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THE TRANSIENT RESPONSE OF A DISK ELECTRODE WITH CONTROLLED POTENTIAL

Kemal Nişancioğlu and John Newman

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The Transient Response of a Disk Electrode with Controlled Potential

Kemal Nişancioğlu and John Newman

Inorganic Materials Research Division,
Lawrence Berkeley Laboratory, and
Department of Chemical Engineering;
University of California, Berkeley

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Abstract

A mathematical treatment is given for the transient behavior of a disk electrode when the potential is varied. The characteristic time constant for decay of the double-layer capacity is assessed.

Key Words: current distribution, time constant, double-layer capacity

Introduction

The authors have recently treated the transient response of a disk electrode to a step change in the applied current.[1] The present paper will report a mathematical analysis developed for the same model but with the electrode potential put under control instead of the current. The results could be relevant to some electroanalytical applications of the disk electrode; for instance, interrupter methods under potentiostatic control are already in common use.[2]

The problem was formulated with certain assumptions in the earlier paper[1] and will not be repeated here. The only difference in the present formulation lies in the fact that the electrode potential is set at zero time as a step to a given value V and maintained at that value thereafter. Our purpose here is therefore to simulate the transient decay of the cell current from an initial value I_o corresponding to the primary distribution[3,4] to a final steady state value I_∞.

Analysis

The potential in the solution can be expressed in terms of a steady state and a transient contribution

$$\Phi = \Phi^{ss} - \Phi^{t} \tag{1}$$

Detailed analyses for the steady state problem have been given elsewhere.[1,5] Earlier treatment of the ideally polarizable electrode,[1] however, does not apply for the present situation; Φ^{ss} vanishes in the absence of an electrode reaction since no net current is associated with the working electrode at steady state when the potential is fixed.

In terms of rotational elliptic coordinates[3] η and ξ, the transient part of the potential can be expressed as

$$\frac{\Phi^t}{V} = \sum_{i=0}^{\infty} \mathcal{C}_i e^{-\theta(\lambda_i+J)} T_i(\eta,\xi) \tag{2}$$

where T_i is a dimensionless potential independent of time, λ_i is an eigenvalue characteristic of the potential T_i, and θ and J are the dimensionless time and exchange current density,[1] respectively. Since Φ^t satisfies Laplace's equation, the functions T_i also satisfy

$$\nabla^2 T_i = 0$$

The boundary conditions associated with T_i are

$$\left.\begin{array}{ll} \dfrac{\partial T_i}{\partial \eta} = 0 \quad \text{at} \quad \eta = 0 & \\ \qquad\qquad \text{(on the insulating portion of the disk)} & \\ T_i = 0 \quad \text{as} \quad \xi \to \infty \quad \text{(far from the disk)} & \\ T_i \ \text{well behaved at} \ \eta = 1 & \\ \qquad\qquad \text{(on the axis of the disk)} & \end{array}\right\} \tag{4}$$

and

$$\frac{\partial T_i}{\partial \xi} + \lambda_i \eta \, T_i = 0 \quad \text{at} \quad \xi = 0 \tag{5}$$
$$\text{(on the disk electrode)}$$

which is obtained by a direct substitution of Eq. (2) into the boundary condition on the disk electrode.[1]

Equations (3) and (5) constitute a Sturm-Liouville system, which can be solved in a straightforward fashion.[1] The solution to Eq. (3) satisfying the conditions (4) is

$$T_i = \sum_{n=0}^{\infty} \mathcal{B}_{i,n} P_{2n}(\eta) M_{2n}(\xi) \tag{6}$$

where $P_{2n}(\eta)$ is the Legendre polynomial of order 2n, and $M_{2n}(\xi)$ is a Legendre function with known properties.[5] Substitution into Eq. (5) for each i and inversion of the resulting set of linear equations with the normalization condition $\mathcal{B}_{i,o} = 1$ yield the numerical values of the eigenvalues λ_i and the coefficients $\mathcal{B}_{i,n}$ (see Table I). The first four eigenfunctions are plotted with respect to the radial position on the surface of the disk in Fig. 1.

The functional behavior of $T_{i,o}$ has much the same significance as the corresponding eigenfunctions $U_{i,o}$ of the galvanostatic problem[1] in depicting the non-uniform state of charge and the pattern of local current flow on the surface of the disk during the transient process. One may note, in fact, that $T_{i,o}$ in Fig. 1 are quite similar to the corresponding curves for $U_{i,o}$ given in reference 1 for $i > 0$. The eigenvalues λ_i also become more similar in numerical value to Λ_i of the galvanostatic series with increasing i.

An important departure from the galvanostatic case is clearly that Φ^t does include a net current in the present situation. This additional contribution is contained, for example, in the first eigenfunction T_o, which unlike U_o is non-zero. The fact that $T_{o,o}$ exhibits no extremum points nor any zeroes suggests that it persists the longest during the

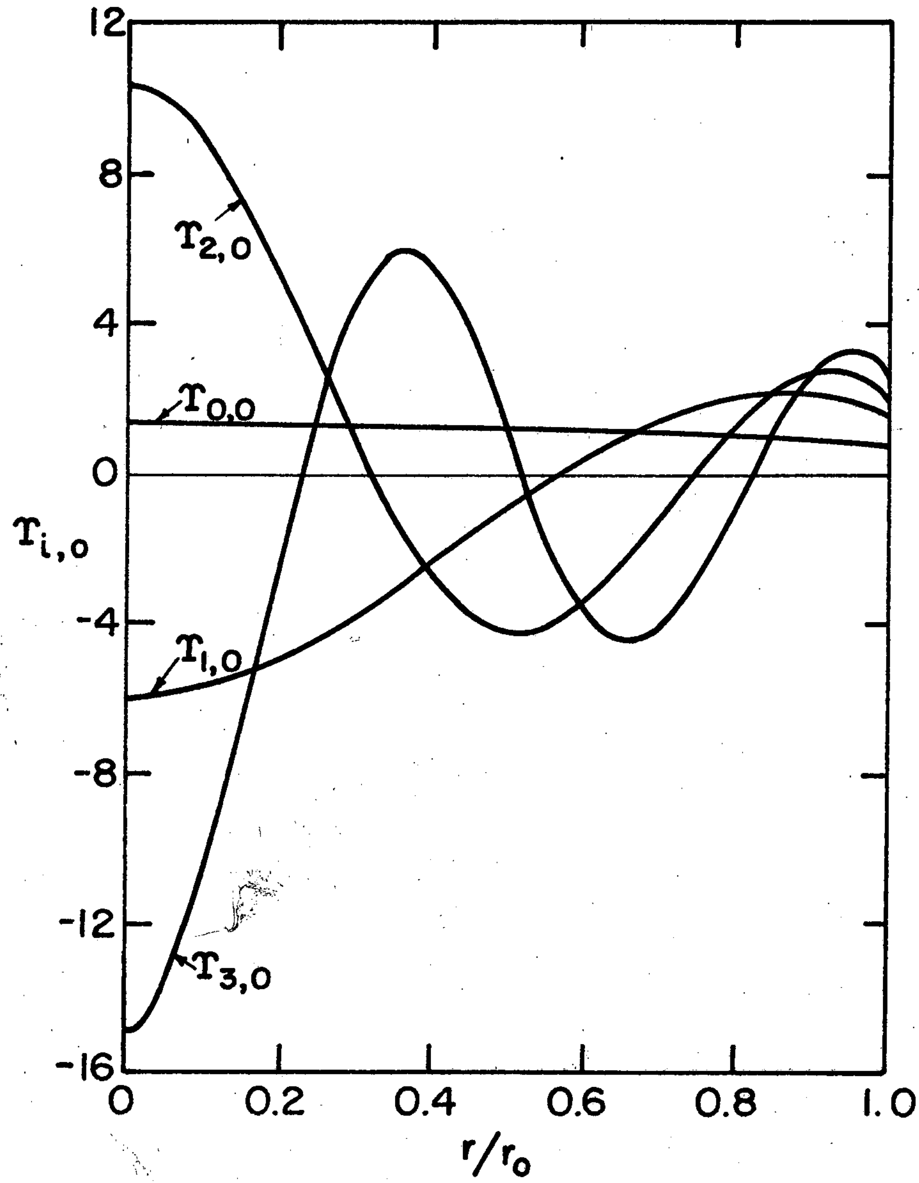

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Fig. 1. Behavior of the first four eigenfunctions on the surface of the disk electrode.

Table I. The first six eigenvalues and the related coefficients $\beta_{n,i}$ of the eigenfunctions.

	λ_0	λ_1	λ_2	λ_3	λ_4	λ_5
	1.15777	4.31680	7.46018	10.6023	13.7441	16.8858
n	i=0	i=1	i=2	i=3	i=4	i=5
0	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
1	0.39451	-3.30704	-3.20144	-3.08673	-3.00260	-2.94030
2	-0.01974	-3.09447	2.69232	3.87544	4.20749	4.29990
3	0.01259	-0.52802	6.45944	0.65745	-2.15584	-3.53764
4	-0.00657	-0.10223	2.64610	-8.32547	-5.09803	-1.69133
5	0.00393	0.02410	0.63787	-6.16121	7.06426	8.21141
6	-0.00256	-0.01843	0.03554	-2.27051	9.75697	-2.49615
7	0.00178	0.01289	0.03502	-0.43176	5.33233	-11.5222
8	-0.00129	-0.00946	-0.02056	-0.10618	1.62964	-9.36731
9	0.00097	0.00718	0.01605	0.01863	0.40730	-4.07287
10	-0.00075	-0.00559	-0.01255	-0.02158	0.02998	-1.27763

decay process and is therefore associated with the largest time constant.

The eigenfunctions $T_{i,o}$ satisfy the orthogonality relationship

$$\int_0^1 \eta T_{i,o} T_{j,o}\, d\eta = \begin{cases} 0 & \text{if } i \neq j \\ -\dfrac{1}{\lambda_i} \displaystyle\sum_{n=0}^{\infty} \dfrac{M'_{2n}(0)}{4n+1} \mathcal{B}^2_{n,i} & \text{if } i = j \end{cases} \tag{7}$$

From the initial condition

$$\Phi = V \quad \text{at} \quad \theta = 0+, \quad \xi = 0 \tag{8}$$

the coefficients $\mathcal{C}_i$ can now be calculated from the equation

$$\mathcal{C}_i = \frac{2\lambda_i}{\pi(\lambda_i + J) \displaystyle\sum_{n=0}^{\infty} \frac{M'_{2n}(0)}{4n+1} \mathcal{B}^2_{n,i}} \tag{9}$$

The current is given by

$$I = -2\pi r_o \kappa \int_0^1 \left.\frac{\partial \Phi}{\partial \xi}\right|_{\xi=0} d\eta$$

$$= I_o \left[\frac{I_\infty}{I_o} - \sum_{i=0}^{\infty} \mathcal{C}_i \, e^{-\theta(\lambda_i + J)} \right] \tag{10}$$

where r_o is the radius of the disk electrode and κ is the solution conductivity. The ratio I_∞ / I_o is a known quantity once the value of J is specified and can be obtained directly from the steady-state analysis. Some calculated values are given in reference 1 (reciprocal of V^{ss}/Φ_o^p).

Figure 2 shows current versus time traces for various J values. Each curve is characterized by a time constant for decay given by

$$\tau = \frac{1}{1.16+J} \frac{r_o C}{\kappa} \tag{11}$$

where C is the double-layer capacity.

The analysis can be generalized by superposition to incorporate an arbitrary time dependence of the applied potential $V(\theta)$. The current is then given by

$$\frac{I}{4r_o\kappa} = V(\theta) + \sum_{i=0}^{\infty} \mathcal{B}_i(\lambda_i+J)e^{-\theta(\lambda_i+J)} \int_0^{\theta} e^{\theta(\lambda_i+J)} V(\theta)d\theta \tag{12}$$

The present results should apply for large and moderately small times without much difficulty in the numerical calculations. For very short times, however, numerical difficulties are inevitable because the current distribution is equal to the primary distribution everywhere on the disk except in a small region near the edge. A large number of terms are thus required in the summation in both Eqs. (2) and (6). The same problem is encountered for large J values.[5] A separate treatment of the edge region for short times or large J values overcomes these difficulties. The authors have formulated this problem, and the results should be published shortly.

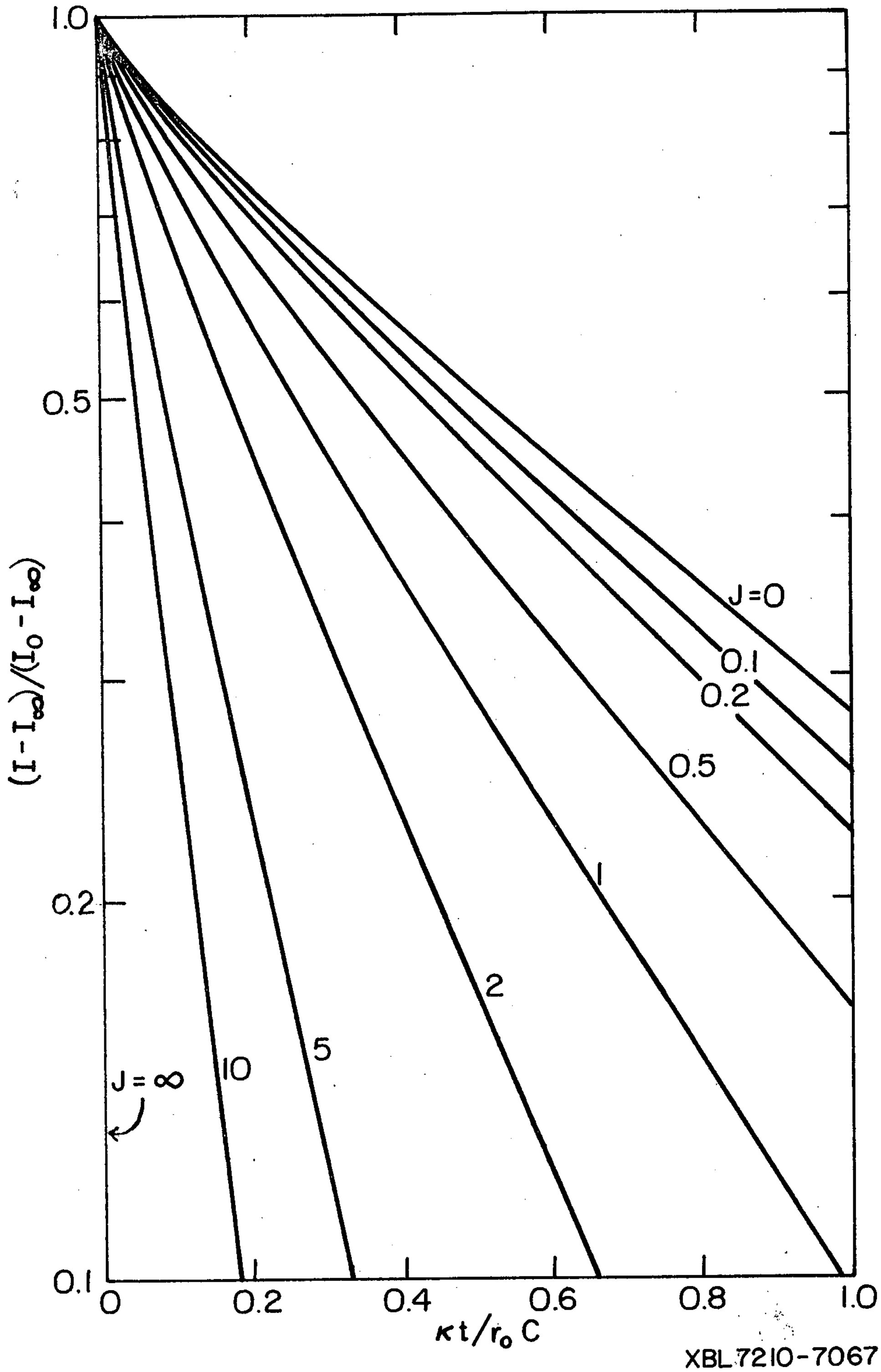

Fig. 2. Current traces at various J values for decay (or charging) of the double-layer capacity. The slope of each curve at large times is related to $\lambda_1 + J$.

Conclusions

The transient response of a disk electrode to step changes in the applied potential has been formulated to yield a well-defined Sturm-Liouville system, which can readily be solved to give solutions in terms of a series of characteristic potential functions. Each function is related to a certain mode of decay of the double-layer capacity and is associated with a characteristic time constant, the first being the dominant one in determining the system behavior at large times. These time constants can accurately be calculated from the eigenvalues of the Sturm-Liouville system. The results can be generalized for arbitrary changes in the applied potential with time by a straightforward application of the superposition integral.

Acknowledgment

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Nomenclature

$\mathcal{B}_{n,i}$	coefficients in series for T_i
C	double-layer capacity (f/cm^2)
$\mathcal{C}_i$	coefficients in series for Φ^t
I	total current (amp)
I_o	total current at $t = 0+(= 4\kappa r_o V)$ (amp)
I_∞	total current at $t = \infty$ (amp)
J	dimensionless exchange current density $= i_o r_o F(\alpha_a+\alpha_c)/RT\kappa$ (see Ref. 1)
M_{2n}	Legendre function discussed in reference (5)
P_{2n}	Legendre polynomial of order 2n
r	radial position from axis of disk (cm)
r_o	radius of disk electrode (cm)
t	time (sec)
V	electrode potential (volt)
η	rotational elliptic coordinate
κ	conductivity of the solution (ohm^{-1}-cm^{-1})
λ_i	eigenvalue
Φ	potential in the solution (volt)
Φ^{ss}	steady state part of Φ (volt)
Φ^t	transient part of Φ (volt)
ξ	rotational elliptic coordinate
τ	characteristic time constant for decay (sec)
θ	$r_o C/\kappa t$, dimensionless time
T_i	eigenfunctions in series for Φ^t
$T_{i,o}$	value of T_i at the electrode surface

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TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720