

Staircase Voltammetry using Rotating Disk Electrode

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Abstract

A theory of staircase voltammetry on the rotating disk electrode is developed. The simulation is based on the method of variable diffusion layer thickness. Critical parameters that define the form of responses are calculated.

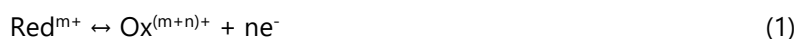
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1. Introduction

Staircase voltammetry is replacing linear scan voltammetry in the new instrumentation [1 - 5]. In this technique the response depends on three variables: the potential step amplitude, the step duration and the current sampling parameter [6 - 12]. Here, we present the theory of staircase voltammetry as applied to the rotating disk electrode. These electrodes are frequently used for the investigation of electrochemical mechanisms [13 - 16]. They are characterized by the mass transport that is controlled by the rotational velocity and by the establishment of steady-state conditions [17 - 20]. Theoretical analysis of linear scan and cyclic voltammetry on the rotating disk electrodes is performed using digital simulation [21] and the so-called "bound – unbound" limiting diffusion approximation [22 - 25]. In this paper we are using the variable diffusion layer thickness approximation [26 - 28]. It was applied to the linear scan voltammetry [28], the pseudo polarography [29] and electro-catalytic reactions [30].

2. Model

A simple, reversible electrode reaction of soluble reactant and product is considered:



On the rotating disk electrode, the mass transport is defined by the following equation:

$$\partial c_R / \partial t = D \partial^2 c_R / \partial x^2 + v_x \partial c_R / \partial x \quad (2)$$

where $v_x = \kappa x^2$ and $\kappa = 0.51 \omega^{3/2} \nu^{-1/2}$. The symbols ω and ν stay for the rotation rate and kinematic viscosity, respectively, and c_R is the reactant concentration. In the applied approximation it is assumed that the concentration depends linearly on the distance from the electrode surface within the diffusion layer and that it is equal to the bulk value (c_R^*) outside this layer:

$$c_R = c_{R,x=0} + (c_R^* - c_{R,x=0}) x / \delta \quad \text{for } 0 \leq x \leq \delta \quad (3)$$

$$c_R = c_R^* \quad \text{for } x > \delta \quad (4)$$

The diffusion layer thickness δ depends on time and the purpose of calculation is to resolve this dependence. Firstly, the differential equation (2) is integrated from $x = 0$ to $x \rightarrow \infty$ and transformed into the following form:

$$d\delta/dt = 2D/\delta - 2\kappa\delta^2/3 + \delta(c_R^* - c_{R,x=0})^{-1} dc_{R,x=0}/dt \quad (5)$$

Under the steady-state conditions ($d\delta/dt = 0$ and $dc_{R,x=0}/dt = 0$) the diffusion layer thickness approaches the limiting value: $\delta_{ss}^3 = 3D/\kappa$. The differential equation (5) can be further transformed by the substitution $u = \delta^2/D$. In this form it can be solved numerically.

$$du/dt = 4 - 4ku^{3/2}/3 + 2u(c_R^* - c_{R,x=0})^{-1} dc_{R,x=0}/dt \quad (6)$$

where $k = \kappa\sqrt{D}$. Electrode reaction (1) satisfies Nernst equation and the reactant concentration at the electrode surface depends on the potential:

$$c_{R,x=0} = c_R^*[1 + \exp(nF(E - E^0)/RT)]^{-1} \quad (7)$$

In the staircase voltammetry the potential is changed for the discrete value

ΔE at the beginning of each step and remains constant during the step. So, the reactant concentration at the electrode surface is changed only when the potential is changed:

$$dc_{R,x=0}/dt = c_R^*\{[1 + \exp(nF(E + \Delta E - E^0)/RT)]^{-1} - [1 + \exp(nF(E - E^0)/RT)]^{-1}\} \quad (8)$$

The formal scan rate is defined as $v = \Delta E/\tau$, where τ is the step duration. The current depends on the concentration gradient at the electrode surface:

$$i = nFSD(c_R^* - c_{R,x=0})/\delta \quad (9)$$

Under steady-state conditions the limiting current appears:

$$i_{lim} = nFSDc_R^*/\delta_{ss} \quad (10)$$

3. Results and discussion

Staircase voltammogram on the rotating disk electrode is either the wave or the curve with the maximum and the limiting current. This is shown in figures 1 and 2. The maximum increases with the scan rate and decreases with the rotation rate. Note that $k = 0.51\omega^{3/2}(D/\nu)^{1/2}$. If the scan rate is low and the rotation rate is high, the maximum disappears, and the response acquires the form of the wave, as in *d.c.* polarography. At high potentials all responses tend to the limiting current that is defined by eq.(10).

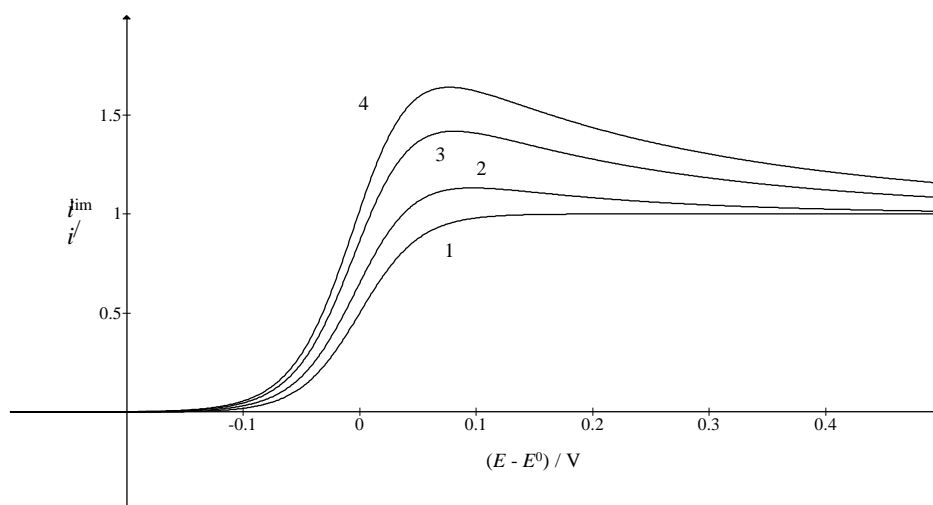


Fig. 1 Staircase voltammograms on the rotating disk electrode, $\Delta E = 1$ mV, $n = 1$, $k = 1$ s^{-3/2} and $v/(V/s) = 0.1$ (1), 0.5 (2), 0.8 (3) and 1 (4).

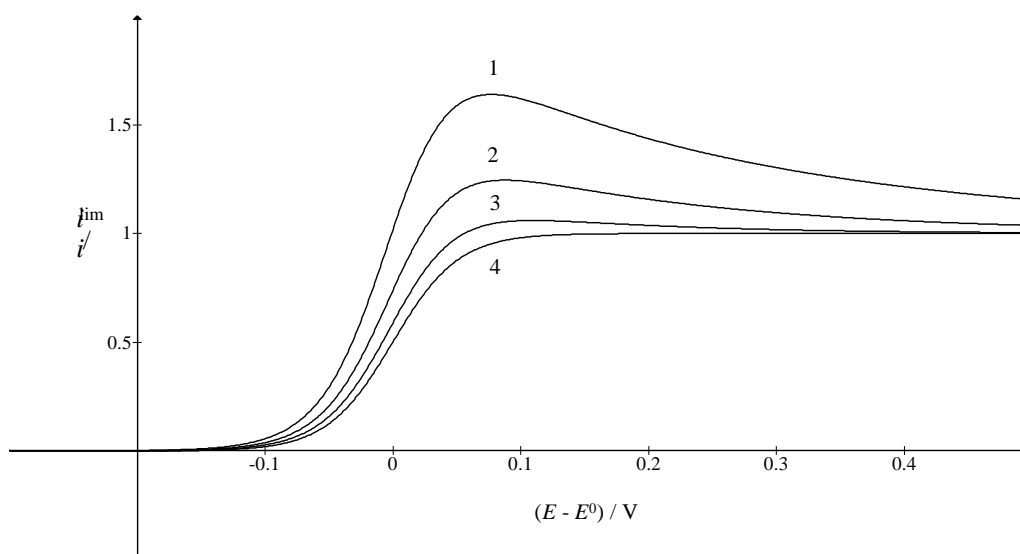
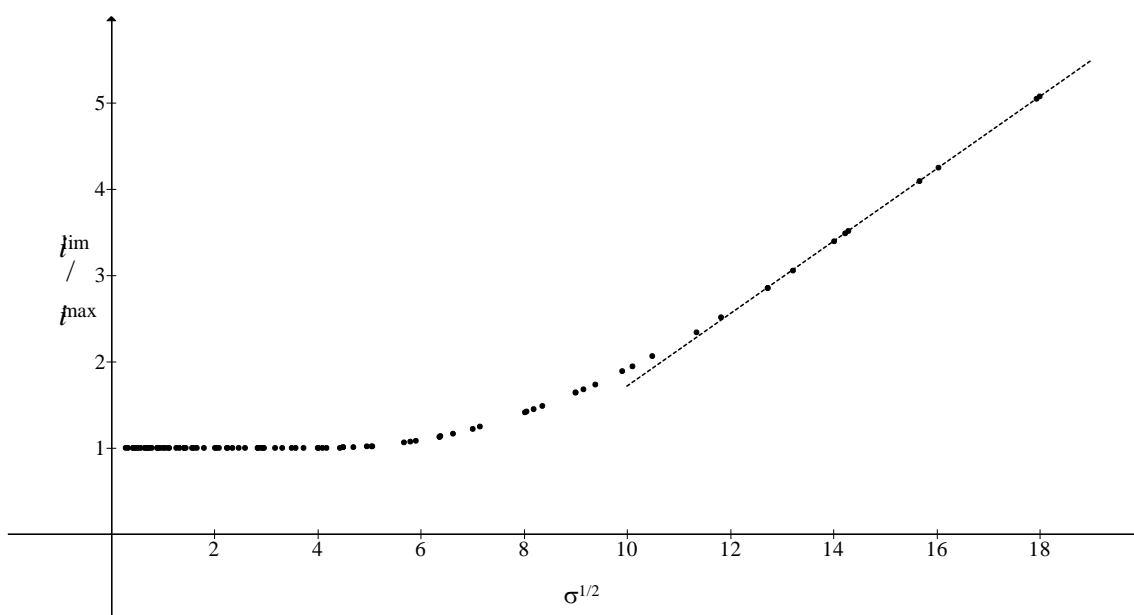


Fig. 2 Staircase voltammograms on the rotating disk electrode, $\Delta E = 1$ mV, $n = 1$, $\nu = 1$ V/s and $k/s^{-3/2} = 1$ (1), 2 (2), 4 (3) and 20 (4).

The current maxima and peak potentials depend on the dimensionless scan rate $\sigma = nF\nu\delta_{ss}^2/DRT$. This variable embrace both the scan rate and the rotation rate because the steady-state diffusion layer thickness is defined by the following equation: $\delta_{ss} = 1.61D^{1/3}\nu^{1/6}\omega^{-1/2}$. These relationships are shown in figures 3 and 4. The dependence of the ratio of maximum and limiting currents on the square root of the variable σ is a curve with two asymptotes: $i_{max} = i_{lim}$, for $\sqrt{\sigma} < 3.50$, and $i_{max}/i_{lim} = 0.42\sqrt{\sigma} - 2.48$ for $\sqrt{\sigma} > 12$. If the potential increment is 2 mV, the slope of the second asymptote is 0.40 and applies for $\sqrt{\sigma} > 12$. The first asymptote corresponds to the responses that resemble polarographic wave and exhibit no maxima. The second asymptote defines the conditions under which the current maximum increases linearly with the square root of scan rate and the slope of this relationship is independent of the rotation rate: $\Delta i_{max}/\Delta\sqrt{\nu} = 0.42nFS c_R^* \sqrt{DF/RT}$. The factor 0.42 is the consequence of the assumption that the current is sampled at the end of each step.

A)



B)

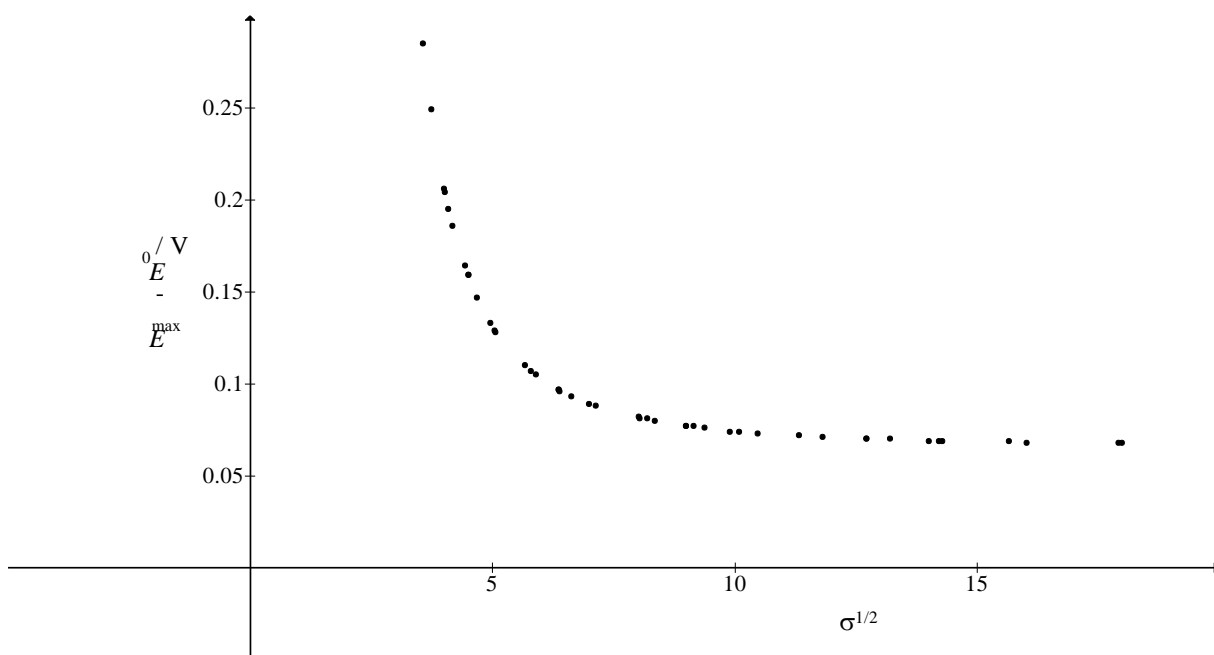


Fig. 3 Dependence of current maxima (A) and peak potentials (B) of staircase voltammograms on the square root of the dimensionless scan rate ($\sigma = nFv\delta_{ss}^2/DRT$) for $n = 1$ and $\Delta E = 1$ mV.

The peak potentials are inversely proportional to the variable σ , as can be seen in Fig. 3B. If $\sqrt{\sigma} < 6$ the peak potential is higher than 0.1 V vs. E^0 and apparently tends to infinity as $\sqrt{\sigma} \rightarrow 3.50$. These are the characteristics of the responses with very small maxima, as can be seen in Fig. 3A. The potentials of significant maxima are lower than 0.075 V if $\sqrt{\sigma} > 10$.

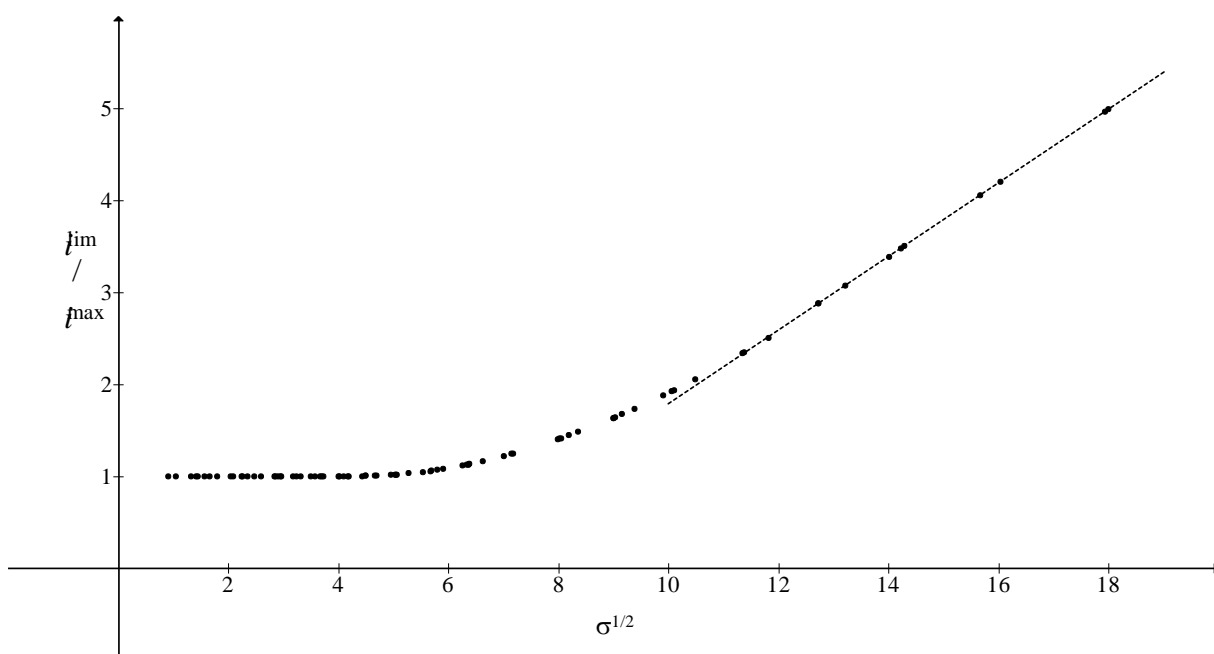


Fig. 4 Relationship between current maxima of staircase voltammograms and the dimensionless scan rate for $n = 1$ and $\Delta E = 2$ mV.

These calculations have shown two critical parameters that determine the form of responses: $\sqrt{\sigma_{crit}} = 3.50$ and $\sqrt{\sigma_{crit}} = 12$. The voltammogram appears in the form of polarographic wave if the ratio of scan rate and the rate of rotation satisfies the following inequality: $v/\omega < 4.726(D/v)^{1/3}RT/nF$. If $n = 1$, $D = 10^{-5}$ cm²/s and $v = 10^{-2}$ cm²/s, this condition is: $v/\omega < 0.012$ V/rad. The second critical parameter defines the condition for voltammograms with well developed maximum: $v/\omega > 55.55(D/v)^{1/3}RT/nF$. In the particular case as above, this condition is: $v/\omega > 0.143$ V/rad.

4. Conclusion

Staircase voltammetry on rotating disk electrode depends on the ratio of scan rate and the rate of rotation. The critical values of this parameter, that are determined in the presented calculations, can serve for the optimization of experimental procedure.

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