

RECONSIDERATION OF THE GALVANOSTATIC DOUBLE-PULSE METHOD

D. J. KOOIJMAN AND J. H. SLUYTERS

Laboratory of Analytical Chemistry, State University, Utrecht (Netherlands)

(Received February 3rd, 1966)

Fast electrode processes can be studied only by relaxation methods. In these methods, the electrode processes should be perturbed with signals of high frequency or short time in order to minimize concentration polarization.

One of the limitations encountered in the study of electrode kinetics with the galvanostatic single-pulse method is the influence of the double-layer capacitance at short pulse lengths. To remove this limitation, GERISCHER AND KRAUSE¹ developed the galvanostatic double-pulse method. The first pulse which is of higher amplitude, i_1 , than the second pulse, primarily charges the double-layer capacitance to the overvoltage required by the current density, i_2 , of the second pulse; *i.e.*, the overvoltage-time curve should start with a horizontal tangent at the beginning of the second pulse. Thus the current, passing the cell, is entirely faradaic at that moment. The value i_1/i_2 must be found by trial and error.

A mathematical analysis of the method, limited to cell responses of small amplitude, has been given by DELAHAY *et al.*² They correct for the concentration polarization occurring within the time, t_1 , of the first pulse. However, they do not consider the errors caused by the experimental difficulty of observing whether or not the cell response starts with a horizontal tangent at time t_1 . In the present paper we shall show that this difficulty seriously limits the double-pulse method.

THEORY

According to DELAHAY *et al.*², the voltage-time relation for the response of an electrode process, that is perturbed by a double-pulse current (Fig. 1), is:

$$\begin{aligned} \eta(t) = & \frac{i_1}{C_d(\gamma - \beta)} \left[\gamma/\beta^2 (\exp \beta^2 t \operatorname{erfc} \beta\sqrt{t} + 2\beta \sqrt{\frac{t}{\pi}} - 1) \right. \\ & \left. - \beta/\gamma^2 (\exp \gamma^2 t \operatorname{erfc} \gamma\sqrt{t} + 2\gamma \sqrt{\frac{t}{\pi}} - 1) \right] \\ & + \frac{i_2 - i_1}{C_d(\gamma - \beta)} \left[\gamma/\beta^2 (\exp \beta^2(t - t_1) \operatorname{erfc} \beta\sqrt{t - t_1} + 2\beta \sqrt{\frac{t - t_1}{\pi}} - 1) \right. \\ & \left. - \gamma/\beta^2 (\exp \gamma^2(t - t_1) \operatorname{erfc} \gamma\sqrt{t - t_1} + 2\gamma \sqrt{\frac{t - t_1}{\pi}} - 1) \right] \end{aligned} \quad (1)$$

and if $\left(\frac{d\eta}{dt}\right)_{t=t_1} = 0$, then

$$\frac{i_2}{i_1} = 1 - \frac{I}{\gamma - \beta} [\gamma \exp \beta^2 t_1 \operatorname{erfc} \beta \sqrt{t_1} - \beta \exp \gamma^2 t_1 \operatorname{erfc} \gamma \sqrt{t_1}] \quad (2)$$

in which

$$\beta + \gamma = \frac{i_0}{nF} \left(\frac{I}{C_{O^*} \sqrt{D_O}} + \frac{I}{C_{R^*} \sqrt{D_R}} \right) \quad \text{and} \quad \beta\gamma = \frac{nFi_0}{RTC_a}$$

The interpretation of eqn. (1) is difficult. Therefore we shall simplify it assuming that $t_1 \rightarrow 0$ and $i_1 t_1 / C_a \rightarrow \eta_0$. Equation (1) then reduces to:

$$\begin{aligned} \eta(t) = & \frac{\eta_0}{\gamma - \beta} [\gamma \exp \beta^2 t \operatorname{erfc} \beta \sqrt{t} - \beta \exp \gamma^2 t \operatorname{erfc} \gamma \sqrt{t}] \\ & + \frac{i_2}{C_a(\gamma - \beta)} \left[\gamma / \beta^2 (\exp \beta^2 t \operatorname{erfc} \beta \sqrt{t} + 2\beta \sqrt{\frac{t}{\pi}} - 1) \right. \\ & \left. - \beta / \gamma^2 (\exp \gamma^2 t \operatorname{erfc} \gamma \sqrt{t} + 2\gamma \sqrt{\frac{t}{\pi}} - 1) \right] \quad (3) \end{aligned}$$

The condition, $(d\eta/dt)_{t=0} = 0$, yields

$$i_2 = \beta\gamma C_a \eta_0 \quad (4)$$

If $i_2 = A\beta\gamma C_a \eta_0$, the curve will not start with a horizontal tangent, and for $A < 1$ the curve will exhibit a minimum at a time t_m , see Fig. 2. Obviously i_2 should be adjusted so that this minimum has just disappeared. This means that $\Delta\eta$ must be distinct for a small deviation of i_2 from the correct value.

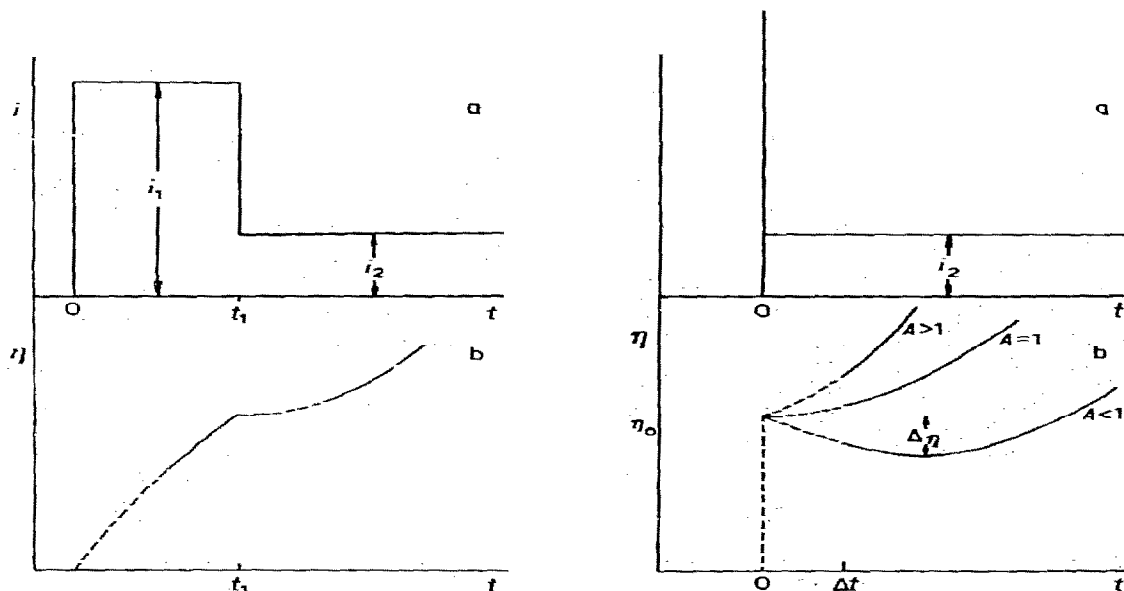


Fig. 1. (a), Shape of a double-pulse current; (b), cell response having a horizontal tangent at time t_1 . The dashed parts of the curve indicate that in these regions the response is obscured by transients.

Fig. 2. (a), Double-pulse current with an infinitely short first-pulse length; (b), cell response having a horizontal tangent at time $t = 0$. The dashed part of the curve indicates the region, Δt , which is obscured by transients.

The values t_m and $\Delta\eta$ can be obtained by expansion in series of the exponential and error functions in eqn. (3) for small values of t :

$$\eta(t) = \eta_0 \left[1 - (1-A)\beta\gamma t + \frac{4}{3\sqrt{\pi}} \beta\gamma(\beta+\gamma)t\sqrt{t} \right] \quad (5)$$

$$\frac{d\eta}{dt} = 0 \quad \text{yields} \quad t_m = \frac{\pi}{4} \left(\frac{1-A}{\beta+\gamma} \right)^2 \quad (6a)$$

and

$$\frac{\Delta\eta}{\eta_0} = -\frac{\pi}{12} (1-A)^3 \frac{\beta\gamma}{(\beta+\gamma)^2} \quad (6b)$$

These equations are valid only if $\beta\gamma t < 1$ and $(\beta+\gamma)t^{3/2} < 1$. These conditions will be checked afterwards.

From Fig. 2 it can be seen that, in order to observe a minimum in the cell response, $\Delta\eta/\eta_0$ must have a finite value. Moreover t_m must be larger than Δt , the time during which the cell response is obscured by transients.

THE VALUES OF Δt AND $\Delta\eta$

Even with good electronic design, transients, due to finite time constants of cables and the cell in the circuit, will be observed at the initial part of the potential-time curve. We have found experimentally that these transients have been damped only after $0.4 \mu\text{sec}$. Consequently, t_m must be larger than $0.4 \mu\text{sec}$. Not only transients will contribute to Δt , but also the rise and decay times of the pulse-generators and the response time of the oscilloscope recording the overvoltage-time curve. If the ohmic drop in the cell is compensated by means of a bridge circuit of DELAHAY³, the value of Δt will be generally larger than $1 \mu\text{sec}$, as a differential oscilloscope with relatively poor rise time must be used. Elsewhere⁴ we have described a set-up for the compensation of the ohmic drop in which an asymmetric fast response oscilloscope can be used. In that case Δt will be about $0.4 \mu\text{sec}$.

The value of $\Delta\eta$ first depends on the line-width of the trace on the screen of the oscilloscope, generally $\Delta\eta/\eta \geq 0.01$. However, if high exchange current densities are measured, the compensation of the ohmic drop will be more important. If e.g. the miscompensation of the ohmic drop for the second pulse is 0.05 mV , the first part of the curve, from 0 to t_1 , will be shifted an amount $(i_1 - i_2)/i_2 \cdot 0.05 \text{ mV}$ with respect to the second part of the curve, $t > t_1$. As a result, $\Delta\eta$ must be larger than 0.01η in order to observe a minimum in the cell response. If the influence of a miscompensation of the ohmic drop is also taken into account, a value of $\Delta\eta/\eta_0 \geq 0.02$ seems reasonable.

SCOPE OF THE DOUBLE-PULSE METHOD

Inserting $t_m \geq 0.4 \mu\text{sec}$ and $\Delta\eta/\eta_0 \geq 0.02$ in eqns. (6a) and (6b), one obtains:

$$\left. \begin{array}{l} \text{for } A = 0.9: \quad \beta + \gamma \leq 140 \quad \text{and} \quad \beta\gamma \geq 76(\beta + \gamma)^2 \\ A = 0.8: \quad \beta + \gamma \leq 280 \quad \beta\gamma \geq 9.6(\beta + \gamma)^2 \\ A = 0.5: \quad \beta + \gamma \leq 700 \quad \beta\gamma \geq 0.61(\beta + \gamma)^2 \end{array} \right\} \quad (7)$$

Taking the following reasonable values: $n = 2$, $T = 300$ °K, $D_{\text{ox}} = D_{\text{R}} = 10^{-5}$ cm²sec⁻¹, $C_a = 25 \cdot 10^{-6}$ Fcm⁻² and $C_{\text{ox}}^* = C_{\text{R}}^* = C^*$, one can calculate the limits of k_{sh} and i_0 , which should not be exceeded if accuracies of 10, 20 and 50% are required, respectively, see Table 1.

TABLE 1

A	C^* (mole cm ⁻²)	i_0 (A cm ⁻²)	K_{sh} (cm sec ⁻¹)
0.9	10^{-7}	$\leq 44 \cdot 10^{-6}$	$\leq 2.2 \cdot 10^{-3}$ (10%)
	$5 \cdot 10^{-7}$	$\leq 1.1 \cdot 10^{-3}$	$\leq 1.1 \cdot 10^{-2}$
	$2.5 \cdot 10^{-6}$	$\leq 27 \cdot 10^{-3}$	$\leq 5.4 \cdot 10^{-2}$
	$10 \cdot 10^{-6}$ and higher	—	$\leq 2.2 \cdot 10^{-1}$
0.8	10^{-7}	$\leq 350 \cdot 10^{-6}$	$\leq 1.7 \cdot 10^{-2}$ (20%)
	$5 \cdot 10^{-7}$	$\leq 8.8 \cdot 10^{-3}$	$\leq 8.8 \cdot 10^{-2}$
	$2.5 \cdot 10^{-6}$ and higher	—	$\leq 4.4 \cdot 10^{-1}$
0.5	10^{-7}	$\leq 5.2 \cdot 10^{-3}$	≤ 0.26 (50%)
	$4 \cdot 10^{-7}$ and higher	—	≤ 1

It should be noted that the error in the measured i_0 or k_{sh} is a systematic one. The measured value for the exchange current density or rate constant is always too low.

A numerical examination* of eqn. (1) revealed that even if $t_1 > 0$, the same limits, as tabulated above, are valid provided that the correction for concentration polarization, occurring within time t_1 , is performed with sufficient accuracy. This may be difficult if the rate constant, k_{sh} , is large, as the extrapolation procedure proposed by DELAHAY² *et al.*, is not always allowed.

DETERMINATION OF THE EXCHANGE CURRENT DENSITY FOR THE Hg/Hg²⁺ ELECTRODE REACTION IN 1 M HClO₄

The Hg/Hg²⁺ electrode has been investigated by means of several relaxation methods and by different authors. IMAI AND DELAHAY⁵ reported for 1 mM Hg₂²⁺, an exchange current of 12 Acm⁻², measured with the faradaic rectification method. SLUYTERS-REHBACH AND SLUYTERS⁶ conclude from a complex plane analysis that i_0 must be larger than 450 mA cm⁻² for 1 mM Hg₂²⁺. BIRKE AND ROE⁷ measured with the galvanostatic single-pulse method an i_0 of about 350 mA cm⁻². The following data are reported from the galvanostatic double-pulse method.

C^* (mM)	i_0 (mA cm ⁻²)		
	Delahay ²	Gerischer ^{1**}	Our data
2	420	350	700
1	250	200	400
0.5	180	120	200
0.2	75		80
0.1			35

* Table of exp x^2 erfc x are tabulated by FADDEYEVA AND TARENT'EV⁹.

** These values are corrected for concentration polarization occurring within the first pulse.

The results obtained with the different relaxation methods are inconsistent. As regards the double-pulse method, it can be shown by means of eqn. (7) (in which, for C_a , the values published by SLUYTERS-REHBACH AND SLUYTERS⁸ are substituted) that the reported data contain errors larger than 50%. Therefore one may conclude that the Hg/Hg₂²⁺ electrode reaction behaves reversibly with respect to the double-pulse method. The inconsistency between our data for 1 mM and 2 mM Hg₂²⁺ and those of DELAHAY AND GERISCHER can be explained by assuming that their value of Δt was larger than ours.

CONCLUSIONS

The galvanostatic double-pulse method has no advantage over the single-pulse method, as the experimental conditions to be fulfilled in order to measure high exchange current densities, cannot be realized. For the same reason, the values of i_0 for the Hg/Hg₂²⁺ electrode reaction measured with the double pulse method, published previously and in this paper, have no meaning.

SUMMARY

A critical examination is made of the voltage response of a cell when a double-pulse current is applied. The limitations of the double-pulse method for studying fast electrode reactions are considered and it is shown that the maximum value of the heterogeneous rate constant measurable with this method is about 0.5 cm sec⁻¹. In this case the error will be 20%.

REFERENCES

- 1 H. GERISCHER AND M. KRAUSE, *Z. Physik. Chem. N.F.*, **10** (1957) 264.
 - 2 H. MATSUDA, S. OKA AND P. DELAHAY, *J. Am. Chem. Soc.*, **81** (1959) 5077.
 - 3 T. BERZINS AND P. DELAHAY, *J. Am. Chem. Soc.*, **77** (1955) 6448.
 - 4 D. J. KOOIJMAN AND J. H. SLUYTERS, *Electrochim. Acta*, submitted.
 - 5 H. IMAI AND P. DELAHAY, *J. Phys. Chem.*, **66** (1962) 1108.
 - 6 M. SLUYTERS-REHBACH AND J. H. SLUYTERS, *Rec. Trav. Chim.*, **83** (1964) 983.
 - 7 R. L. BIRKE AND D. K. ROE, *Anal. Chem.*, **37** (1965) 451.
 - 8 M. SLUYTERS-REHBACH AND J. H. SLUYTERS, *Rec. Trav. Chim.*, **83** (1964) 987.
 - 9 V. N. FADDEYEVA AND N. M. TERENT'EV, *Tables of the probability integral for complex argument*, 1954; Engl. translation, Pergamon Press, Oxford, 1961.
- J. Electroanal. Chem.*, **13** (1967) 152-156