 1,3-BDF in 0.3 M TBAP/DMF on GCE. Estimated parameters for ECE-ECE model are: (A) & (B)– with α variability not included ($\partial\alpha/\partial E=0$ and $\alpha_1=\alpha_2=\alpha_3=\alpha_4$): k_1=0.017±0.001 cms^{-1}, k_2=0.064±0.01 cms^{-1}, k_3=0.041±0.003 cms^{-1}, k_4=0.0065±0.0005 cms^{-1}, $\alpha_1=\alpha_2=\alpha_3=\alpha_4$=0.51±0.01, k_{f1}=1100±200 s^{-1}, k_{f2}=8000±900 s^{-1}; (C) & (D)– with included α variability ($\alpha_1=\alpha_2$, $\alpha_3=\alpha_4$; $\Delta\alpha/\Delta E\neq 0$) in (Sanecki & Skitał, 2007a); (E) & (F)– with included α variability ($\partial\alpha/\partial E\neq 0$) in (Sanecki & Skitał, 2007a). The estimated linear $\alpha=f(E)$ variability along the CV response is shown on the plot. The scale for α is the right vertical axis. [Reproduced by permission of The Electrochemical Society.]

The effect of substituent on elementary α was considered in our previous papers (Sanecki, 2001; Sanecki & Kaczmarski, 1999). Now we compare the reduction of two compounds with $\Delta E_p\approx 0.1$V to show the limit of possibility of α variability detection when two similar (with identical reducible group) compounds are compared (Fig. 8).

The two substituted compounds values of $\partial\alpha/\partial E$ obtained by comparison of respective kinetic parameters are quite reasonable but due to the small difference in α value must be charged with significant error. It suggests that for two substituted compounds, when difference in peak potential is under 0.1 V, the difference in α values is unrecognizable and

variability is not a problem to consider. The similar picture as presented in Fig. 8 and the respective calculation results for two substituted compounds as well as for the series of iodobenzenes examples of α variability can be found in paper (Sanecki, 2001).

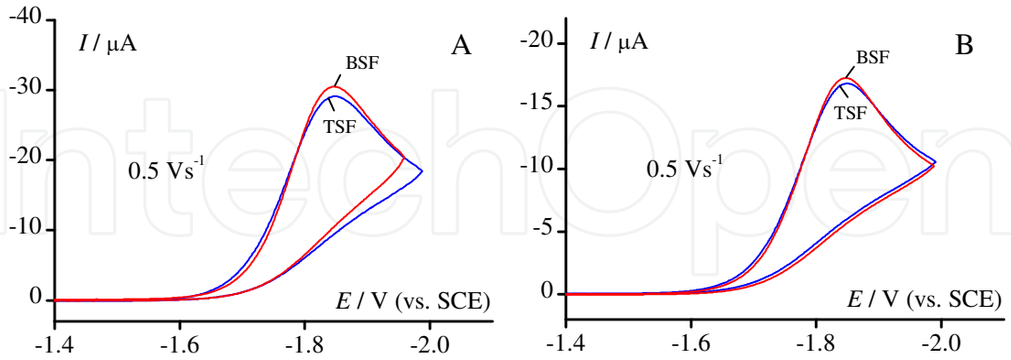


Fig. 8. The comparison of CV reduction of benzenesulfonyl fluoride (BSF) (red line) and TSF (blue line) in 0.3M TBAP/DMF on: (A) GC and (B) Hg electrodes. The curves on plots (A) and (B) were shifted to compare the slopes: plot (A) on GCE by ΔE= –0.122 V, plot (B) on Hg by ΔE= –0.098 V. Note the small difference of slopes which corresponds to a difference of α. The same effect is seen on estimated α values: α_1=0.67±0.02 for BSF and α_1=0.62±0.02 for TSF both on GCE. On Hg electrode for BSF α_1=0.67±0.02, for TSF α_1=0.62±0.02. It results in $\partial\alpha_1/\partial$E = 0.41±V^{-1} for GCE and $\partial\alpha_1/\partial E$=0.61 V^{-1} for Hg electrode. For other parameters see original paper (Sanecki & Skitał, 2007a). [Reproduced by permission of The Electrochemical Society.]

6.5 Comparison of IR_u drop and $\partial\alpha/\partial E$ parameter influence on CV responses

The influence of IR_u effect and non-constant transfer coefficient effect on current response shape can be similar and there is a real risk of making a mistake of detecting a non existing $\partial\alpha/\partial E$ effect. Therefore, the comparison of both effects by simulations is presented in Fig. 9.

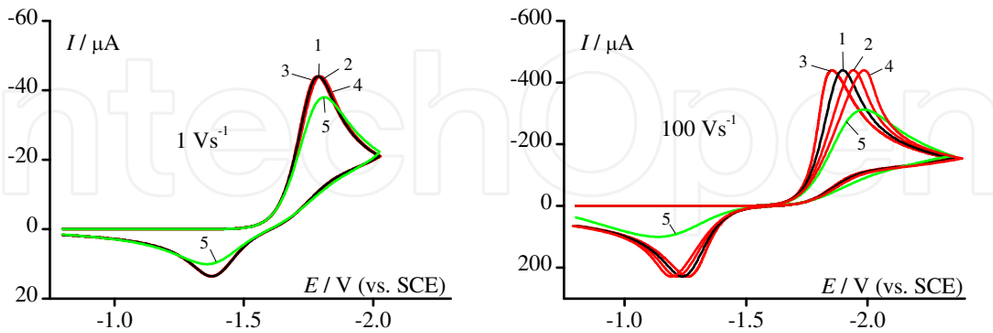


Fig. 9. Theoretical CV current responses for EC kinetic model. The influence of uncompensated resistance R_u and included α variability for 1Vs^{-1} and 100Vs^{-1}. The scan rate value is the one difference between left and right plot. Curves (1),(2),(3),(4): variable α model with $\partial\alpha/\partial E$=0 and R_u=0Ω, 100Ω, -100Ω, 200Ω, respectively; curve (5): variable α model with $\partial\alpha/\partial E$=0.4 and R_u=0Ω. For other parameters see the paper (Sanecki & Skitał, 2007a). [Reproduced by permission of The Electrochemical Society.]

The IR_u compensation problems have been resolved by the method of estimation with the use of theoretical peaks (Sanecki et al., 2003). The series of data in 0.1–100 V/s scan rate range for EC, ECE, and ECE–ECE mechanisms, which correspond to the investigated compounds, were compared.

At first, series of theoretical EC responses were generated, for input set of kinetic parameters. The obtained responses were treated as pseudo-experimental ones and the output kinetic parameters were evaluated from them by a standard estimation procedure. The obtained results indicate that generally, for all kinetic models, IR_u attenuates the determination of exact values not only $\partial\alpha/\partial E$, but all input values of kinetic parameters. For EC model, the influence of IR_u effect is expressed on k_1 to a higher degree, and less on $\partial\alpha/\partial E$ and α_{start}.

The IR_u effect depends on a scan rate value. It is practically invisible at low v up to 1–2 Vs^{-1} (Fig. 9). The effect increases gradually with v and at 25, 50 and 100 V/s is clearly visible, for instance in the range 5–100 Vs^{-1} R_u=100 Ω produces non existing $\partial\alpha/\partial E$ = 0.01–0.04 V^{-1}. Hence, the low scan rate data are safe for $\partial\alpha/\partial E$ determination, even in case of lack of IR_u compensation (not recommended). The $\partial\alpha/\partial E\neq 0$ effect, however, is generally observed as a visible gap in fits for all scan rate peaks (examples: Fig. 9). The influence on the peak shape is different for both effects. The IR_u effect decreases the slope without change of the peak height and passes E_p towards negative potentials. The $\partial\alpha/\partial E$ effect decreases both the slope and the peak height with small influence on E_p.

An overcorrection done on IR_u affected responses is not able to provide a variable α effect, since after IR_u correction CV peaks are steeper which is exactly opposite to observed $\partial\alpha/\partial E$ effect on CV response (Fig. 9). On the contrary, the real risk is the CV response charged with uncompensated IR_u, which can be erroneously considered as comprising an $\partial\alpha/\partial E$ effect.

Other important results obtained from extensive simulations are as follows. For $IR_u>0$ (the case of undercompensation), the obtained $\partial\alpha/\partial E$ (and itself α) increases with v. For $IR_u<0$ (the case of overcompensation), the obtained $\partial\alpha/\partial E$ (and itself α) decreases with v and its negative values can be obtained. For $IR_u=0$ (the proper compensation), the obtained $\partial\alpha/\partial E$ are constant with v.

The recognized rules can be treated as diagnostic criteria. For the other ECE and ECE–ECE models under consideration, the above rules and conclusions hold, although they are less distinct for potential dependent α parameter due to small sensitivity of their kinetic systems.

7. Alkyl iodides electroreduction and α variability

The process of the electroreduction of organic iodides is an example of two-electron reductive cleavage reaction and a subject of extensive investigation in the organic electrochemistry (Andrieux et al., 1979; Caldwell & Hacobian, 1968a, 1968b; Colichman & Kung Liu, 1954; Hush, 1957; Hussey & Diefenderfer, 1967; Jaworski et al., 1992; Mairanovskii, 1969; Mairanovskii & Rubinskaya, 1972; Mairanovskii et al., 1975; Pause et al., 2000; Peters, 1991; Sanecki, 2001; Sawyer et al., 1995; Sease et al., 1968; Stackelberg, 1949;). The established mechanism is relevant for the cleavage of carbon–halogen bond and has been successfully applied also for the other categories of compounds (e.g. (Andrieux et al., 1996, 1997; Jakobsen et al., 1999)).

The influence of carbon chain length and the number of iodine atoms in the molecule was examined. The two-electron reductive cleavage with iodine elimination was numerically resolved into one-electron consecutive steps. The mechanism of the process was discussed in the frames of the two mathematical models: EC(C)E (with radical dimerisation) for one stage electroreduction of RI as well as ECE-EC(C)E kinetic model for two stage electroreduction of RI_2. In both models transfer coefficient variability was included. For electroreduction of diiodomethane the discrimination of elementary α between two reduction stages was determined (Sanecki & Skitał, 2007b). The α variability was determined using estimation procedure in which $\partial\alpha/\partial E$ was treated as other kinetic parameters and included into kinetic model (Corrigan & Evans,1980; McDermott et al.,1992).

The experimental facts and generally accepted relevant literature data suggested EC(E)E model with k_f of very high value (concerted process). Additionally, the estimation results denoted inclusion of ETC variability into the model. The obtained values of $\partial\alpha/\partial E$ parameter for monoalkyl iodides were in range between 0.33–0.36 V^{-1} with maximum confidence interval equal to ±0.09. The respective value for diodomethane was 0.20±0.04 V^{-1} (Fig. 10).

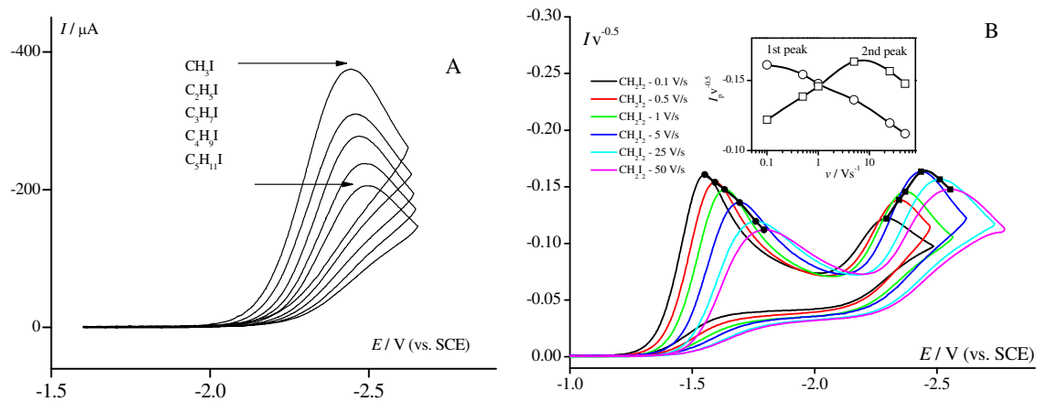


Fig. 10. (A) The CV electroreduction of five alkyl iodides in 0.3 M TBAP in DMF on GCE. The concentration of substrate was 4 mM. Scan rate v = 5 Vs^{-1}. Other details are specified in the original paper (Sanecki & Skitał, 2007b). (B) The CV electroreduction of CH_2I_2 in 0.3 M TBAP/DMF solution on GCE. The normalized CV current responses $Iv^{-0.5}$. The $I_p v^{-0.5}$ values for both reduction stages are shown as respective points on maximum current or, for clarity, separately in the sub-window. Note the different slope of kinetic $I_p v^{-0.5}$ vs v dependence in subwindow. [Reprinted from *Electrochim. Acta*, Vol. 52, Sanecki, P. & Skitał P., The electroreduction of alkyl iodides ..., 4675-4684, Copyright (2007), with permission from Elsevier.]

Conclusions

1. The electroreduction of mono alkyl iodides and diiodomethane on glassy carbon electrode can be described by EC(C)E and ECE-EC(C)E numerical model, respectively. The second electrochemical step of the EC(C)E process is generally slower then the first one.
2. The comparison of CV responses and the values of determined kinetic parameters for a sub-series of five mono iodides indicates that their slope and elementary transfer coefficient do not vary with a change of the alkyl substituent. The fact can be explained

by a small difference of reduction potentials caused by weak substituent effect of alkyl groups.

3. The determined $\partial\alpha/\partial E$ value for diiodomethane is equal to 0.20 V^{-1} and is about two times lower than that obtained in literature for aromatic compound electroreduction on Hg (Sanecki & Kaczmarski, 1999). For the other elementary processes the values in the range 0.174-0.4 V^{-1} were obtained (Savéant & Tessier, 1982). On the other hand, the respective values obtained for monoalkyl iodides are higher (Sanecki & Skitał, 2007b).
4. The respective comparison of elementary kinetic parameters for two-stage diiodomethane electroreduction on GCE indicates the presence of alpha kinetic discrimination with $\partial\alpha/\partial E$=0.15 V^{-1} according to Pearce and Geiger nomenclature (Pierce & Geiger, 1992).

8. Theoretical discovery of *isoalpha points*

8.1 Parameter $\partial\alpha/\partial E$ or non-continuous change of α ($\Delta\alpha$) as a source of revealing particular points on CV curve

The α variability was firstly used as a tool to reveal the particular properties of the investigated system in (Sanecki & Skitał, 2008). It was shown that respective simulations lead to discovery of the new meaningful phenomenon called *isoalpha* effect (Fig. 11,12). The inclusion of the $\partial\alpha/\partial E\neq 0$ parameter or non-continuous variability of α (Δα) into kinetic model of E, EC, ECE, ECE-ECE and of E_rCE_rC–E_rCE_rC mechanisms results in the change of the single CV curve into the set of CV curves comprising specific intersection point(s), called α independent current-potential point or *isoalpha point (iap).* The place of *iap* appearance depends on v and/or k value (Fig. 12). The *isoalpha point* (E_{iap}, I_{iap}) can be, to some extend, treated as electrochemical analog of *isosbestic* point (Sanecki & Skitał, 2008).

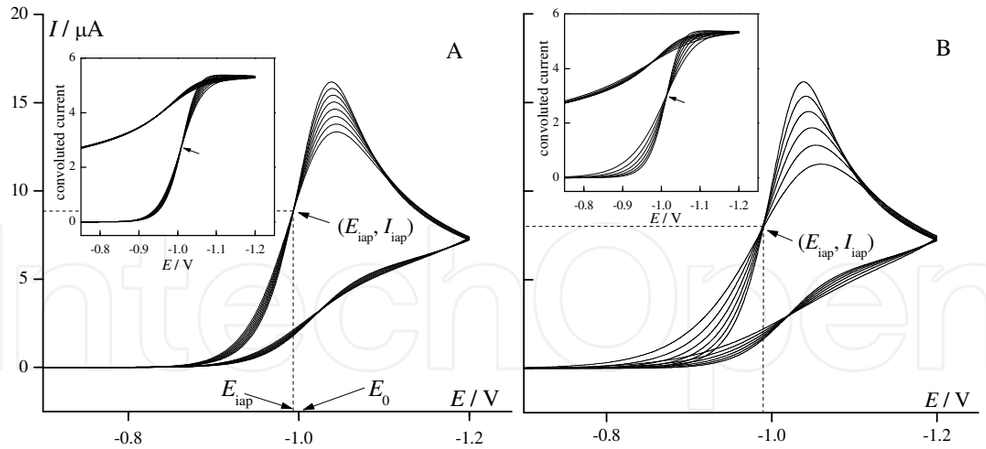


Fig. 11. The discovery of *isoalpha points* as a result of including of $\partial\alpha/\partial E\neq 0$ parameter (A) or different α values (B) into kinetic model of one electron reduction step on the theoretical current response. The one-electron CV responses for E_{irr} process (A): $\partial\alpha/\partial E$ = 0; 0.2; 0.4; 0.6; 0.8; 1.0; 1.2; 1.4 increasing from the top to the bottom curves; (B): α = 1; 0.9; 0.8; 0.7; 0.6; 0.5 decreasing from the top to the bottom curves. The insets show the convoluted form of main plot with revealed *isoalpha point*. Other details are in original paper (Sanecki & Skitał, 2008). [Reprinted from *Electrochim. Acta*, Vol. 53, Sanecki, P. & Skitał P., The mathematical models of kinetics ..., 7711-7719, Copyright (2008), with permission from Elsevier.]

Parameter $\partial\alpha/\partial E$ into respective kinetic equation was previously applied by Corrigan and Evans (Corrigan & Evans, 1980) as well as McDermott and coauthors (McDermott et al., 1992). The application of the non-continuous ETC variability parameter ($\Delta\alpha$), in which each curve is generated for different α value was applied (Sanecki & Kaczmarski, 1999; Sanecki & Skitał, 2007a, 2007b; Sanecki et al., 2006b).

Theoretical curves visualized in Fig. 11A were obtained by the algorithm which includes $\partial\alpha/\partial E$ in the range 0 - 1.4 V^{-1}. Despite the fact, that experimental values of $\partial\alpha/\partial E$ do not exceed 0.5 V^{-1}, the application of wider range of $\partial\alpha/\partial$E results in more extended set of curves. For the same reason α=1 as a starting value was chosen (Fig. 11B). When the variability starts at α=0.5, the intersection point (*iap*) remains the same but the plot is less convincing.

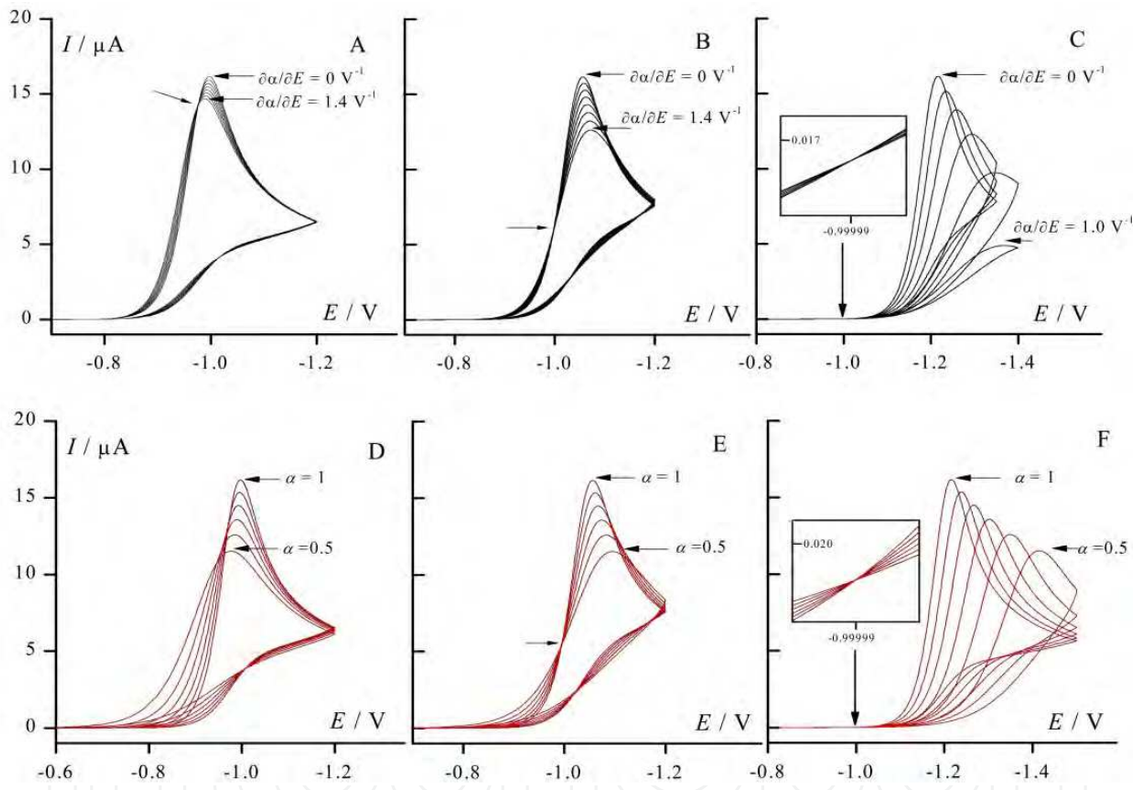


Fig. 12. The effect of including of $\partial\alpha/\partial E\neq0$ parameter (plots (A), (B), (C)) or different α values (plots (D), (E), (F)) into theoretical one-electron kinetic model E_{irr} as well as the influence of *k* value on isoalpha point current response. Plots (A), (B), (C) with $\partial\alpha/\partial E$ = 0; 0.2; 0.4; 0.6; 0.8; 1.0; 1.2; 1.4. (A) *k* =0.05, (B) *k* =0.005, (C) *k* =0.00001. Plots (D), (E), (F) with α = 1; 0.9; 0.8; 0.7; 0.6; 0.5; $\partial\alpha/\partial E$ = 0, (D) *k* =0.05, (E) *k* =0.005, (F) *k* =0.00001. The calculations were done with the use of both *ESTYM_PDE* (black lines, E_{irr}) and *DigiSim*® (red lines, E_rC with k_f=1×10^{10} s^{-1}). Notice, that the both programs provide identical current responses (plots (D), (E), (F)). The insets ((C) and (F)) show the enlarged form of background fragment. Other details are in original paper (Sanecki & Skitał, 2008). [Reprinted from *Electrochim. Acta*, Vol. 53, Sanecki, P. & Skitał P., The mathematical models of kinetics ..., 7711-7719, Copyright (2008), with permission from Elsevier.]

As a result of including of the ETC variation either through $\partial\alpha/\partial E$ parameter or by different values of α, a single curve becomes the set of curves which intersect in one characteristic point in which cathodic current is independent of α (Fig. 11 A and B, respectively). The result is similar to isosbestic point (Berlett et al., 2000; IUAPAC, 1997; Nakajima et al., 2004). The system resembling *iap* and isosbestic point, called *isopotential point* has been described in electrochemistry (Edens et al., 1991; Eichhorn & Speiser, 1994; Fitch & Edens, 1989). Its appearance is associated with the linked multi-sweep experiments when two distinguishable electroactive species interconvert.

The model for totally irreversible process applied with the use of *ESTYM_PDE* was described in paper by Nicholson and Shain (Nicholson & Shain, 1964) and is given in Bard and Faulkner's monograph (Bard & Faulkner, 2001). It is not included in *DigiSim*® software. In *DigiSim*®, however, the E_{irr} mechanism response was easily generated as E_rC with very high k_f value e.g. $k_f = 1\times10^{10}$ s^{-1} (Fig. 12 D,E,F).

A question arises why other authors dealing with the effect of potential-dependent α in voltammetry (Arun & Sangaranarayanan, 2004; Bieniasz & Speiser, 1998a; Bond & Mahon, 1997; Delahay, 1953; Nahir et al., 1994; Tender et al., 1994; Weber & Creager, 1994) did not observe so far such a phenomenon as *iap*, even if Marcus' λ parameter was discussed instead of α. Most probably there are three reasons. Firstly, the range of the phenomenon is not very wide e.g. it appears for $0.05 > k > 1\times10^{-4}$, at v =1Vs^{-1} (for k=0.05, Fig. 12 A,D the *iap* is diffused). At lower k values *iap* occurs but is invisible unless a magnification method is applied (Fig. 12 C,F). Secondly, is the phenomenon to be observed requires at least three (or more) superimposed curves and that was not fulfilled by the other authors. Even if one maintains all parameters constant except for α, no *iap* is observed and CV peak moves towards more negative potentials becoming flatter as α decreases. Examples of the lacking or not visible *iap* can be found in paper by Delahay (Fig. 2 in (Delahay, 1953)).

The third reason in form of examples was shown in Fig. 12 C,F. The data indicate that it is not possible to find *iap* without magnification of the plot and therefore some authors could not notice such a hidden effect. The observed *iap* phenomenon is not contradictory to the well established theory and provides its completion.

The similar, although less distinct *isoalpha points* are obtained for E_rC process when $\partial\alpha/\partial E\neq0$ parameter or different α values mode is introduced into the model (Fig. 12).The influence of scan rate and E_0 value on position *iap* is discussed in (Sanecki & Skitał, 2008). It is seen that *iap* moves down when scan rate increases and its value becomes closer to E_0 value.

8.2 ECE and ECEC mechanisms with included α variability

The kinetics should concern the steps and elementary parameters, which have clear physical meaning as it was performed earlier for E_{irr} process (Fig. 11,12). On the other hand, data applied for ECE process, allowed to generate dependences corresponding to those from Fig. 2 and may be important for ECE process kinetics. Examples of *isoalpha points* for both general (two-electron) peaks and elementary (one-electron) sub-peaks are presented in Fig. 13A,B.

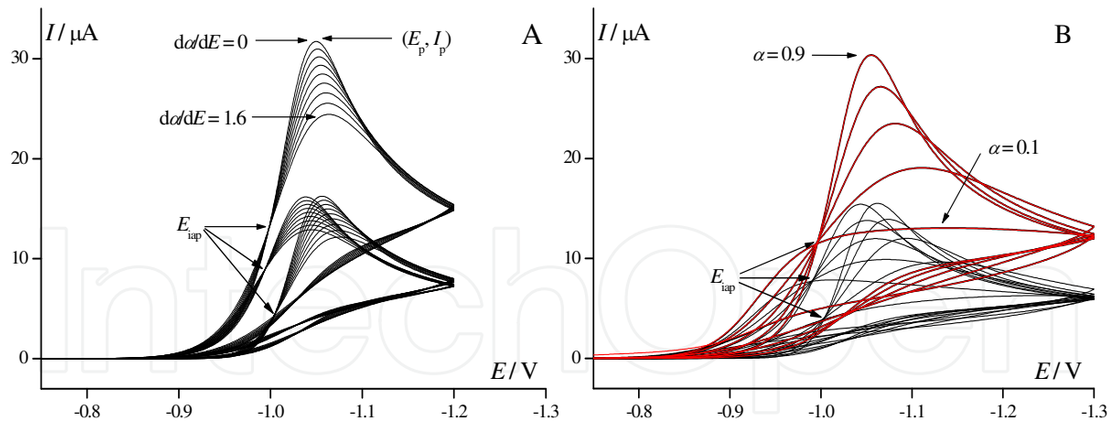


Fig. 13. (A) The *isoalpha* plots for $E_{irr}CE_{irr}$ mechanism. The $\partial\alpha/\partial E$ value is 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6 from the top to the bottom. (B) The *isoalpha* plots for E_rCE_rC mechanism. The α value is 0.1, 0.3, 0.5, 0.7, 0.9 from the bottom to the top. The *isoalpha point* appears on both two-electron and one-electron CV responses. The calculations were done with the use of both *ESTYM_PDE* (black lines) and *DigiSim*® (red lines). Other details are in original paper (Sanecki & Skitał, 2008). [Reprinted from *Electrochim. Acta*, Vol. 53, Sanecki, P. & Skitał P., The mathematical models of kinetics ..., 7711-7719, Copyright (2008), with permission from Elsevier.]

Inclusion of $\partial\alpha/\partial E$ into ECE kinetic model, with other parameters being constant, results in three sets of curves: one for two-electron and two for one-electron stages (Fig. 13A, B). Each set has characteristic intersect point E_{iap} as it was observed earlier for one-electron process (Fig. 11,12).

8.3 E_rCE_rC–E_rCE_rC mechanisms with included α variability

The data presented in Fig. 13A for ECE and ECEC mechanism indicate one E_{iap} point on cathodic part of CV curve. For ECE-ECE and ECEC-ECEC sequences at least two E_{iap} points appear for both continuous (not presented) and non-continuous (Fig. 14A) variability of α, respectively. For the both mechanisms the position of *isoalpha points* is close to $E_{0,i}$ values.

It is worth to notice that apart from α potential dependent kinetic cases considered here, the, to some extent similar, intersection point appears for pure diffusion kinetics, non sensitive to the α value at all (Fig. 14B). The comparable diffusion kinetic case is presented in literature (Greef et al., 1985), Figure 6.5, p. 184) but without discussion in the context presented here.

9. Experimental confirmation of *isoalpha* points reality

This sub-chapter deals with α variability resulting from the change of electrode material properties caused by its modification. Under experimental conditions the change of electrode properties results in both: (1) a change of α i.e. the slope of log k vs. E dependence (electrochemical reaction constant $\alpha = -\rho$); (2) a change of electrochemical rate constant k.

Therefore, the experimental confirmation of predicted by theory *isoalpha point* requires a system with α change separately. For the most of experimental systems, the changes of α and k are coupled together and therefore a shift of CV curves along potential axis is possible

and *isoalpha* point appearance may be disfigured. Despite of the above, experimental confirmation of existence of *isoalpha point* is possible by the use of the set of electrodes with slightly different electronic properties.

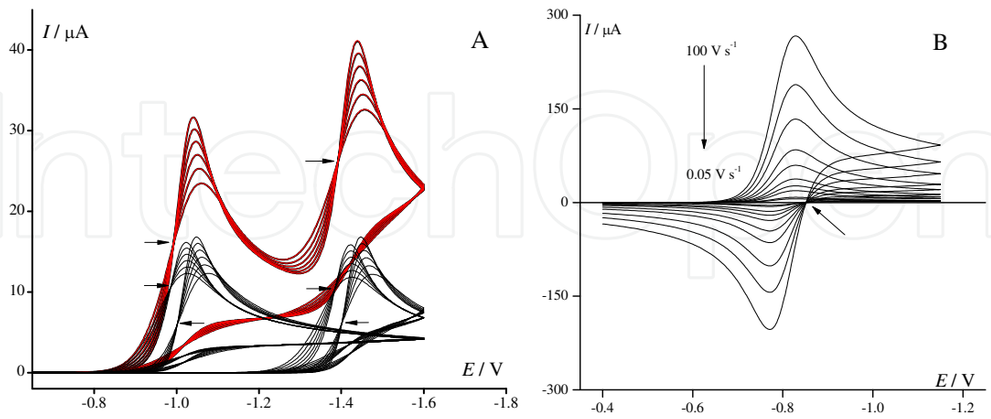


Fig. 14. (A) The theoretical CV current responses of E_rCE_rC–E_rCE_rC process with non-continuous α variability included. Parameter $\alpha_1=\alpha_2=\alpha_3=\alpha_4$=1, 0.9, 0.8, 0.7, 0.6, 0.5 decreases from the top curve to the bottom one. The calculations were done with the use of both *ESTYM_PDE* (black lines) and *DigiSim*® (red lines). Notice that both programs provide exactly the same current responses. Analogical picture is observed when $\partial\alpha/\partial E$ is the source of *isoalpha point.* (B) The appearance of another iso-current point for pure diffusion kinetic case. The one-electron CV responses for E_r process were generated. The v Vs^{-1} decreases from the top to the bottom. Other details are in original paper (Sanecki & Skitał, 2008). [Reprinted from *Electrochim. Acta*, Vol. 53, Sanecki, P. & Skitał P., The mathematical models of kinetics ..., 7711-7719, Copyright (2008), with permission from Elsevier.]

The Hg/Zn system, widely investigated in both aqueous and nonaqueous media, was chosen as a test ((Manzini & Lasia, 1994; Sanecki et al., 2006a) and literature therein). It turned out that Hg drop, after one or more CV cycles, behaves somehow differently even in the situation when metallic Zn was removed from it.

Fig. 15 presents the effect of Hg drop electrode pretreatment on CV response; for details reader is referred to the caption and original paper. The experimental results indicate (Fig. 15D) that an attempt for finding *iap* was successful. The experimental data, selected from Fig. 15 A,B,C, namely curves scanned for 0 and 1 minute intervals (Fig. 15A), provide the possibility of fitting experimental and simulated CV data which exploit *iap* property on rising part of the curve (Fig. 15D plot). The α variability parameter obtained by a comparison of α for both curves equals to $\partial\alpha/\partial E$=0.13. The observed variability of α is due to the change of electrode properties and not to solution parameters in Marcus' sense.

In our case each scan starts with the same concentration of both redox forms. Such conditions are not sufficient for the isopotential point formation of the type described in the literature (Edens et al., 1991; Eichhorn & Speiser, 1994; Fitch & Edens, 1989). In absence of changes of supporting electrolyte concentration, the only source of the *iap* appearance remains $\partial\alpha/\partial E$ or $\Delta\alpha$. Therefore, the occurrence of *iap* indicates that in the investigated system the effect of α variability takes place. Another experimental example of isoalpha

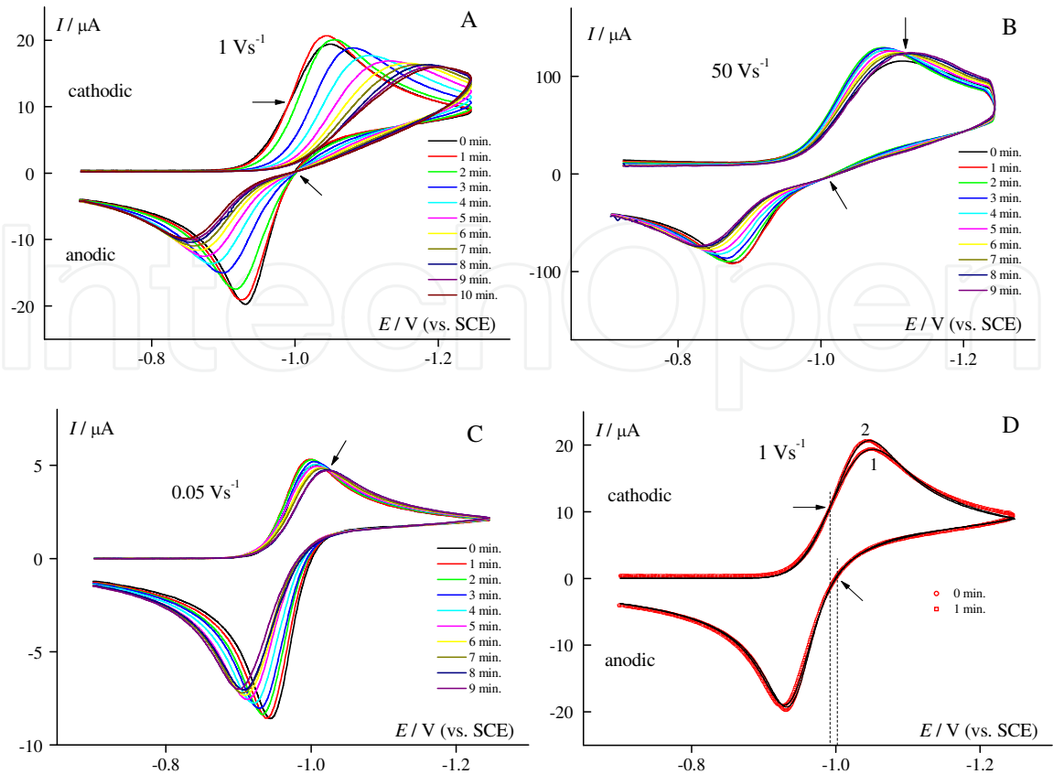


Fig. 15. The effect of non-linked multi scans CV experiment on the same mercury drop. The experimental system: 1mM Zn^{2+} in 1M $NaClO_4$. Plots (A) and (B) the scans were repeated in 1 minute intervals, at open circuit without polarization; $E_{0,exp}$= -0.970 V for Zn/Zn^{2+} system, E_{iap}= -1.000V. Plot (C) – the nine scans were repeated in 1 minute intervals, at starting potential -0.700 V. At the interval metallic Zn was removed from the drop by electrolysis. Plot (D) the comparison of Zn^{2+} electroreduction on pure Hg drop (curve 1, scan 0 min., red points) with the same process on the drop with minor trace of metallic Zn (curve 2, scan 1 min., red points) as well as the respective theoretical curves (black lines) according to extended EE‖Hg(Zn) kinetic model (Sanecki et al., 2006a). The curves 1 and 2 were selected from plot (A). The estimated alpha values: (scan 0) $\alpha_1=\alpha_2=0.66\pm0.02$, (scan 1) $\alpha_1=\alpha_2=0.785\pm0.015$. The observed *isopotential points* and scan rates are indicated on the plots. The other details are in original paper (Sanecki & Skitał, 2008). [Reprinted from *Electrochim. Acta*, Vol. 53, Sanecki, P. & Skitał P., The mathematical models of kinetics ..., 7711-7719, Copyright (2008), with permission from Elsevier.]

point occurrence is provided by hydrogen ions reduction (Fig. 16). Increasing concentration of atomic hydrogen with scan rate decrease is expected to be a source of modification of active electrode surface. In consequence, the *isoalpha point* appeares.

The presented experimental results (Fig. 15, 16) together with theoretical ones (Fig. 11-14) suggest that the change of electrode properties should be considered as an origin of occurrence of the *iap*. It can be supported by a quotation from Corrigan and Evans (Corrigan & Evans, 1980): "*For all of these cases, eq. $d\alpha/dE = F/2\,\lambda$ does not adequately describe the potential dependence of α because λ is a solution parameter which should not depend on surface conditions.*"). The results by Mattheiss and Warren (Matthesiss & Warren, 1977) showed that

anymicroscopic inhomogeneity may significantly affect the Fermi level of electrons and, therefore, the kinetics of electrode process. The similar effect of the change of electrode properties caused by the electrodeposition process is well recognized for solid electrodes (Greef et al., 1985; Sanecki et al., 2006a; Sawyer et al., 1995).

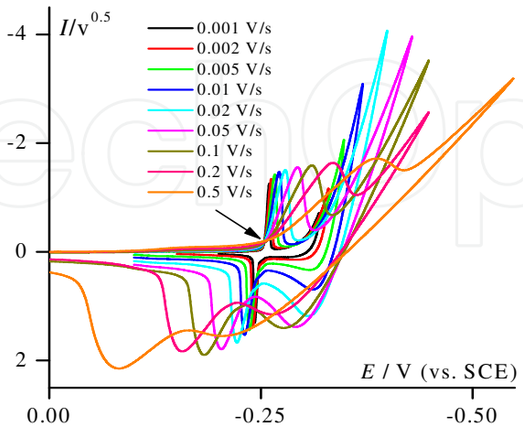


Fig. 16. The normalized complete CV responses $Iv^{-0.5}$ vs. potential E for hydrogen ions – reduction in 0.1M HCl solution. Electrode system: GCE/100 monomolecular Pd layers. The isopotential crossing point is indicated with the arrow (experimental data from ref. (Skitał et al., 2010)). Note the almost vertical position of rising part of CV curves which suggests high increasing of α values. Modification of active electrode surface can be explained by an increasing concentration of atomic hydrogen with scan rate decrease. [Reprinted from *Electrochim. Acta*, Vol. 55, Skitał P. & Sanecki P., The mathematical model of the stripping voltammetry ..., 5604–5609, Copyright (2010), with permission from Elsevier.]

Extended and still growing theory and application of solid electrodes (Horrocks et al., 1994; Kuznetsov & Ulstrup, 1999; Levich, 1966; Wantz et al., 2005) prove that presented results can be useful as an element of theory and practice concerning advanced solid electrodes and thin films dominating in both theoretical and applied electrochemistry (Swain, 2004).

We expect that another experimental *isoalpha points*, analogous to described above, will be found by other investigators.

10. Conclusions

1. Acquisition of rigorous mathematical model of considered mechanism comprising elementary kinetic parameters of electrochemical and chemical steps is fundamental for any discussion of quantitative type.
   MPE method with a proper mathematical model of the considered mechanism, applied to a series of electrochemical responses, is the simple, clear and rigorous way to determine the values of kinetic parameters with their confidence intervals. Additional error space for all estimated kinetic parameters, characteristic for considered mechanism like a fingerprint, can be easily determined basing on obtained theoretical responses. Every mechanism together with its mathematical model can generate electrochemical theoretical responses and its own error space, independently of error space obtained from experimental responses.

2. The common problems with extracting of kinetic parameters basing on selected characteristic points of complex electrochemical responses like half peak method or processed responses (e.g. convolution method) can be avoided by estimation of kinetic parameters on the whole original responses. The actual numerical possibilities and availability of respective software makes it possible to solve practically each of met in practice mechanisms by every researcher. The presented and quoted successful analysis of complex, multi-electron electrode processes with chemical step(s) provides the respective examples.
3. MPE method makes it possible to judge controversial or confused cases of mechanisms. A good example is here a stepwise/concerted mechanism. A uniform approach to understanding of the stepwise/concerted systems was confirmed by respective modeling for ECE mechanism where fluent passage from stepwise to concerted mechanism has been obtained. The only difference between them is the value of $k_{f.}$
4. The mathematical modeling of electrode processes linked with experimental results may become an inspiration for new results and deeper understanding of the nature of electrochemical processes and its description. A good example is here an including of alpha variability into kinetic models and discovery of *isoalpha points*.
5. The occurrence of *isoalpha point* indicates that, under constant composition of the solution, in investigated system $\partial a/\mathrm{d}E$ or Δa type variability takes place. The origin of experimentally found *isoalpha point* can be explained by the change of electrode surface conditions.

11. Acknowledgment

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12. Definitions, abbreviations and symbols

A mechanism can be defined as an system of chemical and electrochemical elementary steps with a set of respective elementary kinetic parameters.

A model is a mathematical description of the considered mechanism or system. Both the mechanism (system) and the model provide an electrochemical response, experimental and theoretical, respectively.

The mathematical model as well as respective electrochemical current or concentration response is a function of multiple variables. Among them there are system variables as electrochemical and chemical rate constants, equilibrium constants, transfer coefficients, standard potentials, etc. as well as variables of experimental type as scan rate, starting potential, concentration, temperature.

AN – acetonitryle
1,3-BDF – 1,3-benzenedisulfonyl difluoride
BSF – benzenesulfonyl fluoride
CV – cyclic voltammetry
DMF – dimethylformamide
$E_{0,i}$ –standard potential of step i (V)

E_{iap} – potential in the isoalpha point (V)
E_p – peak potential (V)
E_{start} – the value of potential where α variability starts
ETC (or α) – elementary transfer coefficient
GCE – glassy carbon electrode
I_{iap} – current in the isoalpha point (A)
iap – isoalpha point
k – electrochemical rate constant for one electron process (cm s^{-1})
k_i (i=1,2,3,...) – electrochemical rate constant for a step of multi electron process (cm s^{-1})
k_f – chemical first order rate constant (s^{-1})
k_{f1}, k_{f2} – chemical first order rate constant of multi stage process (s^{-1})
MPE – multi-parameter estimation
PDE – partial differential equation(s)
ESTYM_PDE - program for solving the models expressed by PDE and estimating their parameters
r; irr (in subscript) – reversible; irreversible
R_u – uncompensated resistance between the working and reference electrode
TBAP – tetrabutylammonium perchlorate
TEAP – tetraethylammonium perchlorate
TSF – *p*-toluenesulfonyl fluoride
v – scan rate
α – transfer coefficient of cathodic process (in electrode kinetics we use elementary kinetic parameters relating to, or describing the single step of kinetic sequence (k_1, k_2, α, α_1, α_2) as well as apparent (general) kinetic parameters i.e. relating to or describing the complex kinetic course or mechanism as a whole (e.g. k_{app}, α_{app}))
β – transfer coefficient of anodic process
α_{start} – the value of α to start with α variability
α_B , β_B – Brønsted acid-base catalysis coefficients
λ – solvent reorganisation factor in Marcus' theory

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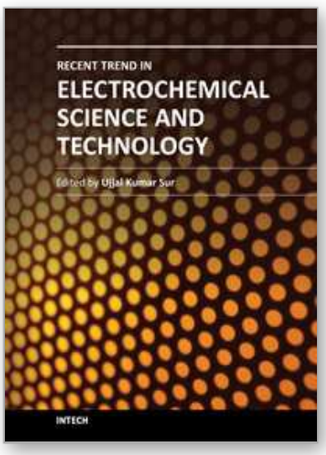
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This book titled "Recent Trend in Electrochemical Science and Technology" contains a selection of chapters focused on advanced methods used in the research area of electrochemical science and technologies; descriptions of electrochemical systems; processing of novel materials and mechanisms relevant for their operation. This book provides an overview on some of the recent development in electrochemical science and technology. Particular emphasis is given both to the theoretical and the experimental aspect of modern electrochemistry. Since it was impossible to cover the rich diversity of electrochemical techniques and applications in a single issue, the focus is on the recent trends and achievements related to electrochemical science and technology.

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