LINEAR SWEEP VOLTAMMETRY AT VERY SMALL STATIONARY DISK ELECTRODES

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ABSTRACT

An expression for linear sweep voltammograms at very small stationary disk electrodes is presented. From numerical calculations theoretical voltammograms are obtained for various values of the dimensionless parameter, \( p = (nF \alpha u/RTD) \), where \( a \) is the radius of the electrode, \( u \) the potential sweep rate and \( D \) the diffusion coefficient. The maximum current and the half-maximum potential are evaluated from the voltammograms as functions of \( p \) and are expressed by approximate equations with high precision. In order to examine the validity of the equations, an experimental study was made at platinum small disk electrodes (\( a = 0.025 \) to \( 0.10 \) mm). The experimental voltammograms were in good agreement with the ones theoretically predicted for various values of the sweep rates and for several different radii of the electrodes.

INTRODUCTION

One of the voltammetric techniques most frequently employed for in vivo measurements is cyclic voltammetry with electrodes of very small size, e.g., stationary disk micro-electrodes [1–6] and cylindrical electrodes [7–9]. Voltammetric currents at such electrodes are often larger than those which would be obtained for linear diffusion at electrodes with the same area, especially in the potential region about the peak. The increase in the current results from non-linear diffusion taking place in the vicinity of an edge or a part of the electrode with small curvature. Taking into account the fact that the mass transfer varies from linear diffusion to non-linear diffusion as time lapses, one can deduce the conclusion that the initial part of the linear sweep voltammogram is controlled by linear diffusion while the final part is governed by non-linear diffusion. On the basis of this conception, Galus et al. attempted to express an equation for the peak current in linear sweep voltammetry as the sum of the linear and the non-linear components [10]. However, their approach was just intuitive and hence describes only qualitatively the peak
current for the limiting cases. Heinze computed cyclic voltammograms with the aid of a two-dimensional simulation based on an implicit difference method and described the dependence of peak current and peak potential on the parameter composed of an electrode radius, potential sweep rate and the diffusion coefficient [11]. The model includes the reversible and quasi-reversible charge transfer. His approach, however, has omitted a discussion of the behavior that is observed at an extremely small electrode and very slow potential sweep rate. By the use of his results, it is quite difficult to evaluate unknown parameters, e.g., diffusion coefficient, from experimentally obtained voltammograms. Therefore the work on linear sweep voltammetry has not been completed.

A number of contributions to progress the understanding of very small disk electrodes have been made in this half decade [10–27]. A few of them are concentrated on the derivation of expressions for the reversible current response to any form of a potential step [14,27]. Application of these expressions may lead also to expressions for linear sweep voltammetry at this electrode. This paper is directed to the derivation and to the calculation of the expression for the reversible linear sweep voltammogram. The maximum current and the potential at half-maximum current are obtained and approximate equations with high accuracy are given for them. These equations are verified experimentally by the linear sweep voltammograms observed at platinum disk electrodes of three different diameters at several sweep rates.

THEORETICAL

Derivation

We consider the simple electrode reaction, \( R = O + ne \), that occurs at the stationary disk micro-electrode with radius \( a \). It is assumed that the electrode reaction takes place so rapidly that the Nernst equation holds at the electrode surface. If the diffusion coefficients of substance \( O \) and \( R \) have a common value of \( D \), the total current, \( I \), passing through the electrode is given by [27]:

\[
I/nF = 4c^*Da\int_0^\infty \left[ f\left(\frac{4D}{a^2}t - u\right)\left(\frac{d}{du}\left[\frac{1}{1 + e^{-f(u)}}\right]\right)\right] du
\]

(1)

where \( c^* \) denotes the bulk concentration of species \( R \), \( t \) the electrolysis time and \( f(t) = (nF/RT)(E(t) - E^0) \). The function \( f \) is defined by:

\[
f(z) = 1 + 0.71835z^{-1/2} + 0.05626z^{-3/2} - 0.00646z^{-5/2}
\]

(2)

for \( z > 0.88 \) and:

\[
f(z) = \left(\frac{\pi}{4z}\right)^{1/2} + \frac{\pi}{4} + 0.094z^{1/2}
\]

(3)

for \( z < 1.44 \). When the electrode potential, \( E \), is swept linearly with the sweep rate, \( v \),
starting at the initial potential, \( E_i \), \( \xi \) or \( E \) is a function of \( t \), given by:

\[
\xi = \xi(t) = \left( \frac{nF}{RT} \right) \left( E_i + \nu t - E^0 \right)
\]  

(4)

Inserting eqn. (4) into eqn. (1) and carrying out the differentiation with respect to \( u \) (or \( t \)) yields:

\[
\frac{1}{4nFc^*Da} = \left( \frac{nF \nu}{4RT} \right) \int_0^1 \left[ f(4D(t-u)/a^2) \right] \text{sech}^2 \left( \frac{\xi(u)}{2} \right) du
\]  

(5)

When we introduce a new integration variable, \( x = 4D(t-u)/a^2 \) and take the initial potential to be sufficiently negative of \( E^0 \), we obtain:

\[
\frac{1}{4nFc^*Da} = \left( \frac{p^5}{16} \right) \int_0^\infty f(x) \text{sech}^2 \left( \frac{p^5 x}{8} - \frac{\xi}{2} \right) dx
\]  

(6)

where:

\[
p = \left( \frac{nFa^2 \nu}{RTD} \right)^{1/2}
\]  

(7)

This is the basic equation for the reversible wave of linear sweep voltammetry.

The parameter \( p \), equivalent to \( 1/\sigma \) in ref. 11, is a significant variable characterizing the wave form. When \( p \) is so large that the first term in eqn. (3) is predominant, eqn. (6) becomes eqn. (16) in ref. 28, which is equivalent to the expression for linear infinite diffusion at a planar electrode. As \( p \) approaches zero, eqn. (2) applies and \( f(z) \) tends to unity because only a large value of \( x \) determines an integral value. Consequently eqn. (6) becomes:

\[
I = \frac{4nFc^*Da}{(1 + e^{-z})}
\]  

(8)

This represents the voltammogram at an electrode with an extremely small radius. Since the right hand side of eqn. (8) does not contain any time-dependent variable except \( \xi \), the voltammogram is under the steady state. As a result, even if the direction of the potential sweep is reversed at any potential, no hysteresis can be observed from the theoretical point of view. The real voltammogram might have hysteresis due to charging current.

**Computation**

Although eqn. (6) is an analytical solution, it is quite difficult to obtain the integral value, as is the case for linear sweep voltammetry due to linear diffusion [29]. We resorted to a numerical method, Simpson's 1/3 rule, for performing the integration. The number of the divisions in Simpson's method was taken to be 100, which yields less than 0.03% errors in comparison with current values calculated with divisions of 1000. The singularity of \( f(z) \) at \( z = 0 \) was eliminated by integration by parts. Equation (2) valid for large \( z \) was connected at \( z = 1.08 \) with eqn. (3) valid for small \( z \).

Voltammograms thus calculated are shown in Fig. 1 for various values of \( p \). The ordinate can be altered to the conventionally used dimensionless current,
Fig. 1. Theoretical linear sweep voltammograms calculated from eqn. (6) for $\rho = (nF\alpha^2v/RTD)^{1/2}$ = (1) 10, (2) 8, (3) 6, (4) 4, (5) 3, (6) 2, (7) 1 and (8) 0.1. The upper abscissa is for 25°C.

Fig. 2. Plots of dimensionless maximum current vs. $\rho$ (solid line) and the corresponding asymptotic line (dashed line) given by eqn. (9).
by multiplying the ordinate by $4/\pi p$. The upper curve in Fig. 1 is similar to the voltammogram resulting from linear diffusion but is larger than the latter by 17% at the peak because of the edge effect. As values of $p$ decrease, the diffusion tail decreases less rapidly than the peak and approaches a constant value, i.e., the steady state current expressed by eqn. (8).

One of the measures characterizing the voltammograms is a maximum current, $I_m$, instead of a peak current, because there is no peak in the voltammogram for a very small value of $p$. In Fig. 2, the dimensionless maximum current, $I_m/4nFe^*Da$, is plotted against $p$. It increases from unity and then approaches asymptotically the (dashed) straight line given by:

$$I_m/4nFe^*Da = 0.351p$$  \hspace{1cm} (9)

which corresponds to the peak current for linear diffusion. The difference between the upper curve and the straight line results from the contribution of the edge effect. This contribution is 10%, 5%, 3%, and 1% for $p = 17, 33, 55, \text{and} 150$, respectively. On the other hand, for $p = 0.6, 0.33, 0.21, \text{and} 0.076$, the voltammograms deviate from the steady state wave by 10%, 5%, 3%, and 1%, respectively. Thus for routine conditions for electrodes with radius ca. 0.1 mm, diffusion is substantially linear for sweep rates larger than about 500 mV/s while steady state behavior is approached only for sweep rates of 1 mV/s or less.

A simple equation expressing the variation of the maximum current with $p$ may be useful for analyzing voltammograms. Therefore we obtained an approximate equation for the maximum current by inspecting the mathematical properties of the various elementary transcendental functions. It is given by:

$$I_m/4nFe^*Da = 0.34 \exp(-0.66p) + 0.66 - 0.13 \exp(-11/p) + 0.351p$$  \hspace{1cm} (10)

The errors involved in this equation are less than 0.23% for any value of $p$.

The parameter, $p$, defined by eqn. (7), contains unknown or only ambiguously determined values of $n$, $D$, and $a$. It is assumed here that values of $n$ are known. If only values of $a$ are known, eqn. (10) can be divided by $p^2$, i.e.,

$$I_mRT/4n^2F^2e^*a^3c = 0.34p^{-2} \exp(-0.66p) + 0.66p^{-2}$$

$$-0.13p^{-2} \exp(-11/p) + 0.351/p$$  \hspace{1cm} (11)

to determine values of $p$, and hence $D$, by calculating the inverse function on the right hand side of eqn. (11), because values on the left hand side are known or measurable. On the other hand, if only values of $D$ are known, one can determine values of $a$ by calculating the inverse function of the following equation:

$$\left(I_m/4e^*\right)^{(v/nFRTD)^{1/2}} = 0.34p \exp(-0.66p) + 0.66p$$

$$-0.13p \exp(-11/p) + 0.35p^2$$  \hspace{1cm} (12)

which has been derived from eqn. (10) by multiplying by $p$. It is easy to compute these inverse functions by applying the well-known Newton method and taking into
account the fact that the curves expressed by eqns. (11) and (12) have concave shapes.

In general, the potential of the peak or maximum current is a significant value identifying electroactive species. Since this potential is ambiguously defined, however, especially for a wave almost under the steady state, it may be convenient to use the potential at half-maximum current instead of the potential at the maximum. In Fig. 3, the half-maximum potential, $E_{m/2}$, is plotted against $p$. With an increase in $p$, the values of $-nF(E_{m/2} - E^*)/RT$ vary from zero to 1.09 which corresponds to $E_{m/2} - E^* = 28/n$ mV at 25°C for linear diffusion [29].

In order to obtain an approximate equation for the half-maximum potential we attempted several trials of curve-fitting by the use of various kinds of elementary functions. We obtained:

$$nF(E_{m/2} - E^*)/RT = -0.694 \tan^{-1}(0.85p)$$

(13)

where the argument of the arctangent is expressed in terms of radians. This equation has an error less than 0.016 for any values of $nF(E_{m/2} - E^*)/RT$, which corresponds to 0.4/n mV at 25°C. It is possible to evaluate $p$ directly by the measurement of only the half-peak potential without any knowledge of either values of $a$ or $D$ if one measures values of $E^*$. Since $E_{m/2} - E^*$ varies only over a narrow range (0 to 28/n mV at 25°C), it is necessary to measure both $E_{m/2}$ and $E^*$ accurately.

Of interest is a comparison of values of peak current, peak potential and half-maximum potential obtained analytically with those determined numerically by

![Graph](image)

Fig. 3. Variation of half-maximum potential with $p$ (solid line) and that at a planar electrode (dashed line).
Heinze with the aid of the difference method [11]. We compared readings of peak current from Fig. 2 in ref. 11 with values calculated from eqn. (10). As a result, values by Heinze are 1.7% less than those calculated from eqn. (10). The deviation would result from participation of sluggish heterogeneous kinetics which Heinze introduced instead of the Nernst equation in the numerical analysis.

In chronoamperometry at very small electrodes, it is possible to determine values of $D$ without knowing $n$-values [13,30,31] by taking advantage of a term expressing non-linear diffusion. However it is not the case for linear sweep voltammetry because the parameter $p$ contains both $n$ and $D$.

**EXPERIMENTAL**

The working micro-electrodes employed here were made from platinum wires 0.025, 0.05 and 0.1 mm in radius. The micro-electrode of 0.1 mm radius was shielded with epoxy resin. It was quite difficult to make the electrode a perfect disk because the platinum spreads on to the shielding epoxy resin during polishing. Hence electrodes less than 0.05 mm in radius were prepared by threading high-purity platinum wire into a drawn glass tube and sealing it with heat. The tip of the electrode was carefully ground so as to expose only a disk of platinum to the solution and then polished with 0.05 µm alumina powder. The diameter of the shielding glass was ca. 2 mm, which is large enough in comparison with the diffusion layer developed even during a rather long electrolysis time, say 60 s. The radius of the electrode was determined by averaging a number of diameters read through a microscope. Only electrodes with less than 5% deviations from readings of the diameter were employed in the experiment.

The cell employed was an H-type cell thermostated at (25 ± 0.2)°C. It was equipped with the working electrode, a Luggin capillary connected to an SCE, an auxiliary electrode of a platinum wire and a tube for passing nitrogen gas. The plane of the electrode disk was mounted horizontally, face down in the cell.

The potentiostat employed was a home made one. Since it has 500 kΩ resistance of the current follower, it allows measurement of at least current greater than 1 nA with little electronic noise. The recorder for cyclic voltammetry was Graphtec LTD, WX 4301 xy-recorder.

All chemicals were of analytical grade. Solutions of hexacyanoferrate(II) (0.1–10 mmol/dm$^3$) in 1.0 mol/dm$^3$ KCl were prepared in twice-distilled water.

Nitrogen gas was bubbled through the solution for 10 min. The electrode potential was swept from 1.2 V vs. SCE to −1.0 V vs. SCE several times for preconditioning the electrode surface before each experimental run.

**RESULTS AND DISCUSSION**

Cyclic voltammograms at an electrode 0.05 mm in radius are shown in Fig. 4 for three values of the potential sweep rate. As predicted by the theory, the voltammogram for slow sweep rate (10 mV/s) shows the limiting current plateau. Therefore
Fig. 4. Cyclic voltammograms measured at an electrode 0.05 mm in radius in a solution of 4 mmol dm$^{-3}$ Fe(CN)$_6^{4-}$ for potential sweep rates of 0.2 (---), 0.04 (-----) and 0.01 (-----) V s$^{-1}$.

Fig. 5. Dependence of $\rho_{\text{exp}}$ on $\sqrt{v}$ measured at electrodes with radii (a) 0.1, (C) 0.05 and (●) 0.025 mm in a solution of 1 mmol dm$^{-3}$ Fe(CN)$_6^{4-}$.
determination of the peak potential becomes ambiguous. The limiting current of the reverse wave for the slow sweep rate treads back on that of the forward wave, but there is a little difference between the half-peak potential on the forward and the reverse waves. This fact demonstrates that the voltammograms do not reach readily the steady state.

We subtracted voltammetric curves obtained in a blank solution from those in a solution containing Fe(CN)$_6^{3-}$ when contribution of residual current was appreciable, especially at a small electrode.

In order to analyze the maximum current by the use of eqns. (11) or (12), it is necessary to estimate either values of $a$ or $D$ in advance. We assume that values of $D$ are unknown while those of $a$ can be determined by geometrical measurement of the radii. Values of $I_m$ were obtained for a variety of sweep rates at electrodes of different radii. We inserted experimental values of $I_m$, $v$, $a$, $T$, $n$ and $c^*$ into the left hand side of eqn. (11), and solved the resulting equation with respect to $p$ by the Newton method. In Fig. 5, the values thus determined, $p_{\text{exp}}$, are plotted against $\sqrt{v}$. The values of $p_{\text{exp}}$ are proportional to $\sqrt{v}$ for three values of $a$, as predicted by eqn. (7).

When values of $p_{\text{exp}}$ are plotted against $a\sqrt{v}$, the plots should fall onto the same line regardless of values of $a$, $v$ and $c^*$, providing that the theory presented here is correct. In Fig. 6, variations of $\log(p_{\text{exp}})$ with $\log(a\sqrt{v})$ are shown for a series of values of $a$, $v$ and $c^*$ in the ranges $0.025 < a/\text{mm} < 0.1$, $0.01 < v/V \text{ s}^{-1} < 0.2$, and

![Image](image-url)

Fig. 6. Plot of $\log(p_{\text{exp}})$ calculated from the maximum current vs. $\log(a\sqrt{v})$. The maximum currents were measured at electrode radii of: (a) 0.1, (O) 0.05, and (●) 0.025 mm. The straight line has a slope of unity.
0.1 < c*/mol dm⁻³ < 4.0. A line with unity slope has been drawn through the points; the fit is quite good. Values of D obtained from the intercept of the line are given in Table 1 together with the D-value obtained with conventional linear sweep voltammetric measurements at an electrode with a radius of 1 mm. The agreement is excellent, indicating that the experimental results support well the theory for the maximum current.

The half-maximum potentials were obtained for the same voltammograms. The equilibrium potentials were measured in solutions with different concentration ratios of Fe(CN)₆³⁻ and Fe(CN)₄⁺ with the total concentration 3.0 mmol dm⁻³; this gave a value for the formal potential, E°′, of 0.232 V vs. SCE. Data for which the quantity Eₘ₀₂ − E°′ was greater than 28 mV were neglected for the analysis. We inserted values of Eₘ₀₂ − E°′ thus obtained into eqn. (13), extracted corresponding values of pₐₓ, and plotted them against log(α/β) in Fig. 7. Although the scatter of the points in Fig. 7 is somewhat greater, the straight line is the same as in Fig. 6. The average value of D evaluated by eqn. (13) is given in Table 1. The deviation of the D-value from that obtained at a planar electrode may result from poor reproducibility of the half-maximum potential due to variation of surface of the platinum electrode. We also tried to determine values of Eₘ₀₂ − E°′ from the midpoint between the half-maximum potentials for the net forward and the net reverse waves. However a scatter bigger than the one in Fig. 7 was found. Therefore this is not a good technique for evaluating the half-maximum potential.

Values of the diffusion coefficient given in Table 1 are larger than 6.32 × 10⁻⁶ cm² s⁻¹ obtained by Stackelberg et al. [32] with a potentiostatic experiment. The deviation may be not due to geometry of the electrode or the electrode area because the value obtained at a small disk electrode is the same as that determined at a large electrode (a = 1 mm). The deviation might result from convection of the solution.

Some micro-electrodes that we constructed were not absolutely flush with the surrounding insulator. A voltammogram at such an electrode has a maximum larger than predicted by the theory, though the shape of the voltammogram looks reasonable. Therefore analysis of the voltammogram might yield an incorrect value of p. In order to obtain correct values of p, it is necessary to construct electrodes which have not only perfect disk form but also planar shapes.

In Fig. 8, variation of the maximum currents with concentrations of Fe(CN)₆⁺⁻ is

<table>
<thead>
<tr>
<th>Obtained</th>
<th>Maximum current, Lₘ</th>
<th>Half maximum potential, Eₘ₀₂</th>
<th>Peak current at large electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>D × 10⁵/cm² s⁻¹</td>
<td>7.30 ± 0.15</td>
<td>7.98 ± 0.43</td>
<td>7.30 ± 0.04</td>
</tr>
<tr>
<td>D × 10⁵/cm² s⁻¹</td>
<td>1.24</td>
<td>3.24</td>
<td>0.30</td>
</tr>
<tr>
<td>Number of runs</td>
<td>71</td>
<td>56</td>
<td>45</td>
</tr>
</tbody>
</table>

*superscript s denotes standard deviation.
Fig. 7. Plot of $\log(p_{\text{ref}})$ calculated from the half-maximum potential vs. $\log(\sigma\sqrt{\sigma})$. The half-maximum potentials were measured at electrode radii of: (△) 0.1, (○) 0.05 and (■) 0.025 mm. The straight line is identical with that in Fig. 6.

Fig. 8. Dependence of maximum currents on concentrations of Fe(CN)$_6^{4-}$. The currents were measured at an electrode radius of 0.025 mm with a sweep rate of 10 mV s$^{-1}$.
shown when currents were measured at the smallest electrode ($a = 0.025$ mm) and the slowest sweep rate ($10$ mV s$^{-1}$) in this experiment. The straight line in Fig. 8 has a slope of unity. Therefore the maximum current exhibits excellent linearity with respect to concentration, as expected by eqn. (10). The measurable lower limit of concentration was $10^{-4}$ mol dm$^{-3}$, below which capacitive current became predominant. In order to detect species at lower concentration, it may be necessary to develop a way to diminish the capacitive component, e.g., by pretreatment of the electrode surface, or by application of square wave voltammetry.

REFERENCES