Diffusion at Ultramicroelectrodes: Chronoamperometric Current Response Using Padé Approximation

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The analysis of transient chronoamperometric current response for various ultramicroelectrode geometries is carried out by solving the mixed boundary value problem for short and long time regimes. A two-point Padé approximant valid for entire time domain is developed. Tabular compilations of dimensionless current for ring and disc electrodes are reported.

1. Introduction

The specification of boundary conditions in diverse domains of interest constitutes the mixed boundary value problem of differential equations and their study arises in various contexts. Among them mention may be made of electrostatic potential theory,[1] heat transfer,[2] soil infiltration,[3] enzyme catalysis involving rototranslational diffusion equation,[4] ultramicroelectrodes,[5] etc. Despite this widespread occurrence, obtaining exact solutions of these problems have proved quite formidable, in general. In the case of electrochemical transport phenomena involving diffusion of electroactive species at ultramicroelectrodes, the “mixed” nature of the boundary conditions consists in formulating flux at one region and surface concentration c at the other viz.

$$\partial c/\partial t = D\nabla^2 c \tag{1}$$

with $c = f$ on S_1 and $(\partial c/\partial n) = g$ on S_2, where S_1 and S_2 refer to the electrode and insulated surface, respectively, f and g are functions dictated by the problem under study, and ∇^2 is the Laplacian operator in the appropriate coordinates.

While no general method of solving these mixed boundary value problems has been proposed, several rigorous procedures such as use of multidimensional integral equations[6] method of matched asymptotic expansions[7] for long time transients, Wiener−Hopf factorization in the case of disk electrodes to obtain steady state current,[8] geometrical constructions pertaining to diverse shapes of microelectrodes for short-time behavior,[9] etc. have been analyzed.

The purpose of this paper is to develop a two-point Padé approximant for approximating non-steady-state chronoamperometric current at ultramicroelectrodes for diffusion-controlled processes. We also provide tabular compilations of current over the entire time domain for ring electrodes of various dimensions and disc electrodes.

2. Analysis of Current for Short and Long Time Regimes

2.1. A General Formulation of the Problem. Assuming that the electrode is plane mounted and axisymmetric, the diffusion equation (1) becomes

$$\frac{\partial c^*}{\partial t} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(\frac{r\partial c^*}{\partial r}\right) + \frac{\partial^2 c^*}{\partial z^2}\right] \tag{2}$$

where $c^* = c_0 - c$, c_0 being the bulk concentration. The mixed boundary conditions are given by

$$c^*(r,0,t) = c_0 \tag{3}$$

on the electrode surface and

$$(\partial c^*/\partial z)_{z=0} = 0 \tag{4}$$

on insulated surface.

The other conditions pertaining to eq 2 are $c^*(r,z,0) = 0$ and $c^*(r,z,t) = 0$ when $z, r \rightarrow \infty$. The chronoamperometric current for the diffusion-limited case is evaluated from

$$i/nFD = 2\pi \int_{\text{electrode surface}} q(r,t) r \, dr \tag{5}$$

where

$$q(r,t) = -\left[\frac{\partial c^*(r,z,t)}{\partial z}\right]_{z=0} \tag{6}$$

Using Hankel transformation of order zero with respect to r and Laplace transform for the time variable, the general solution of eq 2 is given by ref 10

$$c^*(r,z,t) = \frac{1}{2\pi^{1/2} D^{3/2}} \int_0^t \frac{dt'}{(t-t')^{3/2}} \int_{\text{electrode surface}} q(r',t') \times \exp\left[-\frac{(r^2 + r'^2 + z^2)}{4D(t-t')}\right] I_0[rr'/2D(t-t')] r' \, dr' \tag{7}$$

where I_0 represents the modified Bessel function of the first kind and zero order. Equation 7 satisfies the given differential equation and all the given constraints except (3), whatever be the functional form of $q(r,t)$. Thus, the problem of evaluating the current response is now transferred to deriving $q(r,t)$. A simple method originally proposed[2] in soil infiltration studies and subsequently extended to ultramicro disc electrodes[12] consists in exploiting the available information on $q(r,t)$ viz., short and long time domain, and introducing higher order corrections progressively. Elsewhere,[12] two terms for short and long time expansions for $q(r,t)$ in the case of ultramicro disc electrodes have been proposed. However, general treatments valid for all geometries to estimate diffusion current at ultramicroelectrodes when $t \rightarrow 0$ and $t \rightarrow \infty$ are available. Thus, using eq 5, the diffusion current at any microelectrode having

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a closed surface and lying on an essentially infinite support is[7,13,19,25]

$$\frac{i(t)}{nFDc_0} \approx \frac{S}{\sqrt{\pi Dt}} + \frac{P}{2} + \frac{1}{2}(m-r)\sqrt{\pi Dt} \qquad t \to 0 \tag{8}$$

$$\frac{i(t)}{nFDc_0} \approx l_0 + \frac{{l_0}^2}{\sqrt{4\pi^3\, Dt}} \qquad t \to \infty \tag{9}$$

where S is the surface area of the electrode, P is the perimeter m is the number of separate pieces it comprises, and r denotes the number of "holes" in them. For nonplanar geometries the perimeter should be replaced by the appropriate curvature terms in eq 8. Furthermore, the short-time expression for current needs the geometrical characteristics of the electrode while the long-time case requires the information on steady state limit, viz, l_0. For short times, eq 8 is a special case of eq 37 of ref 25 and for long times, Phillips[7] has reported the next term in eq 9 using the method of matched asymptotic expansions.

2.2. Two-Point Padé Approximation for Chronoamperometric Current. In studies involving transient chronoamperometric response at ultramicroelectrodes, the series expansion pertaining to current for small and long time regimes may be written as follows:

$$f(x) = a_0 + a_1 x + O(x^3) \qquad x \to 0 \tag{10}$$

$$= b_0 x + b_1 + b_2 x^{-1} + O(x^{-2}) \qquad x \to \infty \tag{11}$$

where the coefficients a_0 and a_1 depend only on l_0, whereas the coefficients b_0, b_1, and b_2 depend only on S, P, and the topology of the surface (i.e., how many separate pieces it comprises and how many holes there are in them[25]). x in the above equation is equal to $(Dt)^{-1/2}$. A two-point Padé approximation can easily be constructed using first two terms of (10) and (11) as

$$f(x) = \frac{p_0 + p_1 x + p_2 x^2}{1 + q_1 x} \tag{12}$$

where

$$p_0 = a_0; \quad p_1 = b_0 + b_1 q_1; \quad p_2 = b_0 q_1; \quad q_1 = (a_1 - b_0)/(b_1 - a_0) \tag{13}$$

For eqs 8 and 9 the above form leads to

$$\frac{i(t)}{nFDc_0} = \frac{p_0 + p_1 x + p_2 x^2}{1 + q_2 x} \tag{14}$$

where $f(x)$ is identified as $i(t)/nFDc_0$ and $x = (Dt)^{-1/2}$. The coeffieicnts p_0, p_1, p_2, and q_1 are given by

$$p_0 = l_0; \qquad p_1 = \frac{S}{\pi^{1/2}} + \frac{P}{2}q_1$$
$$p_2 = \frac{S}{\pi^{1/2}}q_1; \qquad q_1 = \frac{(l_0^2/2\pi^{3/2} - S/\pi^{1/2})}{(P/2 - l_0)} \tag{15}$$

Equation 14 therefore constitutes a general semiempirical expression that can be employed to evaluate the current for different planar microelectrode geometries with appropriate replacement for the perimeter in the case of nonplanar ones. In what follows, we specialize this result for disc and ring geometries.

3. Non-Steady State Current for Various Geometries

3.1. Ring Electrodes. For ring electrodes $P = 2\pi(a + b)$ and $S = \pi(b^2 - a^2)$ and $m = r = 1$ while l_0 is given by[13]

$$l_0 = \frac{\pi^2(a + b)}{\ln[32a/(b - a) + \exp(\pi^2/4)]} \tag{16}$$

Consequently, eqs 8 and 9 become

$$\frac{i(t)}{4nFDc_0 b} = \frac{\pi^{1/2}}{2}(1 + a/b)y + \frac{\pi}{4}(1 + a/b) \qquad y \gg 1 \tag{17}$$

$$= \frac{l_0}{4b} + \frac{(l_0/b)^2\, y}{4\pi^{3/2}\,(1 - a/b)} \qquad y \ll 1 \tag{18}$$

where $y = \tau_R^{-1/2}$, $\tau_R = (4Dt)/(b - a)^2$. Thus employing eqs 14 and 15 we obtain

$$\frac{i(t)}{4nFDc_0 b} = \frac{p_0 + p_1 y + p_2 y^2}{1 + q_1 y} \tag{19}$$

where

$$p_0 = l_0/4b, \quad p_1 = \pi^{1/2}(1 + a/b)/2 + \pi(1 + a/b)q_1/4 \tag{20}$$

$$p^2 = \pi^{1/2}\,(1 + a/b)q_1/2 \tag{21}$$

$$q_1 = \frac{(l_0/b)^2/(1 - a/b)\pi^{3/2} - 2\pi^{1/2}(1 + a/b)}{\pi(1 + a/b) - l_0/b} \tag{22}$$

We may mention here that a three-term series for short times valid for all geometries is given in refs 19 and 25; however, in the case of ring electrodes, the third term, viz., the term proportional to $t^{1/2}$, is zero as shown in ref 25. Consequently, eq 8 is identical with eq 36 of ref 25 and eq 51 of ref 19. For long time transients, Phillips[7] has provided a three-term expansion valid for all general geometries (cf. eq 18 of ref 7). Further, eq 9 given above is identical to eq 36 of ref 13. In the present analysis, however, we have confined ourselves to employing only two terms of short and long time series expansions. In Table 1, values of the dimensionless current $i(t)/nFDc_0b$ for various a/b ratios and τ are reported and a satisfactory agreement with the recent[26] estimates of Jin et al. is noticed. It should be stated here that other types of functions[18] different from the rational function approximation proposed above can also be constructed empirically in agreement with two limits (17) and (18).

3.2. Disc Electrodes. Substituting $l_0 = 4b$, $S = \pi\, b_2$, $P = 2\pi\, b$, $m = 1$, and $r = 0$ in eqs 8 and 9 we obtain

$$\frac{i(t)}{4nFDc_0 b} = \frac{\pi^{1/2}\, y}{2} + \frac{\pi}{4} + \frac{\pi^{1/2}\, y^{-1}}{16} \qquad y \gg 1 \tag{23}$$

$$= 1 + 4\pi^{-3/2} y \qquad y \ll 1 \tag{24}$$

where $y = \tau_D^{-1/2}$ and $\tau_D = (4Dt)/b^2$. As in the earlier case, we

TABLE 1: Chronoamperometric Current at Ultramicroring Electrodes for Various τ_R Values and a/b Ratios Evaluated Using (19)[a]

	a/b					
τ_R	0	0.3	0.5	0.7	0.8	0.9
0.01	9.6717	12.5423	14.4133	16.3767	17.3458	18.3162
	(9.6505)	(12.5416)	(14.4499)	(16.3991)	(17.3645)	(18.3298)
0.05	4.7963	6.1747	7.0279	8.0229	8.5059	8.9921
	(4.7614)	(6.1731)	(7.0624)	(8.0656)	(8.5439)	(9.0209)
0.10	3.6496	4.6663	5.2695	6.0324	6.4010	6.7748
	(3.6162)	(4.6640)	(5.2978)	(6.0861)	(6.4511)	(6.8140)
0.50	2.1406	2.6556	2.9102	3.3422	3.5575	3.7863
	(2.1031)	(2.6495)	(2.9223)	(3.4164)	(3.6402)	(3.8607)
1	1.7920	2.1812	2.3476	2.6870	2.8635	3.0591
	(1.7612)	(2.1715)	(2.3549)	(2.7621)	(2.4574)	(3.1522)
5	1.3407	1.5635	1.5953	1.7759	1.8861	2.0301
	(1.3275)	(1.5272)	(1.5953)	(1.8275)	(1.9769)	(2.1569)
10	1.2377	1.4463	1.4139	1.5468	1.6327	1.7561
	(1.2296)	(1.3679)	(1.4149)	(1.5836)	(1.7080)	(1.8831)
∞	1.0000	0.9904	0.9793	0.9406	0.8990	0.8220
	(1.0000)	(0.9904)	(0.9793)	(0.9406)	(0.8990)	(0.8220)

[a] The numbers in parentheses denote estimates obtained using (31).

construct the two-point Pade approximant such that eq 24 and the first two terms of eq 23 are reproduced, viz.

$$\frac{i(t)}{4nFDc_0b} = \frac{p_0 + p_1y + p_2y^2}{1 + q_1y} \tag{25}$$

where

$$p_0 = 1; \quad p_1 = \pi^{1/2}/2 + \pi\, q_1/4; \quad p_2 = \pi^{1/2}q_1/2$$

$$q_1 = (4\pi^{-3/2} - \pi^{1/2}/2)/(\pi/4 - 1) \tag{26}$$

Equations 25 and 26 can also be obtained by substituting $a/b = 0$ and $l_0 = 4b$ in eqs 19−22. The comparison of digital simulation data with the prediction of eq 25 has been discussed earlier.[12]

4. Incorporation of Higher Order Terms in Short and Long Time Domain

In the analysis presented above, only two terms of short and long time series expansions have been considered. In general, the coefficient a_2 in eq 10 is zero. However, the coefficient b_2 is zero only for ring electrode. The accuracy of rational function approximation discussed above can be improved by considering higher order terms in eqs 10 and 11. For this purpose, we consider [3/2] Padé approximation such that three terms of short time expansion (eq 11) as well as two terms of long time expansion (eq 10) are reproduced. In this case, $f(x)$ is constructed as

$$f(x) = \frac{p_0 + p_1x + p_2x^2 + p_3x^3}{1 + q_1x + q_2x^2} \tag{27}$$

where

$$p_0 = a_0; \quad p_1 = b_0 + b_1q_1 + b_2q_2; \quad p_2 = b_0q_1 + b_1q_2; \quad p_3 = b_0q_2$$

$$q_1 = \frac{(b_0 - a_1)(a_0 - b_1)}{(a_0 - b_1)^2 + b_2(a_1 - b_0)}; \quad q_2 = \frac{(a_1 - b_0)q_1}{(b_1 - a_0)} \tag{28}$$

For eqs 8 and 9 the above form leads to

$$\frac{i(t)}{nFDc_0} = \frac{p_0 + p_1x + p_2x^2 + p_3x^3}{1 + q_1x + q_2x^2} \tag{29}$$

where $f(x)$ is identified as $i(t)/nFDc_0$ and $x = (Dt)^{-1/2}$. The coefficients p_0, p_1, p_2, p_3, q_1, and q_2 are given by

$$p_0 = l_0; \quad p_1 = S\pi^{-1/2} + Pq_1/2 + (1/2)(m - r)\pi^{1/2}\, q_2$$

$$p_2 = Sq_1\pi^{-1/2} + Pq_2/2; \quad p_3 = Sq_2\pi^{-1/2} \tag{30}$$

$$q_1 = \frac{(S\pi^{-1/2} - (1/2)l_0^{\,2}\pi^{-3/2})(l_0 - P/2)}{(l_0 - P/2)^2 + (1/2)(m - r)\pi^{1/2}[(1/2)l_0^{\,2}\pi^{-3/2} - S\pi^{-1/2}]}$$

$$q_2 = \frac{[(1/2)l_0^{\,2}\pi^{-3/2} - S\pi^{-1/2}]q_1}{(P/2 - l_0)}$$

The results for ring and disc geometries, arising from eqs 29 and 30, are reported below.

4.1. Ring Electrodes. Substitution of appropriate expressions for S, P, l_0, m, and r pertaining to ring electrodes in eqs 29 and 30 leads to the chronoamperometric current as

$$\frac{i(t)}{4nFDc_0b} = \frac{p_0 + p_1y + p_2y^2 + p_3y^3}{1 + q_2y + q_2y^2} \tag{31}$$

where $y = \tau_R^{-1/2}$ and $\tau_R = (4Dt)/(b - a)^2$. The coefficients p_0, p_1, p_2, p_3, q_1, and q_2 are given by

$$p_0 = l_0/4b; \quad p_1 = (1 + a/b)[\pi^{1/2}/2 + \pi\, q_1/4]$$

$$p_2 = (1 + a/b)[\pi^{1/2}q_1/2 + \pi\, q_2/4]; \quad p_3 = (1 + a/b)q_2\pi^{1/2}/2$$

$$q_1 = \frac{[(l_0/b)^2/4(1 - a/b)\pi^{3/2} - \pi^{1/2}(1 + a/b)/2]}{[\pi(1 + a/b)/4 - l_0/4b]} \tag{32}$$

and

$$q_2 = q_1^2$$

In Table 1, values of dimensionless current $i(t)/4nFDc_0b$ for various ring dimensions and time intervals are reported.

4.2. Disc Electrodes. If the appropriate values for S, P, l_0, m, and r pertaining to disc electrodes are substituted in eqs 29 and 30, we obtain the chronoamperometric current as

$$\frac{i(t)}{4nFDc_0b} = \frac{p_0 + p_1y + p_2y^2 + p_3y^3}{1 + q_1y + q_2y^2} \tag{33}$$

where $y = \tau_D^{-1/2}$ and $\tau_D = (4Dt)/b^2$. The coefficients p_0, p_1, p_2, p_3, q_1, and q_2 are given by

$$p_0 = 1 \quad ;p_1 = \pi^{1/2}/2 + \pi\, q_1/4 + \pi^{1/2}\, q_2/16;$$

$$p_2 = \pi^{1/2}q_1/2 + \pi\, q_2/4; \quad p_3 = \pi^{1/2}\, q_2/2$$

$$q_1 = \frac{(\pi^{1/2}/2 - 4\pi^{-3/2})(1 - \pi/4)}{(1 - \pi/4)^2 + (\pi^{1/2}/16)(4\pi^{-3/2} - \pi^{1/2}/2)}$$

$$q_2 = \frac{(4\pi^{-3/2} - \pi^{1/2}/2)q_1}{(\pi/4 - 1)} \tag{34}$$

TABLE 2: Comparision of Various Results for Chronoamperometric Current $i(t)/4nFDc_0b$ for Disc Electrodes

$(b^2/Dt)^{1/2}$	Cottrell behavior	Padé approximation		Fleischmann et al.[22]	digital simulation of Shoup et al.[23]	Aoki et al.[24] approximation at	
		eq 25	eq 35			short t	long t
0.01	0.00443	1.004	1.004	0.9269	1.004		1.004
0.02	0.00886	1.007	1.007	0.9285	1.007		1.007
0.03	0.01329	1.011	1.011	0.9302	1.011		1.011
0.04	0.01772	1.014	1.014	0.9319	1.014		1.014
0.05	0.01963	1.018	1.018	0.9335	1.018		1.018
0.06	0.02659	1.025	1.022	0.9352	1.022		1.022
0.10	0.04431	1.036	1.036	0.9418	1.036	↑	1.036
0.30	0.1329	1.110	1.108	1.012	1.109	diverges	1.108
0.50	0.2216	1.186	1.182	1.072	1.183	positive	1.180
0.70	0.3102	1.264	1.256	1.134	1.259		1.254
0.90	0.3988	1.343	1.332	1.198	1.335	1.471	1.328
1.00	0.4431	1.383	1.370	1.231	1.374	1.416	1.366
2.00	0.8862	1.792	1.770	1.586	1.770	1.683	1.762
3.00	1.329	2.213	2.188	1.974	2.181	2.117	2.169
4.00	1.772	2.641	2.615	2.381	2.603	2.558	2.473
5.00	2.216	3.073	3.048	2.798	3.031	3.001	2.413
6.00	2.659	3.507	3.483	3.222	3.465	3.444	1.534
7.00	3.102	3.944	3.921	3.650	3.901	3.887	−0.859
8.00	3.545	4.381	4.360	4.081	4.340	4.330	
9.00	3.987	4.820	4.799	4.514	4.780	4.773	diverges
10.00	4.431	5.259	5.240	4.950	5.221	5.216	negative
11.00	4.874	5.699	5.681	5.386	5.665	5.650	↓
12.00	5.317	6.139	6.122	5.823	6.105	6.103	
13.00	5.760	6.580	6.564	6.261	6.547	6.546	
14.00	6.204	7.021	7.006	6.700	6.990	6.989	
15.00	6.647	7.462	7.447	7.139	7.433	7.432	
16.00	7.090	7.903	7.890	7.579	7.846	7.875	
17.00	7.533	8.345	8.332	8.019	8.319	8.318	
18.00	7.976	8.786	8.774	8.460	8.762	8.761	
19.00	8.419	9.228	9.217	8.900	9.205	9.204	
20.00	8.862	9.670	9.659	9.341	9.648	9.648	
21.00	9.305	10.112	10.102	9.782	10.091	10.091	
25.00	11.078	11.881	11.872	11.548	11.863	11.863	
35.00	15.509	16.306	16.301	15.969	16.294	16.294	
50.00	22.156	22.948	22.945	22.608	22.941	22.941	
70.00	31.018	31.806	31.806	31.465	31.803	31.803	
100.00	44.311	45.095	45.098	44.754	45.095	45.095	

[a] Diverges.

If the numberical values of p_0, p_1, p_2, p_3, q_1 and q_2 are employed, we obtain

$$\frac{i(t)}{4nFDc_0b} = \frac{1 + 2.0297y + 1.96739y^2 + 0.9086584y^3}{1 + 1.3113y + 1.02534y^2} \quad (35)$$

where $y = \tau_D^{-1/2}$ and $\tau_D = (4Dt)/b^2$.

Table 2 indicates the dimensionless chronoamperometric current for disc electrodes evaluated using (25) and (35). A satisfactory agreement with other estimates can be noticed. The results of Fleischmann et al.[22] were derived by replacing the boundary condition at the electrode surface with one of uniform flux, while those of Shoup et al.[23] represent a fit to numberically calculated results, and those of Aoki et al.[24] are calculated for short and long time by Wiener−Hopf factorization procedure. Shoup and Szabo's expression is within 0.6% of the digital simulation results. Equation 25 reported earlier[12] leads to estimates within about 1.5% of Shoup and Szabos[23] results, whereas computed values using eq 35 are accurate to within 0.56% of the same.

In summary, a simple method of estimating non-steady-state chronoamperometric current for general ultramicroelectrode geometries has been suggested with the help of the Padé approximant. Explicit results for ring geometries are reported. The extension of the procedure to other geometries such as hemisphere, band electrodes, etc. apart from the study of scanning electrochemical microscope (SECM) response for different tip shapes[21] seems possible.

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(18) To combine eqs 17 and 18 we can also consider the function of the form. $i(t)/4nFDc_0b = a_1 + b_1y + c_1 \exp(-d_1 y)$ using (17) and (18) we get $a_1 = \pi(1 + a/b)/4$, $b_1 = \pi^{1/2} (1 + a/b)/2$, $c_1 = l_0/4b - \pi(1 +$

$a/b)/4$, and

$$d_1 = \frac{(l_0/b)^2/4(1 - a/b)\pi^{3/2} - \pi^{1/2}(1 + a/b)/2}{\pi(1 + a/b)/4 - I_0/4b}$$

where $y = \tau_R^{-1/2}$ and $\tau_R = (4Dt)/(b - a)^2$.

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