

ON SECOND ORDER EFFECTS IN A GALVANIC CELL

PART I. POLARIZATION BY A SINE WAVE MODULATED HIGH FREQUENCY CURRENT*

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(Received 11th January 1975)

INTRODUCTION

The faradaic rectification method, introduced by Doss and Agarwal¹ and further elaborated by Barker² and Delahay *et al.*³, is, next to second harmonic polarography⁴, the best known second order technique; it is useful both for electroanalytical purposes and for the study of electrode processes. Nevertheless, the number of applications is still quite small, most probably because of the complexity of the theory and the difficulties inherent to the experimental procedure.

Concerning the latter, one has to deal with the evaluation of the rectification voltage which is relatively small as compared with the amplitude of the applied a.c. voltage, with hum and with fluctuations in the mean electrode potential caused by drop growth, changes in temperature, etc. The high frequency a.c. voltage needs to be separated from the rectification voltage by means of filters that should be absolutely free of any spurious rectification effects. In order to distinguish the rectification signal from the other, slower, fluctuations (and to minimize heating of the solution), the HF polarizing current is usually chopped into short trains of sine waves, obtained either by mechanical switching or by modulating the sine wave generator with pulses of a milliseconds duration. The resulting pulse-shaped rectification signals can be measured on the screen of an oscilloscope.

However, this chopping technique introduces an extra complication into the theory, because the charging of the double layer, involved in the change of interfacial potential, is usually not completed within the short times during which the polarizing current is applied to the cell. Consequently the measured rectification signal is a complex function of time, as has been derived by Delahay *et al.*³.

Generally, an amplitude modulated perturbation signal, *e.g.* a current, can be represented by⁵

$$i = i_A [\varphi(t)] \sin \omega_0 t \quad (1)$$

where $i_A \sin \omega_0 t$ is the unmodulated current and $\varphi(t)$ is an arbitrary function of time. As mentioned before, in the faradaic rectification technique $\varphi(t)$ has the shape of a repetitive pulse, but for the purpose of measuring the rectification effect, any

* Dedicated to Prof. K. S. G. Doss on the occasion of his reaching his 70th year.

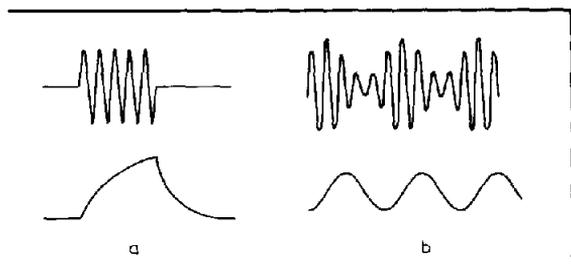


Fig. 1. High-frequency polarizing currents and demodulation responses for pulse modulation (a) and sine-wave modulation (b).

other repetitive or periodic function may be applied. An obvious alternative is a sinusoidal modulating function: $\varphi(t) = 1 + m \cos \omega_m t$. Then the technique becomes similar to the demodulation technique, known from publications by Brocke⁶ and Zheleztsov⁷. These authors described the *demodulation current* flowing through a cell which is perturbed by a *sinusoidally amplitude-modulated voltage*, superimposed on a d.c. ramp; the technique is called demodulation polarography (see Fig. 1).

As compared with the pulse-modulated rectification technique the sine wave-modulated technique has the interesting advantage that the demodulation signal can be measured with the aid of modern synchronous detection instead of the old-fashioned oscilloscopic measurements. However, the theory developed by Brocke⁶ is limited to very fast electrode reactions that are still reversible at the high frequencies of the polarizing voltage usually applied, whereas the more general expressions given by Zheleztsov⁷ for the faradaic current are extremely complicated. In comparison with this, the theory for faradaic rectification polarography, developed by us to express the rectification *voltage response* of a cell to a sine wave *current perturbation*, is relatively simple. Moreover, in this case the electrical set-up is also relatively simple, because no high-frequency potentiostat is needed, as opposed to a set-up for voltage perturbation.

Because, essentially, a voltage response to a current perturbation provides the same information as a current response to a voltage perturbation³⁻⁵, we considered it worthwhile to approach the demodulation technique starting from the former principle. In this paper this will be done on the basis of the analogy with the rectification technique, whereas more general considerations will be presented in a succeeding paper.

THEORY

(1) *The theory of faradaic rectification polarography*

In this section we will summarise briefly the theory of faradaic rectification, as far as it is relevant for our purpose. As has been done previously, we will assume that there is no coupling between the charging of the double-layer and the faradaic process.

Analysis of the processes occurring at the electrode after the start of the polarizing current is usually done in terms of two limiting cases.

(i) If there were no double-layer capacity shunting the faradaic process, the

faradaic rectification voltage ΔE_F could be measured directly across the electrode, provided that the impedance Z_F of the cell is negligible with respect to the input impedance of the measuring circuit.

(ii) If there were no electrode reaction, the charging of the double-layer would involve a non-faradaic rectification voltage ΔE_C , which is also built-up immediately, provided the rectification current is prevented from flowing by the high input impedance of the measuring circuit.

Normally both processes are in parallel with each other (see Fig. 2). Then we may describe the situation after the start of the polarizing a.c. current as though the two ideal voltage sources ΔE_F and ΔE_C are switched on simultaneously⁸. Consequently two currents Δi_F and Δi_C are generated, which can be expressed in terms of the processes accompanying them:

(i) The faradaic current Δi_F can be considered as the first order response to the "perturbation" $-(\Delta E_F - \Delta E_M)$ (see Fig. 2), accompanied by the changes in surface concentrations Δc_O and Δc_R :

$$\Delta i_F = -\frac{\partial i}{\partial E}(\Delta E_F - \Delta E_M) + \frac{\partial i}{\partial c_O} \Delta c_O + \frac{\partial i}{\partial c_R} \Delta c_R \quad (2)$$

where Δc_O and Δc_R are functions of Δi_F , given by the well-known integral equation

$$nF\Delta c_i = \pm(\pi D_i)^{-\frac{1}{2}} \int_0^t \Delta i_F(t-u)^{-\frac{1}{2}} du \quad (3)$$

in the case of mass transport by semi-infinite linear diffusion.

(ii) The current flowing through the double-layer capacity C_d is given by

$$\Delta i_C = -C_d \frac{d(\Delta E_C - \Delta E_M)}{dt} \quad (4)$$

with $\Delta E_M(t=0) = \Delta E_C$ leading to

$$\Delta E_C - \Delta E_M = -\frac{1}{C_d} \int_0^t \Delta i_C dt \quad (5)$$

(iii) Since no external current is flowing, one has

$$\Delta i_C = -\Delta i_F \quad (6)$$

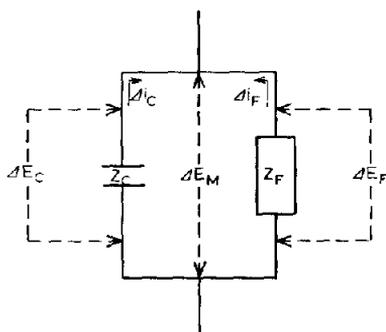


Fig. 2. Equivalent circuit for the combination of ΔE_F and ΔE_C to the measured rectification voltage, c.q. the demodulation voltage.

The solution for ΔE_M from eqns. (2)–(6) has been given by Delahay *et al.*³. It can be written in the form

$$\Delta E_M = \Delta E_F(1 - \tau) + \Delta E_C \tau \quad (7)$$

where for pulse modulation

$$\tau = \frac{(H - G)^{-1}}{\theta C_d} \{ G^{-1} \exp(G^2 t) \operatorname{erfc}(Gt^{\frac{1}{2}}) - H^{-1} \exp(H^2 t) \operatorname{erfc}(Ht^{\frac{1}{2}}) \} \quad (8)$$

where $\theta = (\partial i / \partial E)^{-1}$ is the charge transfer resistance and

$$G, H = 2^{-\frac{1}{2}} \{ (p')^{-1} \pm [(p')^{-2} - 2(\theta C_d)^{-1}]^{\frac{1}{2}} \} \quad (9)$$

In eqn. (9), p' is the irreversibility quotient, equal to

$$p' = nF 2^{-\frac{1}{2}} \left[\frac{\partial i_F}{\partial c_R} D_R^{-\frac{1}{2}} - \frac{\partial i}{\partial c_O} D_O^{-\frac{1}{2}} \right] \quad (10)$$

The solution, given by eqns. (7)–(10), was originally derived for the rectification voltage at electrodes initially in equilibrium. In the case of faradaic rectification polarography we have a d.c. current i flowing through the faradaic branch. Then $\Delta i_F = i - \bar{i}$ and $\Delta c_i = c_i - \bar{c}_i$, where \bar{c}_i is the mean surface concentration of Ox or Red. On the assumption that the concentration gradient caused by the d.c. current is linear and invariable as compared to that of the rectification current ($\partial^2 \bar{c} / \partial x^2 \ll \partial^2 c / \partial x^2$ and $\partial \bar{c} / \partial t \ll \partial c / \partial t$) it can be shown that the first order relations (2) and (3), and thus eqns. (7)–(10), are still valid.

(2) The nature of the rectification voltages

Both ΔE_F and ΔE_C originate from the second order contributions to the series expansions of the $i - E$ characteristics of the faradaic and the non-faradaic branch respectively. In the derivation these second order contributions can all be expressed in terms of $i_F(\omega_0)^2$ and $i_C(\omega_0)^2$, where $i_F(\omega_0)$ and $i_C(\omega_0)$ are the faradaic and the non-faradaic a.c. current with frequency ω_0 , the sum of which is equal to the total current i . Consequently, the rectification voltages can, with a view to eqn. (1), be written quite formally as

$$\Delta E_F = S_F i_A^2 [\varphi(t)]^2 \quad (11)$$

and

$$\Delta E_C = S_C i_A^2 [\varphi(t)]^2 \quad (12)$$

where, with 100% pulse modulation, we have $\varphi(t) = 0$ for $t < 0$ and $\varphi(t) = 1$ for $t > 0$.

The expression for S_F can be given in a more or less explicit form, depending on the way in which the rate equation describing charge transfer is assigned^{2,3,9,10}, and also depending on the mode of mass transfer⁵. The general operator formalism presented by Rangarajan⁵ may be followed, but at present we prefer to confine ourselves to an implicit rate expression $i = f(E, c_O, c_R)$ and the explicit mass transfer equations pertaining to semi-infinite linear diffusion. Then we have for S_F ^{9,10}

$$S_F = -\frac{1}{2}\theta^2 \left\{ \theta \frac{p_0^2 + 2p_0 + 2}{p_0^2} (FF) + \frac{p_0 + 2}{nFp_0(2\omega_0)^{\frac{1}{2}}} [(OF)D_O^{-\frac{1}{2}} - (RF)D_R^{-\frac{1}{2}}] \right. \\ \left. + \frac{1}{n^2 F^2 \theta \omega_0} [(OO)D_O^{-1} + (RR)D_R^{-1} - ORD_O^{-\frac{1}{2}} D_R^{-\frac{1}{2}}] \times \frac{a_0^2}{(p_0 + 1)^2 + (a_0 + 1)^2} \right\} \quad (13)$$

where $(FF) = \frac{1}{2} \partial^2 i_F / \partial E^2$, $(OF) = \partial^2 i_F / \partial c_O \partial E$, $(RF) = \partial^2 i_F / \partial c_R \partial E$, $(OO) = \frac{1}{2} \partial^2 i_F / \partial c_O^2$, $(RR) = \frac{1}{2} \partial^2 i_F / \partial c_R^2$ and $(OR) = \partial^2 i_F / \partial c_O \partial c_R$. Further

$$p_0 = p' \omega_0^{\frac{1}{2}} \quad (14)$$

and

$$a_0 = p' / \theta C_d \omega_0^{\frac{1}{2}} \quad (15)$$

The term in a_0 and p_0 at the end of eqn. (13) represents the relation $|Z(\omega_0)|^2 / |Z_F(\omega_0)|^2$ between the squared amplitudes of the faradaic and the total current.

Similarly, the expression for S_C in eqn. (12), as deduced from the second order expansion of the charge density-potential relationship, reads^{2,9}

$$S_C = -\frac{1}{4C_d} \frac{dC_d}{dE} (C_d \omega)^{-2} \left[1 - \frac{a_0^2}{(p_0 + 1)^2 + (a_0 + 1)^2} \right] \quad (16)$$

where $C_d = dq/dE$ is the double-layer capacity. The term between brackets represents the relation $|Z(\omega_0)|^2 / |Z_C(\omega_0)|^2$ between the squared amplitudes of the capacitive and the total current.

(3) The theory of demodulation polarography

With a sinusoidal modulation function, eqn. (1) may be written as

$$i = i_A [1 + m \cos \omega_m t] \sin \omega_0 t \\ = i_A \sin \omega_0 t + \frac{1}{2} m i_A \sin(\omega_0 - \omega_m) t + \frac{1}{2} m i_A \sin(\omega_0 + \omega_m) t \quad (17)$$

So, the current flowing through the cell is composed of three parts, with frequencies $(\omega_0 - \omega_m)$, ω_0 and $(\omega_0 + \omega_m)$. Consequently the fluctuations in the surface concentrations c_O and c_R will be composed of three terms too, corresponding to these frequencies. The second order response of a non-linear element will consist of contributions at various frequencies:

- (i) zero frequency: rectification effects from the three terms
- (ii) $2(\omega_0 - \omega_m)$, $2\omega_0$ and $2(\omega_0 + \omega_m)$: second harmonics
- (iii) ω_m and $2(\omega_0 - \omega_m)$: intermodulation between $(\omega_0 - \omega_m)$ and ω_0
- (iv) ω_m and $2(\omega_0 + \omega_m)$: intermodulation between ω_0 and $(\omega_0 + \omega_m)$
- (v) $2\omega_m$ and $2\omega_0$: intermodulation between $(\omega_0 - \omega_m)$ and $(\omega_0 + \omega_m)$.

The spectrum of these contributions is represented in Fig. 3. In principle a rigorous derivation of these effects should be set up, inserting the proper expressions for ΔE , Δc_O and Δc_R in the Taylor expansion of the $i - (c_O, c_R, E)$ characteristic. If, however, $\omega_m \ll \omega_0$, it can be said that the modulation function $\varphi(t)$ is varying slowly with time as compared to the carrier function⁵. In that case eqns. (11) and (12) still hold⁵, so that for example, the rectification and demodulation effects become

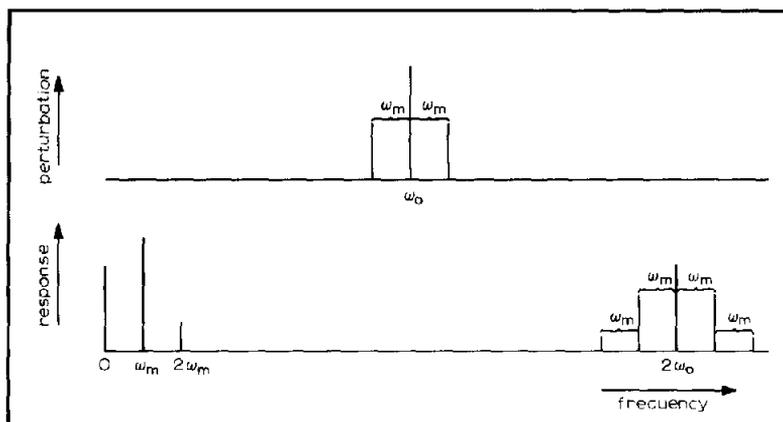


Fig. 3. Spectrum of the applied alternating current and the resulting second-order responses.

$$\overline{\Delta E_{F,C}} = S_{F,C} i_A^2 (1 + \frac{1}{2} m^2) \quad (18a)$$

$$\Delta E_{F,C}(\omega_m) = S_{F,C} i_A^2 \times 2m \cos \omega_m t \quad (18b)$$

$$\Delta E_{F,C}(2\omega_m) = S_{F,C} i_A^2 \times \frac{1}{2} m^2 \cos 2\omega_m t \quad (18c)$$

(4) The resulting demodulation response

Returning to Fig. 2, it will be clear that the same reasoning as in section 1, will be applicable to the *alternating* voltage sources $\Delta E_F(\omega_m)$ and $\Delta E_C(\omega_m)$. However, the problem becomes much simpler when it is realized that ΔE_F is acting as a voltage source with internal impedance Z_F , and ΔE_C as a voltage source with internal impedance Z_C . Since, as in section (1), the currents Δi_F and Δi_C are first order responses to ΔE_F and ΔE_C , Z_F can be identified with the faradaic impedance and Z_C with the double-layer impedance $-j/\omega C$ ($j = \sqrt{-1}$). From Fig. 2 it follows that

$$\begin{aligned} \Delta E_M(\omega_m) &= \Delta E_F(\omega_m) + \Delta i_F(\omega_m) Z_F(\omega_m) \\ &= \Delta E_C(\omega_m) + \Delta i_C(\omega_m) Z_C(\omega_m), \end{aligned} \quad (19)$$

from which, with $\Delta i_F = -\Delta i_C$,

$$\Delta E_M(\omega_m) = \Delta E_F(\omega_m) \frac{Z_C(\omega_m)}{Z_C(\omega_m) + Z_F(\omega_m)} + \Delta E_C(\omega_m) \frac{Z_F(\omega_m)}{Z_C(\omega_m) + Z_F(\omega_m)} \quad (20)$$

For the demodulation effect at frequency $2\omega_m$ the same reasoning applies, and thus eqn. (20) holds using $2\omega_m$ instead of ω_m . After all, Delahay's result for pulse-modulated rectification could also be obtained by considering ΔE_F and ΔE_C as voltage sources with internal operation impedances $Z_F(s)$ and $Z_C(s)$, leading to an equation similar to eqn. (20) for the Laplace transforms of ΔE_M , ΔE_F and ΔE_C .

It is also possible to derive an expression for the external demodulation current which will flow if the cell is connected to a measuring circuit with a low input impedance Z_M (see Fig. 4). We have for the potential difference ΔV across the interface, if R_Ω is the ohmic resistance:

$$\begin{aligned} \Delta V(\omega_m) &= \Delta E_F(\omega_m) + \Delta i_F(\omega_m) Z_F(\omega_m) \\ &= \Delta E_C(\omega_m) + \Delta i_C(\omega_m) Z_C(\omega_m) \\ &= [-\Delta i_F(\omega_m) - \Delta i_C(\omega_m)][R_\Omega + Z_M] \end{aligned} \tag{21}$$

from which with $\Delta i = \Delta i_F + \Delta i_C$

$$\Delta i(\omega_m) = -\left\{ \frac{\Delta E_C(\omega_m)}{Z_C(\omega_m)} + \frac{\Delta E_F(\omega_m)}{Z_F(\omega_m)} \right\} \left[1 + (R_\Omega + Z_M) \left(\frac{1}{Z_C(\omega_m)} + \frac{1}{Z_F(\omega_m)} \right) \right]^{-1} \tag{22}$$

and with a similar equation for $\Delta i(2\omega_m)$. The signs in eqns. (19)–(22) have been chosen such, that a current corresponding to a cathodic reaction at the indicator electrode is negative.

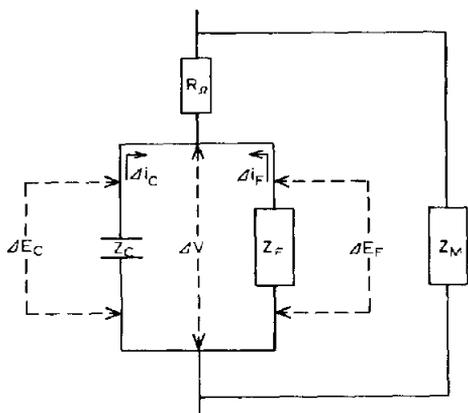


Fig. 4. Equivalent circuit for the derivation of the demodulation current.

DISCUSSION

Eqn. (20) is written quite generally in terms of the complex impedances Z_F and Z_C . Since both ΔE_F and ΔE_C are in phase with the modulating signal, *cf.* eqn. (18), ΔE_M will be complex too and can be split up into an in-phase part $\Delta E'_M$ and a quadrature part $\Delta E''_M$. Under the conditions assumed in this paper, *i.e.* no coupling between faradaic process and charging process, and mass transport by semi-infinite diffusion, we have¹¹

$$Z_F = \theta [1 + (1-j)p_m^{-1}] \tag{23}$$

and

$$Z_C = -j(\omega C)^{-1} \tag{24}$$

Then with eqns. (18) and (20) we can express $\Delta E'_M$ and $\Delta E''_M$ by

$$\Delta E'_M = [S_F(1-\tau') + S_C\tau'] 2mi_\lambda^2 \cos \omega_m t \tag{25}$$

with

$$\tau' = \frac{(p_m + 1)^2 + a_m + 1}{(p_m + 1)^2 + (a_m + 1)^2} \tag{26}$$

and

$$\Delta E_M'' = -(S_F - S_C)\tau'' 2mi_A^2 \sin \omega_m t \quad (27)$$

with

$$\tau'' = \frac{a_m(p_m + 1)}{(p_m + 1)^2 + (a_m + 1)^2} \quad (28)$$

in which $p_m = p'\omega_m^{\frac{1}{2}}$ and $a_m = (p'/\theta C_d)\omega_m^{-\frac{1}{2}}$.

Considering the extremes one can see that:

(i) At low modulation frequency, which is comparable with large modulation times in pulse modulation, both τ' and τ'' tend to zero; consequently $\Delta E_M''$ becomes zero and $\Delta E_M'$ contains only the faradaic contribution.

(ii) At high modulation frequency τ' tends to unity and τ'' again to zero; $\Delta E_M''$ approaches zero and $\Delta E_M'$ contains only the demodulation effect of the double-layer. Note, however, that for the theory described here, $\omega_m \ll \omega_0$ is required.

(iii) At potentials far removed from the half-wave potential, where the faradaic impedance is very large ($a_m \approx 0$), one has also $\tau' \approx 1$ and $\tau'' \approx 0$.

Similar considerations hold for $\Delta E_M(2\omega_m)$. However, it seems of little interest to measure this response, because no further information can be obtained from it, while its magnitude is at best four times smaller than that at the fundamental modulation frequency.

The measurement of $\Delta E_M'$ and $\Delta E_M''$ can be performed with the aid of a tuned phase-sensitive amplifier. The modulating signal can be used as a reference, but it seems more appropriate to tap the high-frequency polarizing alternating current across a small resistance R , as was done in ref. 12, to square it with a fast multiplier, and to measure the component in ω_m of the resulting voltage

$$\Delta E_R(\omega_m) = 2mi_A^2 R^2 \cos \omega_m t \quad (29)$$

alternately with ΔE_M on the same entrance. ΔE_R serves as a calibration voltage. The quotients $\Delta E_M'/\Delta E_R$ and $\Delta E_M''/\Delta E_R$ should be independent of i_A and m , so that it is possible to check whether heating of the electrode by the polarizing current occurs. As in the faradaic rectification technique, the measurements may be performed at varying d.c. potential, *i.e.* in the form of "demodulation polarography". An experimental set-up, based on these ideas, is being constructed in this laboratory.

The information provided by $\Delta E_M'$ and $\Delta E_M''$ is twofold. First, by inspection of the dependency on the modulation frequency, it is possible to determine the first order parameters p' and θC_d , together with S_F and S_C , which are independent of ω_m . Once p' and θC_d are known, S_F and S_C can be determined for various values of the carrier frequency ω_0 . Analysis of these results yields the second order parameters or their combinations, as they appear in eqns. (13) and (16), together with the first order parameters governing these equations. It can also be said that on variation of ω_0 one may examine the high-frequency behaviour of the cell and on variation of ω_m information is obtained concerning the low-frequency behaviour. In both cases there is no interference from the ohmic resistance, since no external current is flowing. It therefore seems that, by virtue of the advantageous method of measurement, the demodulation technique is also a useful method for the study of electrode processes.

SUMMARY

A theoretical study is presented concerning the application of a high-frequency alternating current, amplitude modulated by a low-frequency sine wave, to a galvanic cell. Based on the correlation with the faradaic rectification technique, expressions are given for the low-frequency demodulation voltages of the faradaic process and for the double-layer capacity. Both responses, which are in-phase with the modulation signal, are combined by considering them as voltage sources, having respectively the faradaic impedance and the double-layer impedance as internal impedances. The resulting demodulation voltage appears to possess an in-phase and a quadrature component, from which information can be obtained of the high-frequency as well as the low-frequency behaviour of the cell.

LIST OF SYMBOLS

<i>Symbol</i>	<i>Unit</i>	<i>Meaning</i>
a_0, a_m		$p'/\theta C_d \omega^{\frac{1}{2}}$ at frequency ω_0, ω_m
C_d	F cm ⁻²	double-layer capacity
c_0, c_R	mol cm ⁻³	concentration of the ox-/red component
E	V	electrode potential
F	C mol ⁻¹	Faraday constant
i	A cm ⁻²	current density
i_A	A cm ⁻²	amplitude of the hf-polarizing current
m		modulation depth
n		number of electrons transferred
p'	s ^{1/2}	$nF\sqrt{\frac{1}{2}}[D_R^{-\frac{1}{2}}(\partial i/\partial c_R) - D_O^{-\frac{1}{2}}(\partial i/\partial c_O)]^{-1}$
p_0, p_m		irreversibility quotient ($p'\sqrt{\omega}$ at frequency ω_0, ω_m)
$S_{F.C}$	V A ⁻² cm ⁴	$\Delta E_{F.C}/i_A^2 [\varphi(t)]^2$
t	s	time
Z_C	Ω cm ²	double layer impedance
Z_F	Ω cm ²	faradaic impedance
$\Delta E_C, \Delta E_C(\omega_m)$	V	rectification, <i>c.q.</i> demodulation, voltage of the double-layer
$\Delta E_F, \Delta E_F(\omega_m)$	V	faradaic rectification, <i>c.q.</i> demodulation voltage
$\Delta E_M, \Delta E_M(\omega_m)$	V	measured rectification, <i>c.q.</i> demodulation voltage
$\Delta E'_M(\omega_m)$	V	in-phase of $\Delta E_M(\omega_m)$
$\Delta E''_M(\omega_m)$	V	quadrature of $\Delta E_M(\omega_m)$
$\Delta E_R(\omega_m)$	V	squared voltage drop across current measuring resistance
Δi_C	A cm ⁻²	current discharging the double-layer from ΔE_C
Δi_F	A cm ⁻²	current charging the double-layer to ΔE_F
$\Delta c_0, \Delta c_R$	mol cm ⁻³	fluctuations in c_0 and c_R with respect to the bulk concentrations caused by Δi_F
θ	Ω cm ⁻²	charge transfer resistance
τ, τ', τ''		charging function
$\varphi(t)$		modulation function

ω_0	s^{-1}	angular frequency of polarizing current
ω_m	s^{-1}	angular frequency of modulation signal

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