



Original scientific paper

## New complex dimensionless variable in cyclic staircase voltammetry on the rotating disk electrode\*

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### Abstract

Cyclic staircase voltammograms of a simple, reversible oxidation on the rotating disk electrode is analysed by the digital simulation. It is demonstrated that the peak currents and potentials depend on the single dimensionless variable that considers nonlinear relationship between peak currents and the potential increment. The reverse, cathodic branch of voltammograms depends on this variable differently than the anodic one.

### Keywords

reversible oxidation; sigmoidal dependence; digital simulation.

### Introduction

In the linear scan voltammetry on the rotating disk electrode the maximum current depends on the product of steady state diffusion layer thickness and the square root of scan rate [1]. However, in the staircase voltammetry on this electrode, the relationship between peak current and the above mentioned product depends on the potential increment [2]. This is because in the later technique the peak current does not depend linearly on the square root of the formal scan rate  $\Delta E / \tau$  (where  $\Delta E$  is the potential increment and  $\tau$  is the step duration), but on the ratio  $\Delta E^{0.446} / \tau^{0.5}$  [3]. For this reason, a new complex variable for the staircase voltammetry on the rotating disk electrode is proposed here.

### Model

A simple, fast and reversible electrode reaction is investigated:



Both components of this redox couple are solution soluble and only Red is initially present in the solution. On the rotating disk electrode, the mass transport can be described by the following differential equations and boundary conditions [1,4]:

\*Dedicated to the memory of Dr. Šebojka Komorsky-Lovrić.

$$\partial c_R / \partial t = D \partial^2 c_R / \partial x^2 - v \partial c_R / \partial x \quad (2)$$

$$\partial c_O / \partial t = D \partial^2 c_O / \partial x^2 - v \partial c_O / \partial x \quad (3)$$

$$v = -0.510 \omega^{3/2} \nu^{1/2} x^2 \quad (4)$$

$$t = 0, x \geq 0: \quad c_R = c_R^*, c_O = 0 \quad (5)$$

$$t > 0, x \rightarrow \infty: \quad c_R \rightarrow c_R^*, c_O \rightarrow 0 \quad (6)$$

$$x = 0: \quad c_{O,x=0} = c_{R,x=0} \exp(F(E-E^0) / RT) \quad (7)$$

$$D(\partial c_R / \partial x)_{x=0} = I / FS \quad (8)$$

$$D(\partial c_O / \partial x)_{x=0} = -D(\partial c_R / \partial x)_{x=0} \quad (9)$$

The meanings of all symbols are reported in Table 1.

Table 1. List of parameters

Symbol	Meaning
$c_O$	Concentration of product
$c_R$	Concentration of reactant
$c_R^*$	Bulk concentration of reactant
$D$	Diffusion coefficient
$\delta$	Diffusion layer thickness
$\Delta E$	Potential increment
$\Delta t$	Time increment
$\Delta x$	Space increment
$E$	Potential
$E^0$	Standard potential
$F$	Faraday constant
$I$	Current
$\nu$	Kinematic viscosity
$\omega$	Rotation rate
$R$	Gas constant
$S$	Electrode surface area
$T$	Temperature
$\tau$	Step duration
$v$	Flow rate of solution

The differential equations (2) and (3) are solved by the finite difference method [1]. A cyclic staircase voltammetry is applied and the currents flowing at the end of each potential step are calculated. The following fixed parameters are used:  $D = 10^{-5} \text{ cm}^2/\text{s}$ ,  $\nu = 10^{-2} \text{ cm}^2/\text{s}$ ,  $\Delta t = 10^{-5} \text{ s}$  and  $D\Delta t / \Delta x^2 = 0.4$ . The results are reported as the relationship between the dimensionless current  $\Phi$  and electrode potential:

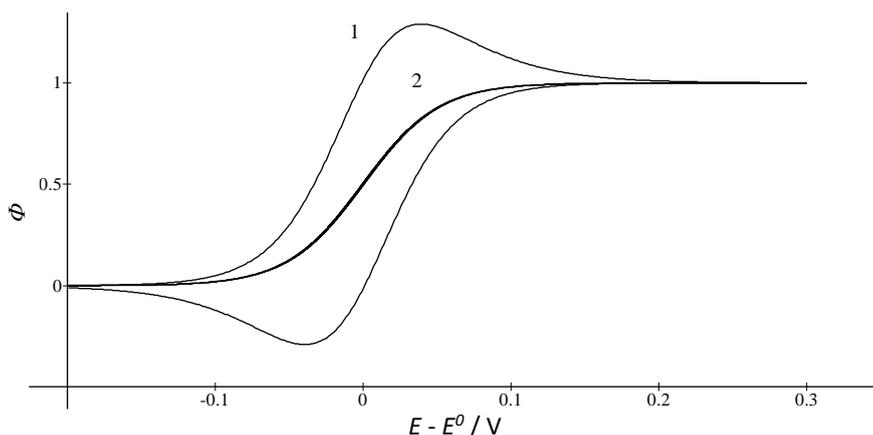
$$\Phi = I \delta_{SS} / FSDc_R^* \quad (10)$$

$$\delta_{SS} = 1.61D^{1/3}\nu^{1/6}\omega^{-1/2} \quad (11)$$

## Results and discussion

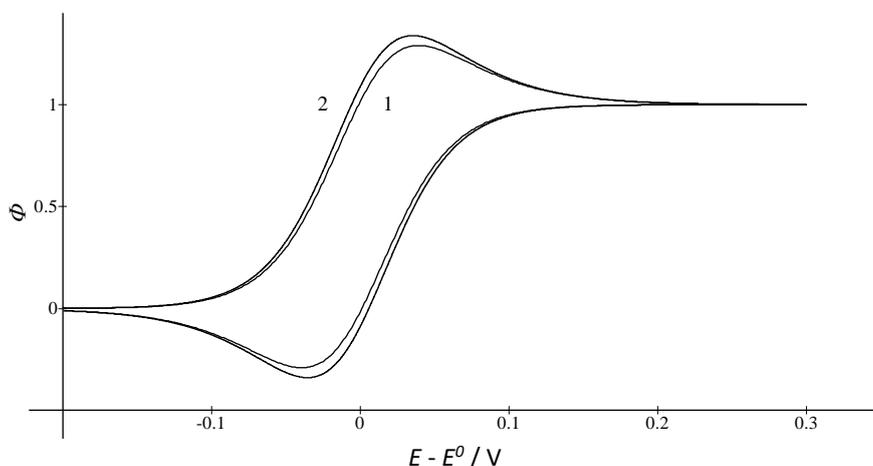
Cyclic staircase voltammograms on the rotating disk electrode depend on the formal scan rate and the electrode reaction rate. Two examples are shown in Figure 1. The anodic and cathodic branches of the response are either separated and characterized by the maximum and minimum,

respectively, or overlapped and resembling polarographic wave. This transformation is achieved either by the decreasing scan rate or by the increasing rotation rate.

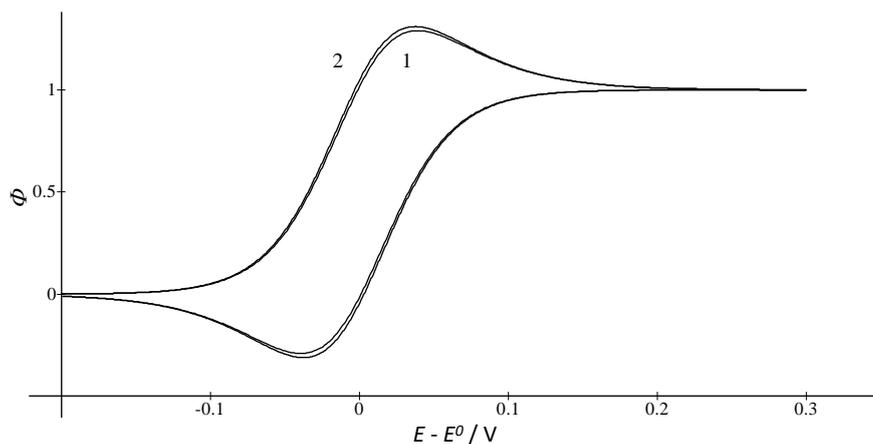


**Figure 1.** Cyclic staircase voltammograms of the reaction (1) on the rotating disk electrode;  $\tau = 10^{-3}$  s,  $\omega = 40 \pi$  rad / s and  $\Delta E = 10^{-3}$  (1) and  $10^{-5}$  (2) V

In the analog linear scan voltammetry, the response depends on the complex, dimensionless variable  $\sigma = F(dE/dt)\delta_{ss}^2 / DRT$  [1], but in the digital staircase voltammetry this variable cannot be used because the same formal scan rate  $\Delta E / \tau$  can be obtained by combining various  $\Delta E$  and  $\tau$  pairs. Figures 2 and 3 show two examples of many in which responses corresponding to the same  $\sigma$  value are not identical.

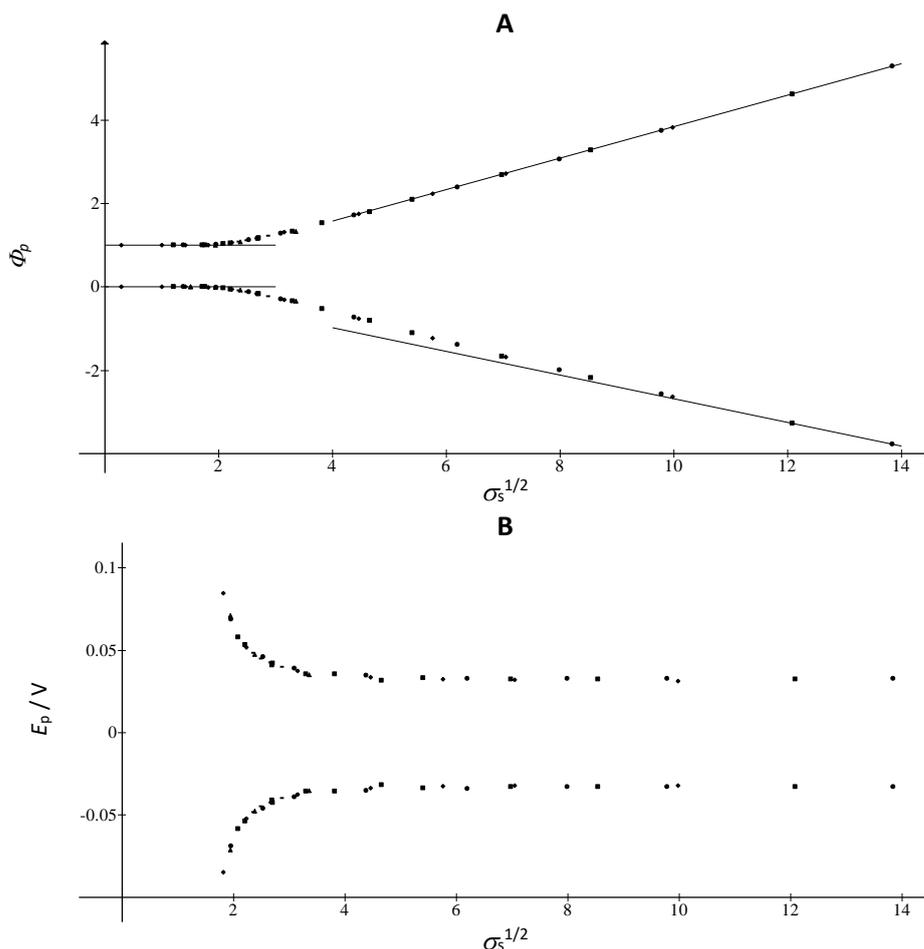


**Figure 2.** CSV on RDE;  $\tau = 10^{-3}$  s,  $\omega = 40 \pi$  (1) and  $4$  (2)  $\pi$  rad  $s^{-1}$  and  $\Delta E = 10^{-3}$  (1) and  $10^{-4}$  (2) V



**Figure 3.** CSV on RDE;  $\omega = 40 \pi$  rad  $s^{-1}$ ,  $\tau = 10^{-3}$  s and  $5 \times 10^{-4}$  (2) s and  $\Delta E = 10^{-3}$  (1) and  $5 \times 10^{-4}$  (2) V

In Figure 2, the experimental conditions are similar only in  $\tau$ , but the variable  $\sigma^{1/2} = 2.8335$  is common by the coincidence. Still, the second anodic peak current is 3.75 % higher than the first one and the difference between the peak potentials is 3 mV. The curves in Figure 3 have common  $\omega$  and the formal scan rate, but different  $\Delta E$  and  $\tau$ . Again, the difference in anodic peak currents is 1.56 % of the smaller one. Three different peak currents for the same  $\sigma^{1/2}$  can be ascribed to different  $\Delta E$  values, in the agreement with our calculations that the peak currents on the stationary planar electrode depend on  $\Delta E^{0.446}$  [3]. For this reason, a new dimensionless variable  $\sigma_s = (F\Delta E / RT)^{0.892} \delta_{SS}^2 / D\tau$  is proposed here. An advantage of this variable is that various pairs of  $\Delta E$  and  $\tau$  values cannot give the same  $\sigma_s$  value. The curve 1 in Figures 2 and 3 corresponds to  $\sigma_s^{1/2} = 3.09$ , while the curves 2 in these figures correspond to  $\sigma_s^{1/2} = 3.29$  and 3.15, respectively. By the variation of  $\omega$ ,  $\Delta E$  and  $\tau$  the relationship between anodic and cathodic peak currents and potentials and the square root of the variable  $\sigma_s$  is calculated and presented in Figure 4.



**Figure 4.** Dependence of peak currents (A) and peak potentials (B) on the square root of the complex dimensionless variables  $\sigma_s = (F\Delta E / RT)^{0.892} \delta_{SS}^2 / D\tau$

The peak currents, both anodic and cathodic, vanish if  $\sigma_s^{1/2} < 1.8$ . Under this condition, the response acquires the form of polarographic wave, and its dimensionless limiting current is equal to 1. If  $\sigma_s^{1/2} > 4$ , the anodic peak currents tend to the asymptote  $\Phi_p = 0.378 \sigma_s^{1/2} + 0.060$ . This means that the real peak current is not entirely independent of the rotation rate:  $I_p = FSC_R * D^{1/2} [0.378 (F\Delta E/RT)^{0.446} \tau^{1/2} + 0.060 D^{1/2}/\delta_{SS}]$ . The anodic peak potentials tend to 0.033 V vs.  $E^0$  if  $\sigma_s^{1/2} > 6$ . As the peak currents gradually disappear below  $\sigma_s^{1/2} = 3$ , the peak potentials increase to 0.090 V. The cathodic and anodic peak potentials are symmetrical versus  $E^0$ . The cathodic peak currents depend on  $\sigma_s^{1/2}$  as sigmoidal

function. Within the interval  $3 < \sigma_s^{1/2} < 6$  the slope  $\Delta\Phi_p / \Delta\sigma_s^{1/2}$  is equal to -0.36 and then the peak currents tend to the asymptote  $\Phi_p = -0.284 \sigma_s^{1/2} + 0.160$  if  $\sigma_s^{1/2} > 9$ .

The values of parameters  $\Delta E$  and  $\tau$  used in these calculations are rather high with the purpose to obtain pronounced effects, while in the experiments they can be as much as one hundred times lower. However, the limit of the ratio  $(F\Delta E / RT)^{0.892} / \tau$  as  $\Delta E$  and  $\tau$  tend to zero is infinite, which means that the described effect does not disappear at very low  $\Delta E$  and  $\tau$  values.

Nonlinear relationship between the peak current and the potential increment can be described by the function  $0.446 / (1 + 0.375(nF\Delta E / RT)^{0.52})$  [5]. This function and the exponential one fit the results of simulation equally well [3]. These results are relevant for the application of the rotating disk electrode in the investigation of electrochemical mechanisms [6-8].

## Conclusions

Nowadays the cyclic staircase voltammetry is frequently used electroanalytical technique [9]. Our calculations explain the difference between this method and the analog linear scan voltammetry when applied to the rotating disk electrodes. A sigmoidal dependence of the peak currents in the reverse branch of cyclic voltammogram on the newly proposed dimensionless variable  $\sigma^{1/2}$  is discovered.

## Data availability

All relevant data are available on demand.

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