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Cyclic Voltammetry at Shallow Recessed Microdisc Electrode: Theoretical and Experimental Study

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Abstract

This study focuses on the cyclic voltammetry behavior at shallow recessed microdisc electrode, particularly on the transition from cottrellian behavior to steady state behavior. Diffusion to the inlaid and recessed microdisc electrode is simulated. From the shape of the CVs, for a given radius and potential scan rate, the transition time from planar diffusion to hemispherical diffusion presents a minimum as the recess increases. Theoretical prediction was confirmed by fitting the simulated CVs with experimental results. Dimensionless transition scan rate has been defined and determined by simulation for inlaid and recessed microdisc electrodes.

Keywords

Recessed electrode; Microdisc; Voltammetry

1. Introduction

Photolithographic techniques are widely used to fabricate microelectrode arrays with well-defined and reproducible geometries of micron dimensions [1]. These microelectrode arrays have shown their advantages in many electroanalytical applications [2,3]. The individual microelectrodes in the microelectrode arrays produced by photolithography are generally with shallow recess. Recessed disc electrodes have attracted renewed interest because its miniaturization to nanometer scales [4]. Nanoporous electrodes with large l/a ratio (where l is the recess depth and a is the orifice radius of the recessed microdisc electrode) were utilized to study the photon gated [5] and electrostatic gated [6] transport of molecules through the pore orifice. Mirkin and co-workers used shallow recessed nanodisk electrodes to perform electrochemical experiments in nanometer sized, sub zeptoliter volume thin layer cells [7,8] in which only limited number of redox molecules were trapped.

Cyclic voltammetry is a commonly used electroanalytical technique to characterize microelectrode arrays and detect analytes. The cyclic voltammograms at microhole electrode arrays has been treated theoretically [9], however, to the best of our knowledge, no one has reported the theory of cyclic voltammetry at single shallow recessed microdisc electrode or microelectrode arrays. A microhole electrode is a deep recessed microelectrode, where the concentration of redox species at the “mouth” of the microhole is the same as in the bulk of

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the solution during the experiment. This can be achieved by stirring the solution. Under such conditions the mass transport outside of the well has no or little effect on the mass transport in the well as it has been revealed in the chronoamperometric studies of inlaid and recessed microelectrodes by Bond et al. [10]. The mass transport in shallow recessed microelectrodes is more complex. In shallow recessed microelectrodes the transition from planar diffusion to hemispherical diffusion has to be considered. In their chronoamperometric studies with recessed microdisc electrodes Bartlett and Taylor [11] noted that the Cottrellian current decay for deep recess microdiscs at short times “switching” to steady-state behavior at long times. However, neither Bond [10], nor Bartlett [11] discussed the theory of cyclic voltammetry in their studies. Understanding the cyclic voltammetric behavior at shallow recessed microelectrodes is essential for the quantitative description of the voltammetric behavior of shallow recessed microelectrode arrays and to formulate design guidelines for such commonly utilized sensor structures [12]. In this paper, we present the numeric simulation study of cyclic voltammetry at shallow recessed microdisc electrode and validate the theory with experimental data.

2. Theory

2.1. Model

To simulate the cyclic voltammetric response, a simple one-electron transfer reaction with Butler-Volmer kinetics is considered

The forward and backward rate constants, k_f and k_b , are defined by

$$k_f = k^0 \exp\left(-\frac{\alpha F}{RT}(E - E^{0'})\right) \quad (2)$$

$$k_b = k^0 \exp\left(-\frac{(1 - \alpha) F}{RT}(E - E^{0'})\right) \quad (3)$$

where k^0 is the standard heterogeneous rate constant for the redox couple¹, α is the transfer coefficient ($\alpha = 0.5$ is taken in this work), $E^{0'}$ is the formal potential, E is the applied potential on the electrode/solution interface. Fig. 1 shows the coordinate system used in the model. The diffusion of species O and R in a quiescent solution can be pressed as

$$\frac{\partial c_o(r, z, t)}{\partial t} = D_o \left[\frac{\partial^2 c_o(r, z, t)}{\partial r^2} + \frac{1}{r} \frac{\partial c_o(r, z, t)}{\partial r} + \frac{\partial^2 c_o(r, z, t)}{\partial z^2} \right] \quad (4)$$

¹Rate constants characteristic for Nernstian CVs were chosen.

$$\frac{\partial c_R(r, z, t)}{\partial t} = D_R \left[\frac{\partial^2 c_R(r, z, t)}{\partial r^2} + \frac{1}{r} \frac{\partial c_R(r, z, t)}{\partial r} + \frac{\partial^2 c_R(r, z, t)}{\partial z^2} \right] \quad (5)$$

where the c_O , c_R , D_O and D_R are the concentrations and diffusion coefficients of respective species. Before the experiment starts, only the species O is present in the solution with initial bulk concentration of c_b . With the assumption of $D_O = D_R$, then $c_R = c_b - c_O$ applies to the entire simulation domain. For a recessed microdisc electrode with a radius of a and the recess depth of l , the initial conditions are:²

$$c_O = c_b \quad 0 \leq r \leq 200a, \quad 0 \leq z \leq 200a \quad (6)$$

$$c_R = 0 \quad 0 \leq r \leq 200a, \quad 0 \leq z \leq 200a \quad (7)$$

The boundary conditions for a recessed microdisc electrode are:

$$\begin{aligned} D_O \left[\frac{\partial c_O(r, z, t)}{\partial z} \right]_{z=-l} &= -D_R \left[\frac{\partial c_R(r, z, t)}{\partial z} \right]_{z=-l} \\ &= k_f c_O(r, z, t) \\ &\quad - k_b c_R(r, z, t) \quad 0 < r < a \end{aligned} \quad (8)$$

$$\begin{aligned} D_O \left[\frac{\partial c_O(r, z, t)}{\partial r} \right]_{r=0} &= D_R \left[\frac{\partial c_R(r, z, t)}{\partial r} \right]_{r=0} \\ &= 0 \quad -l < z < 200a \end{aligned} \quad (9)$$

$$\begin{aligned} D_O \left[\frac{\partial c_O(r, z, t)}{\partial r} \right]_{r=a} &= D_R \left[\frac{\partial c_R(r, z, t)}{\partial r} \right]_{r=a} = 0 \quad -l < z < 0 \end{aligned} \quad (10)$$

²The boundary condition for z was selected as $200a$ because this distance is sufficiently larger than the diffusion layer thickness at all times considered in our simulations and experiments in this work. This has been confirmed by comparing the simulation results obtained with $z_{\max} = 200a$ and $z_{\max} = 1000a$. The two solutions were the same.

$$\begin{aligned}
 D_o \left[\frac{\partial c_o(r, z, t)}{\partial r} \right]_{r=200a} \\
 = D_R \left[\frac{\partial c_R(r, z, t)}{\partial r} \right]_{r=200a} = 0 \quad 0 < z < 200a
 \end{aligned} \quad (11)$$

$$\begin{aligned}
 D_o \left[\frac{\partial c_o(r, z, t)}{\partial z} \right]_{z=0} \\
 = D_R \left[\frac{\partial c_R(r, z, t)}{\partial z} \right]_{z=0} = 0 \quad a < r < 200a
 \end{aligned} \quad (12)$$

$$c_o = c_0 \quad z = 200a, 0 < r < 200a \quad (13)$$

$$c_R = 0 \quad z = 200a, 0 < r < 200a \quad (14)$$

The time scale (t_{cv}) of the cyclic voltammetric experiment is

$$t_{cv} = \frac{2(E_h - E_l)}{v} \quad (15)$$

where the E_h is the highest and E_l is the lowest applied potential in the cyclic voltammetric experiment and v is the potential scan rate. The triangle wave of E - t in cyclic voltammetry can be expressed as:³

$$E = E_i + (E_r - E_i) \cdot \frac{2}{\pi} \sin^{-1} \left\{ \sin \left[\frac{\pi v t}{2(E_h - E_l)} \right] \right\} \quad 0 \leq t \leq t_{cv} \quad (16)$$

where E_i is the initial potential, E_r is the reversal potential in cyclic voltammetry.

The current passing through the microelectrode/solution interface can be calculated by

$$i = 2\pi F D_o \int_0^a r \left[\frac{\partial c_o(r, z, t)}{\partial z} \right]_{z=-l} dr \quad (17)$$

The time-dependent diffusion problems defined above were solved by a COMSOL Multiphysics® version 3.2 (COMSOL, Inc., Burlington, MA, USA) program, which applies the finite element method. Simulation of cyclic voltammetry using this software has been first

³The $\sin^{-1}$ function has been selected to describe a triangle wave, instead of a widely adopted two segments function, because the commercial software used in our simulations did not work with the latter.

proven accurate by White and co-workers [4,13]. For a general treatment the following dimensionless parameters were used:

$$C_o = c_o / c_0 \quad (18)$$

$$C_R = c_R / c_0 \quad (19)$$

$$R = r / a \quad (20)$$

$$Z = z / a \quad (21)$$

$$L = l / a \quad (22)$$

$$K_0 = \frac{k_0 a}{D} \quad (23)$$

$$\varepsilon = \frac{nFE}{RT} \quad (24)$$

$$\tau = \frac{4Dt}{a^2} \quad (25)$$

$$V = \frac{nF}{4RT} \cdot \frac{va^2}{D} \quad (26)$$

Simulation of each CV takes 3-4 minutes on a PC equipped with a Pentium D 3.4 GHz processor and 4 GB memory and Windows XP Professional Edition operating system.

2.2 Dimensionless transition scan rate vs. recess depth

In most applications steady state responses are desired in measurements with microelectrode arrays. However, to obtain sigmoidal shape CVs with microdisc electrode arrays certain requirements must be met, e.g., the experimental conditions should be adequate for obtaining sigmoidal shape CVs with single microdisc electrodes. Here we define a dimensionless transition scan rate (V_{tr}) for a single microdisc electrode, at which the ratio of the maximum current in the reverse scan⁴ to the maximum current in the forward scan ($\gamma = I_{rmax}/I_{fmax}$) is

⁴The maximum current in the reverse scan is the absolute current value at the reverse "peak".

0.05. The CVs with $\gamma > 0.05$, which are obtained with dimensionless scan rates larger than V_{tr} , are considered significantly deviated from sigmoidal shape, while CVs with $\gamma \leq 0.05$ are considered sigmoidal, i.e., very close to steady state response. For an inlaid microdisc electrode ($L = 0$), V_{tr} was found to be 0.0856^5 (Fig 2a). With this value, the real transition scan rate (v_{tr}) for a given microelectrodes radius can be easily calculated. At the reversal point of a CV simulated with V_{tr} the current is $1.064 \times I_{ss}$, where I_{ss} is the steady state current of the inlaid microelectrode. The overpotential at the reversal point is 0.25 V ($E_r - E_{1/2} = 0.25$ V).

When the effect of increasing recession depth on the shape of CVs is considered at a given V , one might intuitively think that γ will monotonically increase as L increases. But the simulations for shallow recessed microdisc electrode show that γ passes a minimum at e.g., $V = 0.08562$ at ca $L = 1$, (Fig 2a and b). This phenomenon is a consequence of the difference in the chronoamperometric behaviors of shallow recessed and coplanar microelectrodes [10, 11]. Shallow recessed microelectrodes reach steady state faster than coplanar microdisc electrodes and the transition from cottrellian behavior to steady state behavior in their chronoamperometric response is more abrupt than with coplanar microdisc electrodes.

In a numerical simulation study of chronoamperometry at shallow recessed microdisc electrodes, Bartlett and Taylor interpreted the minimum time required to reach a certain percentage of steady state current [11]. Here, with increasing recess depth and at the same V and τ , the concentration of reactant (C_0) at the orifice approaches to the bulk concentration (Fig 3), so that a steady state beyond the orifice reaches faster. But when L exceeds a certain value, cottrellian behavior in the well dominates during the potential scan and a peak shaped CV will be observed at a given V .

The dimensionless transition scan rates present a maximum value at ca. $L = 0.75$ as L increases (Fig 4), for the same reason. These V_{tr} are important for finding design guidelines for microdisc electrode arrays, which is discussed in consequent paper. When is $0 \leq L \leq 2$, the peak has been fitted to an asymmetric double sigmoidal function for the convenience of rebuilding the curve

$$V_{tr} = A + B \cdot \frac{1}{1 + e^{-\frac{L-C}{D}}} \cdot \left(1 - \frac{1}{1 + e^{-\frac{L-C}{E}}} \right) \quad (27)$$

where $A = -0.00687$, $B = 0.164$, $C = 0.203$, $D = 0.275$, $E = 1.345$. When $2 < L < 30$, V_{tr} shows a good linear correlation to L in logarithm scale (Fig 4, inset), which gives

$$V_{tr} = 0.1233 * L^{-1.784} \quad (28)$$

3. Experiment

3.1 Chemicals

Ferrocenemethonal (FcMeOH, 97%) was obtained from Sigma-Aldrich (St. Louis, MO). Other chemicals were reagent grade and were used as received from commercial sources. All aqueous solutions were prepared with $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$ deionized water (Nanopure, Barnstead, Dubuque, IA)

⁵The value of γ depends on the difference of reverse potential and the formal electrode potential, i.e., how far the potential has been swept beyond the formal electrode potential. However, at V_{tr} , when the CVs are quite close to the ideal sigmoidal wave, the effect of is almost negligible in practical experimental conditions.

3.2 Fabrication of inlaid and recessed electrode

A ~7 mm length 25- μ m-dia Au wire (99.99+%, Goodfellow, Oakdale, PA) was sealed in a borosilicate glass tube with O.D of 2 mm and I.D of 1.16 mm (Sutter, Novato, CA). The electrode tip was polished to a flat and smooth surface on successively finer grades of emery papers, and then polished with 0.05 μ m alumina. Electrical contact was made with silver epoxy (EPO-TEK, Billerica, MA) and a copper wire.

The recessed microdisc electrode was prepared by electrochemically etching the gold in a solution containing 1M KI and 0.1 M phosphate buffer (pH 7.2) [14]. The etching cell was immobilized in an ultrasonic bath (Cole-Parmer 8890) by a plastic frame. The electrochemical etching process was facilitated by sonication.

3.3 Electrochemical measurement

Electrochemistry experiments were performed with a CHI 760C electrochemical workstation (CH Ins., Austin, TX). A Pt wire served as the counter electrode. A 1.5-mm-dia silver wire (99.9%, Aldrich, Milwaukee, WI) was employed as quasi-reference electrode for the sonication facilitated etching process. Ag/AgCl reference electrode in 3M KCl solution was used in other cases.

3.4 Fitting of experimental results

CVs were recorded at 10 mV/s and 40 mV/s with inlaid and recessed 25- μ m-dia microdisc electrodes in a 1 mM FcMeOH solution with 0.1 M NaNO₃. The recess depths were determined from the steady state current by

$$\frac{i_{ss,recessed}}{i_{ss,inlaid}} = \frac{\pi}{4L+\pi} \quad (29)$$

for $L \geq 1$ [10] and

$$\frac{i_{ss,recessed}}{i_{ss,inlaid}} = \frac{1}{1+1.6843L - 1.3237L^2 + 1.7116L^3 - 0.7585L^4} \quad (30)$$

for $0 < L < 1$ [11]. In the later case, a curve of steady state current ratio over L was plotted from Eq. (30), and the L was determined from the corresponding current ratio.

When $v = 0.04$ V/s and $D = 7.4 \times 10^{-6}$ cm²/s [15] for ferrocenemethanol were taken, the dimensionless scan rate V is 0.0842 for a 25- μ m-dia electrode. The value is very close to V_{tr} of inlaid microdisc electrode. Simulated CVs are fitted very well with the experimental results (Fig 5a). More comparisons between theoretical and experimental results can be found in Fig 5b, where γ was plotted versus $\log L$. These comparisons confirmed the theoretical finding that γ passes a minimum as L increases, and validated the simulations and other theoretical results presented above.

4. Conclusion

A dimensionless transition scan rate of inlaid electrode was determined by simulations, which divides the CVs into two types: cottrellian behavior dominated and steady state behavior

dominated. At a given V , γ presents a minimum value rather than monotonically increases as L increases for shallow recessed microdisc electrodes. The experimental results confirmed the theoretical predictions and validated the simulations. The values of V_{tr} for shallow recessed electrodes for various L were determined from simulations, and a maximum value was found around $L = 0.75$.

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Fig. 1. Mesh in the simulation domain near the recessed microdisc electrode. Inset is the schematic diagram for the whole simulation domain.

Fig. 2. Computed CVs (a) and γ (b) at $V = 0.08562$ for various L from 0 to 4

Fig. 3. Time depended concentration profile of the reactant at the orifice of the recessed disc in CVs with $V = 0.08562$, (a) at the edge and (b) at the center. $L = 0.2, 0.5, 1, 2, 3, 4$ from bottom to top

Fig. 4. Dimensionless transition scan rate for recessed disc electrodes determined by simulations (circle), and the fitted curve (solid line) for $0 \leq L \leq 2$. Logarithm scale plot of V_{tr} vs. L for $2 < L \leq 30$ are shown in the inset (circle) with the linear fitting.

Fig. 5.

(a) Experimental CVs recorded at 40 mV/s in a 1 mM FcMeOH solution with 0.1 M NaNO₃ at 25- μ m-dia inlaid (solid green) and recessed microdisc electrodes with $L = 0.89$ (solid blue) and $L = 3.10$ (solid red). Computed CVs are shown as dashed lines with corresponding colors. (b) Comparison of γ from computed (triangle) and experimental (square) CVs