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ELECTRODE

P.C. Andricacos and P.N. Ross, Jr.

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DIFFUSION CONTROLLED MULTI-SWEEP CYCLIC VOLTAMMETRY

II. REVERSIBLE DEPOSITION ON A STATIONARY PLANAR ELECTRODE

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ABSTRACT

Multi-sweep cyclic voltammetry applied to electrodeposition at a stationary planar electrode under conditions of semi-infinite linear diffusion is analyzed in terms of current and charge density functions. A hypothetical periodic state obtained at an infinite reversal overpotential serves as a lower bound for the values of the current function, which has as an upper bound the current measured on the first sweep. Another hypothetical periodic state reached by continuous cycling depends on the chosen finite value of the reversal overpotential. A quasi-periodic state is defined when current functions do not change significantly with further cycling. Whereas fewer cycles are necessary for quasi-periodic behavior in the current with increasing reversal overpotential, the opposite is true for the cathodic charge. It is found that the cathodic current always exhibits a maximum; multiple sweeping significantly reduces its height and shifts its position towards more cathodic overpotentials, but not by much. As in linear sweep voltammetry, the height of the cathodic maximum obtained by multiple sweeping depends linearly on the square root of the sweep rate, whereas the charge associated with each sweep depends linearly on its inverse. Each complete cycle results in a net accumulation of deposit, with the amount on each cycle decreasing with the total number of previous cycles. Whereas the first cathodic sweep starts from

zero current, the current at the start of the second cathodic sweep is anodic; the value of this anodic current depends both on sweep rate and the reversal overpotential. Relative to linear sweep voltammetry, multi-sweep cyclic voltammetry generates characteristic currents that are unique to each sweep, thereby multiplying the criteria for reversibility manyfold. However, cyclic voltammetry also creates a substantial net deposit on each sweep, and any resulting surface area change with repeated cycling would make the multi-sweep diagnostics meaningless.

Key Words: Electrode, deposition, mass transport, voltammetry.

1. Introduction

Whereas the application of single sweep potential cycles to stationary electrodes has become a technique with long history in electrochemistry, multi-sweep methods have almost never been investigated. An exception is the paper by Matsuda⁽¹⁾ in which a reversible reaction with soluble product is examined under conditions of multi-sweep cyclic voltammetry (CV) occurring on a hanging drop electrode. In this investigation, we examine cyclic voltammograms obtained when multi-sweep CV is applied to a stationary planar electrode under conditions of semi-infinite linear diffusion. The reaction mechanism is that of a reversible deposition with the deposit at unit activity. Linear sweep voltammetry (LSV) results for this reaction have been reported previously by Berzins and Delahay.⁽²⁾ The first anodic sweep has been analyzed by White and Lawson⁽³⁾ who also included the case of time-dependent deposit activity. A comparison is made where appropriate with the corresponding theory⁽⁴⁾ for a rotating disk electrode (RDE). A complete description of the problem would require computation of concentration, current and charge density functions. Since the computation of concentration functions is a major task and it would add little information to that available from RDE theory,⁽⁴⁾ we have restricted ourselves to an analysis of current and charge density functions only.

By appropriately defining these functions, it has been possible to obtain expressions which depend only on the reversal overpotential. In this respect, they are different from the RDE functions, even if the latter were to be expressed in terms of dimensional quantities. To

emphasize this point, different notation has been chosen for their representation. By analogy to RDE theory, a reversal overpotential has been sought which would guarantee periodic behavior immediately after the LSV sweep. It was found that this behavior is observed only with infinite overpotential. Both the mathematical and physical interpretation of the periodic current function at infinite reversal overpotential is difficult. It is thus being used only as a computational result, and the discussion will emphasize the quasi-periodic state. This is achieved when, for a given reversal overpotential, a sufficient number of cycles has been applied so that current density does not change significantly upon further cycling.

2. Statement of the Problem and Definitions

The absence of a time-independent characteristic length associated with a stationary electrode does not allow the definition of dimensionless distance, time, and sweep rate. If 2θ is the duration of a complete cycle, the surface concentration during the cathodic sweep changes exponentially through the Nernst equation from c^b to $c^b \exp(-a\theta)$, where c^b is the bulk concentration; during an anodic sweep the variation is from $c^b \exp(-a\theta)$ back to c^b . For

$$a = (nF/RT)v, \quad [1]$$

the parameter $a\theta$ is a dimensionless reversal overpotential; similarly, at , where t is dimensional time, is a dimensionless overpotential. In eq. [1], v is the sweep rate, and n , F , R and T have their usual meaning. For reasons of consistency with previously published work,⁽²⁾ we retain the notation $(at, a\theta)$ as opposed to (H, H_c) introduced in the RDE theory.⁽⁴⁾

If ℓ is the number of already applied cycles, we can define dimensional time into a cathodic sweep, t_c , or into an anodic sweep, t_a , by the following equations

$$t = 2\ell\theta + t_c ; 0 \leq t \leq \theta ; t \text{ during a cathodic sweep} \quad [2a]$$

$$t = (2\ell+1)\theta + t_a ; 0 \leq t \leq \theta ; t \text{ during an anodic sweep} \quad [2b]$$

Since the surface concentration, $c(0,t)$, is a known function of time, current densities can be computed by the application of Duhamel's theorem (4,5):

$$i(t) = - nF(D/\pi)^{1/2} \int_0^t \frac{\partial c}{\partial t}(0,\lambda) \cdot (t-\lambda)^{-1/2} d\lambda \quad [3]$$

For instance, combination of eqs. [2a] and [3] yields the current density during the $(\ell+1)^{th}$ cathodic cycle, i_c^ℓ , as a function of ℓ , v , and θ . As has been demonstrated by Berzins and Delahay⁽²⁾ in the LSV case, the combination $i_c^\ell v^{-1/2}$ depends only on at_c . Since this property is retained in multi-sweep CV, the relevant current density functions are defined as follows:

$$I_c^\ell(at_c; a\theta) = i_c^\ell / (nF D^{1/2} a^{1/2} c^b) \quad [4]$$

$$I_a^\ell(at_a; a\theta) = i_a^\ell / (nF D^{1/2} a^{1/2} c^b) \quad [5]$$

where I_c^ℓ refers to the $(\ell+1)^{th}$ cathodic sweep and I_a^ℓ to the $(\ell+1)^{th}$ anodic sweep.

Note that I 's are dimensionless and that the factor $nFD^{1/2} a^{1/2} c^b$ is not related to a limiting current density, as is the case for J 's in RDE theory; in addition, a transformation such as $J\sigma^{-1/2}$ for the RDE still depends on both σ and $\sigma\theta'$ rather than $\sigma\theta'$ ($=a\theta$) alone.

The charge density during the $(\ell+1)^{th}$ cathodic or anodic sweep, q_c^ℓ and q_a^ℓ , respectively, can be obtained by integrating i_c^ℓ and i_a^ℓ over the time interval, 0 to θ . As for $i_v^{-1/2}$, the quantity $q_v^{1/2}$ depends only on $a\theta$. The charge density functions, Q_c^ℓ and Q_a^ℓ , can then be defined as follows:

$$Q_c^\ell(a\theta) = q_c^\ell / (nF D^{1/2} a^{-1/2} c^b) = \int_0^{a\theta} I_c^\ell(at_c; a\theta) d(at_c) \quad [6]$$

$$Q_a^\ell(a\theta) = q_a^\ell / (nF D^{1/2} a^{-1/2} c^b) = \int_0^{a\theta} I_a^\ell(at_a; a\theta) d(at_a) \quad [7]$$

The net charge density function, $Q_n^\ell(a\theta)$, associated with the complete $(\ell+1)^{th}$ cycle is:

$$Q_n^\ell(a\theta) = Q_c^\ell(a\theta) + Q_a^\ell(a\theta) \quad [8]$$

Expressions for I_c^ℓ , I_a^ℓ and Q_c^ℓ , Q_a^ℓ are derived in the Appendix.

3. Results and Discussion

In the limit $a\theta \rightarrow \infty$, both I_c^ℓ and I_a^ℓ became ℓ -independent, indicating the existence of a hypothetical periodic state denoted by $I_c(at_c; \infty)$ and $I_a(at_a; \infty)$. Since an infinite amount of charge is consumed during the LSV sweep in the overpotential range 0 to ∞ , this periodic state is unrealizable. From the mathematical viewpoint, the boundary condition an infinite distance away from the electrode surface, dictates that the concentration should be retained at the bulk value,

c^b , but over finite times. Indeed, concentration functions for the LSV sweep derived in the Appendix contain forms which cannot be determined when both distance away from the electrode surface and time are infinite.

Despite difficulties in the physical and mathematical interpretation of I_c and I_a , numerical evaluation of I_c^ℓ and I_a^ℓ over a large range of $a\theta$ and ℓ values has indicated that

$$I_c^\ell > I_c \text{ and } I_a^\ell > I_a. \quad [9]$$

Since,

$$I_c^0 > I_c^\ell \text{ and } I_a^0 > I_a^\ell \quad [10]$$

we can write,

$$I_c < I_c^\ell < I_c^0 \text{ and } I_a < I_a^\ell < I_a^0 \quad [11]$$

indicating that the LSV current function and the periodic cathodic at infinite reversal overpotential are upper and lower bounds, respectively, for I_c^ℓ irrespective of the value of ℓ or $a\theta$. Similarly, I_a^ℓ is bounded from the above by the current function during the first anodic sweep and from below by the periodic anodic at infinite reversal overpotential.

No closed form expressions have been derived for the periodic states obtained by letting $\ell \rightarrow \infty$. However, they can be shown to exist and are generally different from each other depending on the chosen finite value of $a\theta$. They also obey eq. [11]. Since these periodic states involve infinite times, their physical and mathematical interpretation is under doubt.

Numerical investigations of current density functions has shown that for a given finite value of $a\theta$, a state is reached beyond which increasing the number of cycles does not effect significant changes in their value. This type of behavior can be termed quasi-periodic and is attained within fewer cycles as the reversal overpotential is increased. This is expected since in the limit of infinite $a\theta$ the first cathodic sweep is sufficient for periodic behavior. The following discussion will focus on λ -dependent functions and their relation to the hypothetical periodic state at infinite reversal overpotential.

Figures 1 and 2 are drawn for two different values of the dimensionless reversal overpotential, 6 and 24, respectively. As for the RDE, no extremum is expected to appear in the anodic sweeps, since no limitations have been imposed on the amount of material that can be stripped from the electrode surface. However, all cathodic curves exhibit a maximum. Thus, there are three criteria of diagnostic importance. These are: i) the foot of the cathodic wave, $I_c^\lambda(0; a\theta) = I_a^{\lambda-1}(a\theta; a\theta)$; ii) the position of the cathodic maximum on the potential axis, $(at_c)_{\max}^\lambda$; and iii) the height of the cathodic peak, $I_{c,\max}^\lambda$. The values of these quantities for the two bounds, i.e. the first cathodic wave⁽²⁾ and the periodic wave at infinite overpotential are as follows:

$$I_c^0(0) = 0. ; (at_c)_{\max}^0 = 0.854 ; I_{c,\max}^0 = 0.610 \quad [12]$$

$$I_c(0, \infty) = -1. ; (at_c)_{\max} = 1.3 ; I_{c,\max} = 0.194 \quad [13]$$

As mentioned previously, these numbers define the total range of variation of the current functions. For instance, the cathodic maximum can never exceed 0.61 or be lower than 0.19, irrespective of ℓ and $a\theta$. Furthermore, since $I_c(0, \infty) = -1$, a meaning can be assigned to the quantity $nFD^{1/2} a^{1/2} c^b$ as that current density measured in the anodic direction at the foot of the periodic cathodic wave with infinite reversal overpotential.

A considerable reduction of the height of the cathodic peak during the second wave as compared to the first is one of the most important predictions of the present model. Its position is also shifted in the cathodic direction but not by much, as can be inferred by a comparison of the $(at_c)_{\max}$ values in eqs. [12] and [13]. The subsequent development of the current function profiles is mostly defined by the value of the reversal overpotential. For large such values, the height and position of the second cathodic wave maximum do not change significantly with further cycling. On the other hand, for values of the reversal overpotential which are near the maximum, current functions for different values of ℓ show marked variations. This is a consequence of the slower approach to quasi-periodic behavior for smaller values of $a\theta$.

A summary of numerical results for the three diagnostic criteria is shown in Table 1, over a range of $a\theta$ values of practical interest. For a single electron transfer reaction ($n=1$), the reported range of $a\theta$ values corresponds to a cathodic reversal overpotential of approximately 0.35-1.4 volts. The way of using this table is as follows: let $i_c^\ell(0; a\theta)$ be the current density measured at the beginning of the $(\ell+1)^{th}$ cathodic wave (or the end of the ℓ^{th} anodic) at a fixed reversal

overpotential of $(RT/nF)a\theta$, and $i_{c,max}^{\ell} [(at_{c,max})^{\ell}, a\theta]$ be the peak current density; then,

$$i_c^{\ell}(0; a\theta) = A c^b v^{1/2} I_0^{\ell}(0; a\theta) \quad [14]$$

$$i_{c,max}^{\ell} [(at_{c,max})^{\ell}; a\theta] = A c^b v^{1/2} I_{c,max}^{\ell} [(at_{c,max})^{\ell}; a\theta] \quad [15]$$

$$A = (nF)^{3/2} (RT)^{-1/2} D^{1/2} \quad [16]$$

where $I_c^{\ell}(0; a\theta)$ and $I_{c,max}^{\ell}$ can be read off Table 1 (or computed from eq. [A16] of the Appendix). For example, if $a\theta=24$, a plot of the peak current density measured during the fifth sweep ($\ell=4$) vs. $v^{1/2}$ should be linear with a slope of $0.238 A c^b$. Similarly, a plot of the absolute value of the current density at the foot of the same wave should also be linear with a slope of $0.961 A c^b$. It should be remembered that these slopes also depend on the diffusion coefficient and the bulk concentration of the reacting ion; in addition, increasing ℓ should not greatly affect these values (for instance, the maximum measureable slope for the current density at the foot of the wave vs. $v^{1/2}$ is $A c^b$ to be compared against $0.961 A c^b$ for $\ell=4$).

We now turn our attention to the charge density functions. In the hypothetical periodic states, these functions possess interesting properties; these can be summarized as follows:

$$Q_c(\infty) = 1 ; Q_a(\infty) = -1 ; Q_n(\infty) = 0 \quad [17]$$

$$Q_n^{\infty}(a\theta) = 0 \quad [18]$$

Equation [18] indicates that for any value of $a\theta$, no net deposit is formed or stripped from the electrode in the periodic state reached by letting $\ell \rightarrow \infty$; similarly, for the periodic state of $a\theta \rightarrow \infty$ (eq. [17]). As in the case of $I_c(0; \infty)$, the limiting values of $Q_c(\infty)$ and $Q_a(\infty)$, eq. [17], assign a meaning to the quantity $(\pm) nFD^{1/2} a^{-1/2} c^b$, as the charge density obtained during a periodic cathodic (+) or anodic (-) sweep at infinite reversal overpotential.

Regarding quasi-periodic behavior of the charge functions, it should be noted that increasing number of cycles is required for increasing $a\theta$. This is contrary to the current function behavior, but should be expected since small variations in the current density acquire greater significance as $a\theta$ increases; this is a consequence of integrating currents over the entire $a\theta$ range.

Figures 3 and 4 are plots of cathodic, anodic, and net charge density functions with $a\theta$ as the variable and ℓ as the parameter. As shown in Fig. 4, Q_n^ℓ is always positive indicating that a multi-sweep CV experiment for a reversible deposition reaction always results in the formation of a net deposit on the electrode surface, except in the hypothetical periodic state reached by $\ell \rightarrow \infty$ (eq. 18) when no net material is deposited (or stripped) irrespective of the reversal overpotential. Apart from the implications of this result on transient surface morphology, it also indicates that a thin film of deposit originally existing on the surface is sufficient for the performance of the experiment. However, its presence is necessary to prevent underpotential deposition effects and for the electrode to have a well-defined equilibrium potential.

The definition of charge density functions shows that the actual charge density measured during a cathodic, anodic, or complete potential cycle should be correlated to the inverse of the square root of the sweep rate, $v^{-1/2}$, rather than $v^{1/2}$. If $q_n^{\ell}(a\theta)$ is the measured net charge density during the $(\ell+1)^{th}$ complete cycle, then

$$q_n^{\ell}(a\theta) = Bc_v^{-1/2} Q_n^{\ell}(a\theta) \quad [19]$$

$$B = (nFRTD)^{1/2} \quad [20]$$

where $Q_n^{\ell}(a\theta)$ values are read off Fig. 4. Similar expressions can be written down for q_c^{ℓ} and q_a^{ℓ} in terms of Q_c^{ℓ} , Q_a^{ℓ} , and $v^{-1/2}$. Figure 3 can be used to provide values for Q_c^{ℓ} and Q_a^{ℓ} .

4. Conclusions

Analysis of a reversible deposition reaction occurring on a stationary planar electrode under multi-sweep cyclic voltammetry conditions has demonstrated the absence of an experimentally realizable periodic state. Instead, all quantities of potential diagnostic use, such as the height of the cathodic current maximum, its position on the potential axis, and the magnitude of the anodic current at the equilibrium potential, vary continuously with the parameters of the method, such as the number of applied cycles and the reversal overpotential. These variations are most pronounced between the first and second sweeps and they diminish with continued cycling, eventually leading to quasi-periodic behavior. Relative to linear sweep voltammetry, multi-sweep cyclic voltammetry multiplies the characteristic criteria of reversibility manyfold.

Except in the hypothetical periodic states achieved by an infinite reversal overpotential or by an infinite number of applied cycles, in which no net deposit is formed during a complete potential sweep, all other states result in the formation of an appreciable net deposit on the electrode surface. The resulting changes in surface area may invalidate the detailed information that can be obtained in principle by multi-sweep measurements. Since the most important changes for diagnostic purposes occur on the first two sweeps, metal deposition studied by cyclic voltammetry should be limited to three sweeps or less to avoid the roughness complication.

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List of Symbols

a	defined by eq. [1]
$a\theta$	dimensionless reversal overpotential
at_a	dimensionless overpotential into an anodic sweep
at_c	dimensionless overpotential into a cathodic sweep
$(at_c)_{\max}$	value of at_c at the maximum of the periodic current density function at infinite reversal overpotential; eq. [13]
$(at_c)^0_{\max}$	value of at_c at the maximum of the LSV current density function; eq. [12]
A	constant defined by eq. [16]
B	constant defined by eq. [20]
c	concentration
c'	dimensionless concentration defined by eq. [A5]
c^b	bulk concentration
c'_s	dimensionless concentration obtained when an infinite potential step is applied to a planar electrode; eq. [A6]
c^0_c	concentration during LSV sweep; eq. [A18]
D	diffusion coefficient
i	current density
I_a	periodic anodic current density function at infinite reversal overpotential; eq. [A20]
I_c	periodic cathodic current density function at infinite reversal overpotential; eq. [A19]
I^0_a	current density function during the first anodic sweep; eq. [A15]
I^0_c	LSV current density function; eq. [A14]
I^ℓ_a	current density function during the $(\ell+1)$ th anodic sweep eq. [A17]

I_c^ℓ	current density function during the $(\ell+1)$ th cathodic sweep; eq. [A16]
$I_{c,max}$	maximum value of I_c
$I_{c,max}^0$	maximum value of I_c^0
ℓ	number of applied complete potential cycles
Q_a	anodic charge density function at infinite reversal overpotential; eq. [A37]
Q_c	cathodic charge density function at infinite reversal overpotential; eq. [A36]
Q_n	net charge density function at infinite reversal overpotential; eq. [A38]
Q_n^∞	net charge density function after an infinite number of cycles; eq. [A38]
Q_a^ℓ	charge density function during the $(\ell+1)$ th anodic sweep; eq. [A32]
Q_c^ℓ	charge density function during the $(\ell+1)$ th cathodic sweep; eq. [A31]
Q_n^ℓ	net charge density function during the complete $(\ell+1)$ th sweep; eq. [A33]
t	time
t_a	time into an anodic sweep; eq. [2b]
t_c	time into a cathodic sweep; eq. [2a]
v	sweep rate
θ	reversal time
λ	dummy variable of integration

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Table 1. Numerical results for the current density function at the foot of the cathodic wave (a), the position of the cathodic maximum (b), and its height (c), in terms of the number of cycles, l , and the dimensionless reversal overpotential, $a\theta$. The range of values reported in columns (b) indicates that over this range the maximum value of the cathodic current density function was the same to 4 significant figures. Negative numbers refer to anodic currents.

l	$a\theta=6$			$a\theta=8$			$a\theta=10$			$a\theta=12$			$a\theta=14$		
	a^*	b	c	a	b	c	a	b	c	a	b	c	a	b	c
1	-0.868	1.324-8	0.355	-0.890	1.338-43	0.334	-0.903	1.345-51	0.319	-0.913	1.349-55	0.309	-0.920	1.355	0.300
2	-0.886	1.343-6	0.320	-0.906	1.351-5	0.301	-0.918	1.357-8	0.289	-0.926	1.359-61	0.280	-0.933	1.359-64	0.273
3	-0.896	1.346-52	0.304	-0.915	1.354-9	0.286	-0.927	1.359-61	0.275	-0.935	1.361-3	0.267	-0.941	1.361-6	0.261
4	-0.904	1.349-53	0.294	-0.922	1.357-9	0.277	-0.933	1.361-2	0.266	-0.940	1.362-5	0.259	-0.946	1.361-7	0.253
5	-0.909	1.351-4	0.287	-0.927	1.358-60	0.271	-0.937	1.360-4	0.260	-0.944	1.361-6	0.253	-0.950	1.363-6	0.248
10	-0.923	1.352-6	0.270	-0.940	1.359-62	0.255	-0.949	1.363	0.246	-0.956	1.361-7	0.240	-0.960	1.363-7	0.235
20	-0.935	1.354-6	0.257	-0.950	1.360-1	0.244	-0.959	1.360-6	0.235	-0.964	1.363-6	0.230	-0.968	1.363-7	0.226
30	-0.940	1.351-2	0.252	-0.955	1.359-63	0.239	-0.963	1.361-6	0.231	-0.969	1.362-8	0.226	-0.972	1.363-7	0.222
50	-0.945	1.354-7	0.246	-0.960	1.359-63	0.233	-0.968	1.361-6	0.226	-0.973	1.363-6	0.221	-0.976	1.365	0.218

l	$a\theta=16$			$a\theta=18$			$a\theta=20$			$a\theta=22$			$a\theta=24$		
	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
1	-0.926	1.354-60	0.294	-0.930	1.357-61	0.288	-0.934	1.358-62	0.283	-0.938	1.359-63	0.279	-0.940	1.360-3	0.275
2	-0.938	1.360-6	0.268	-0.942	1.361-6	0.263	-0.945	1.363-5	0.259	-0.948	1.363-6	0.256	-0.951	1.362-8	0.253
3	-0.945	1.362-7	0.256	-0.949	1.362-7	0.252	-0.952	1.365	0.249	-0.954	1.363-8	0.246	-0.957	1.363-9	0.243
4	-0.950	1.363-7	0.249	-0.954	1.365-6	0.245	-0.956	1.363-7	0.242	-0.959	1.364-8	0.240	-0.961	1.364-8	0.238
5	-0.954	1.365	0.244	-0.957	1.362-7	0.241	-0.960	1.364-7	0.238	-0.962	1.363-9	0.235	-0.964	1.364-8	0.233
10	-0.964	1.363-8	0.232	-0.966	1.365-6	0.229	-0.969	1.365-8	0.227	-0.971	1.364-9	0.225	-0.972	1.364-9	0.223
20	-0.971	1.363-8	0.223	-0.974	1.364-8	0.221	-0.976	1.365-7	0.219	-0.977	1.365-8	0.217	-0.979	1.364-9	0.216
30	-0.975	1.364-8	0.219	-0.977	1.365-8	0.217	-0.979	1.365-8	0.215	-0.980	1.365-8	0.214	-0.982	1.365-8	0.213
50	-0.979	1.365-6	0.215	-0.981	1.365-7	0.213	-0.982	1.364-8	0.212	-0.984	1.365-8	0.211	-0.985	1.365-8	0.210

* $a: I_c^l(0, a\theta)$; $b: (at_c)^l_{\max}$; $c: I_{c, \max}^l$

Figure Captions

Fig. 1. Current density functions for a reversal overpotential of $6RT/nF$.

Fig. 2. As in Fig. 1, but for a reversal overpotential of $24RT/nF$; I_c ($at_c; \infty$) is very close to I_c^{100} and is not included in the figure.

Fig. 3. Cathodic and anodic charge density functions in terms of dimensionless reversal overpotential, $a\theta$, and number of cycles.

Fig. 4. Net charge density functions.

Fig. 1

XBL 825-639

Fig. 2

XBL 825-628

Fig. 3

XBL 825-635

Fig. 4

APPENDIX

Mathematical Derivation of Current and Charge Density Functions

Since no time independent characteristic length is associated with a stationary electrode, the diffusion problem is described in terms of dimensional quantities, such as distance, x , away from the electrode surface, time, t , and the concentration, $c(x,t)$, of the reacting species. Assuming semi-infinite linear diffusion and excluding natural convection, double layer capacitance, pseudocapitance, and electrolyte resistance effects, we can write

$$c(\infty, t) = c^b, \quad t \text{ positive and finite} \quad [A1]$$

where c^b is the bulk - also initial - concentration of the reacting species, and,

$$c(0, t) = \begin{cases} c^b \exp[-a(t-2n\theta)]; & 2n\theta \leq t \leq (2n+1)\theta; \text{ cathodic cycle} \\ c^b \exp[-(2n+2)a\theta] \exp(at); & (2n+1)\theta \leq t \leq (2n+2)\theta; \text{ anodic cycle} \end{cases} \quad [A2]$$

$$a = (nF/RT)v \quad [A3]$$

where v is the dimensional sweep rate and n , F , R and T have their usual meaning. Equation [A2] describes the dependence of the surface concentration on time; this is defined from the potential through the Nernst equation. It is assumed that the potential starts at the equilibrium value based on c^b , and changes linearly at a rate v for a time θ . The cycle is repeated in the opposite direction for the interval $(\theta, 2\theta)$ and so on (see Fig. 1 in Ref. 4).

Expressions for the functions of interest are reported in terms of dimensional times, t_c and t_a , into a cathodic and anodic cycle, respectively. These are defined as follows:

$$t = 2\ell\theta + t_c; \quad 0 \leq t_c \leq \theta; \quad t \text{ during a cathodic sweep} \quad [A4a]$$

$$t = (2\ell + 1)\theta + t_a; 0 \leq t_a \leq \theta; t \text{ during an anodic sweep} \quad [A4b]$$

a. Current Density Functions

For the purposes of the derivations in this work, we introduce two concentration functions, c' and c'_s , defined as follows:

$$c'(x,t) = 1 - c(x,t)/c^b \quad [A5]$$

$$c'_s(x,t) = 1 - \operatorname{erf}\left[\frac{1}{2} x (Dt)^{-1/2}\right] \quad [A6]$$

where D is the diffusion coefficient of the reacting ion and "erf" is the error function (6)

$$\operatorname{erf} x = 2\pi^{-1/2} \int_0^x \exp(-\zeta^2) d\zeta \quad [A7]$$

Both Eqs. [A5,6] are related to the applicability of Duhamel's theorem. By Eq. [A5], the initial condition on $c(x,t)$ changes from c^b to 0. Equation [A6] is the solution to the infinite potential step problem. Transforming Eq. [A2] according to Eq. [A5], Duhamel's theorem yields:

$$c'(x,t) = \int_0^t \frac{\partial c'}{\partial t}(0,\lambda) \cdot c'_s(x,t-\lambda) d\lambda \quad [A8]$$

Since

$$i(t) = -nFD c^b \frac{\partial c'}{\partial x}(0,t) \quad [A9]$$

we obtain

$$\begin{aligned} i(t) &= -nFD c^b \int_0^t \frac{\partial c'}{\partial t}(0,\lambda) \cdot \frac{\partial c'_s}{\partial x}(0,t-\lambda) d\lambda \\ &= -nF(D/\pi)^{1/2} \int_0^t \frac{\partial c}{\partial t}(0,\lambda) \cdot (t-\lambda)^{-1/2} d\lambda \end{aligned} \quad [A10]$$

Equation [A10] can be used directly for the computation of current density when combined with [A2], [A4a or 4b].

As has been demonstrated for the case of LSV (2), the cathodic current i_c depends on $v^{1/2}$ and at . However, the quantity $i_c v^{-1/2}$ depends only on at . This property is the origin of the definition of current density functions for stationary electrodes. It should be noted that the corresponding quantity, $\frac{i_c}{\tau_L} \sigma^{-1/2}$, for the RDE is still a function of the dimensionless sweep rate, σ , instead of $\sigma\tau$ or $\sigma\theta'$ alone (where τ and θ' are dimensionless t and θ , respectively). In order to emphasize that stationary electrode current density functions are defined differently than RDE functions, we represent them with the symbol I , instead of J . (4). We can then write

$$I_c^{\ell} (at_c; a\theta) = i_c^{\ell} / (nFD^{1/2} a^{1/2} c^b) \quad [A11]$$

$$I_a^{\ell} (at_a; a\theta) = i_a^{\ell} / (nFD^{1/2} a^{1/2} c^b) \quad [A12]$$

where i_c^{ℓ} is the current density measured during the $(\ell+1)^{th}$ cathodic sweep and i_a^{ℓ} is the current density measured during the $(\ell+1)^{th}$ anodic sweep. Combination of Eq. [A10] with [A4a] or [4b] yields expressions for I_c^{ℓ} and I_a^{ℓ} in terms of the error function and Dawson's integral (6,7)

$F(x)$

$$F(x) = \exp(-x^2) \int_0^x \exp(\tau^2) d\tau \quad [A13]$$

i) single-sweep CV; cathodic (also LSV): (2)

$$I_c^0(at_c) = 2\pi^{-1/2} F[(at_c)^{1/2}] \quad [A14]$$

ii) single-sweep CV; anodic* (3)

$$I_a^0(at_a; a\theta) = 2\pi^{-1/2} \left\{ F[(at_a + a\theta)^{1/2}] - \exp(-a\theta) F[(at_a)^{1/2}] \right\} - \exp(-a\theta) \exp(at_a) \operatorname{erf}[(at_a)^{1/2}] \quad [A15]$$

iii) multi-sweep CV; cathodic

$$I_c^\ell(at_c; a\theta) = 2\pi^{-1/2} F[(at_c)^{1/2}] - 2\pi^{-1/2} \sum_{n=1}^{\ell} \exp(-a\theta) F[(at_c + (2n-1)a\theta)^{1/2}] - F[(at_c + 2na\theta)^{1/2}] + \sum_{n=1}^{\ell} \exp(at_c) \exp[(2n-2)a\theta] \left\{ \operatorname{erf}[(at_c + (2n-2)a\theta)^{1/2}] - \operatorname{erf}[(at_c + (2n-1)a\theta)^{1/2}] \right\} \quad [A16]$$

iv) multi-sweep CV; anodic

$$I_a^\ell(at_a; a\theta) = -\exp(-a\theta) \exp(at_a) \operatorname{erf}[(at_a)^{1/2}] - 2\pi^{-1/2} \sum_{n=0}^{\ell} \exp(-a\theta) F[(at_a + 2na\theta)^{1/2}] - F[(at_a + (2n+1)a\theta)^{1/2}] + \sum_{n=1}^{\ell} \exp(at_a) \exp[(2n-1)a\theta] \left\{ \operatorname{erf}[(at_a + (2n-1)a\theta)^{1/2}] - \operatorname{erf}[(at_a + 2na\theta)^{1/2}] \right\} \quad [A17]$$

* This expression does not agree with the one reported in Ref. 3; in the latter, the multiplying factor for $F[(at_a)^{1/2}]$ is 1, rather than $\exp(-a\theta)$.

Whereas Eqs. [A16],[A17] possess an $\ell \rightarrow \infty$ -independent limit as $a\theta \rightarrow \infty$, no closed form expression can be obtained for $\ell \rightarrow \infty$. The condition $a\theta \rightarrow \infty$ is similar to the condition $\theta' \rightarrow \infty$ in RDE theory, except that in the latter $\theta' \gg 1$ is sufficient to simulate infinity. Furthermore, $a\theta \rightarrow \infty$ is devoid of any physical sense because an infinite amount of charge would be consumed for the reversal overpotential to assume such high values. Mathematically, examining such a limiting behavior is not proper because the boundary condition, [A1], is not satisfied. To demonstrate this, we examine the concentration profiles during the first cathodic sweep (LSV). Using Eq. 8 we obtain*

$$c_c^0(x,t)/c^b = \text{erf}\left[\frac{x}{2(Dt)^{1/2}}\right] + 1/2 \exp\left(-\frac{x^2}{4Dt}\right) \left\{ w[(at)^{1/2} + \frac{ix}{2(Dt)^{1/2}}] + w[-(at)^{1/2} + \frac{ix}{2(Dt)^{1/2}}] \right\} \quad [A18]^\dagger$$

from which it becomes obvious that expressions such as $x/(Dt)^{1/2}$ or x^2/Dt are indeterminate when both x and t tend to ∞ . Similar arguments hold for $\ell \rightarrow \infty$

Letting $a\theta \rightarrow \infty$ in Eqs. 16 and 17 we obtain:

$$I_c(at_c; \infty) = 2\pi^{-1/2} F[(at_c)^{1/2}] - \exp(at_c) \left\{ 1 - \text{erf}[(at_c)^{1/2}] \right\} \quad [A19]$$

$$I_a(at_a; \infty) = - \exp(-a\theta) \exp(at_a) \text{erf}[(at_a)^{1/2}] \quad [A20]$$

* For the definition of the function $w(z)$, see Ref. 6.

† $i = (-1)^{1/2}$ in this equation.

Numerical evaluation of Eqs. 16 and 17 has indicated that

$$I_c^\ell > I_c^0 ; I_a^\ell > I_a^0 \quad [A21]$$

in other words, I_c and I_a are lower bounds for I_c^ℓ and I_a^ℓ , respectively.

In addition,

$$I_c^\ell < I_c^0 \text{ and } I_a^\ell < I_a^0 \quad [A22]$$

Since doubts exist about the physical interpretation of the limits of the current functions at infinite times (obtained by letting either $a\theta$ or ℓ tend to ∞), it is more practical to investigate quasi-periodic behavior achieved when increasing ℓ does not change the values of the current functions appreciably. Numerical investigations have shown that attainment of quasi-periodic behavior requires larger number of cycles, ℓ , as the reversal overpotential, $a\theta$, decreases.

One final point needs clarification: namely, that the hypothetical periodic state obtained by allowing $a\theta \rightarrow \infty$ is not identical to the one obtained for $\ell \rightarrow \infty$ but with finite $a\theta$. In the case of the cathodic current function, this can be demonstrated by examining the difference, ΔI_c^ℓ , between I_c^ℓ and I_c :

$$\begin{aligned} \Delta I_c^\ell(at_c; a\theta) &= I_c^\ell(at_c; a\theta) - I_c(at_c; \infty) \\ &= \exp(at_c) \left\{ 1 - \operatorname{erf}[(at_c + a\theta)^{1/2}] \right\} \end{aligned}$$

$$\begin{aligned}
 & + \sum_{n=2}^{\ell} \exp(at_c) \exp[(2n-2)a\theta] \left\{ \operatorname{erf}[(at_c + (2n-2)a\theta)^{1/2}] \right. \\
 & \quad \left. - \operatorname{erf}[(at_c + (2n-1)a\theta)^{1/2}] \right\} \\
 & - 2\pi^{-1/2} \sum_{n=1}^{\ell} \exp(-a\theta) F[(at_c + (2n-1)a\theta)^{1/2}] \\
 & \quad - F[(at_c + 2na\theta)^{1/2}]^*
 \end{aligned} \tag{A23}$$

whereas $\Delta I_c^{\ell}(at_c; \infty) \rightarrow 0$ as expected, $\Delta I_c^{\infty}(at_c; a\theta) \neq 0$ in general and depends on the particular $a\theta$ value.

We end the section on current density functions by a discussion of some computational details. Expressions involving a dependence on ℓ inside a series have been simplified by employing identities such as

$$\sum_{n=0}^{\ell} f(2\ell-2n-1) g(2\ell-2n) = \sum_{n=1}^{\ell} f(2n-1) g(2n) \tag{A24}$$

where f and g are generally different functions of the argument. In several occasions, numerical evaluation of expressions such as

$$\exp(2na\theta) \left\{ \operatorname{erf}[(2na\theta)^{1/2}] - \operatorname{erf}[(2n+1)a\theta]^{1/2} \right\} \tag{A25}$$

can be difficult, since it may involve multiplication of a very large with a very small number. This difficulty can be circumvented by using an asymptotic expansion (6,8) of the error function for large arguments:

$$\operatorname{erfx} = 1 - \pi^{-1/2} \exp(-x^2) \left\{ x^{-1} + \sum_{j=1}^{\infty} (-1)^j [1.3 \dots (2j-1)] 2^{-j} x^{-2j-1} \right\} \tag{A26}$$

* For $\ell=1$, the series beginning with $n=2$ is set equal to 0.

The implications of the divergence of the series on the accuracy of the approximation are discussed in Ref. 8. It should be noted that Eq. [A25] converges to 0 when either n or $a\theta$ tend to ∞ . This can be shown by applying de l' Hôpital's rule.

b. Charge Density Functions

The charge q_c^ℓ associated with the $(\ell+1)^{th}$ cathodic current wave (not a cumulative quantity) is:

$$q_c^\ell = \int_0^{\theta} i_c^\ell dt_c \quad [A27]$$

A similar expression can be written down for q_a^ℓ . In view of Eq. [A11] an obvious change of variable yields

$$Q_c^\ell(a\theta) = q_c^\ell / (nFD^{1/2}a^{-1/2}c^b) = \int_0^{a\theta} I_c^\ell(at_c; a\theta) d(at_c) \quad [A28]$$

and, for anodic waves,

$$Q_a^\ell(a\theta) = q_a^\ell / (nFD^{1/2}a^{-1/2}c^b) = \int_0^{a\theta} I_a^\ell(at_a; a\theta) d(at_a) \quad [A29]$$

As in the case of $i_v^{\ell-1/2}$, the quantity $q_v^{\ell-1/2}$ is independent of v and depends on $a\theta$ alone. It seems natural then to chose Q 's as the charge density functions. Since charge densities in RDE models are defined differently, the symbol Q (rather than R) has been chosen to refer to stationary electrodes. The net charge contribution to the $(\ell+1)^{th}$ cycle, can be related to the net charge density function

$$Q_n^\ell(a\theta) = Q_c^\ell(a\theta) + Q_a^\ell(a\theta) \quad [A30]$$

As noted previously, positive values for Q's indicate the net formation of a deposit. Expressions for the charge density functions are obtained from Eqs. [A28] and [A29]:

i) multi-sweep CV; cathodic

$$\begin{aligned}
 Q_c^{\ell}(a\theta) = & - 2\pi^{-1/2} F [(a\theta)^{1/2}] + 2\pi^{-1/2}(a\theta)^{1/2} [(2\ell+1)^{1/2} - (2\ell)^{1/2}] \\
 & - 2\pi^{-1/2} \sum_{n=1}^{\ell} F [((2n+1)a\theta)^{1/2}] - [1 + \exp(-a\theta)] F [(2na\theta)^{1/2}] \\
 & + \exp(-a\theta) F [((2n-1)a\theta)^{1/2}] \\
 & + \sum_{n=1}^{\ell} \exp[(2n-1)a\theta] \left\{ \operatorname{erf} [((2n-1)a\theta)^{1/2}] - \operatorname{erf} [(2na\theta)^{1/2}] \right\} \\
 & - \exp[(2n-2)a\theta] \left\{ \operatorname{erf} [((2n-2)a\theta)^{1/2}] - \operatorname{erf} [((2n-1)a\theta)^{1/2}] \right\} \quad [A31]
 \end{aligned}$$

ii) multi-sweep CV; anodic

$$\begin{aligned}
 Q_a^{\ell}(a\theta) = & - \operatorname{erf} [(a\theta)^{1/2}] + 2\pi^{-1/2}(a\theta)^{1/2} [(2\ell+2)^{1/2} - (2\ell+1)^{1/2}] \\
 & - 2\pi^{-1/2} \sum_{n=0}^{\ell} F [((2n+2)a\theta)^{1/2}] - [1 + \exp(-a\theta)] F [(2n+1)a\theta)^{1/2}] \\
 & + \exp(-a\theta) F [(2na\theta)^{1/2}] \\
 & + \sum_{n=1}^{\ell} \exp(2na\theta) \left\{ \operatorname{erf} [(2na\theta)^{1/2}] - \operatorname{erf} [((2n+1)a\theta)^{1/2}] \right\} \\
 & + \exp[(2n-1)a\theta] \left\{ \operatorname{erf} [((2n-1)a\theta)^{1/2}] - \operatorname{erf} [(2na\theta)^{1/2}] \right\} \quad [A32]
 \end{aligned}$$

iii) multi-sweep CV; net

$$\begin{aligned}
 Q_n^{\ell}(a\theta) = & 2\pi^{-1/2}(a\theta)^{1/2} [(2\ell+2)^{1/2} - (2\ell)^{1/2}] - 2\pi^{-1/2} \left\{ F [((2\ell+2)a\theta)^{1/2}] \right. \\
 & \left. - \exp(-a\theta) F [((2\ell+1)a\theta)^{1/2}] \right\}
 \end{aligned}$$

$$+ \exp(2\ell a\theta) \left\{ \operatorname{erf}[(2\ell a\theta)^{1/2}] - \operatorname{erf}[(2\ell+1)a\theta]^{1/2} \right\} \quad [\text{A33}]$$

For very large $a\theta$ values, the dependence of Q_c^ℓ and Q_a^ℓ on ℓ and $a\theta$ is as follows:

$$Q_c^\ell = 1 + 2\pi^{-1/2}(a\theta)^{1/2}[(2\ell+1)^{1/2} - (2\ell)^{1/2}] \quad [\text{A34}]$$

$$Q_a^\ell = 1 + 2\pi^{-1/2}(a\theta)^{1/2}[(2\ell+2)^{1/2} - (2\ell+1)^{1/2}] \quad [\text{A35}]$$

whereas integration of eqs. [A19] and [A20] yields

$$Q_c(\infty) = 1 \quad [\text{A36}]$$

$$Q_a(\infty) = -1 \quad [\text{A37}]$$

Since ℓ and $a\theta$ can be varied independently, eqs. [A34] and [A35] can be made to converge to eqs. [A36] and [A37] irrespective of how high the value of $a\theta$ is. It is concluded then that for increasing values of $a\theta$, a larger number of cycles is necessary for the attainment of periodic behavior for the charge functions. This is contrary to the behavior of current functions and is probably due to the fact that small variations in the current cause greater variations in the charge with increasing $a\theta$, since the charge is the integral of the current over the total $a\theta$ range.

For the hypothetical periodic states, it should be noted that

$$Q_n(\infty) = 0; Q_n^\infty(a\theta) = 0 \quad [\text{A38}]$$

indicating that for these cases, no net charge is dissolved or deposited during the passage of a complete cycle.

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