Polarographic Diffusion Current Observed with Square Wave Voltage. II. Basic Theory for a Reversible Electrode

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(Received February 26, 1954)

In the preceding paper[1] the diffusion current, observed when the voltage applied to a reversible electrode is suddenly changed, is discussed theoretically. The theory is so easily to be extended that the electrolysis with a square wave voltage as shown in Fig. 1(a) can be elucidated as follows.

Our problem is now to solve the differential equation:

$$\partial C/\partial t = D\cdot\partial^2 C/\partial x^2 \tag{1}$$

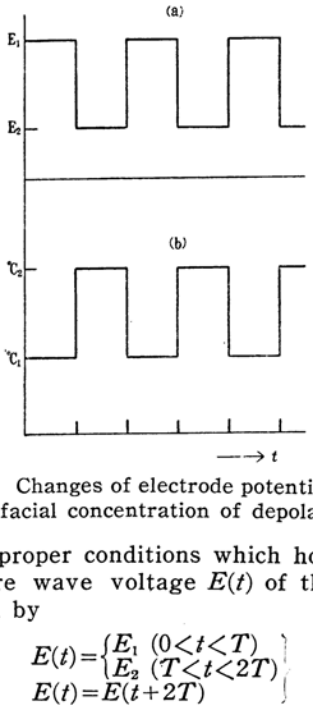

Fig. 1. Changes of electrode potential and interfacial concentration of depolarizer.

with the proper conditions which hold when the square wave voltage $E(t)$ of the period $2T$ shown by

$$\left.\begin{array}{l} E(t)=\begin{cases} E_1 \ (0<t<T) \\ E_2 \ (T<t<2T) \end{cases} \\ E(t)=E(t+2T) \end{array}\right\} \tag{2}$$

is applied. Since the concentration of depolarizer shows everywhere the constant value $^{*}C$ before the electrolysis, the initial condition is given by

$$t=0,\ 0\leq x\leq\infty,\ C={}^{*}C. \tag{3}$$

Next as for the interfacial concentration, it is shown in the previous paper that the conception that the concentrations of the oxidized and reduced forms are at a state of equilibrium at the electrode surface leads to a simplified supposition that each interfacial concentration shows a constant value according to the applied potential. Thus it is seen that the boundary condition is given by $x=0,\ t>0$,

$$C=\left\{\begin{array}{l} {}^{\circ}_{1}C(E=E_1;\ 2nT<t<(2n+1)T) \\ {}^{\circ}_{2}C(E=E_2;\ (2n+1)T<t<(2n+2)T) \end{array}\right\} \tag{4}$$

where n is an integer. This relationship is illustrated in Fig. 1(b).

(1) Solution by Means of the Principle of Superposition.—Let the function $C(x,\ t)$ be an algebraic sum of the functions $C(\mathrm{I})$, $C(\mathrm{II})$,……, etc.; namely

$$C=C(\mathrm{I})+C(\mathrm{II})+C(\mathrm{III})+C(\mathrm{IV})+\cdots\cdots, \tag{5}$$

and it is supposed that each function is governed by Fick's law of diffusion. As shown in Part I of this study, the following relations hold for the function $C(\mathrm{I})$.

$$\left.\begin{array}{l} t=0,\ 0\leq x\leq\infty,\quad C(\mathrm{I})={}^{*}C; \\ t>0,\ x=0,\qquad C(\mathrm{I})={}^{\circ}_{1}C; \\ \qquad C(\mathrm{I})={}^{\circ}_{1}C+({}^{*}C-{}^{\circ}_{1}C)\cdot\mathrm{erf}\dfrac{x}{2\sqrt{Dt}} \end{array}\right\} \tag{6}$$

Further, as for the function $C(\mathrm{II})$, the following relations hold.

$$\left.\begin{array}{l} t-T\leq 0,\ 0\leq x\leq\infty,\ C(\mathrm{II})=0; \\ t-T>0,\ x=0,\ C(\mathrm{II})={}^{\circ}_{2}C-{}^{\circ}_{1}C; \\ \qquad C(\mathrm{II})=({}^{\circ}_{2}C-{}^{\circ}_{1}C)\cdot\mathrm{erfc}\dfrac{x}{2\sqrt{D(t-T)}}. \end{array}\right\} \tag{7}$$

When such a calculation is carried out repeatedly, next it is found that $C(\mathrm{III})$ is shown by

$$\left.\begin{array}{l} t-2T\leq 0,\ 0\leq x\leq\infty,\ C(\mathrm{III})=0; \\ t-2T>0,\ x=0,\ C(\mathrm{III})={}^{\circ}_{1}C-{}^{\circ}_{2}C; \\ \qquad C(\mathrm{III})=({}^{\circ}_{1}C-{}^{\circ}_{2}C)\cdot\mathrm{erfc}\dfrac{x}{2\sqrt{D(t-2T)}} \end{array}\right\} \tag{8}$$

Upon generalizing this procedure, it is found that the concentration of depolarizer $C(x,\ t)$ is demonstrated by

$$C={}^{\circ}_{1}C+({}^{*}C-{}^{\circ}_{1}C)\cdot\mathrm{erf}\frac{x}{2\sqrt{Dt}}+$$

$$+\sum_{n=1}^{n}(-1)^n({}^{\circ}_{1}C-{}^{\circ}_{2}C)\cdot\mathrm{erfc}\frac{x}{2\sqrt{D(t-nT)}}, \tag{9}$$

which holds at the time interval given by

$$nT<t<(n+1)T$$

That this expression can satisfy the conditions shown by the Eqs. (1), (3) and (4), is

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[1] T. Kambara, This Bulletin, **27**, 523 (1954).

to be easily verified; and it is comprehensible that the interfacial concentrations are at a state of equilibrium and that the fluxes of oxidant and reductant are continuous at the electrode surface, when the above developed theoretical treatment is applied both to oxidant and reductant.

(2) **Solution by Means of the Laplace-Transformation.**—Next the above deduced conclusion will be derived by the aid of the Laplace-transformation. Upon applying the Laplace-transformation defined by

$$\mathfrak{L}C(x,\ t)=p\int_0^\infty e^{-pt}\cdot C(x,\ t)\cdot dt=u(x,\ p),$$

the differential equation (1) with the initial condition shown by Eq. (3) is converted into

$$p(u-{}^*C)=D\cdot\partial^2u/\partial x^2. \tag{10}$$

The general solution of this equation is given by

$$u={}^*C+A\cdot\exp\sqrt{\frac{p}{D}}x+B\cdot\exp\left(-\sqrt{\frac{p}{D}}x\right).$$

Since the relationship $u={}^*C$ must always hold for $x=\infty$, the integral constant A is clearly zero. Next the remaining constant B must be determined. Eq. (4), showing the boundary condition, can be written in the form:

$$x=0,\ t>0,\ C=\frac{1}{2}({}^{\circ}_{1}C+{}^{\circ}_{2}C)$$

$$+\frac{1}{2}({}^{\circ}_{1}C-{}^{\circ}_{2}C)\cdot M(T,\ t), \tag{11}$$

where the function $M(T,\ t)$ is the "square wave" or "meander" function shown in Fig. 2 and is defined as follows.

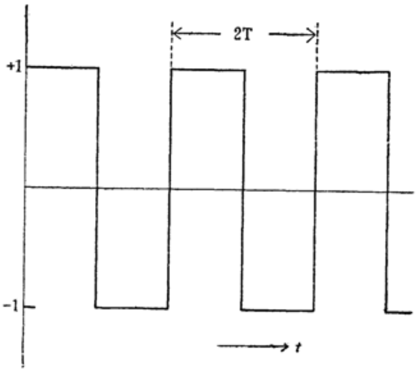

Fig. 2. Schematic representation of square wave function shown by Eq. (12).

$$M(T,\ t)=\begin{cases}+1 & (0<t<T);\\ -1 & (T<t<2T);\end{cases}$$
$$M(T,\ t+2T)=M(T,\ t). \tag{12}$$

Furthermore it can be shown that the function $M(T,\ t)$ has the following transformation.

$$\mathfrak{L}M(T,\ t)=\tanh\frac{pT}{2} \tag{13}$$

If the interfacial concentration is represented by

$$C(0,\ t)={}^{\circ}C=\mathfrak{L}^{-1}\ {}^{\circ}u,$$

it is found that

$${}^{\circ}u=B+{}^*C={}^{\circ}_{2}C+\frac{1}{2}({}^{\circ}_{1}C-{}^{\circ}_{2}C)\cdot\left(1+\tanh\frac{pT}{2}\right)$$
$$={}^{\circ}_{2}C+({}^{\circ}_{1}C-{}^{\circ}_{2}C)\cdot\{1+\exp\ (-pT)\}^{-1};$$

thus the constant B is determined, and it follows that

$$u(x,\ p)={}^*C+({}^{\circ}_{2}C-{}^*C)\cdot\exp\left(-\sqrt{\frac{p}{D}}x\right)$$

$$+({}^{\circ}_{1}C-{}^{\circ}_{2}C)\cdot\exp\left(-\sqrt{\frac{p}{D}}x\right)\cdot\{1+\exp(-pT)\}^{-1} \tag{14}$$

Upon utilizing the expansion:

$$\frac{1}{1+\exp(-pT)}=1-\exp(-pT)$$
$$+\exp(-2pT)-\ \ldots\ldots,$$

Eq. (14) can be transformed into

$$u(x,\ p)={}^*C+({}^{\circ}_{2}C-{}^*C)\cdot\exp\left(-\sqrt{\frac{p}{D}}x\right)$$

$$+({}^{\circ}_{1}C-{}^{\circ}_{2}C)\sum_{n=0}^{n}{}'(-1)^n\cdot\exp\left(\sqrt{\frac{p}{D}}x\right)\cdot\exp(-npT). \tag{14a}$$

In order to execute the inverse transformation, we can legitimately employ the following theorems; i. e.

$$\left.\begin{array}{l}\mathfrak{L}^{-1}\exp\left(-\sqrt{\frac{p}{D}}x\right)=\mathrm{erfc}\frac{x}{2\sqrt{Dt}};\\ \text{and if we have}\\ \quad\mathfrak{L}^{-1}f(p)=A(t),\\ \text{then it is found that}\\ \quad\mathfrak{L}^{-1}[e^{-kp}\cdot f(p)]=A(t-k).\end{array}\right\} \tag{15}$$

It must be noticed here that $A(t-k)=0$ for $t<k$ and that $A(t-k)$ implies the "translated function". There is no doubt that by means of the Eqs. (15) the expression for $u(x,\ p)$ shown by Eq. (14a) can be inversely transformed into Eq. (9).

Thus the basic expression for the concentration distribution in the case that a square wave voltage is applied upon a reversible electrode is theoretically obtained by means of the two mathematically different methods. It follows immediately from the above conclusion that the concentration gradient at the electrode surface is manifested by

$$\left(\frac{\partial C}{\partial x}\right)_{x=0}=\frac{{}^*C-{}^{\circ}_{1}C}{\sqrt{\pi Dt}}$$

$$+\sum_{n=1}^{n}{}'(-1)^{n+1}\frac{{}^{\circ}_{1}C-{}^{\circ}_{2}C}{\sqrt{\pi D(t-nT)}} \tag{16}$$

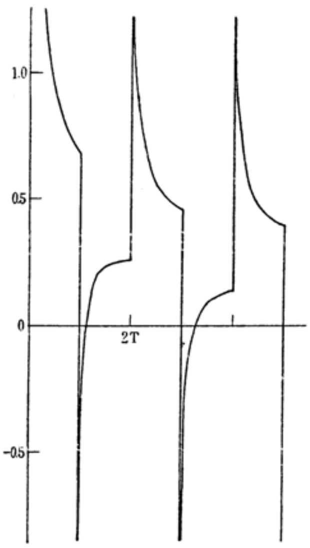

Fig. 3. Schematic representation of the course of instantaneous currents intensity due to the application of a square wave voltage. Curve shows the equation by

$$I=\frac{\alpha}{\sqrt{t}}+\sum_{n=1}^{n}(-1)^{n}\frac{\beta}{\sqrt{t-nT}},$$

The numerical values employed are as follows:

$\alpha=3;\quad \beta=1;\quad T=20.$

The instantaneous current intensity is readily obtainable from this equation, and in Fig. 3 is illustrated an example of the function given by Eq. (16). In our laboratory Dr. Suzuki[2] has investigated the electrolysis with square wave voltage by the aid of a rotating switch and the electro-magnetic oscillograph, and the recordings thereof are, in the case of reversible electrode reactions, quite in harmony with the present theoretical consideration. The validity of the above developed mathematical treatment will be amply and convincingly shown in the following article, in which many experimental facts will be rationally elucidated.

Summary

By means of the principle of superposition and of the Laplace transformation, the differential equation of diffusion is integrated, and the result thus obtained gives the fundamental theoretical expression for the electrolysis with a square wave voltage.

The author wishes to express his sincere thanks to Prof. I. Tachi for his kind guidance. The author's thanks are also due to Dr. M. Suzuki, who helped the author with many oscillographic data.

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[2] M. Suzuki, *J. Electrochem. Soc. Japan*, **22**, 63, 112, 162, 221 (1951); *Memoirs College Agr., Kyoto Univ.*, No. 67 (1954).