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The Current-Impulse Relaxation Technique and the Kinetics of Rapid Electrochemical Reactions. I. General Considerations

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The current-impulse relaxation technique, which extends the time domain experimentally accessible to kinetic investigations and permits direct assessment of charge-transfer kinetics without mass-transport polarization of the interphase, is described. The electrochemical system is displaced from equilibrium by a constant current impulse of restricted duration relative to the system relaxation time. From the slope of the charging curve and the value of the applied current density the differential capacitance is directly calculated; the subsequent relaxation of the overpotential is directly related to the kinetics of the faradaic process through which relaxation proceeds. By drastic restriction of the coulombic content of the impulse and reduction of the time interval before relaxation data are acquired, the kinetic parameters of the charge-transfer process are found without correction for mass-transport contributions. As a consequence of its conceptual and experimental simplicity, the technique offers operational and interpretive advantages over other methods.

Introduction

A dominant characteristic of the development of the study of the rates and mechanisms of electrochemical reactions through the past decade has been the introduction of techniques by which ever more rapid processes may be investigated. The fundamental problem in the extension of these techniques to the investigation of very rapid electrochemical processes is the difficulty of discrimination between the kinetic effects of charge-transfer and mass-transport processes. Satisfactory resolution of this problem requires the establishment of well-defined boundary conditions in the electrode-electrolyte interphase, appropriate to the direct application of a solution to the corresponding boundary-value problem for the mass-transport contribution to the over-all process.

The step-functional transient relaxation techniques² offer distinct limitations in imposing the definition of boundary conditions required for the study of very rapid reactions, and they involve practical difficulties of observation of the resulting system response at sufficiently brief intervals following the perturbation. That both of these limitations might be avoided if the perturbation was an impulse rather than a step function was recognized in the proposals of Reinmuth

and Wilson³ and of Delahay^{4,5} that the charge-step technique⁶ be applied to the study of rapid electrochemical reactions. In a charge-step experiment, the potential of the electrochemical cell under study is observed in response to a very brief impulse of undefined form but of known coulombic content. Because for a sufficiently abrupt pulse the transient impedance of the capacitive double layer is quite small relative to the partially resistive faradaic impedance, the double layer is charged to a new potential before appreciable

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(2) For a thorough review, see P. Delahay, *Advan. Electrochem. Electrochem. Eng.*, **1**, 233 (1961). A more recent appraisal is given by W. H. Reinmuth, *Anal. Chem.*, **36**, 211R (1964).

(3) W. H. Reinmuth and C. E. Wilson, *ibid.*, **34**, 1159 (1962); W. H. Reinmuth, *ibid.*, **34**, 1272 (1962).

(4) P. Delahay, *ibid.*, **34**, 1161 (1962).

(5) P. Delahay, *J. Phys. Chem.*, **66**, 2204 (1962).

(6) P. Delahay and D. M. Mohilner, *J. Am. Chem. Soc.*, **84**, 4247 (1962); P. Delahay and D. M. Mohilner, *J. Phys. Chem.*, **66**, 959 (1962); P. Delahay, *ibid.*, **67**, 135 (1963). It is to the study of adsorption processes, with which these papers deal, that the technique owes an alternative (if not generally applicable) name, the "coulostatic" method. The more satisfactory designation "charge-step" is also due to Delahay, although its use was not preferred by him.

charge is consumed by the faradaic process. If the impulse is applied in such a manner that the cell is decoupled from the pulse source upon termination of the impulse, the double-layer capacitance is effectively in series only with the faradaic impedance and dissipation of the excess charge of the double layer can occur only as charge is consumed progressively by the electrode reaction. The relaxation of the overpotential from the initial value imposed by the impulse as the system approaches equilibrium is directly related to the kinetics of the reaction through which relaxation proceeds.

If the duration of the coulombic impulse is restricted to a time quite small relative to the relaxation time constant, the boundary conditions at the initiation of relaxation are well defined on the time scale of the relaxation process. Because the perturbation is of impulse rather than step-functional form, no ohmic correction of the overpotential response observed during relaxation is required. The very large ohmic drop across the cell during the interval of the impulse may drive the detector amplifier into saturation, however, and its recovery may be slow; extended transient oscillation due to stray inductance and capacitance present in cells of conventional design and to coupling capacitance also may prohibit reliable measurements for a significant interval following the impulse. Each of the published kinetic investigations in which the charge-step technique has been applied has demonstrated this restriction from measurements at short times: the experimental studies of Zn(II)-Zn(Hg) by Delahay and Aramata⁷ and by Hamelin⁸ and those of Bi(III)-Bi(Hg) by Hamelin⁹ graphically depict measurements to 5 μ sec. Reinmuth and Wilson³ reported satisfactory relaxation behavior at times greater than 2 μ sec following an impulse.

This prohibition from short time measurements imposes a distinct upper bound upon the rate of processes which can be examined. For adequate sensitivity and to assure applicability of the mass-transport equations, measurements of response must be initiated at times of the order of the time constant of the relaxation process. For a simple R-C model of the electrode process, as appropriate to the description of a small-amplitude relaxation through a simple charge-transfer reaction, assuming a nominal differential capacitance of 20 μ f cm⁻², a 2- μ sec time constant for the discharge of a univalent ion corresponds to a maximum value for the apparent exchange current of approximately 0.2 amp cm⁻². The restriction from short time measurements also necessitates an extended extrapolation of the observed response to $t = 0$ for the determination of the perturbation overpotential η_0 . The resulting uncertainty in η_0 is reflected in the value calculated for the differential

capacitance and leads to a substantial uncertainty in the calculated apparent exchange current.

The current-impulse relaxation technique was conceived to permit direct assessment of differential capacitance and to extend the time domain accessible to impulse relaxation measurements.

The Current-Impulse Relaxation Technique

In a current-impulse relaxation experiment, electrode potential is observed as a function of time in response to a constant-current pulse of brief duration; the technique is a direct but significant refinement of the charge-step technique in which a rectangular coulombic pulse replaces the "pseudoderivative" pulse of the charge-step method as the forcing function.

The response to such a perturbation may most conveniently be analyzed in terms of an equivalent linear network consisting of the electrolyte resistance, R_e , in series with the parallel combination of the capacitance of the double layer, C_1 , and the faradaic impedance. The faradaic impedance, in the time domain, is a series combination of charge-transfer resistance, R_c , and time-dependent mass-transport impedance, $Z_m(t)$. In the short time limit, or for negligible perturbation, the mass-transport contribution to the faradaic impedance vanishes, and the customary simplified network results. The behavior of the parallel arms is described by the equation

$$i_p = C_1(d\eta/dt) + \eta/R_c \quad (1)$$

where i_p is the external (pulse) current, η the overpotential, and t the time. The contribution of the electrolyte resistance, R_e , in series with the parallel arms is specified by the expression

$$\xi = i_p R_e + \eta \quad (2)$$

where ξ is the observable displacement of the cell potential from its equilibrium value. From the initiation of the constant-current impulse, charging response is given by

$$d\xi/dt = d\eta/dt = (i_p/C_1) \exp(-t/R_e C_1) \quad (3)$$

At the instant of impulse termination ($t = T$) the ohmic component of the observed potential vanishes, and only the perturbation overpotential, symbolized by η_0 , remains

$$\eta_0 = i_p R_c [1 - \exp(-T/R_e C_1)] \quad (4)$$

If following the impulse the cell is essentially at open circuit, the observed response must be simply

$$\xi = \eta = \eta_0 \exp[-t/R_e C_1] \quad (5)$$

(7) P. Delahay and A. Aramata, *J. Phys. Chem.*, **66**, 2208 (1962).

(8) A. Hamelin, *Compt. Rend.*, **257**, 1709 (1963).

(9) A. Hamelin, *ibid.*, **259**, 362 (1964).

where the origin at the time axis is redefined at the instant of impulse termination.

During the current pulse, the slope of the charging curve, $d\xi/dt$, must be i_p/C_1 for measurement times much less than the time-constant product $R_c C_1$; from the experimentally observed linear charging slope in the short time limit and the measured value of the impulse current, the differential capacitance is directly calculated.¹⁰ The capacitance can also be estimated from the relaxation plot, as with the charge-step method. Determination of R_c is made directly from the relaxation response of the system: a plot of $\ln \xi$, against t yields a slope $-(1/R_c C_1)$; with the value of C_1 assessed from the charging slope, R_c is calculated. Because this analysis requires only a determination of the slope of the logarithmic plot, and not its intercept at $t = 0$, there is no need for precise experimental definition of $t = 0$. Over the small excursions of potential for which the analysis is valid, the current-overpotential characteristic may be linearized; the charge-transfer resistance is then

$$R_c = \nu_d R T / n f i_a^0$$

where ν_d is the stoichiometric number for the rate-determining step, R is the gas constant, T the absolute temperature, n the number of electrons per unit advancement of the over-all electrochemical reaction, f the faraday, and i_a^0 represents the apparent exchange current density. Where this simple model is applicable, the exchange current density of a process is directly calculated from the value of R_c obtained from relaxation data if a value of n/ν_d is assumed or evaluated (*e.g.*, by analysis of the current overpotential characteristic over an extended potential range). Analysis of the dependence of exchange current density upon the concentration(s) of the reactant species in accordance with an electrochemical reaction-order treatment yields a value for the transfer coefficient of the charge-transfer reaction.

Application of an analysis which neglects the contribution of mass transport to the faradaic impedance requires that the concentrations of reactant and product be constrained to negligible changes in the course of a relaxation measurement. This requirement is implemented in the current-impulse technique by a drastic restriction of the quantity of charge transferred in each experiment and by a substantial reduction in the time interval between pulse termination and acquisition of the first reliable relaxation data.

Experimental Considerations

Operationally, a current-impulse relaxation experiment requires first that the charge density of the test

electrode be abruptly changed from its equilibrium value by a constant-current impulse of time duration negligible with respect to the time constant of the relaxation process in such a way that the cell is essentially at open circuit when the charging is completed, and second, that some means be available for observation of the resulting displacement of the electrode potential and its relaxation as the system approaches equilibrium.

To supply the current impulse to the cell, a fast-rise dc-coupled pulse generator with high output impedance and moderately high output voltage capability is required. The instrument used in exploratory studies was the General Radio 1217-B pulse generator with its associated 1201-B power supply. The dc component normally present at the positive output of this instrument was removed by a simple diode clamp. The pulse generator was coupled to the cell through a 1-kilohm load resistor to assure constant impulse current and two 1N-914 switching diodes with polarity appropriate to pass a pulse but to reject counterflow of current. This method of coupling offers the additional advantage relative to capacitive coupling of substantially decreasing the settling time of the series R - L - C loop to which the input circuit is equivalent. The settling time increases with increasing LC product for the loop; with diode coupling L is the inductance of cell leads and electrode geometry and C is essentially the decoupling diode interelectrode capacitance, 5 pf or less, while for capacitive coupling the inductance is equivalent but the capacitance becomes that of the coupling capacitor, typically of the order of 500 pf. The decreased settling time with diode coupling manifests itself in substantially abbreviated post-impulse ringing.

With this input arrangement, current pulses continuously variable in amplitude from 0 to 20 ma and of duration as brief as 100 nsec were applied to the cell.

The overpotential response to the constant-current perturbation was amplified by a Tektronix 1121 amplifier (rise time 21 nsec). Although the limitation of its first amplification stage is nominally 10 mv, the unit recovers quickly from overload. The amplified signal was cabled to a Tektronix 535A sweep-delay oscilloscope with a type H plug-in preamplifier (rise time 31 nsec). The delayed trigger output pulse of the oscilloscope was used to trigger the pulse generator and the

(10) Measurement of the "initial slope" of the overpotential response of a system to a constant-current pulse, first reported by F. P. Bowden and E. K. Rideal, *Proc. Roy. Soc. (London)*, **A120**, 59, 80 (1928), has been extensively applied in determinations of differential capacitance in the presence of irreversible or quasi-reversible electrochemical reactions. The present technique simply extends this procedure to the class of highly reversible processes.

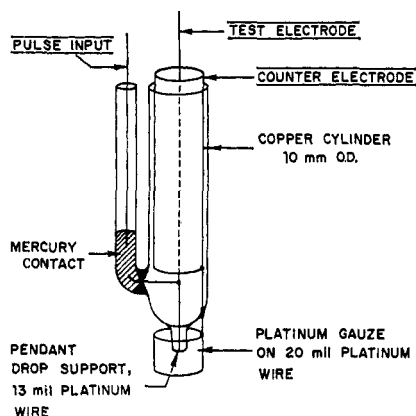


Figure 1. Low-inductance two-electrode probe with auxiliary pulse input for current-impulse relaxation measurements.

experiment was controlled by the oscilloscope time base "A." Single-sweep triggering was employed to avoid significant polarization.

With this system, an over-all deflection sensitivity as great as $50 \mu\text{V cm}^{-1}$ was achieved on a 100-nsec cm^{-1} time base. With appropriate calibration, current, overpotential, and time can be measured with an accuracy of 1%. Charging curves and relaxation response were recorded photographically with a Tektronix 350/C 35-mm camera system using Kodak Tri-X (ASA 400) film.

The transient response observed during and following an abrupt perturbation of a reactive system is relatively sensitive to the effects of stray capacitance and inductance, which may increase rise time and introduce extended ringing; to optimize response, an adaptation of the coaxial two-electrode configuration proposed by Blomgren, Inman, and Bockris¹¹ was employed. The two-electrode probe is illustrated in Figure 1. The pulse current is applied through the auxiliary contact to the test electrode, with the shield held at ground, and the response is observed between the inner conductor and the shield. In principle, there is no inductive coupling between the pulse input lead and the potential-measuring part of the system since the output lead is external to the shield. The mutual inductance between the shield and the inner conductor and the self-inductance of the shield cancel with the result that the over-all inductance of the cell is reduced to that of the loop: test electrode-counter electrode-shield.

The effect of electrolyte resistance upon the observed current-impulse response also may be substantial; as a consequence of the high current level of the impulse, the detection system is subjected to a voltage pulse which may be many times the magnitude of the

overpotential to be observed subsequent to the impulse (for $R_e = 5$ ohms, for example, up to 100 mv). Although iR compensation would provide the most direct solution to this problem, the recovery time of the detection system for overloads of such brief duration was of the order of 200 nsec, so an iR compensation scheme was not required.

The system 10–90% rise time was less than 100 nsec; however, overshoot and transient ringing due to uncompensated inductance and stray capacitance prohibited reliable ($\pm 100 \mu\text{V}$) observation of relaxation for an interval of up to 400 nsec following termination of the current pulse. Ringing was evident only following the pulse and did not obscure charging response. With excessive overload of the 1121 amplifier, however, the charging slope is suppressed, and care must be taken that the input attenuation is adequate to eliminate this distortion. System noise was observed to be of the order of $50 \mu\text{V}$ peak-to-peak; no interference by line frequency noise is possible over the time scale of a measurement.

Applicability and Scope

The unique advantage of the current-impulse relaxation technique has been identified as its capability for assessing the kinetic parameters of an electrochemical charge-transfer reaction directly, without correction for mass-transport polarization of the electrode-electrolyte interphase. The compatibility of a strict limitation of the charge passed in an experiment with the generation of experimentally significant response can be demonstrated in terms of the capabilities of the measurement system described.

If one estimates that the magnitude of the perturbation overpotential, η_0 , must be 5 mv to assure accurate relaxation measurements, a perfectly polarizable electrode with a differential capacitance of $20 \mu\text{F cm}^{-2}$ will require a 1×10^{-7} coulomb cm^{-2} impulse to assume this overpotential. This corresponds, for deposition of a univalent ion from solution, to approximately 0.05% of a monolayer, assuming 10^{16} deposition sites cm^{-2} . Even with this quite conservative estimate of the detection sensitivity, the polarization should introduce only a negligible mass-transport contribution to the observed overpotential at short times. Because the effects of mass-transport polarization are relatively more pronounced at longer times, examination of a semilogarithmic plot of the relaxation data for linearity permits immediate confirmation that these effects are inappreciable in the time interval of observation.

The maximum rate of an electrochemical reaction

(11) E. Blomgren, D. Inman, and J. O'M. Bockris, *Rev. Sci. Instr.*, **32**, 11 (1961).

which can be investigated with the current-impulse relaxation technique may be directly calculated. Two sets of limiting conditions are involved, the minimum conditions for adequate assessment of the value of C_1 during charging and the condition of a sufficient overpotential at the time of impulse termination to permit satisfactory analysis of the relaxation response. If one assumes that a satisfactory "initial slope" determination of the capacitance can be made if the time constant of the relaxation process, $R_c C_1$, is greater than twice the duration T of the impulse (cf. eq 3), the requirement $T > 0.2 \mu\text{sec}$ based upon a typical 80-nsec system rise time yields directly the over-all condition $0.2 \mu\text{sec} < 0.5 R_c C_1$, or $R_c C_1 > 0.4 \mu\text{sec}$. The specification that the time constant of the process must be greater than $0.4 \mu\text{sec}$ is also compatible with the $0.4\text{-}\mu\text{sec}$ interval following pulse termination before reliable relaxation data can be recorded: the overpotential at one time constant must be η_0/e , or for $\eta_0 = 5 \text{ mv}$, almost 2 mv , which is certainly adequate to assure accurate measurements. For a nominal differential capacitance of $20 \mu\text{f cm}^{-2}$ the restriction on the relaxation time constant corresponds to a minimum charge-transfer resistance of 0.02 ohm cm^2 . What might be a more severe limitation on the minimum value of R_c arises as a consequence of the 20-ma maximum pulse current of the apparatus described. Applying the condition $T < 0.5 R_c C_1$ to eq 4

$$\eta_0 < i_p R_c [1 - \exp(-0.5)] = 0.4 i_p R_c$$

if, as before, a minimum value of 5 mv is required for η_0 , then $i_p R_c > 0.0125 \text{ v}$. For $i_p = 20 \text{ ma}$, this places a minimum value of 0.625 ohm on R_c . With an impulse current of 20 ma applied to an electrode of surface area 0.01 cm^2 , $R_c \geq 0.00625 \text{ ohm cm}^2$, corresponding, for η/ν_d assumed to be unity, to a maximum exchange current density of approximately 4 amp cm^{-2} . Thus within the range of parameters experimentally attainable with commercial instrumentation, the current-impulse technique permits determinations of the kinetic parameters for electrochemical reactions about one order of magnitude more rapid than have been investigated with other transient relaxation methods.

The simplicity and power of the current-impulse relaxation technique promote its applicability to a wide range of problems in electrochemical kinetics and the elucidation of the mechanisms of electrode processes. The direct determination of differential capacitance in conjunction with kinetic measurements suggests application of the technique to the study of the dynamic properties of the electrochemical double layer and the influence of the double layer upon charge-transfer kinetics. Work is proceeding in each of these areas and detailed examinations of the kinetics of model metal deposition and oxidation-reduction reactions are underway.

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