INVESTIGATION ON CYCLIC RECIPROCAL DERIVATIVE CHRONOPOTENTIOMETRY. PART II. THEORETICAL EQUATION FOR AN IRREVERSIBLE REACTION

Shuping BI[1,]*, Jian CHEN and Tao CHEN

Department of Chemistry, Nanjing University, Nanjing 210093, People Republic of China;
e-mail: [1] bisp@nju.edu.cn

Received November 5, 1999
Accepted February 10, 2000

Presented at International Conference on Modern Electroanalytical Methods, Seč, September 19–23, 1999.

A rigorous mathematical analysis is presented for an irreversible electrode process in the cyclic reciprocal derivative chronopotentiometry. Influences of basic electrochemical parameters, such as transfer coefficient α, rate constant k_s, current density j, number of the electrons involved in the electrode reaction n and reactant concentration c_0^* on the properties of the dt/dE–E chronopotentiogram are described.

Key words: Cyclic reciprocal derivative chronopotentiometry; Irreversible reactions; Electrode processes; Electrochemistry; Voltammetry.

Cyclic reciprocal derivative chronopotentiometry (CRDCP) is a novel electrochemical method developed recently. It is derived from the cyclic derivative chronopotentiometry[1]. The first paper from this laboratory has dealt with the general principle and treatment of reversible electrode process[2]. The chronopotentiogram of CRDCP has a shape similar to the classic cyclic voltammetry (CV), possessing some unique electrochemical characteristics. It may be considered as the CV under the galvanostatic conditions. In this paper, we continued its theoretical study for an irreversible reaction.

THEORETICAL

Consider a reduction $O + ne \rightarrow R$, involving only one rate-determining step and neglecting the effect of the backward process. The cathodic process can be written as $(0 < t < \tau)$ (refs[3,4]);

E–t curve:

$$E_c = E^{0\prime} + \frac{RT}{\alpha nF} \ln \frac{2k_s}{\sqrt{\pi \mathrm{D_O}}} + \frac{RT}{\alpha nF} \ln\left(\sqrt{\tau} - \sqrt{t}\right) , \qquad (1)$$

dt/dE–t curve:

$$\frac{\mathrm{d}t}{\mathrm{d}E} = \frac{2\alpha nF}{RT} \sqrt{t}\left(\sqrt{t} - \sqrt{\tau}\right) . \qquad (2)$$

From Eqs (*1*) and (*2*), the dt/dE–E curve can be obtained:

$$\frac{\mathrm{d}t}{\mathrm{d}E} = \frac{\alpha nF}{RT} \frac{\sqrt{\pi D_O}}{k_s} P \left(\sqrt{\tau} - \frac{\sqrt{\pi D_O}}{2k_s} P \right) , \qquad (3)$$

in which

$$P = \exp \frac{(E_c - E^{0\prime})\alpha nF}{RT} . \qquad (4)$$

Transition time obeys the equation

$$\sqrt{\tau} = \frac{nF\sqrt{\pi D_O}\, c_0^*}{2j} . \qquad (5)$$

Notations in the above equations are as follows: E is the electrode potential, $E^{0\prime}$ standard formal electrode potential, t time from the start of the experiment, α transfer coefficient, n number of electrons involved in the over-all electrode reaction, k_s heterogeneous rate constant, j density of the current through the electrolytic cell, D_O and D_R diffusion coefficients of substances O and R, respectively.

At $t = \tau/4$, dt/dE–E the curve achieves its maximum value. The peak height, $y_{P,c}$, is

$$y_{P,c} = -\frac{\alpha nF}{2RT} \tau ; \qquad (6)$$

the peak potential:

$$E_{P,\mathrm{c}} = E^{0\prime} + \frac{RT}{\alpha nF} \ln \frac{k_\mathrm{s}\sqrt{\tau}}{\sqrt{\pi D_\mathrm{O}}} \,. \tag{7}$$

Combinig Eqs (*3*), (*4*) and (*6*), the half-peak width can be obtained

$$W_{P/2,\mathrm{c}} = \frac{1.763RT}{\alpha nF} \,. \tag{8}$$

At time τ, the current through the cell is reversed and, consequently, substance R is reoxidized. Let $\alpha + \beta = 1$; the anodic branch can be described as: ($\tau < t < \tau'$, $t' = t - \tau$) (refs[5,6]);

E–*t* curve:

$$E_\mathrm{a} = E^{0\prime} - \frac{RT}{\beta nF} \ln \frac{2k_\mathrm{s}}{\sqrt{\pi D_\mathrm{R}}} - \frac{RT}{\beta nF} \ln \left[\left(\tau + t'\right)^{1/2} - 2t'^{1/2} \right] ; \tag{9}$$

d*t*/d*E*–*t* curve:

$$\frac{\mathrm{d}t}{\mathrm{d}E} = -\frac{\beta nF}{RT} \left\{ \frac{\left[(\tau + t')^{1/2} - 2t'^{1/2} \right] \left[2t'^{1/2} \left(\tau + t'\right)^{1/2} \right]}{t'^{1/2} - 2\left(\tau + t'\right)^{1/2}} \right\} . \tag{10}$$

Equations (*9*) and (*10*) are very complicated and hence cannot be solved directly; we applied the numerical simulation method. The results indicate that at $t' = 2/7\tau' = 2/21\tau$ ($\tau' = \tau/3$ as in the case of the reversible electrode process, the transition time for the reoxidation process is one third of the transition time for the preceding cathodic processes[7,8]), d*t*/d*E*–*E* achievs its maximum value

$$y_{P,\mathrm{a}} = 0.1554 \frac{\beta nF}{RT} \tau \,, \tag{11}$$

the peak potential is

$$E_{P,\mathrm{a}} = E^{0\prime} - \frac{RT}{\beta nF} \ln \frac{0.8586 k_\mathrm{s} \sqrt{\tau}}{\sqrt{\pi D_\mathrm{R}}} , \tag{12}$$

the half-peak width can be expressed as:

$$W_{P/2,\mathrm{c}} = \frac{1.901 RT}{\beta nF} . \tag{13}$$

Similarly to cyclic voltammetry, we also emploied following parameters to represent the properties of CRDCP:

the ratio of cathodic and anodic peak heights:

$$\frac{y_{P,\mathrm{c}}}{y_{P,\mathrm{a}}} = -\frac{3.218\alpha}{\beta} ; \tag{14}$$

the distance of cathodic and anodic peak potentials:

$$\Delta E_P = E_{P,\mathrm{a}} - E_{P,\mathrm{c}} = -\frac{RT}{\beta nF} \ln \frac{0.8586 k_\mathrm{s} \sqrt{\tau}}{\sqrt{\pi D_\mathrm{R}}} - \frac{RT}{\alpha nF} \ln \frac{k_\mathrm{s} \sqrt{\tau}}{\sqrt{\pi D_\mathrm{O}}} ; \tag{15}$$

the half-peak width for both cathodic and anodic branches (T = 298 K):

$$W_{P/2,\mathrm{c}} = 45.3/\alpha n \quad (\mathrm{mV}) , \tag{16}$$

$$W_{P/2,\mathrm{a}} = 48.8/\beta n \quad (\mathrm{mV}) . \tag{17}$$

RESULTS AND DISCUSSION

No attempt was made to verify the theoretical equations for the electrochemical reaction in the present case, because the accuracy of oscillographic recordings in such a short time period under the irreversible condition is not sufficient. A computer-aided numerical simulation method was used to calculate theoretical *E*–*t*, d*t*/d*E*–*t* and d*t*/d*E*–*E* chronopotentiograms and investigate its electrochemical properties. A Pentium 586 computer and Turbo C 2.0 language were used for the programming.

As an example, variations of three curves *E*–*t*, d*t*/d*E*–*t* and d*t*/d*E*–*E* with parameters α and k_s are shown in Figs 1 and 2. This diagram was constructed using the following data: $j = 2 \cdot 10^{-4}$ A cm^{-2}, $n = 2$, $c_0^* = 1 \cdot 10^{-7}$ mol cm^{-3}, $D_O = D_R = 1 \cdot 10^{-5}$ cm^2 s^{-1} and $T = 298$ K.

Influences of important electrochemical parameters (α, k_s, j, n and c_0^*) on the properties of CRDCP were also investigated theoretically. The values of $y_{P,c}/y_{P,a}$, ΔE_P, $W_{P/2,c}$ and $W_{P/2,a}$ were computed and are tabulated in Table I along with other pertinent information. Inspection of the information in Table I also reveals several important points:

1. $y_{P,c}/y_{P,a}$ is related explicitly to α and independent of k_s, j, n and c_0^*.

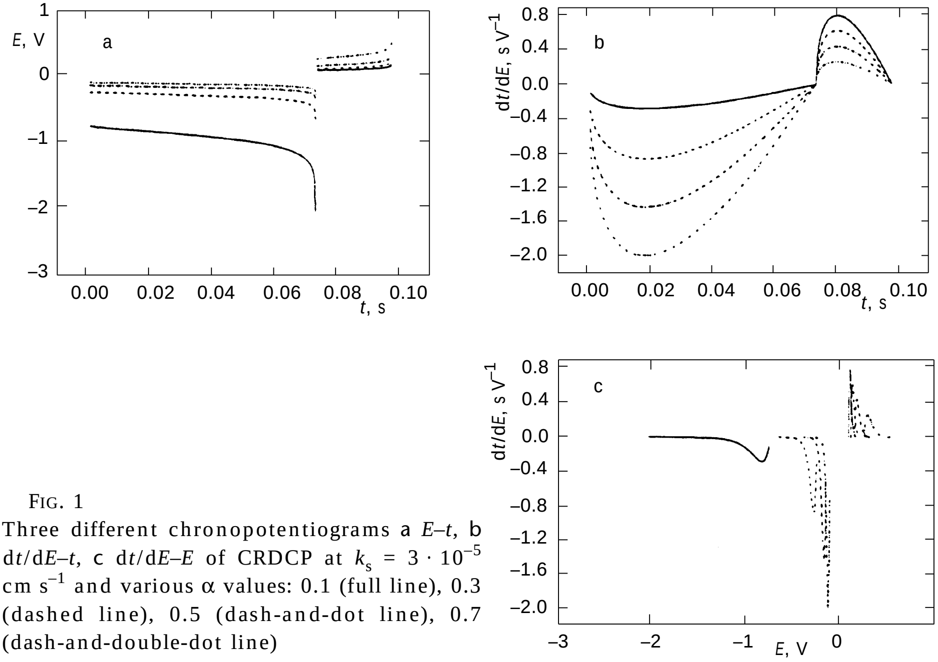

FIG. 1

Three different chronopotentiograms a *E*–*t*, b d*t*/d*E*–*t*, c d*t*/d*E*–*E* of CRDCP at $k_s = 3 \cdot 10^{-5}$ cm s^{-1} and various α values: 0.1 (full line), 0.3 (dashed line), 0.5 (dash-and-dot line), 0.7 (dash-and-double-dot line)

2. ΔE_P is a function of α, k_s, j and c_0^*. With increasing n, α, k_s and c_0^* , ΔE_P decreases (opposite trend for increasing j).

3. $W_{P/2,c}$ and $W_{P/2,a}$ only depend on transfer coefficient α and n, and are not related with k_s, j and c_0^*.

CONCLUSIONS

It is possible to develop a rigorous mathematical analysis of CRDCP for the irreversible process discussed in the present paper. The characteristics of the $dt/dE–E$ curve appears to be particularly useful in evaluating thermodynamic and kinetic quantities for both reduction and oxidation. In such studies, the method is more advantageous than classic chronopotentiometry. For example, the transfer coefficent α is estimated from the slope and E intercept of a plot of E *vs* log $(I – (t/\tau)^{1/2})$ in chronopotentiometry. Determination of accurate transition time is difficult because τ is obscured

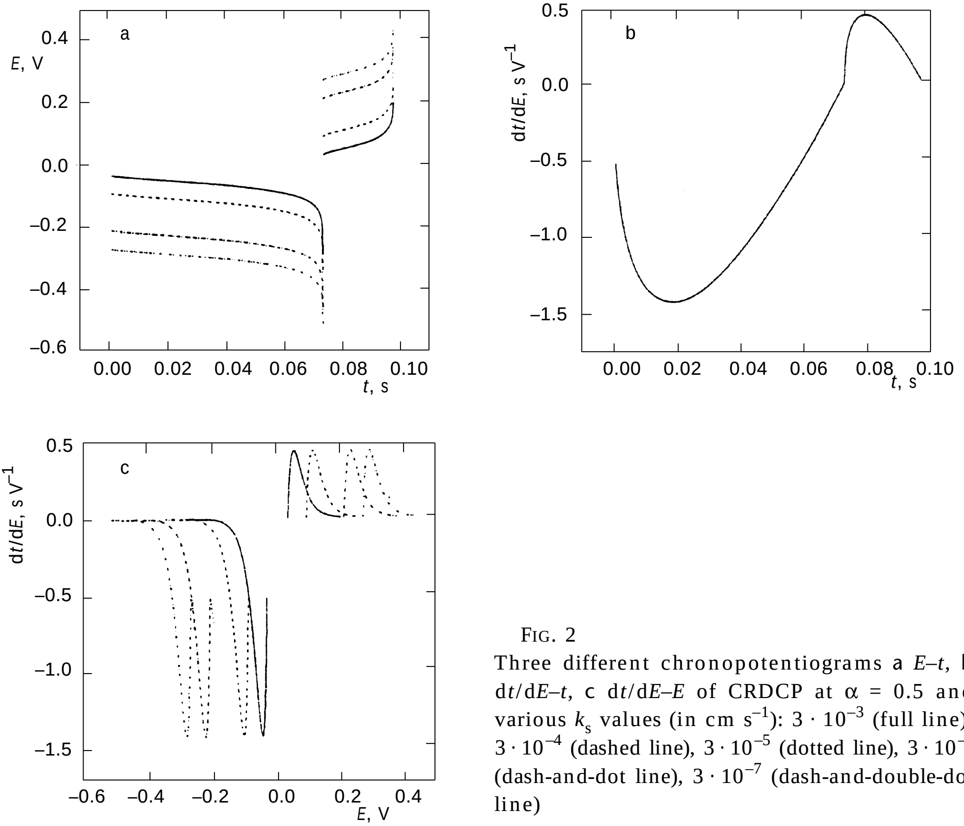

FIG. 2

Three different chronopotentiograms a $E–t$, b $dt/dE–t$, c $dt/dE–E$ of CRDCP at α = 0.5 and various k_s values (in cm s^{-1}): $3 \cdot 10^{-3}$ (full line), $3 \cdot 10^{-4}$ (dashed line), $3 \cdot 10^{-5}$ (dotted line), $3 \cdot 10^{-6}$ (dash-and-dot line), $3 \cdot 10^{-7}$ (dash-and-double-dot line)

TABLE I
Influences of parameters α, k_s, c_0^*, j and n on the properties of dt/dE–E chronopotentiogram (except specified, the parameters are: $j = 2 \cdot 10^{-4}$ A cm^{-2}, $n = 2$, $c_0^* = 1 \cdot 10^{-7}$ mol cm^{-3}, T = 298 K, $D_O = D_R = 1 \cdot 10^{-5}$ cm^2 s^{-1}, $\alpha = 0.5$ and $k_s = 3 \cdot 10^{-5}$ cm s^{-1})

Parameter	Properties	Results					Conclusion
k_s	k_s, cm s^{-1}	$3 \cdot 10^{-7}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-5}$	$3 \cdot 10^{-4}$	$3 \cdot 10^{-3}$	k_s affects $\Delta E_{P,ac}$ only
	$\Delta E_{P,ac}$/V	0.5761	0.4579	0.3396	0.2214	0.1030	
	$y_{P,c}/y_{P,a}$			3.218			
	$W_{P/2,c}$/mV			45.3			
	$W_{P/2,a}$/mV			48.8			
α	α	0.1	0.3	0.5	0.7		α affects $\Delta E_{P,ac}$, $y_{P,c}/y_{P,a}$ $W_{P/2,c}$ and $W_{P/2,a}$
	$\Delta E_{P,ac}$/V	0.9347	0.4025	0.3396	0.4062		
	$y_{P,c}/y_{P,a}$	0.3576	1.379	3.218	7.509		
	$W_{P/2,c}$/mV	226.5	75.5	45.3	32.4		
	$W_{P/2,a}$/mV	27.1	34.9	48.8	81.3		
j	j, A cm^{-2}	$1 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$8 \cdot 10^{-4}$	$12 \cdot 10^{-4}$	j affects $\Delta E_{P,ac}$ only
	$\Delta E_{P,ac}$/V	0.3040	0.3396	0.3752	0.4108	0.4316	
	$y_{P,c}/y_{P,a}$			3.218			
	$W_{P/2,c}$/mV			45.3			
	$W_{P/2,a}$/mV			48.8			
c_0^*	c_0^*, mol cm^{-3}	$1 \cdot 10^{-7}$	$2 \cdot 10^{-7}$	$4 \cdot 10^{-7}$	$6 \cdot 10^{-7}$	$8 \cdot 10^{-7}$	c_0^* affects $\Delta E_{P,ac}$ only
	$\Delta E_{P,ac}$/V	0.3396	0.3040	0.2684	0.2476	0.2329	
	$y_{P,c}/y_{P,a}$			3.218			
	$W_{P/2,c}$/mV			45.3			
	$W_{P/2,a}$/mV			48.8			
n	n	1	2	3			n affects $\Delta E_{P,ac}$ $W_{P/2,c}$ and $W_{P/2,a}$
	$\Delta E_{P,ac}$/V	0.7504	0.3396	0.2125			
	$y_{P,c}/y_{P,a}$			3.218			
	$W_{P/2,c}$/mV	90.6	45.3	30.2			
	$W_{P/2,a}$/mV	97.6	48.8	32.5			

due to the effects of capacitance of the double layer[9,10]. However, α can be readily obtained by measuring both cathodic and anodic peak heights in CRDCP using Eq. (*14*). The proposed approach provides a very simple experimental method for the determination of transfer coefficient; it should be credited with reviving interest in related chronopotentiometric techniques.

This project is supported by the National Natural Science Foundation of China (No. 49831005 and No. 29777013) and Fok Ying Tung Education Foundation of Hong Kong. The authors thank Profs R. Kalvoda, L. Pospíšil, Rongshi Cheng and Hongyuan Chen for their support and help.

REFERENCES

1. Bard A. J., Faulkner L. R.: *Electrochemical Methods – Fundamentals and Applications*. Wiley, New York 1980.
2. Bi S. P., Yu J.: *J. Electroanal. Chem.* **1996**, *405*, 51.
3. Reinmuth W. H.: *Anal. Chem.* **1960**, *32*, 1514.
4. Peters D. G., Burden S. L.: *Anal. Chem.* **1966**, *38*, 530.
5. Paunovic M.: *J. Electroanal. Chem.* **1967**, *14*, 447.
6. Delahay P., Mattax C. C.: *J. Am. Chem. Soc.* **1954**, *76*, 5314.
7. Berzins T., Delahay P.: *J. Am. Chem. Soc.* **1953**, *75*, 4205.
8. Macero D. J., Anderson L. B.: *J. Electroanal. Chem.* **1963**, *6*, 221.
9. Olmstead M. L., Nicholson R. S.: *J. Phys. Chem.* **1968**, *72*, 1650.
10. Bard A. J.: *Anal. Chem.* **1963**, *35*, 340.