ADDITIVE CYCLIC SQUARE WAVE VOLTAMMETRY FOR ADSORPTIVE - COMPLEX IRREVERSIBLE SYSTEM (1) —— CONTROLL ED BY THE RATE OF COMPLEXING REACTION

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The Faradaic current of adsorptive - complex irreversible electrode processes can be written as

\[ i(t) = nF Ak_f \Gamma_0(t) \]  

(1)

where

\[ k_f = k_n \exp\left[-\frac{nF(E - E^*)}{RT}\right] \]  

(2)

\[ \Gamma_0(t) = \int_0^t \left( \frac{\partial G}{\partial X} \right)_{X=0} dt + \int_t^t \frac{\partial G}{\partial X} \left|_{X=0} \right. dt - \int_t^t k_f \Gamma_0(t) dt \]  

(3)

and

\[ \left( \frac{\partial G}{\partial X} \right)_{X=0} = C_k D_0^{-1/2} \left[ K_k C_k^2 C_0^2 \cdots \right]^{1/2} \]  

(4)

\[ \Gamma_0(t) \] is the surface concentration (in moles per unit area) of the reactant MLxQy... (i.e. O), \( \tau_a \) is adsorptive time before scanning, \( C_k \) & \( C_0 \) are complexants concentration, \( K = C_0/C_k \), and \( C_k^2 \) is the determinand M ion bulk concentration. Then

\[ i(t) = nFA(D_0 K_k C_k^2 C_0^2 \cdots)^{1/2} C_k \tau_a k_f \]  

\[ \cdot \left[ 1 + 1/\tau_a \int_0^t \exp\left( \int_0^t k_f dt \right) dt \right] \cdot \exp\left( -\int_0^t k_f dt \right) \]  

(5)

Eq. (5) is suited for any waveform of polarization potential. For cyclic square wave voltammetry, the sweep potential equations are expressed as follows

\[ E(j) = E_i - INT[(j - 1)/2] \Delta E + (-1)^j E_s \]  

(when \( j = 1, 2 \ldots 2H + 1 \))

\[ E(j) = E_i - 2H \Delta E + INT(j/2) \Delta E + (-1)^j E_s \]  

(when \( j = 2H + 2 \ldots 4H + 1 \))

(6)

\( (\Delta E, E_s > 0) \)

For forward sweep \( 1 \leq j \leq 2H + 1 \), but for reverse sweep \( 2H + 1 \leq j \leq 4H + 1 \), where \( H \) is the staircase number of forward or reverse sweep. In eq. (5), the two integral parts can be solved by means of the superposition principle

\[ \int_0^t k_f dt = \int_0^t k_{t_1} dt + \int_0^t k_{t_2} dt + \cdots + \int_0^t k_{t_{2H+1}} dt = \tau T(J) \]

(7)

\[ T(J) = \sum_{j=1}^{2H+1} k_{t_j} \]

(8)

\[ \int_0^t \exp\left( \int_0^t k_f dt \right) dt = \int_0^t \exp\left[ \tau T(J) \right] dt = \tau \sum_{j=1}^{2H+1} \exp\left[ \tau T(J) \right] \]

(9)

where \( \tau \) is a pulse duration, \( t = \tau_a + j \tau \), and \( J \) is pulse ordinal number. Thus, for cyclic square wave voltammetry, the current at any pulse \( J \) is

\[ i(J) = nFA(D_0 K_k C_k^2 C_0^2 \cdots)^{1/2} C_k \tau_a X(J) \]

(10)

\[ X(J) = k_f \left[ 1 + \frac{\tau}{\tau_a} \sum_{j=1}^{2H+1} \exp\left[ \tau T(J) \right] \right] \exp\left[ -\tau T(J) \right] \]

(11)

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Therefore, the additive current for square wave voltammetry is given by

\[ i_a(J) = nF A(D_0 k_1 C_1^0 C_2^0 \cdots)^{1/2} C_n^* \Delta t [X(J) + X(J+1)] \]  

(12)

For forward sweep \( J = 1, 3, 5 \cdots 2H-1 \), and for reverse sweep \( J = 2H + 2, 2H + 4 \cdots 4H \). Then, the additive cyclic current equation

\[ i_{ca}(J) = nF A(D_0 k_1 C_1^0 C_2^0 \cdots)^{1/2} C_n^* \Delta t \]  

\[ \cdot \left[ X(J) + X(J+1) + X(4H+1-J) + X(4H+2-J) \right] \]  

(13) 

\[ (J = 1, 3, 5 \cdots 2H-1) \]

all-order derivative convolution and derivative equation

\[ i_\beta = nF A(D_0 k_1 C_1^0 C_2^0 \cdots)^{1/2} C_n^* \Delta t \]  

\[ \cdot \lim_{N \to \infty} \frac{1}{N-1} \sum_{l=0}^{N-1} \sum_{l=0}^{N-1} \frac{\Gamma(l-q) X(l)}{\Gamma(-q) \Gamma(l+1)} \]  

(14) 

\[ [l = q, q + 1, 4H + 1 - q, 4H + 2 - q; \text{for practical calculation } N = (J + 1)/2] \]

can be obtained. When \( q = -0.5, 0, 0.5, 1, 1.5, i_\beta \) is convolution, normal, deconvolution, first derivative & second derivative convolution convolution current respectively. The peak potential equation of additive cyclic current was deduced as follows

\[ E_p = E^* + \frac{RT}{a nF} \ln \left( \frac{2RTk_1 \tau}{a nF \Delta E} \right) + \text{INT} \left( \frac{E_s - \Delta E}{2 \Delta E} \right) \Delta E \]  

(15)

It could be known from (13) and (14) that additive cyclic current and its all-order derivative convolution & derivative currents were proportional to \( C_n^*, C_1^{1/2}, C_2^{1/2} \). By the treatment of eqs. (10), (12) to (15) with a microcomputer, some conclusions were obtained: 1) For forward sweep, the positive and negative pulse currents \( i_{pa}, i_{pn} \) are in same direction, the peak shapes are asymmetrical, \( i_{pa} > i_{pn} \), and the additive current of forward sweep \( i_{pa} \) is also-asymmetrical. 2) For reverse sweep, the positive and negative pulse currents \( i_{pr}, i_{pn} \) approach to zero, and there are no appearance of the reduction peak. 3) The peak shape of additive cyclic current \( i_{ca} \) is asymmetrical. 4) \( i_{ca} \) increases rapidly with \( q \) value, and the resolution improved. 5) A linear dependence of \( i_{ca} \) on \( \Delta E^{1+\tau}, (1/\tau)^{1+\tau} \) and \( \tau \) is predicted, \( i_{ca} \) is linear decreased slightly as \( E \) increases, and the more \( q \) value is, the faster it decreases. 6) \( E_p \) moves to positive potential as \( E \) increases. All current equations given above are also suited for the system of complexant reducted, but in the case, "n" is the electron number of a complexant (Q or L) reducted.

Experiments with Zn(II) - Zincon complex were carried out to verify the theory. The results were in good agreements with the theoretical conclusions.