

LINEARIZATION OF THE CURRENT/VOLTAGE CHARACTERISTIC OF AN ELECTRODE PROCESS. APPLICATION TO RELAXATION METHODS*

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Abstract—Generally, an electrode process is assumed to behave as a linear element at potential departures from equilibrium not exceeding 5 mV. In this paper a rigorous examination is presented of the maximum overpotential at which linearization of the i/E relationship for charge-transfer and mass-transfer controlled electrode processes is allowed. It appears that the 5-mV limit is an overestimate. Mostly the excursion from equilibrium potential should not exceed 0.5 mV.

Study of kinetics of electrode reactions with pulse methods is not feasible at such low potential levels. A considerable improvement of these methods can be obtained if a two-indicator electrode cell is used, one electrode functioning as the cathode and the other as the anode. Then, first-order deviations from linearity of each electrode cancel. The maximum value of the applied overpotential may be extended by one order of magnitude. In the faradaic impedance methods first-order deviations, giving rise to second harmonics, are not important provided higher harmonics than the fundamental are rejected by a tuned amplifier. In this case a 5-mV excursion from the equilibrium potential is allowed.

Résumé—En général le comportement d'un processus rédox à une électrode est supposé linéaire si la déviation d'équilibre ne dépasse pas la valeur de 5 mV. On présente un examen rigoureux des valeurs maximum des surtensions permises afin que la linéarisation de courbe courant-tension soit correcte. La limite de 5-mV est démontrée être une surestimation. Le plus souvent l'excursion d'équilibre ne doit pas excéder la valeur de 0,5 mV.

L'étude de la cinétique électrochimique à une électrode rédox avec des impulsions galvanostatiques n'est pas praticable à des potentiels tellement bas.

Une amélioration considérable de ces méthodes est possible en appliquant une cellule à deux électrodes indicatrices, l'une fonctionnant comme anode, l'autre comme cathode. Des déviations de linéarité d'ordre premier des deux électrodes se compensent en ce cas, la valeur maximum du potentiel permis s'élevant d'un ordre de grandeur. Dans la méthode de l'impédance faradique des déviations d'ordre premier, qui produisent des deuxième harmoniques, ne sont pas importantes pourvu que la réponse de la cellule passe un amplificateur syntonisé. En ce cas des excursions d'équilibre de 5 mV sont permis.

Zusammenfassung—Die Stromspannungsbeziehung bei einem Elektrodenprozess wird im allgemeinen als linear angenommen, wenn die Überspannung 5 mV nicht überschreitet. Es wird eine eingehende Untersuchung darüber angestellt, bis zu welchen maximalen Überspannungen die Linearisierung für durchtritts- und diffusionskontrollierte Elektrodenvorgänge erlaubt ist. Man kommt zum Ergebnis, dass die 5 mV-Grenze zu hoch gewählt ist. In den meisten Fällen sollte die Abweichung vom Gleichgewichtspotential 0,5 mV nicht überschreiten.

Kinetische Untersuchungen mit instationären Methoden sind bei derartig kleinen Überspannungen kaum durchführbar. Die Methodik lässt sich jedoch bedeutend verbessern, wenn eine Zelle mit zwei Indikator-Elektroden verwendet wird, die eine Elektrode als Kathode, die andere als Anode. In diesem Falle kompensieren sich die Abweichungen von der Linearität in erster Näherung gegeneinander. Der zulässige Überspannungswert darf deshalb um eine Größenordnung erhöht werden. Bei Faraday-Impedanzmethoden sind die Abweichungen erster Ordnung, welche harmonische zweiter Ordnung ergeben, ohne Einfluss, falls auf die Grundfrequenz abgestimmte Verstärker verwendet werden. In diesem Fall darf die zulässige Überspannung maximal 5 mV betragen.

INTRODUCTION

KINETIC parameters of fast electrode processes are mostly determined with relaxation methods. In these methods only small excursions from the equilibrium potential are

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allowed. The reason for this is twofold: first, mass transfer polarization is small at slight perturbations of equilibrium; secondly correction for mass transfer polarization can be performed only after the solution of Fick's equations

$$i = nFD \frac{dC}{dx} \quad \text{and} \quad \frac{dC}{dt} = D \frac{d^2C}{dx^2}, \quad (1)$$

together with the current/voltage relationship

$$i = i_0 \left[\frac{C_R}{C_R^*} \exp \left(\alpha \frac{nF}{RT} \eta \right) - \frac{C_{ox}}{C_{ox}^*} \exp \left\{ -(1 - \alpha) \frac{nF}{RT} \eta \right\} \right], \quad (2)$$

in which C_R and C_{ox} are the concentrations at the electrode surface, C_{ox}^* and C_R^* the bulk concentrations, and $\eta = (E - E_{eq})$.

In many cases this problem is too difficult to be solved without linearization of (2), by expansion of the exponentials, into

$$i = i_0 \left[\frac{C_R}{C_R^*} - \frac{C_{ox}}{C_{ox}^*} + \frac{nF}{RT} \eta \right]. \quad (3)$$

Generally (3) is assumed to be correct for overpotentials not exceeding 5 mV. It will be shown that this limit is valid only at special conditions and that mostly much lower overpotentials should be applied.

THEORY

We shall treat successively the following three types of electrode processes:

A. The rate-determining step of the reaction is the charge-transfer at the electrode surface.

B. The rate of the electrode process is solely controlled by mass transfer of the electro-active species from and to the electrode surface.

C. The intermediate case.

A. Charge-transfer control

In this case the concentrations at the electrode surface are equal to the bulk concentrations. (2) then becomes

$$i = i_0 \left[\exp \left(\alpha \frac{nF}{RT} \eta \right) - \exp \left\{ -(1 - \alpha) \frac{nF}{RT} \eta \right\} \right], \quad (4)$$

whence, after expansion of the exponential terms and rearranging:

$$\eta = \frac{RT}{nF i_0} \left[1 - \frac{2\alpha - 1}{2!} \frac{i}{i_0} + \frac{(3\alpha - 1)(3\alpha - 2)}{3!} \frac{i^2}{i_0^2} - \frac{(4\alpha - 1)(4\alpha - 2)(4\alpha - 3)}{4!} \frac{i^3}{i_0^3} + \dots \right] \quad (5)$$

It is evident that deviation from linearity is a function of α and is larger the more α differs from 0.5. Higher order terms in (5) will be sufficiently small, <1%, under the conditions represented in Table 1.

TABLE 1. MAXIMUM VALUES OF η , AT WHICH A CHARGE-TRANSFER CONTROLLED ELECTRODE REACTION BEHAVES AS A LINEAR ELEMENT WITHIN 1%. THESE VALUES SHOULD NOT BE EXCEEDED IN PULSE MEASUREMENTS IF ONE INDICATOR ELECTRODE IS USED

α or $(1 - \alpha)$	0.0	0.1	0.25	0.40	0.50
η_{\max}	$\frac{0.5}{n}$ mV	$\frac{0.7}{n}$ mV	$\frac{1}{n}$ mV	$\frac{2.5}{n}$ mV	$\frac{12}{n}$ mV

B. Mass-transfer control

This means that the exchange current density i_0 is so large that (2) may be written

$$\frac{C_R}{C_R^*} \exp \alpha \frac{nF}{RT} \eta - \frac{C_{ox}}{C_{ox}^*} \exp -(1 - \alpha) \frac{nF}{RT} \eta = 0$$

or

$$\eta = \frac{RT}{nF} \ln \frac{C_{ox}}{C_{ox}^*} \frac{C_R^*}{C_R}. \quad (6)$$

Introducing $C_{ox} = C_{ox}^* - \Delta C_{ox}^*$ and $C_R = C_R^* + \Delta C_R^*$ into (6), one obtains

$$\eta = \frac{RT}{nF} \left[\ln \left(1 - \frac{\Delta C_{ox}^*}{C_{ox}^*} \right) - \ln \left(1 + \frac{\Delta C_R^*}{C_R^*} \right) \right],$$

whence, after expansion of the logarithmic terms

$$\eta = -\frac{RT}{nF} \left[\left(\frac{\Delta C_{ox}^*}{C_{ox}^*} + \frac{\Delta C^*}{C^*} \right) + \frac{1}{2} \left(\frac{\Delta C_{ox}^{*2}}{C_{ox}^{*2}} - \frac{\Delta C_R^{*2}}{C_R^{*2}} \right) + \frac{1}{3} \left(\frac{\Delta C_{ox}^{*3}}{C_{ox}^{*3}} + \frac{\Delta C_R^{*3}}{C_R^{*3}} \right) + \dots \right]. \quad (7)$$

For low values of η , (7) may be linearized

$$\eta = -\frac{RT}{nF} \left(\frac{\Delta C_{ox}^*}{C_{ox}^*} + \frac{\Delta C_R^*}{C_R^*} \right) = \frac{RT}{nF} \left(\frac{C_{ox}}{C_{ox}^*} - \frac{C_R}{C_R^*} \right). \quad (8)$$

Evidently deviation from linearity depends on C_{ox}^*/C_R^* , in other words on the difference between equilibrium potential and half-wave potential. Higher order terms in (7) will contribute less than 1% to η at potential departures from equilibrium given in Table 2.

TABLE 2. MAXIMUM VALUES OF η AT WHICH A MASS-TRANSFER CONTROLLED ELECTRODE PROCESS BEHAVES AS A LINEAR ELEMENT WITHIN 1%. THESE VALUES SHOULD NOT BE EXCEEDED IN PULSE MEASUREMENTS IF ONE INDICATOR ELECTRODE IS USED

$\pm(E_{eq} - E_{1/2})$	∞ mV	$\frac{60}{n}$ mV	$\frac{30}{n}$ mV	$\frac{20}{n}$ mV	0 mV
η_{\max}	$\frac{0.5}{n}$ mV	$\frac{0.6}{n}$ mV	$\frac{1}{n}$ mV	$\frac{1.5}{n}$ mV	$\frac{9}{n}$ mV

C. The intermediate case

Expansion of the exponential terms in (2) yields

$$\eta = \frac{RT}{nF} \left[\left(\frac{i}{i_0} - \frac{\Delta C_{\text{ox}}^*}{C_{\text{ox}}^*} - \frac{\Delta C_R^*}{C_R^*} \right) - \frac{2\alpha - 1}{2} \frac{i^2}{i_0^2} - \frac{1}{2} \left(\frac{\Delta C_{\text{ox}}^{*2}}{C_{\text{ox}}^{*2}} - \frac{\Delta C_R^{*2}}{C_R^{*2}} \right) + \frac{i}{i_0} \left(\frac{\alpha \Delta C_{\text{ox}}^*}{C_{\text{ox}}^*} - \frac{(1 - \alpha) \Delta C_R^*}{C_R^*} \right) \right] + \dots \quad (9)$$

In this case the maximum value of the potential excursion η , at which higher order terms in (9) may be dropped, is now a complex function of i_0 , α and the equilibrium potential. Dependent on the dominating type of polarization, a choice must be made between Tables 1 and 2.

Obviously a 5-mV departure from equilibrium potential introduces serious errors unless measurements are performed at potentials close to the half-wave potential and if α is near to 0.50.

APPLICATION TO RELAXATION METHODS

Faradaic impedance methods^{1,2}

The electrode process is perturbed by an ac potential or current. Non-linearity of the electrode impedance gives rise to overtones. A sine-wave response, however, can be amplified with a tuned amplifier rejecting harmonics higher than the fundamental one. This means that first-order deviations of linearity, giving rise to a second harmonic and a rectification signal, will have no appreciable effect on the

TABLE 3. VALUES OF η GIVING RISE TO ERRORS LESS THAN 1%, FOR CHARGE-TRANSFER CONTROLLED-ELECTRODE PROCESSES NOT TO BE EXCEEDED IN FARADIC IMPEDANCE METHODS (AND IN PULSE METHODS PROVIDED THAT A TWO-INDICATOR ELECTRODE CELL IS USED)

α or $(1 - \alpha)$	0.0	0.10	0.25	0.40	0.50
η_{max}	$\frac{5}{n}$ mV	$\frac{6}{n}$ mV	$\frac{12}{n}$ mV	$\frac{17}{n}$ mV	$\frac{14}{n}$ mV

TABLE 4. VALUES OF η GIVING RISE TO ERRORS LESS THAN 1%, FOR MASS-TRANSFER CONTROLLED-ELECTRODE PROCESSES NOT TO BE EXCEEDED IN FARADIC IMPEDANCE METHODS (AND IN PULSE METHODS PROVIDED THAT A TWO-INDICATOR ELECTRODE CELL IS USED)

$\pm(E_{1/2} - E_{\text{eq}})$	∞ mV	$\frac{60}{n}$ mV	$\frac{30}{n}$ mV	$\frac{20}{n}$ mV	0 mV
η_{max}	$\frac{5}{n}$ mV	$\frac{6}{n}$ mV	$\frac{8}{n}$ mV	$\frac{9}{n}$ mV	$\frac{10}{n}$ mV

measurements. Second-order deviations do have influence, as a Fourier expansion of $eg \sin^3 \omega t$ contributes to a third harmonic but also to the fundamental frequency. As a result, the maximum value of the overpotential across the faradaic impedance may be taken larger than the values in Tables 1 and 2. Such values are given in Tables 3 and 4. It must be stressed, however, that Tables 3 and 4 may be applied only if the cell response goes to a tuned amplifier.

Faradaic rectification

The rectification signal is caused by the non-linearity of the electrode process. Theoretical discussions³ consider only first order deviations. Higher order deviations from linearity contribute less than 1% to the rectification signal if ΔE_∞ does not exceed the values given in Tables 5 and 6.

TABLE 5. VALUES OF ΔE_∞ , GIVING RISE TO ERRORS LESS THAN 1%, FOR CHARGE-TRANSFER CONTROLLED ELECTRODE PROCESSES NOT TO BE EXCEEDED IN THE FARADAIC RECTIFICATION METHOD

α or $(1 - \alpha)$	0.0	0.10	0.20	0.25	0.30	0.40	0.45	0.50
$(\Delta E_\infty)_{\max}$	$\frac{125}{n} \mu\text{V}$	$\frac{200}{n} \mu\text{V}$	$\frac{550}{n} \mu\text{V}$	$\frac{2000}{n} \mu\text{V}$	$\frac{400}{n} \mu\text{V}$	$\frac{100}{n} \mu\text{V}$	$\frac{50}{n} \mu\text{V}$	$0 \mu\text{V}$

TABLE 6. VALUES OF ΔE_∞ GIVING RISE TO ERRORS LESS THAN 1%, FOR MASS TRANSFER CONTROLLED ELECTRODE PROCESSES NOT TO BE EXCEEDED IN THE FARADAIC RECTIFICATION METHOD

$\pm(E_{\text{eq}} - E_{1/2})_\infty$	$\infty \text{ mV}$	60 mV	20 mV	0 mV
$(\Delta E_\infty)_{\max}$	$\frac{125}{n} \mu\text{V}$	$\frac{125}{n} \mu\text{V}$	$\frac{100}{n} \mu\text{V}$	$0 \mu\text{V}$

Pulse methods

Studying electrode processes with galvanostatic step,⁴ double pulse⁵ or coulostatic step,⁶ one may apply overvoltages not exceeding the values in Tables 1 and 2. Accurate measurements at such low overpotentials, however, are not feasible as the noise and hum-to-signal ratio becomes too high. Obviously, in the case of mass-transfer control, the equilibrium potential should preferably be kept close to the half-wave potential. This involves, however, serious drawbacks: preparation of stable amalgams of low concentrations is very difficult; determination of α is impossible; study of an electrode reaction of the type $\text{Me}^{n+} + ne \rightleftharpoons \text{Me}$ is not possible.

This type of electrode reaction was recently discussed by Birke and Roe.⁷ They stated that "approximations previously used to obtain a linearized relationship between overpotential and current are not adequate to represent the situation when the reduced phase is of unit activity". They do not fully recognize, however, that these approximations are hardly adequate, except close to the half-wave potential (see Table 2). Furthermore the formula derived by them⁷ (equation (6)) to correct for non-linearity is likely to be in error, as η still depends on α even if the exchange current becomes infinite. A better formula is obtained by substituting the concentration changes at the electrode surface calculated by Berzins and Delahay⁸ into the expanded current/voltage relation for the intermediate case, (9) in this paper.

A real improvement can be obtained, if both electrodes—instead of one of them—contribute to the response of the cell, in other words if the counter electrode is made identical to the indicator electrode. The measured response of the whole cell will be the sum of responses of the oxidation reaction at the anode and the reduction reaction at the cathode. From (5), (7) and (9) it appears that first-order deviations from linearity cancel. So using two indicator electrodes, one may apply in the pulse methods, mentioned above, overpotentials as high as those tabulated for the impedance methods (see Tables 3 and 4). Sometimes it will be impossible to

have a cell with two identical electrodes, *eg* if a dme is used. Then two experiments must be performed in which alternatively the indicator electrode is exposed to the same current but with opposite sign, and the two responses added.

EXPERIMENTS AND RESULTS

In order to illustrate experimentally the influence of the non-linearity of the current/voltage relationship, we have studied the $\text{Hg}_2^{2+}/\text{Hg}$ -electrode in 1 M HClO_4 , applying galvanostatic single- and double-pulse methods.

The charge-transfer resistance of the reaction $\text{Hg}_2^{2+} + 2e \rightleftharpoons \text{Hg}$ is low. In the single pulse method the response of the cell was measured 1.6 ms after the start of the pulse. This time is sufficiently long to ascertain that the response of the cell is entirely determined by mass transfer. Furthermore the ratio C_0^*/C_R^* is extreme.

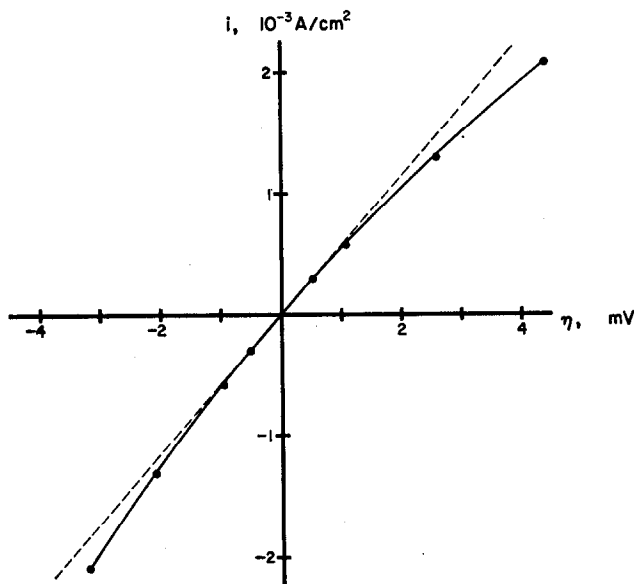


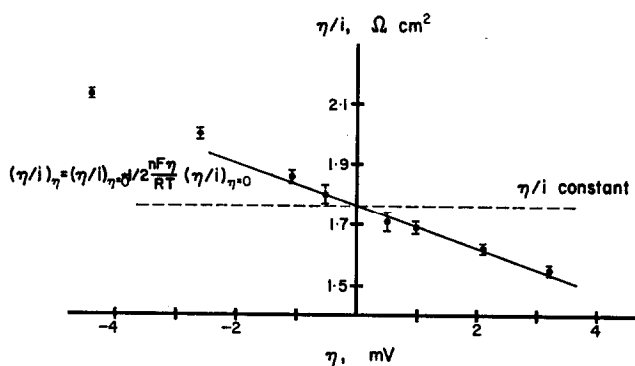
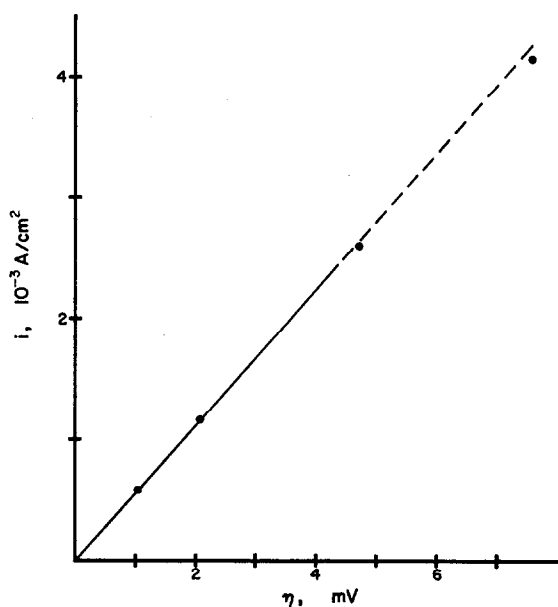
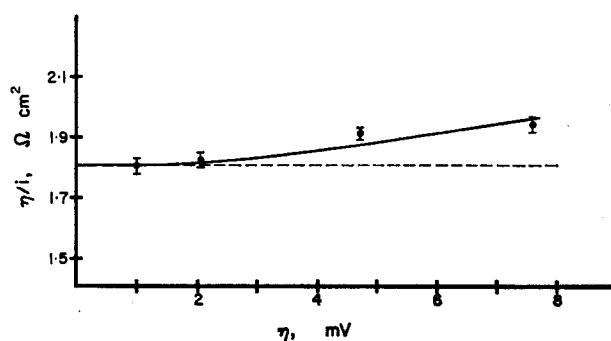
FIG. 1(a). Plot of the overpotential of a one-indicator electrode cell against the applied current density for the Hg_2^{2+} (0.52×10^{-4} M/cm³)/Hg electrode reaction in 1.0 M HClO_4 at 25°C.

Time elapsed after the start of the galvanostatic pulse, 1.6 ms.

Therefore we may expect that a deviation from linearity will be distinct at very low overpotentials, if a cell is used with one indicator electrode only.

This is confirmed by Fig. 1a, in which the cell response—corrected for the ohmic drop with the bridge circuit as described by Delahay⁴—has been plotted against the applied current. The cell with one indicator electrode behaves as a linear element only at very low overpotentials. This becomes more evident in Fig. 1b where η/i has been plotted against η . In such a plot a linear element should give a horizontal line. If only first-order deviations from linearity are important it can be derived from (7) that for the reduction of Hg_2^{2+} or the oxidation of Hg the following relation holds:

$$(\eta/i)_\eta = (\eta/i)_{\eta=0} - \frac{1}{2} \frac{nF}{RT} \eta (\eta/i)_{\eta=0}. \quad (10)$$


 FIG. 1(b). Plot of η/i vs η for the data of Fig. 1(a).

 FIG. 2(a). Plot of η vs i for a two-indicator electrode cell. Other circumstances identical to those described for Fig. 1(a).

 FIG. 2(b). Plot of η/i vs η for the data of Fig. 2(a).

Up to 4 mV this equation appears to be correct, see Fig. 1b. Generally such a plot can be used to correct for first-order deviations. The value $(\eta/i)_{\eta=0}$ can be graphically determined from

$$(\eta/i)_{\eta} = (\eta/i)_{\eta=0} + A\eta(\eta/i)_{\eta=0} \quad (10a)$$

in which A is a constant dependent on i_0 , α and E_{eq} . Such a method, correcting for first-order non-linearity, is, however, no better and more time-consuming than the direct measurement of the response of a cell containing two identical electrodes.

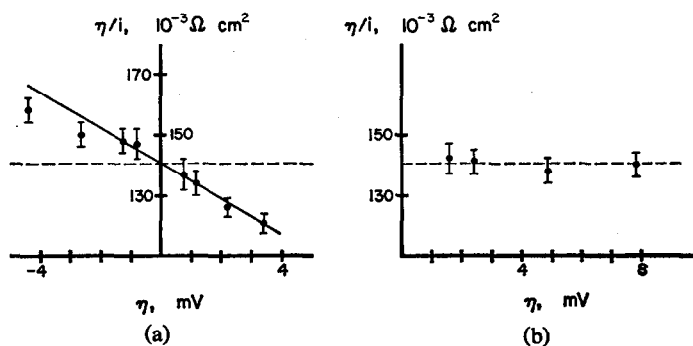


FIG. 3. Plot of η/i vs η for the double pulse method. Length of the first pulse was 4 μ s.

Other circumstances identical to Fig. 1(a).

(a), data for a one indicator electrode cell.

(b), data for a two indicator cell.

Similar plots, constructed with data obtained from a two-indicator electrode cell, clearly demonstrate that in this case the range of overpotentials may be extended by one order of magnitude.

Further experiments were performed with the double-pulse method at a time of 4 μ s, Figs. 3a, 3b. Here too, large errors are involved if the overpotential is chosen higher than 1 mV. Using, however, a two-indicator electrode cell one may apply much higher overpotentials.

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