

GALVANOSTATIC PULSE FOLLOWED BY COULOSTATIC IMPULSE WITH REVERSED SIGN: A NEW DOUBLE-PULSE METHOD FOR THE DETERMINATION OF THE KINETIC PARAMETERS OF ELECTRODE REACTIONS

I. THEORY AND CLASSIFICATION

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INTRODUCTION

A number of relaxation methods for the determination of the kinetic parameters of electrode reactions are known. In these methods the equilibrium state of the electrode under study is perturbed by a controlled current or voltage function and the response, defined by the kinetic properties of the electrode process, is measured and analyzed.

In the widely utilized faradaic impedance method the indicator electrode is perturbed by a sine wave current or potential and the kinetic parameters are determined from the measured electrode impedance. The technique was first applied to relatively fast electrode reactions by Randles¹ and afterwards by others. At present there are two methods of analyzing the experimental data: Randles' vector construction method and its extension, the complex plane method of Sluyters².

Perturbation of the equilibrium state is achieved by means of current pulses in the galvanostatic single pulse method and by means of charging impulses in the coulomatic (im)pulse method. In these transient methods the overvoltage, arising from the galvanostatic current or the coulomatic charge injection, is measured as a function of time. The correspondence between these pulse methods and the faradaic impedance method has been fully clarified with the introduction of a transformation procedure by which transients are converted into impedances³. Subsequent analysis by means of the complex plane method offers the possibility of avoiding the difficulty of analyzing the overvoltage-time curve according to cumbersome theoretical expressions. However, this convenient way of analyzing pulse data does not alter the fact that the study of the faster electrode reactions remains limited by three fundamental complications, *viz.* the ohmic drop, concentration polarization and double-layer charging current.

Gerischer and Krause⁴ were the first to attempt experimentally to remove one of these limitations. Recognizing that at short pulse times an important fraction of the cell current is non-faradaic, they developed the galvanostatic double-pulse method. The first pulse primarily charges the double-layer capacitance to the overvoltage required by the current density of the second pulse; *i.e.*, the overvoltage-time

curve should start with a horizontal tangent at the beginning of the second pulse. The current is thus entirely faradaic at that moment but the overvoltage generally contains an element of concentration polarization⁵. Besides, ohmic drop compensation is still critical⁶, especially when high exchange current densities are measured. The essence of the double-pulse galvanostatic experiment is simply the discontinuous lowering of the galvanostatic current to a value equal to the faradaic current at that particular moment.

From these considerations a better approach would seem to be to combine a first galvanostatic pulse, which builds up a certain overvoltage, with a following coulостatic pulse instead of a second galvanostatic one. The charge injection, caused by this coulостatic impulse, can be chosen such that the overvoltage-time curve starts with a horizontal tangent just as in the galvanostatic double-pulse method. Clearly, such a situation can be achieved only if the polarities of the coulостatic charging impulse and the galvanostatic pre-pulse are opposite. After the (dis)charging has been completed, no net current flows through the cell and consequently the measured overvoltages contain no contribution from the ohmic resistance of the cell. This feature permits a favourable comparison with the galvanostatic double-pulse technique, which is seriously limited by the ohmic overpotential.

Because the tangent in the overvoltage-time curve is bound to be horizontal after cessation of the coulостatic impulse, not only the net current through the cell but also the capacitance and faradaic currents are zero. This means that a pseudo-equilibrium state has been created where the potential is, simply by Nernst's law, prescribed by the surface concentrations of the electroactive species at that moment. The overvoltage thus represents the mass transfer polarization built up during the application of the pre-pulse, and contains no component due to activation polarization. Apparently, combination of a galvanostatic pulse with a following coulостatic impulse offers the possibility of splitting the overvoltage into a charge transfer polarization part and a mass transfer polarization part.

The proposed technique is therefore a step forward from the existing double-pulse method where only a separation between charging current and faradaic current is achieved. The choice of a coulостatic second pulse enables a direct experimental determination of charge transfer polarization with the logical consequence that the algebra is restricted mainly to Ohm's law. In the following the technique will be referred to as the G(alvanostatic) R(eversed) C(oulостatic) pulse method, a notation which clearly expresses the mixed double-pulse character and the opposite polarities of the two pulses.

THEORY

In a general way, an electrochemical transient method can be characterized by a relationship between the parameters: current, potential, time and concentration.

Considering the simple electrode process:



and taking the double-layer capacity into account, Astruc and Bonastre⁷ gave a unified mathematical derivation of these relationships for most important aperiodic relaxation methods. For the galvanostatic single pulse method the resulting ex-

pression, first derived by Berzins and Delahay⁸, is rather cumbersome as it contains exponential error functions with possibly complex argument. For any given set of values for time, current density and bulk concentrations of Ox and R, the overvoltage is, in a complex way, defined by the charge transfer parameters k_{sh} and α , the mass transfer parameters D_{Ox} and D_R and the double layer parameter C_d .

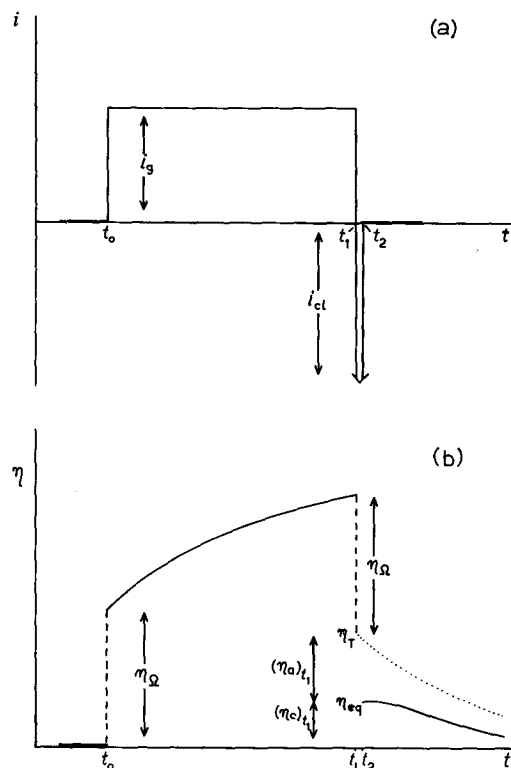


Fig. 1. (a) Shape of a GRC-current pulse; (b) cell response having a horizontal tangent at time t_2 . (...) Response in the absence of the coulostatic pulse.

On applying a GRC-pulse signal to an electrochemical cell with an impedance that can be represented by the classical Randles' equivalent circuit, the resulting overvoltage η will generally vary with time as is shown in Fig. 1. The input signal—current as a function of time—is characterized by the galvanostatic current i_g , the galvanostatic pulse width t_g and the coulostatic charge density q_{cl} which, in its turn, is defined by current i_{cl} and duration t_{cl} according to

$$q_{cl} = i_{cl} t_{cl} \quad (2)$$

The charge injection q_{cl} should be such that the principal condition of the GRC method, *viz.* a horizontal tangent in the η, t curve at t_2 :

$$(d\eta/dt)_{t_2} = 0 \quad (3)$$

is fulfilled. The response signal (see Fig. 1b) is sufficiently characterized by: η_{eq} , the potential difference between the real equilibrium state and the pseudo-equilibrium

created, an "equilibrium overvoltage", and η_T , the "total" overvoltage that appears if only a galvanostatic pulse is applied.

Figure 1 shows clearly that, the current through the cell being zero, neither η_T nor η_{eq} contain the ohmic overpotential η_Ω .

The first part of the η, t curve in Fig. 1b, that is for $t_0 < t < t_1$, represents in essence a normal galvanostatic response and could be described by the potential-time relationship as derived for a galvanostatic current perturbation. However, the use of the complicated expression will not be necessary in the theoretical characterization of the GRC method. It is sufficient to state that at time t_1 the overvoltage η contains, η_Ω being zero, contributions from charge transfer polarization and from concentration polarization so that:

$$\eta_T = (\eta_a)_{t_1} + (\eta_c)_{t_1} \quad (4)$$

In order to specify $(\eta_a)_{t_1}$, it will first be necessary to find an expression for the faradaic current i_f at time t_1 . The net current flowing through the cell, denoted by i_t , is at any moment equal to the algebraic sum of the charging current i_c and i_f :

$$i_t = i_c + i_f \quad (5)$$

For the present current function, represented by Fig. 1a, the conditions are:

$$i_t = i_g \quad t_0 < t < t_1 \quad (6a)$$

$$i_t = i_{c1} \quad t_1 < t < t_2 \quad (6b)$$

$$i_t = 0 \quad t \geq t_2 \quad (6c)$$

At any t the change in charge density on the electrode, q_M , is related to the tangent in the η, t curve

$$(dq_M/dt) = i_c = C_d(d\eta/dt) \quad (7)$$

Consequently, using (5), (6a) and (7), the faradaic current at time t_1 can be written as:

$$(i_f)_{t_1} = i_g - C_d(d\eta/dt)_{t_1} \quad (8)$$

Under conditions where the current-voltage characteristic may be linearized (these conditions will be discussed in detail below), the charge transfer polarization is assumed to be caused by a simple resistance θ , related to the apparent exchange current density i_0 according to:

$$\theta = RT/nFi_0 \quad (9)$$

Combination of Ohm's law with eqns. (8) and (9) results in the general relationship:

$$(\eta_a)_{t_1} = (RT/nFi_0)[i_g - C_d(d\eta/dt)_{t_1}] \quad (10)$$

An expression for the concentration polarization overvoltage η_c is easily found as it is caused simply by the differences in concentrations of the electroactive species at the electrode surface and in the bulk of the solution. Applying Nernst's law, $(\eta_c)_{t_1}$ is the difference between the Nernstian equilibrium potentials of the redox system at $t=t_0$ and $t=t_1$, the real equilibrium and the polarized state respectively:

$$(\eta_c)_{t_1} = (RT/nF)[\ln [(c_{Ox})_{t_1}/(c_R)_{t_1}] - \ln c_{Ox}^*/c_R^*] \quad (11)$$

The overvoltage at t_1 being characterized, it will, in a first approach, be assumed that the duration of the coulstatic charging impulse is so short that leakage by the faradaic reaction can be neglected between t_1 and t_2 . In other words, it is supposed that $(c_{\text{Ox}})_{t_1} = (c_{\text{Ox}})_{t_2}$ and $(c_{\text{R}})_{t_1} = (c_{\text{R}})_{t_2}$ and hence the concentration polarization at t_2 will be the same as at $t = t_1$:

$$(\eta_c)_{t_2} = (\eta_c)_{t_1} \quad (12)$$

From the fundamental condition for the response signal (a horizontal tangent as is represented by (3)) together with (5), (6c) and (7), it can be concluded that not only i_t is zero at t_2 but also:

$$(i_c)_{t_2} = (i_f)_{t_2} = 0 \quad (13)$$

This means that neither a charging nor a faradaic process is taking place at time t_2 and the electrode is at a pseudo-equilibrium state. The potential of the electrode in this state is defined by the $c_{\text{Ox}}/c_{\text{R}}$ ratio at the electrode surface as is given by (11) and does not, because of (13), contain a contribution from charge transfer polarization. This is in fact the crucial characteristic of the GRC method, as it leads to the conclusion that the measured overvoltage at time t_2 , η_{eq} , represents pure concentration polarization. Using (12) this can be formulated as:

$$\eta_{\text{eq}} = (\eta_c)_{t_1} \quad (14a)$$

and, using (4):

$$\eta_{\text{T}} - \eta_{\text{eq}} = (\eta_a)_{t_1} \quad (14b)$$

Equation (14b) states that the pseudo-overvoltage $\eta_{\text{T}} - \eta_{\text{eq}}$ (see Fig. 1b) represents the charge transfer polarization built up during the galvanostatic pre-pulse. Combination of (14b) with (10) yields, after rearranging, a very simple expression for i_0 as a function of the several experimentally accessible quantities:

$$i_0 = \frac{RT}{nF} \frac{i_g - C_d(d\eta/dt)_{t_1}}{\eta_{\text{T}} - \eta_{\text{eq}}} \quad (15)$$

The sudden change in charge density on the electrode between t_1 and t_2 not only forces $(d\eta/dt)_{t_2}$ to be zero but at the same time alters the potential across C_d . The difference is equal to $(\eta_{\text{T}} - \eta_{\text{eq}})$ and, the current being completely capacitive, can be correlated with q_{cl} and C_d by the relation:

$$\eta_{\text{T}} - \eta_{\text{eq}} = q_{\text{cl}}/C_d \quad (16)$$

In spite of its simplicity, eqn. (16) is of great importance as it expresses the possibility of determining C_d in the presence of the electroactive species, at time t_2 . i_0 also is obtained by means of (15) and thus pertains to the same surface concentrations of Ox and R. The study of more complicated electrode reactions, *e.g.* where C_d is affected by Ox and R, is possible. Combination of (16) with (15) results in:

$$i_0 = \frac{RT}{nF} \left[\frac{i_g}{\eta_{\text{T}} - \eta_{\text{eq}}} - \frac{q_{\text{cl}}(d\eta/dt)_{t_1}}{(\eta_{\text{T}} - \eta_{\text{eq}})^2} \right] \quad (17)$$

where it is easily seen that the value of C_d does not need to be known in the evaluation of i_0 but can be determined separately. Provided the electrode behaves classically,

eqn. (16) could, independently of (17), be used as an internal check on the correctness of the experiments.

At times beyond t_2 the electrode potential will relax to its initial equilibrium value in a way resembling the normal coulstatic impulse relaxation, where also C_d is discharged through the faradaic reaction. The pseudo-equilibrium state, in principle existing only at t_2 , is distorted by the transport of electroactive species to and from the electrode. This mass transport is dictated by the differences between $(c_{Ox})_{t_2}$ and c_{Ox}^* and between $(c_R)_{t_2}$ and c_R^* . A complete theoretical description will not be easy because the relaxation process corresponds to the breakdown of diffusion layers that have been built up during the galvanostatic pre-pulse. The thicknesses of these layers at t_2 are mainly governed by t_g and the diffusion coefficients of Ox and R. Their rates of breakdown, after t_2 , are jointly determined by i_0 , C_d , D_{Ox} and D_R . Consequently, a study of the η , t curve at times larger than t_2 could, in a complicated way, reveal information about the diffusion coefficients. However, the determination of these constants should preferably be left to simpler and better techniques such as d.c. polarography or the faradaic impedance method. In order to judge the potentialities of the present method as regards attainable ranges of values of k_{sh} in comparison with other relaxation methods, the consequences of a finite coulstatic pulse time and other non-ideal behaviour of the system will be discussed later in this paper.

CONDITIONS OF LINEARITY

The electrode process so far has been considered as behaving as a linear element. Kooijman *et al.*⁹ pointed out that the maximum overpotential at which linearization of the i , E relation is allowed, depends on the c_{Ox}^*/c_R^* ratio for a mass transfer controlled reaction and on the transfer coefficient α for a charge transfer controlled reaction. In the GRC method the mass transfer polarization part of η_T is eliminated. Thus there is no need for linearization of (11) and, consequently, only the magnitude of $(\eta_a)_{t_1}$, the charge transfer part of η_T , should be considered. The kinetic parameters that are determined from (17) or (15) do not pertain to c_{Ox}^* and c_R^* but to $(c_{Ox})_{t_1}$ and $(c_R)_{t_1}$, which are defined by η_{eq} according to eqns. (11) and (14a). For the latter reason it is, from a theoretical point of view, not entirely correct to make use of a two-indicator electrode cell in the GRC method, as two charge transfer overvoltages different, in principle, are added and later averaged. The use of such a "twin cell" becomes especially tricky if the mechanism of the electrode reaction under study is more complicated, *e.g.* when anodic and cathodic processes are different. It seems therefore the safest way to chose a one-indicator electrode system since there is, in the GRC method, also the possibility of a direct check on linearity by plotting $(\eta_a)_{t_1}$ against $(i_t)_{t_1}$. The limitations caused by linearity conditions of the mass transfer process are not met in the GRC method which is especially favourable in the study of electrode reactions of the type $Me^{n+} + ne \rightleftharpoons Me$, where the equilibrium potential cannot be kept close to the half-wave potential.

MORE COMPLICATED ELECTRODE REACTIONS

'Extending the discussion to more complicated models for the electrode process,

e.g. to a less simple equivalent circuit of the electrode impedance, the reasoning will also become more intricate. So far, the simplicity of GRC and its algebra has been governed by the splitting of η_T into $(\eta_a)_{t_1}$ and $(\eta_c)_{t_1}$ as is, in terms of the equivalent circuit, shown schematically in Fig. 2. The direct measurement of potential across, and current through, the charge transfer resistance θ makes the theoretical background very simple. However, in the case of an electrode reaction with a complication where the Randles' circuit does not hold, the interpretation of η_{eq} is not at once obvious. As an example we will treat the case of an electrode process that is coupled by a heterogeneous chemical reaction as is often the case in the electrocrystallization of metals. So-called adatoms are formed which become incorporated in the lattice of the electrode, or adsorbed at particular growth sites of the electrode surface. In the most general treatment, both surface diffusion of the adatoms and a finite rate of metal lattice formation must be considered, leading to the relatively complicated equivalent circuit¹⁰ of Fig. 3.

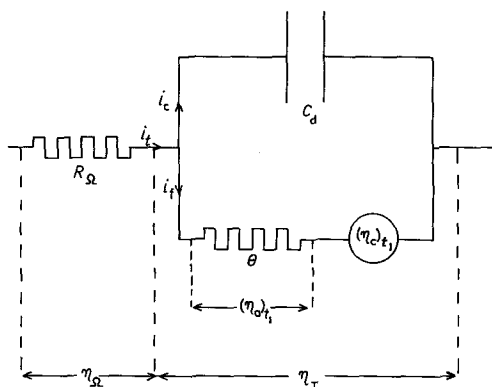


Fig. 2. Distribution of current and overvoltage at time t_1 in terms of Randles equivalent circuit. $(\eta_c)_{t_1}$ represents an impedance-less voltage source which stands for the concn. polarization at t_1 .

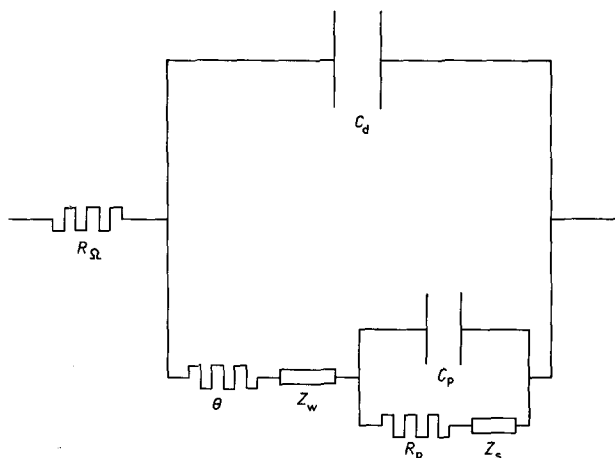


Fig. 3. Equivalent circuit for the case of an electrocrystallization process where both surface diffusion and slow lattice formation are considered.

The capacitance C_p , the so-called "adsorption pseudocapacitance", is directly related to the adatom concentration c_{ad} (mol cm⁻²), according to:

$$C_p = (n^2 F^2 / RT) c_{ad} \quad (18)$$

and the determination of this quantity *in situ* is of importance in the elucidation of the electrodeposition mechanism. Assuming a "parallel-step structure" for the metal surface, Fleischmann *et al.*¹⁰ described the diffusion of adatoms along the electrode surface to the lattice-building sites. The resulting impedance Z_s is in series with the resistance R_p , accounting for the finite rate at which the adatoms that reach the edge are incorporated into the lattice. As compared with the original Randles' circuit, some extra components are added, in series with θ and Z_w , to the faradaic impedance.

In the most general case where none of the components in the equivalent circuit of Fig. 3 can be neglected, the cell response to a GRC input signal should be interpreted with care. The pseudo-equilibrium overvoltage η_{eq} not only pertains to concentration polarization in the solution (Z_w), but also to the overvoltage across C_p . Provided that the condition:

$$R_p C_p \gg t_{c1} \quad (19)$$

holds, no appreciable current will flow through C_p between t_1 and t_2 and hence the potential across it will not change. As a consequence $(\eta_T - \eta_{eq})$ still represents the charge transfer overvoltage across θ at time t_1 and therefore i_0 can be evaluated just as easily as in the case of the simpler equivalent circuit. Further inspection of η_{eq} as a function of the input parameters i_g and t_g should yield information about the other components of the faradaic impedance. However, an easier way to obtain this

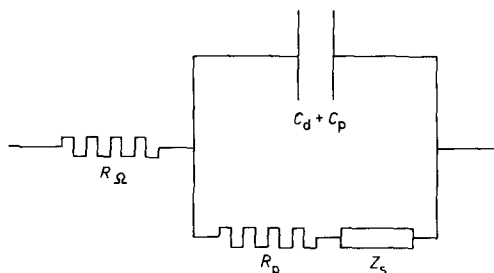


Fig. 4. Equivalent circuit for the case of an electrocrystallization process where both bulk diffusion and the charge transfer step can be neglected.

information is to raise the bulk concentration of the metal ion to values where θ and Z_w become negligible. The adatom concentration is not, or only slightly¹¹, dependent on the metal ion concentration and the equivalent circuit of the electrode impedance is reduced to a Randles-like scheme as represented in Fig. 4. The rate of lattice formation and the adatom concentration can then be evaluated by means of the procedure described for the classical case. We intend to investigate this experimentally in the near future.

SCOPE

In the case of very fast electrode reactions the total cell impedance is largely determined by the ohmic resistance R_Ω and this seriously limits the potentialities of most relaxation methods. In the GRC method, none of the experimental quantities utilized (see eqn. (17)) is affected by R_Ω and limitations could, in principle, now arise from the following basic sources of error.

(a) Even within the very short duration of the coulostatic charging impulse, some part of the total current will be faradaic. This leakage *via* the faradaic path which has been neglected up to this point, has a twofold consequence:

1. The surface concentrations of the electroactive species are not the same before and after application of the coulostatic impulse. Thus the observed η_{eq} is not equal to the concentration polarization overvoltage at time t_1 and eqn. (14a) is no longer valid:

$$\eta_{eq} \neq (\eta_c)_{t_1}$$

and the "loss of concentration polarization" is represented by the difference $[(\eta_c)_{t_1} - \eta_{eq}]$.

2. The coulostatic charge density q_{cl} is not completely consumed by C_d . Therefore the application of (16) should, as for q_{cl} , be attended by some correction for the faradaic leakage.

(b) In spite of 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 η, t curve after time t_2 . The damping time of these transients Δt is about $0.3 \mu s$. The possible errors caused by this experimental complication are clarified by Fig. 5a and b, the former pertaining to a normal galvanostatic pulse relaxation and the latter to a characteristic GRC curve.

The total overvoltage η_T will be found too low by an amount $\Delta\eta_T$, caused by relaxation between t_1 and $(t_1 + \Delta t)$. Apart from the inequality of η_{eq} and $(\eta_c)_{t_1}$ (see (a) 1), η_{eq} will be observed too low by $\Delta\eta_{eq}$ because the observer makes $(d\eta/dt)_{t_2 + \Delta t}$ zero instead of $(d\eta/dt)_{t_2}$. Figure 5b shows that the η, t curve starts with a horizontal tangent at $t_2 + \Delta t$ whereas the fundamental GRC condition (3) is not fulfilled.

(c) The powers of the pulse generators available are limited, which means that t_{cl} cannot be chosen infinitely small and that the charge transfer polarization $(\eta_a)_{t_1}$ cannot be raised to any required value. Furthermore, oscilloscope readings are rather inaccurate which affects the accuracy of η_{eq} , in a twofold sense: (i) the reading of η_{eq} itself contains a random error (of at least 2%) and (ii) misreading of the tangent $(d\eta/dt)_{t_2 + \Delta t}$ involves another random error in η_{eq} .

The limitations following from the arguments under (c) are simple and well-defined but those under (a) and (b) are all concerned with constant-current faradaic relaxation ($i_t = i_{cl}$, or $i_t = 0$). These relaxations are difficult to describe because of competing charging current and complicated initial (time t_1) conditions. However, if some reasonable assumptions are made, estimations of the different errors will be possible and predictions about the potentialities of the GRC method can be made on the basis of an example worked out in detail.

The case considered is where the galvanostatic pre-pulse causes a charge transfer overvoltage at time t_1 of 2.0 mV, irrespective of the magnitude of concentra-

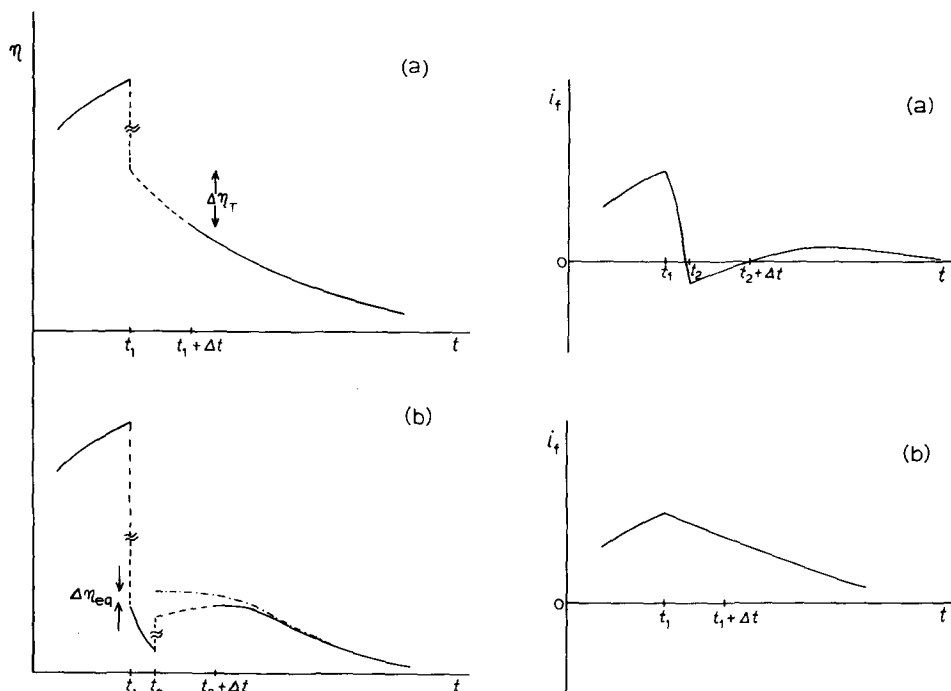


Fig. 5. Cell response to: (a) galvanostatic single pulse, showing the error in η_T ; (b) GRC pulse, showing the error in η_{eq} ; (-----) curve with a horizontal tangent at t_2 . The dashed parts of the curves indicate that in these regions the response is obscured by transients.

Fig. 6. The course of the faradaic current for a: (a) GRC expt., (b) galvanostatic single pulse expt.

tion polarization, so that $(\eta_a)_{t_1} = \eta_T - (\eta_c)_{t_1} = 2.0$ mV (it will be checked later if the values chosen in this example are experimentally attainable or may even be exceeded). If it is assumed that the change in concentration polarization overvoltage arising between t_1 and t_2 also amounts to 2.0 mV, the exchange current density, evaluated according to (15) and neglecting possible errors in C_d , will be too small by a factor of two.

During the short time interval between t_1 and t_2 the electrode process behaves almost as a transfer resistance θ shunted by the double layer capacitance C_d (leaving R_Ω out of consideration). Starting from the overvoltage η_T , the voltage-time response of such a network, if a constant current pulse with amplitude i_{cl} and duration t_{cl} is applied, is:

$$\eta_t = \eta_T - i_{cl}\theta \{1 - \exp - [(t - t_1)/\theta C_d]\} \quad (20a)$$

with $t_1 < t < t_2 (= t_1 + t_{cl})$.

The current i_f flowing through the resistance θ in the same time interval follows from (20a):

$$(i_f)_t = i_{cl} \{1 - \exp - [(t - t_1)/\theta C_d]\} \quad (20b)$$

and its complete course is shown schematically in Fig. 6a. The "change" in η_{eq} ,

$[(\eta_c)_{t_1} - \eta_{eq}]$ can be correlated with the faradaic current between t_1 and t_2 if the time dependent $(i_f)_t$, as defined by (20b), is replaced by a mean constant faradaic current \bar{i}_f during t_{cl} according to:

$$\bar{i}_f = \frac{1}{t_{cl}} \int_{t_1}^{t_1+t_{cl}} (i_f)_t dt = i_{cl} - \int_0^{t_{cl}} \exp(-t/\theta C_d) dt \quad (21)$$

Taking $D_{Ox} = D_R = D$, the corresponding concentration variation Δc for both Ox and R follows from the well-known Sand equation¹²:

$$\Delta c = (2\bar{i}_f/nF) (t_{cl}/\pi D)^{\frac{1}{2}} \quad (22)$$

The following values are assumed: $D_{Ox} = D_R = D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $c_{Ox}^* = c_R^* = c^*$, $n=2$, $T=25^\circ\text{C}$, $C_d = 25 \times 10^{-6} \text{ F cm}^{-2}$ and for t_{cl} a minimum value of 50 ns. The value of 2.0 mV for $[(\eta_c)_{t_1} - \eta_{eq}]$ corresponds, simply according to Nernst' law, to a 16% alteration in the ratio c_{Ox}/c_R at the electrode surface and, for not too high values of $(\eta_c)_{t_1}$, approximately to $\Delta c_{Ox} = \Delta c_R = 0.08 c^*$. Inserting this in (22) and taking $c^* = 10^{-6} \text{ mol cm}^{-3}$, \bar{i}_f is found to be 0.2 A cm^{-2} . The charging current necessary to change the potential across C_d by 4.0 mV within the time interval t_{cl} , is 2 A cm^{-2} which is thus about 90% of the total current. Applying (21) and using (5), a minimum value of θ is obtained, corresponding to a rate constant k_{sh} of 7 cm s^{-1} . The determination of C_d by means of (16) involves a systematic error of only 10% as 90% of q_{cl} is utilized to discharge C_d . This also justifies the assumption that the influence of the error in C_d on the k_{sh} evaluated is negligible in relation to the error caused by decrease of concentration polarization.

In the present example a value for $\Delta\eta_T$, the main error under (b), can be found by assuming that the relaxation process between t_1 and $t_1 + \Delta t$ behaves as a capacitance C_d which is discharged through the resistance θ .

Shortly after t_1 the apparent overvoltage across C_d (with regard to the pseudo-equilibrium potential, defined by c_{Ox}/c_R at that moment) is equal to the charge transfer overvoltage $(\eta_a)_{t_1}$, being 2.0 mV. The corresponding $\Delta\eta_T$, equal to 1.4 mV, is a minimum value because of the fact that the RC-model does not account for additional rises in the pseudo-overvoltage caused by concentration changes during t_1 and $t_1 + \Delta t$. This value already represents a large proportion of the initial 2.0 mV and $\Delta\eta_T$ is therefore likely to be considerably higher. However, it will not exceed the maximum value of 2.4 mV which is prescribed by the initial slope in the η, t relaxation curve.

The same reasoning also applies to the influence of Δt on the observed η_{eq} which will always be smaller than $\Delta\eta_T$ because $(d\eta/dt)$ is made close to zero so that there is no pseudo-overvoltage. Furthermore, there will always be a tendency to extrapolate the observed η, t curve back to t_2 and to adjust i_{cl} such that $(d\eta/dt)_{t_2}$ —rather than $(d\eta/dt)_{t_2+\Delta t}$ —is zero. An exact calculation of $\Delta\eta_{eq}$ would be possible by means of the complete voltage–time relation for a GRC response but considering the minor influence of $\Delta\eta_{eq}$ we will confine ourselves to an estimation. Making allowance for the maximum extra variation in $\Delta\eta_T$, 1.0 mV, a value of 0.5 mV for $\Delta\eta_{eq}$ seems quite reasonable.

Adding all the errors caused by faradaic leakage between t_1 and the time of measurement, it is obvious that in the case of the c^* chosen, the two main and opposite sources of error, $[(\eta_c)_{t_1} - \eta_{eq}]$ and $\Delta\eta_T$, are about equal. This is represented schematical-

ly in Fig. 6a and b where the faradaic current beyond t_1 is outlined for a GRC and for a classical galvanostatic pulse experiment. In GRC the polarity of (di_f/dt) again changes sign at t_2 (see Fig. 6a) and this gives the appearance that the deviation $[(\eta_c)_{t_1} - \eta_{eq}]$ is somewhat compensated between t_2 and $t_2 + \Delta t$. However, the reversed faradaic current only arises because i_{c1} is chosen (apart from faradaic "loss" between t_1 and t_2) too high in order to make $(d\eta/dt)_{t_2 + \Delta t}$ zero instead of $(d\eta/dt)_{t_2}$. A horizontal tangent at t_2 would require a lower coulstatic charge and for this reason $\Delta\eta_{eq}$ does not partially compensate $[(\eta_c)_{t_1} - \eta_{eq}]$ but represents another error acting in the same direction. In the case of the present example, η_{eq} is thus lowered by, in total, about 2.5 mV, and η_T by roughly 1.5–2.5 mV leading to an observed value between 2.0 and 3.0 mV for $(\eta_T - \eta_{eq})$. The computed value of the rate constant will on average be 25% too small and for still higher rate constants the uncertainty will evidently increase.

It should be emphasized that evaluation of C_d using (16) now leads to serious errors. The applied charge injection q_{c1} : (i) corresponds to a total potential difference of 4.0–4.5 mV instead of the observed 2.0–3.0 mV and (ii) is not fully (about 90%) utilized to discharge C_d . It is easily seen that the value of C_d will be found too high by about a factor of two. If C_d is known beforehand, (15) should be used to calculate i_0 , inserting the correct C_d . If the value of C_d is not available, or known to be seriously affected by the presence of an extremely reversible redox couple, its value could still be estimated by extrapolating the η , t curve for the galvanostatic relaxation back to t_1 , thus approximating η_T . In this way the uncertainty will be reduced to about 25%. The constancy of $q_{c1}/(\eta_T - \eta_{eq})$ now being doubtful, an experimental check on the reliability of the evaluated k_{sh} could very well be performed by variation of t_{c1} which strongly influences $[(\eta_c)_{t_1} - \eta_{eq}]$.

With regard to the limitations mentioned under (c) it can be stated that modern pulse generators are sufficiently powerful to meet the requirements of the example chosen:

(i) a galvanostatic pulse with an amplitude such that, after the chosen time interval t_g , an overvoltage of 2.0 mV has been built up across the minimum θ of about 0.3Ω (for a HMDE).

(ii) a coulstatic impulse with a width not exceeding 50 ns, representing a charge of 3.5×10^{-9} C.

The inaccuracy of oscilloscope readings and, combined with this, the experimental difficulty of observing a horizontal tangent at t_2 , determine the accuracy of the GRC method for moderately fast electrode reactions. As limiting factors controlling the potentialities of the method, they can be neglected with respect to the other sources of error.

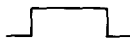


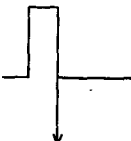
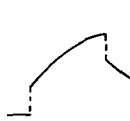
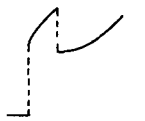
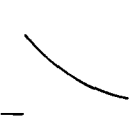
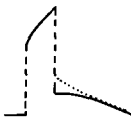
Summarizing, we may conclude that there are two main errors both of which represent an unwanted faradaic relaxation process for roughly the same time interval. Because of their opposite signs and equal orders of magnitude, the maximum rate constant that could be evaluated within 50% accuracy is about 10 cm s^{-1} . Extensive treatment of experimental details and a verification of the method will be given in a separate paper¹³.

CLASSIFICATION

Very recently, Rangarajan¹⁴ classified the existing linear relaxation methods

according to the number of input parameters. In this "parametric approach" the galvanostatic pulse (GP) and the coulostatic impulse (CI) method are examples of one-parameter methods because in the former the current and in the latter the charge only can be varied. The galvanostatic double pulse (GDP) method involves three input parameters *viz.* the magnitudes of the two pulses and the duration of the first pulse. In analogy with this, the proposed GRC method is easily fitted into this scheme as a 3-parameter method with i_g , t_1 and q_{cl} as input parameters. Table 1 gives a survey of the most important characteristics of the galvanostatic single and double pulse methods as constant current relaxation methods, the coulostatic charging impulse method and the new mixed-pulse GRC method which combines a constant current pulse with a charging impulse. In GRC evaluation of the kinetic parameters

TABLE 1

Technique	GP (galvanostatic single pulse)	GDP (galvanostatic double pulse)	CI (coulostatic impulse)	GRC (galvanostatic reversed coulo- static)
number of input parameters	1	3	1	3
input parameters	i_g	i_{g1} , t_1 , i_{g2}	q_{cl}	i_g , t_1 , q_{cl}
input signal: i as $f(t)$				
response signal: η as $f(t)$				
constraints	—	adjust i_{g1} and i_{g2} such that $(d\eta/dt)_{t_1} = 0$	—	adjust i_g and q_{cl} such that $(d\eta/dt)_{t_2} = 0$
features	transient analysis	analysis of η_{t_1} as a function of t_1	transient analysis	charge transfer overvoltage is obtained directly
elimination of: ohmic drop (iR)	—	—	iR	iR
mass transfer polarization (m.t.)	—	—	—	m.t.
double layer charging current (i_c)	—	i_c	—	—

is indirectly affected by the double layer capacitance because of its presence in the expressions for $(i_t)_{t_1}$ (eqns. (8) and (15)). To remove this complication completely, the GDP method, as a means of measuring $(i_t)_{t_1}$ directly, could be combined with the GRC method in order to determine the corresponding charge transfer overvoltage.

In conclusion, the most interesting features of the proposed GRC method will be compared with the other pulse methods mentioned:

(a) The experimental work is more complicated than with GP or CI and also more extensive than with GDP. Two pulse generators are needed but compensation of the ohmic drop, which requires the accurate adjustment of a variable resistor¹⁵, is not necessary as the measured overvoltages do not contain contributions from the ohmic resistance.

(b) The electrolysis time t_g , especially in the case of fast electrode reactions, is chosen so short that the exposed electrode has been relaxed within a comparatively short time. This means that in one second a number of pulses can be forced through the cell without affecting the initial (equilibrium) conditions. Thus a repetitive signal can be applied to the cell and the response can be read from the oscilloscope screen without photographic recording.

(c) At the cost of a relatively small extension of experimental work, the elaboration of the data obtained has been greatly simplified. The possibility of eliminating concentration polarization led to a confining of the calculus to the explicit eqns. (15) and (17) for i_0 . Compared with GDP, this elimination implies the presence of C_d in these equations. As stated above, the combination of GRC with GDP would completely remove the double layer influence.

(d) The value obtained for the differential double layer capacity C_d pertains, as with the kinetic data, to the situation at the electrode as it exists at time t_1 . At this moment the electrode is not at equilibrium but in a polarized state where the surface concentrations of Ox and R are generally different from the bulk values but readily calculable from η_{eq} . Especially in the case of a solid electrode system, where the "adatom capacity" C_p has an important role, the possibility of determining C_d *in situ* after a well-defined electrolysis seems promising.

(e) The elimination of mass transfer polarization has the additional result that the condition of linearity for the electrode process applies only to the charge transfer part of the total overvoltage. This means that, except when α or $(1 - \alpha)$ is close to unity, $(\eta_a)_{t_1}$ is allowed to be of the order of a few mV where the simple, linear eqn. (10) still holds. Also, it is no longer necessary to keep the equilibrium potential close to the half-wave potential as is required when overvoltages that contain a dominant contribution from mass transfer polarization are analyzed. This feature offers, for instance, the possibility of studying an electrode reaction of the type $Me^{n+} + ne \rightleftharpoons Me$ which is less feasible for other pulse methods.

(f) In the case of very fast electrode reactions the two main sources of error partly cancel out thus permitting distinctly higher rate constants to be measured than is possible with GP, CI or GDP¹⁶.

(g) Finally it should be emphasized that the only purpose of the galvanostatic pre-pulse is to build up a certain overvoltage and that it should be chosen such that $(i_t)_{t_1}$ and $(\eta_a)_{t_1}$ have optimum values. Clearly, any other input signal that could bring about the same situation would do just as well. For instance a coulostatic double impulse method could be envisaged where a coulostatic pre-pulse is, after some time

interval, followed by another coulостatic impulse with necessarily reversed sign and carrying less charge. The essence of the method would remain unchanged except that the determination of $(i_f)_{t_1}$ would be different because this parameter is associated with the cell response at time t_1 , that is at the end of the pre-pulse.

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SUMMARY

A new double pulse method is presented in which a galvanostatic pre-pulse is followed by a coulостatic impulse with reversed sign. The coulостatic charge density selected is such that the overvoltage–time curve starts with a horizontal tangent after the impulse has ceased. As both the net current through the cell and the charging current through the double layer capacity are zero, the faradaic current must also be zero. This allows the elimination of both concentration polarization and ohmic drop so that the charge transfer overvoltage is obtained directly. The method, denoted as GRC, is mainly distinguished by very simple analysis of experimental data and good potentialities. In addition it seems to be especially promising for the study of electrode processes where determination of double layer capacity *in situ* is vital.

LIST OF SYMBOLS

i_c	charge current density
i_{cl}	coulостatic current density
i_f	faradaic current density
\bar{i}_f	mean faradaic current density
i_g	galvanostatic current density
i_t	total current density
q_{cl}	coulостatic charge density
t	time
Δt	time region during which the overvoltage is obscured by transients
t_{cl}	coulостatic impulse width
t_g	galvanostatic pulse width
t_0	time at which the galvanostatic pulse starts
t_1	time at which the galvanostatic pulse ends
t_2	time at which the coulостatic impulse ends
η	overvoltage
η_a	charge transfer overvoltage
η_c	mass transfer overvoltage
η_{eq}	overvoltage in the pseudo-equilibrium state
$\Delta\eta_{eq}$	variation in η_{eq}

- η_T total overvoltage at time t_1
 $\Delta\eta_T$ variation in η_T
 η_Ω overvoltage invoked by ohmic resistance

All the other symbols have their usual meaning; if necessary, see ref. 2.

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