

ON SECOND ORDER EFFECTS IN A GLAVANIC CELL

PART II. A UNIFIED TREATMENT OF THE THEORETICAL PRINCIPLES OF THE SECOND ORDER TECHNIQUES FOR THE STUDY OF ELECTRODE PROCESSES AND FOR ELECTROCHEMICAL ANALYSIS

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ABSTRACT

A general formalism is developed for the theory of the second order contribution to the non-linear behaviour of an electrochemical cell. The derivations result into a set of linear relationships for both the faradaic process and the double-layer charging process, which can be combined to deduce the ultimate cell response under various experimental conditions. The treatment is applicable to any accepted input waveform and gives a clear insight in the close connection between the so-called potentiostatic and galvanostatic approach. As an example the second harmonic distortion and the rectification effect arising from a single harmonic perturbation are briefly discussed. The implications of the treatment for the study of charge transfer kinetics are indicated in a general way, i.e. without specifying an a priori model, but in terms of operational parameters.

(1) INTRODUCTION

The non-linear nature of the current-potential characteristics of an electrode reaction is the basis of a number of electrochemical techniques, which are classified as second order relaxation methods. Since the recognition of second-order effects as rectification [1] and second-harmonic distortion [2], a rather prosperous development of second order techniques has taken place during the last two decennia. In the several contributions to this development a difference in philosophy can be sharply distinguished, connected to the original purpose:

(a) Methods for the determination of charge transfer parameters of very fast electrode reactions: the faradaic rectification [3–6] and the demodulation [7] techniques.

(b) Analytical techniques for extremely low concentrations and with high resolving power: radio-frequency polarography [8], second harmonic a.c. polarography [9], intermodulation polarography [10] and demodulation polarography [11,12].

In the former class the performance is galvanostatic, *with or without* additional d.c. polarization, which is not considered as essential. In the methodology also the presence of the electrical double layer is carefully accounted for. In

the latter class it is attempted to minimize double-layer effects so that they apparently can be neglected. The potentiostatic performance *with* d.c. polarization is essential, because one is interested in peak currents occurring at a certain d.c. potential.

One exception in these arguments should be made for the second harmonic polarographic technique, which has been elaborated almost to the same extent as fundamental a.c. polarography [13], and proves to be equally valuable for kinetic studies, or even more so in special cases (e.g. possible coupled chemical reactions) [14,15]. In our opinion this suggests that also the other techniques are equally valuable.

The established merits of the second order techniques as compared to first order (linear) techniques are the diminished influences of both the double-layer capacity and the ohmic resistance, thus leaving more content of information on the faradaic process in the ultimate cell response. However, Reinmuth has shown that there is a much more fundamental difference [16]: First order effects yield, in fact, only *one* kinetic parameter (the "operational" exchange current density), if desired as a function of d.c. potential, from which an unambiguous reaction mechanism cannot be deduced. From second order effects *three* parameters can be deduced, which, in combination with the first order parameter, provide the necessary information about the rate equation describing charge transfer.

From a practical point of view there appear to be two disadvantages in the second order approach as compared to the linear impedance method: (1) instrumentation is more difficult and more likely to be affected by artefacts, and (2) the theory is much more complex. The latter is accentuated by the fact that, at the birth of each new principle of performance, the inventors derived their own theory, using their own notations, etc. Moreover, in some cases misconceptions have sneaked in, leading to erroneous results. The only general treatment is to our knowledge that of Rangarajan, who outlines a very formalistic procedure to derive theories for non-linear relaxation methods (of arbitrary order), separately for the potentiostatic approach [17] and the galvanostatic approach [18]. This work is almost entirely restricted to the faradaic interfacial process.

The aim of the paper presented here is to derive a more explicit theory, which is generally applicable to all possible perturbations which may lead to second order responses. Both the faradaic and the non-faradaic process will be considered. Especially we intend to show the close relation between the generated second order current and voltage response, as they show up in practical situations of an ohmic resistance being in series with the interfacial process.

(2) DEFINITIONS, NOTATIONS, PREMISES

(i) In order to detect a second order effect separately the system under investigation should be excited by a *periodic input signal* and the response to this signal should be decomposed by selective detection. In the methods mentioned before the input signal is a more or less composite *sinusoidal waveform* as specified in Table 1. The nomenclature is based on the manner in which the system "manipulates" this waveform.

(ii) In order to avoid contributions of higher order to the selected output, the

TABLE 1

Input waveforms in use in second order techniques and the components of the second order responses (the frequency of the detected signal is underlined).

Input waveform	Frequencies occurring in second order response				Technique
$E_m \sin \omega_m t$	d.c.	$2\omega_m$			Second harmonic
$E_m \sin \omega_m t + E_n \sin \omega_n t$	d.c.	$2\omega_m$	$\omega_m + \omega_n$	$\omega_m - \omega_n$	Intermodulation
$E_H f(t) \sin \omega_H t$	$f(t)$	$2\omega_H$			Rectification
$E_{HL} \sin \omega_H t \sin \omega_L t$	d.c.	$2(\omega_H + \omega_L)$	$2\omega_H$	$2\omega_L$	Demodulation
$E_H \sin \omega_H t(1 + E_L \sin \omega_L t)$	d.c.	$2(\omega_H + \omega_L)$	$2(\omega_H - \omega_L)$	$2\omega_L$	Demodulation (double sideband)

input waveform should have a limited amplitude [19]. Its application can be performed either to a system which is initially at equilibrium (no d.c. current) or to a system which is polarized to a certain d.c. potential. In view of this we adopt the following notations:

j_F = faradaic current density

$j_{F,dc}$ = initial d.c. faradaic current density

Δj_F = small amplitude faradaic current density, due to the sinusoidal excitation

Δj_C = small amplitude charging current density, due to the sinusoidal excitation

E = interfacial d.c. potential

ΔE = small amplitude interfacial potential, due to the sinusoidal excitation

ΔV = total small amplitude voltage across the cell

To simplify formulae writing we introduce

$$\varphi = (nF/RT)(E - E^\circ) \quad (1)$$

and

$$\epsilon = (nF/RT)\Delta E \quad (2)$$

(iii) In general, it is assumed that currents and potentials are additively composed of the several order contributions:

$$\Delta j_F = \Delta j_{F,1} + \Delta j_{F,2} + \Delta j_{F,3} + \dots = \sum_{n=1}^{\infty} \Delta j_{F,n} \quad (3a)$$

$$\Delta j_C = \Delta j_{C,1} + \Delta j_{C,2} + \Delta j_{C,3} + \dots = \sum_{n=1}^{\infty} \Delta j_{C,n} \quad (3b)$$

$$\Delta E = \Delta E_1 + \Delta E_2 + \Delta E_3 + \dots = \sum_{n=1}^{\infty} \Delta E_n \quad (3c)$$

$$\epsilon = \epsilon_1 + \epsilon_2 + \epsilon_3 + \dots = \sum_{n=1}^{\infty} \epsilon_n \quad (3d)$$

(iv) When a finite current flows through the cell, the surface concentrations c_O and c_R of the faradaic reactants will differ from the initial "bulk" concentrations c_O^* and c_R^* . Strictly, c_O and c_R should be solved from the appropriate mass transport equations for the *total current*, but it is allowed to split them into a "d.c. part" \bar{c}_O , \bar{c}_R and an "a.c. part" Δc_O , Δc_R due to the excitation, provided that \bar{c}_O and \bar{c}_R vary much slower in time than Δc_O and Δc_R [20,21]. We will assume that this is the case and moreover that the "d.c. problem" has been solved separately, i.e. \bar{c}_O and \bar{c}_R are known functions of the d.c. current or the d.c. potential.

Following Rangarajan [17], we postulate that Δc_O and Δc_R are related to Δj_F by some function $\tilde{\gamma}_O$, resp. $\tilde{\gamma}_R$. For example, for the most simple mode of mass transfer one has [22]

$$nFD_O^{1/2}\Delta c_O = \tilde{\gamma}_O(\Delta j_F) = + \int_0^t \frac{\Delta j_F(t-u)}{(\pi u)^{1/2}} du \quad (4a)$$

$$nFD_R^{1/2}\Delta c_R = \tilde{\gamma}_R(\Delta j_F) = - \int_0^t \frac{\Delta j_F(t-u)}{(\pi u)^{1/2}} du \quad (4b)$$

In view of eqn. (3a) it can be stated that $\tilde{\gamma}_O$ and $\tilde{\gamma}_R$ must also consist of a series of increasing order:

$$\tilde{\gamma}_O = \tilde{\gamma}_{O,1} + \tilde{\gamma}_{O,2} + \tilde{\gamma}_{O,3} + \dots = \sum_{n=1}^{\infty} \tilde{\gamma}_{O,n} \quad (5a)$$

$$\tilde{\gamma}_R = \tilde{\gamma}_{R,1} + \tilde{\gamma}_{R,2} + \tilde{\gamma}_{R,3} + \dots = \sum_{n=1}^{\infty} \tilde{\gamma}_{R,n} \quad (5b)$$

Equations (4) are valid for mass transfer control solely by semi-infinite linear diffusion towards a planar electrode. They are commonly accepted to hold for small amplitude sinusoidal perturbations at not too low frequencies (>10 Hz), even if the electrode is spherical or non-stationary (dropping mercury electrode). When complications are involved, such as the occurrence of chemical reactions preceding or following charge transfer and/or reactant adsorption, the convolution integrals in (4) need to be more complex. From the theories known thus far, however, it can be inferred that the additive character of the different order contributions, expressed in eqns. (5), is maintained.

(v) As mentioned in the Introduction, two types of practical performance are possible, viz. (a) the application of a *controlled potential waveform* on the electrode (potentiostatic approach), or (b) the enforcement of a *controlled current waveform* through the cell (galvanostatic approach). Intuitively one would infer that in the former case second order currents are to be detected and in the latter case the generated second order voltages. Delahay et al. [3] have argued that — at least theoretically — the reverses are also possible: e.g., when in case (a) the second order current is prevented to flow (by appropriate filters and resistances in the detecting circuit) the net result will be a generated second order potential shift; similarly in case (b) the generated voltage distortion may be short-circuited and the result is a second order current.

When this is understood, it becomes obvious that it is difficult to predict a priori what will be measured in the practical situation, because of the following considerations:

(1) The interface provides two pathways for current, the faradaic one and the double layer charging, which are shunting each other.

(2) The total cell voltage is the sum of the interfacial potential and the voltage across the ohmic resistance. A real potentiostatic perturbation is therefore only possible if the potentiostat provides the possibility of 100% feed-back resistance compensation. Practical realizability of this is doubtful.

In view of this we will first discuss the relevant aspects of the faradaic and the non-faradaic process separately, and combine them afterwards with special regard to the modes of control. This procedure automatically implies that both processes are assumed to be independent of each other, i.e. the electroactive species do not play a significant role in the charging process [23].

(vi) A final point of discussion in this section is the question how to characterize the faradaic charge transfer process. Mostly the techniques collected in

Table 1 are described in terms of the well-known Butler-Volmer Theory (BVT), i.e. in terms of a standard heterogeneous rate constant k_{sh} and a transfer coefficient α , which both are considered as constants with a physical significance. Reinmuth [16] has argued, however, that adopting the BVT expression (or any other one) a priori, should be discouraged, since it is by no means certain whether it is valid. If it is not, anomalous and discrepant results may be observed, especially when different methods to determine k_{sh} and α are compared. Therefore it is strongly advocated [16] provisionally to leave the rate equation undefined, and only to postulate that the faradaic current is some function of the surface concentrations (in the double layer!) of the reactants and the interfacial potential. In the most simple case this is expressed by

$$j_F = f(c_O, c_R, \varphi) \quad (6)$$

Of course, for any practical situation eqn. (6) needs to be made explicit in terms of a suitable model, which inevitably invokes the forward and backward rate constants of the (partial) processes which determine the overall rate of charge transfer. We will give no further specification of these rate constants, but notice that it is always possible to compose the whole mechanism, whatever its complexity, into an "overall" reaction, characterized by the "overall" rate constants k_f and k_b , which must obey the Nernst equation in the form:

$$k_b/k_f = \exp \varphi \quad (7)$$

(3) THE FARADAIC PROCESS

In order to divide the "response-perturbation" relation into parts of several order eqn. (6) is subjected to the Taylor expansion, written in the form

$$\Delta j_F = \sum_{k=1}^{\infty} (1/k!) [\Delta c_O \partial / \partial c_O + \Delta c_R \partial / \partial c_R + \epsilon \partial / \partial \varphi]^k j_F \quad (8)$$

Since all variables are presumed to be composed of several order contributions, eqn. (8) must be elaborated:

$$\sum_{n=1}^{\infty} \Delta j_{F,n} = \sum_{k=1}^{\infty} (1/k!) \left[\sum_{n=1}^{\infty} \Delta c_{O,n} \partial / \partial c_O + \sum_{n=1}^{\infty} \Delta c_{R,n} \partial / \partial c_R + \sum_{n=1}^{\infty} \epsilon_n \partial / \partial \varphi \right]^k j_F \quad (9)$$

Now, by definition, the different orders in this series can be separated by combining the terms in the following way:

- first order: all terms with $k = 1$ and $n = 1$
- second order: all terms with $k = 1, n = 2$ and $k = 2, n = 1$ (also cross-terms!)
- third order: all terms with $k = 1, n = 3$ and $k = 3, n = 1$
- fourth order: all terms with $k = 1, n = 4, k = 2, n = 2, k = 4, n = 1$ etc.

Using the operator notation for Δc_O and Δc_R (cf. eqns. 4 and 5) this procedure leads to the following relations:

first order:

$$\Delta j_{F,1} - \frac{1}{nF} [\tilde{O} D_O^{-1/2} \tilde{\gamma}_{O,1} + \tilde{R} D_R^{-1/2} \tilde{\gamma}_{R,1}] - \tilde{F} \epsilon_1 = 0 \quad (10)$$

second order:

$$\begin{aligned} \Delta j_{F,2} - \frac{1}{nF} [\tilde{O} \tilde{D}_O^{-1/2} \tilde{\gamma}_{O,2} + R \tilde{D}_R^{-1/2} \tilde{\gamma}_{R,2}] - \tilde{F} \epsilon_2 \\ = \frac{\tilde{F}\tilde{F}}{2} \epsilon_1^2 + \frac{1}{nF} [\tilde{O}\tilde{F} \tilde{D}_O^{-1/2} \tilde{\gamma}_{O,1} + \tilde{R}\tilde{F} \tilde{D}_R^{-1/2} \tilde{\gamma}_{R,1}] \epsilon_1 \\ + \frac{1}{n^2 F^2} \left[\frac{\tilde{O}\tilde{O}}{2} \tilde{D}_O^{-1} \tilde{\gamma}_{O,1}^2 + \tilde{O}\tilde{R} \tilde{D}_O^{-1/2} \tilde{D}_R^{-1/2} \tilde{\gamma}_{O,1} \tilde{\gamma}_{R,1} + \frac{\tilde{R}\tilde{R}}{2} \tilde{D}_R^{-1} \tilde{\gamma}_{R,1}^2 \right] \end{aligned} \quad (11)$$

where \tilde{O} , \tilde{R} , \tilde{F} are the first order partial derivatives, and $\tilde{O}\tilde{O}$, $\tilde{R}\tilde{R}$, $\tilde{F}\tilde{F}$, $\tilde{O}\tilde{R}$, $\tilde{O}\tilde{F}$ and $\tilde{R}\tilde{F}$ the second order partial derivatives (see Table 2).

The first order relation, eqn. (10), is naturally a linear equation which enables us to calculate the first order current from a given ϵ_1 , or conversely to calculate the interfacial potential response to a given $\Delta j_{F,1}$. For sinusoidal perturbations eqn. (10) is actually the basis for the derivation of the faradaic impedance or admittance, which can be performed by Laplace transformation with imaginary Laplace parameter $i\omega$ [25].

The second order relation, eqn. (11), has a similar structure, except that the right-hand side is not zero, but contains all quadratic and cross-terms of first order quantities (ϵ_1 , $\tilde{\gamma}_{O,1}$ and $\tilde{\gamma}_{R,1}$). The right-hand side, therefore, can always be calculated with the aid of eqn. (10) for either a given $\Delta j_{F,1}$ or a given ϵ_1 . Equation (11) clearly demonstrates the interrelation between the two approaches mentioned in the foregoing section:

(a) When the *interfacial potential* is controlled to be equal to $(RT/nF)\epsilon_1$, one has $\epsilon_2 = 0$. Then the right-hand side in eqn. (11) can be considered as the voltage source which enforces the second order current $\Delta j_{F,2}$ to flow.

(b) When the *faradaic current density* is controlled to be equal to $\Delta j_{F,1}$, one has $\Delta j_{F,2} = 0$ and also $\tilde{\gamma}_{O,2} = \tilde{\gamma}_{R,2} = 0$, so that the right-hand side in eqn. (11) provides immediately the second order interfacial potential response $(RT/nF)\epsilon_2$.

(4) THE DOUBLE-LAYER CHARGING

Thus far, the second order aspects of double-layer charging have not always been properly treated, as has been pointed out by Rangarajan [17]. In fact the

TABLE 2

Partial derivatives and their significance in Butler-Volmer Theory (under non-equilibrium conditions)

Partial derivative	Symbol	Expression in BVT
$\partial j_F / \partial \varphi$	\tilde{F}	$nFk_f[\alpha \tilde{c}_O + (1 - \alpha) \tilde{c}_R \exp \varphi]$
$\partial j_F / \partial c_O$	\tilde{O}	$-nFk_f$
$\partial j_F / \partial c_R$	\tilde{R}	$nFk_f \exp \varphi$
$\partial^2 j_F / \partial \varphi^2$	$\tilde{F}\tilde{F}$	$-nFk_f[\alpha^2 \tilde{c}_O - (1 - \alpha)^2 \tilde{c}_R \exp \varphi - \alpha'(\tilde{c}_O - \tilde{c}_R \exp \varphi)]$
$\partial^2 j_F / \partial c_O \partial \varphi$	$\tilde{O}\tilde{F}$	$nF\alpha k_f$
$\partial^2 j_F / \partial c_R \partial \varphi$	$\tilde{R}\tilde{F}$	$nF(1 - \alpha)k_f \exp \varphi$
$\partial^2 j_F / \partial c_O^2$	$\tilde{O}\tilde{O}$	0
$\partial^2 j_F / \partial c_R^2$	$\tilde{R}\tilde{R}$	0
$\partial^2 j_F / \partial c_O \partial c_R$	$\tilde{O}\tilde{R}$	0

k_f = forward rate constant, $\alpha = -d(\ln k_f)/d\varphi$, $\alpha' = d\alpha/d\varphi$.

error made is that one considers the "current—voltage" relation for a capacitor as the starting point. However, this is already a first order relationship, deduced from the *basic function* characterizing a capacitive process:

$$q = f(E, c_1, c_2 \dots c_i) \quad (12)$$

where q is the charge density on the electrode; $c_1 \dots c_i$ are surface concentrations of species which in principle, via adsorption in the double layer, may influence the value of q . In this paper we will assume that either the surface concentrations of the species concerned are constant, or their influence on q is negligible (no adsorption of electroactive species) so that q is only a function of E . Consequently the Taylor expansion is relatively simple:

$$\Delta q = \sum_{k=1}^{\infty} (1/k!) [\Delta E \, d/dE]^k q \quad (13)$$

and, with eqn. (3c):

$$\sum_{n=1}^{\infty} \Delta q_n = \sum_{k=1}^{\infty} (1/k!) \left[\sum_{n=1}^{\infty} \Delta E_n (d/dE) \right]^k q \quad (14)$$

where Δq_n represents the n th order term in Δq . With the same rules as applied to the faradaic case eqn. (14) can be separated into the different orders, but before doing this we will modify the notation by introducing the differential double layer capacity:

$$dq/dE = C_d \quad (15a)$$

and

$$(d/dE)^k q = (d/dE)^{k-1} C_d \quad (15b)$$

so that we obtain the relationships:

first order:

$$\Delta q_1 - C_d \Delta E_1 = 0 \quad (16)$$

second order:

$$\Delta q_2 - C_d \Delta E_2 = (dC_d/dE) (\Delta E_1)^2/2 \quad (17)$$

These equations are needed to derive the corresponding relations in terms of the charging current components, by applying either

$$\Delta j_{c,n} = d\Delta q_n/dt \quad (18a)$$

or

$$\Delta q_n = \int \Delta j_{c,n} \, dt \quad (18b)$$

Like eqn. (11), eqn. (17) describes the second order double layer response in terms of the linearly related quantities Δq_2 and ΔE_2 , with the right-hand side in principle defined by the first order input-output relation.

(5) BEHAVIOUR OF THE TOTAL CELL

As has been done earlier [4,26], the combined effects of the faradaic process and the charging process will be considered with the aid of the "equivalent circuit" in Fig. 1. This circuit is very similar to the well-known Randles' circuit containing the *faradaic impedance* Z_F , the *double-layer impedance* Z_C and the *ohmic resistance* R_Ω . The extensions needed for the second order behaviour are the (virtual) "*voltage sources*" S_F and S_C in the faradaic branch and the capacitive branch respectively. It is supposed that Kirchhoff's laws must be applicable to this scheme.

The magnitude of S_F must be taken equal to that value of the generated second order interfacial potential, which would occur when $\Delta j_{F,2}$ equalled zero, i.e. [cf. eqn. (11)]:

$$S_F = -\frac{RT}{nF} \tilde{F}^{-1} \left\{ \frac{\tilde{F}\tilde{F}}{2} \epsilon_1^2 + \frac{1}{nF} [\tilde{O}\tilde{F}D\tilde{O}^{-1/2}\tilde{\gamma}_{O,1} + \tilde{R}\tilde{F}D\tilde{R}^{-1/2}\tilde{\gamma}_{R,1}] \epsilon_1 + \frac{1}{n^2F^2} \left[\frac{\tilde{O}\tilde{O}}{2} D\tilde{O}^{-1}\tilde{\gamma}_{O,1}^2 + \tilde{O}\tilde{R}D\tilde{O}^{-1/2}D\tilde{R}^{-1/2}\tilde{\gamma}_{O,1}\tilde{\gamma}_{R,1} + \frac{\tilde{R}\tilde{R}}{2} D\tilde{R}^{-1}\tilde{\gamma}_{R,1}^2 \right] \right\} \quad (19)$$

Similarly, S_C is that value of the generated second order interfacial potential, which would occur when $\Delta j_{C,2}$ equalled zero, i.e. [cf. eqn. (17)]:

$$S_C = -C_d^{-1} (dC_d/dE) (\Delta E_1)^2/2 \quad (20)$$

It should be noted that the equivalent elements Z_F and Z_C have not yet been specified, and could not yet be specified for two reasons: (a) the operators $\tilde{\gamma}_O$ and $\tilde{\gamma}_R$ depend on the mode of mass transfer, and (b) it can be foreseen that the frequencies (or the time scale) involved in the experiment play a role. At this stage of our reasonings nothing more can be said than that Z_F and Z_C must be considered as "*operational impedance*", defined as the quotient of the Laplace transforms of voltage and current. In view of Fig. 1 this means that one can write

$$\overline{\Delta E_1}(s) = Z_F(s) \overline{\Delta j_{F,1}}(s) = Z_C(s) \overline{\Delta j_{C,1}}(s) \quad (21)$$

as usual, but

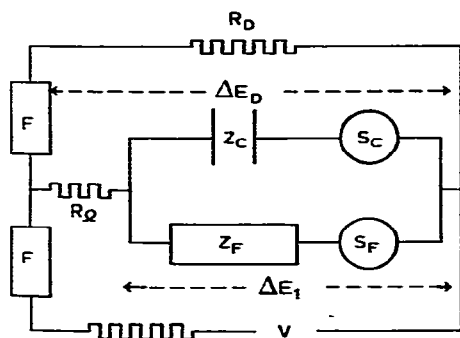


Fig. 1. Equivalent circuit of the electrochemical cell connected to perturbation source V and detector input resistance R_D (see text).

$$\begin{aligned}\overline{\Delta E_2}(s) &= \overline{S_F}(s) + Z_F(s)\overline{\Delta j_{F,2}}(s) \\ &= \overline{S_C}(s) + Z_C(s)\overline{\Delta j_{C,2}}(s)\end{aligned}\quad (22)$$

where the bars indicate Laplace transforms of currents or voltages. For derivations to follow, it may also be convenient to define the operational admittances $Y_F(s)$ and $Y_C(s)$ as the reciprocals of the impedances:

$$Y_F(s) = 1/Z_F(s), \quad Y_C(s) = 1/Z_C(s) \quad (23)$$

The final items in this section are the representation of the perturbation and of the response measurement. Although many instrumental features are important, it is for our purpose sufficient to represent the cell as a four-pole, having two connections to the perturbation source (either a potentiostat or a galvanostat) and two others to the detection device, which has an input resistance R_D (see Fig. 1). Appropriate filters prevent the fundamental current from flowing through the detector circuit and the second order current from flowing through the perturbation circuit.

Evidently the magnitude of R_D determines what kind of response is measured: if $R_D \gg Z_{\text{cell}}$, the external current is prevented from flowing, so that the interfacial potential is measured; reversely, if $R_D \ll Z_{\text{cell}}$, the voltage across R_D must be proportional to the external cell current. It must be noted that in the latter case the ohmic resistance R_Ω may be also determining the measured signal, since it causes an ohmic loss in the second order circuit [$\Delta E_D = \Delta E_2 - R_\Omega \Delta j_2$].

The same problem troubles the discussion about the perturbation circuit, which necessarily precedes the final derivation of the second order effects. For example, when a single frequency perturbation is applied, it is common use to specify in theory the interfacial first order potential as

$$\Delta E_1 = E_m \sin \omega_m t \quad (24)$$

which is, of course, attractive in view of eqns. (19) and (20). However, unless a potentiostat with ideal feed-back facility is used, ΔE_1 is not the primary experimental quantity. Consequently, experimental results are always subject to some kind of error discussion including non-ideality of the potentiostat.

TABLE 3

Relations between the first order interfacial potential and the perturbing signal

Perturbation	Relations
(a) Current $\Delta j_1 = j_m \sin \omega_m t'$	$\Delta E_1 = E_m \sin \omega_m t = E_m \sin(\omega_m t' - \theta'_m)$ $E_m^2 = j_m^2 [(Z'_{el})^2 + (Z''_{el})^2] = j_m^2 [(Y'_{el})^2 + (Y''_{el})^2]^{-1}$ $\cot \theta'_m = Z'_{el}/Z''_{el} = Y''_{el}/Y'_{el}$
(b) Voltage: $\Delta V_1 = V_m \sin \omega_m t''$	$\Delta E_1 = E_m \sin \omega_m t = E_m \sin(\omega_m t'' - \theta''_m)$ $E_m^2 = V_m^2 \{1 + 2R_\Omega Y'_{el} + R_\Omega^2 [(Y'_{el})^2 + (Y''_{el})^2]\}^{-1}$ $\cot \theta''_m = (Y'_{el}/Y''_{el}) + (1/R_\Omega Y'_{el})$

Z'_{el} , Z''_{el} = real and imaginary component of interfacial impedance.

Y'_{el} , Y''_{el} = real and imaginary component of interfacial admittance.

R_Ω = ohmic resistance.

Moreover at very high frequencies the idea of using a potentiostat must be rejected anyway because of the enormous ohmic drop. Still, the most surveyable solution is to maintain the formulation in eqn. (24), but to realize that there is a defined phase and amplitude relation between the interfacial potential and the actual perturbing voltage or current. Of course this relation can be immediately derived from the well-known theories of cell impedance with the aid of eqn. (21) and similar relations, for example between total current Δj_1 and total cell voltage ΔV_1 . A summary of such relations is given in Table 3.

The conclusion of our theory developed thus far is that with eqns. (10), (11) and (16)–(22) the second order behaviour of an electrochemical cell is formally described, except for the definition of the operators $\tilde{\gamma}_{O,n}$ and $\tilde{\gamma}_{R,n}$, which must follow from a model accepted for the mode of mass transport. Implementation of these equations in a practical case only requires specification of such a model and, in addition, specification of the mode of perturbation, e.g. one of the examples in Table 1. In the next sections we will briefly discuss the implications of such a procedure.

(6) SINGLE FREQUENCY PERTURBATION: SECOND HARMONIC AND RECTIFICATION EFFECTS

Among the second order techniques, the so-called faradaic rectification method has been elaborated most extensively, i.e. including account for double layer charging and rectification by the double layer [3–5], but usually with a simple mode of mass transfer, viz. semi-infinite linear diffusion. Theories of second harmonic polarography extend sometimes to cases of preceding or following chemical reactions [13–15], but usually neglect the presence of the double layer. Just for a demonstration, we will elaborate our formulae assuming semi-infinite linear diffusion (i.e. eqns. 4), to find comparable expressions for both techniques.

According to eqns. (4) and (5) $\tilde{\gamma}_{R,n} = -\tilde{\gamma}_{O,n}$, which enables to write eqns. (10), (11) and (19) in a more transparent form:

$$[\Delta j_{F,1} + \lambda \tilde{\gamma}_{O,1}] R_{ct} - \Delta E_1 = 0 \quad (25)$$

$$[\Delta j_{F,2} + \lambda \tilde{\gamma}_{O,2}] R_{ct} - \Delta E_2 = -S_F \quad (26)$$

$$-S_F = R_{ct} [(1/R'_{ct}) \Delta E_1^2/2 + (nF/RT) \lambda'_i \tilde{\gamma}_{O,1} \Delta E_1 + \lambda'_c \gamma_{O,1}^2/2] \quad (27)$$

where the meaning of the new symbols R_{ct} , R'_{ct} , λ , λ'_i and λ'_c is given in Table 4.

For the procedure to follow it will be useful to specify the operational impedances mentioned in eqns. (21) and (22). Since the Laplace equivalent of eqn. (4) is

$$\tilde{\gamma}_O(s) = s^{-1/2} \overline{\Delta j_F}(s) \quad (28)$$

it is easily found from e.g. eqns. (21) and (25) that

$$Z_F(s) = R_{ct} [1 + \lambda s^{-1/2}] \quad (29)$$

Similarly, eqns. (16), (18) and (21) lead to

$$Z_C(s) = [sC_d]^{-1} \quad (30)$$

TABLE 4

Specification of symbols used in section (6)

Symbol	Meaning	Expression in BVT
λ	$-\tilde{O}D_0^{-1/2} - \tilde{R}D_R^{-1/2}/nF$	$k_f[D_0^{-1/2} + D_R^{-1/2} \exp \varphi]$
λ'_f	$-\tilde{O}FD_0^{-1/2} - \tilde{R}FD_R^{-1/2}/nF \quad (= \partial \lambda / \partial \varphi)$	$-k_f[\alpha D_0^{-1/2} + (1 - \alpha)D_R^{-1/2} \exp \varphi]$
λ'_c	$-\tilde{O}OD_0^{-1} - 2\tilde{O}RD_0^{-1/2}D_R^{-1/2} + \tilde{R}RD_R^{-1}/n^2F^2$	0
p_m	$(2\omega_m)^{1/2}/\lambda$	
p_{2m}	$(4\omega_m)^{1/2}/\lambda$	
R_{ct}	$(RT/nF)\tilde{F}^{-1}$	$(RT/n^2F^2)k_f^{-1}[\alpha\tilde{c}_O + (1 - \alpha)\tilde{c}_R \exp \varphi]^{-1}$
R'_{ct}	$(RT/nF)\tilde{F}\tilde{F}^{-1}$	$(RT/nF)[(2\alpha - 1)/R_{ct} + (n^2F^2/RT)k_f(c_O - c_R \exp \varphi)(\alpha - \alpha^2 - \alpha')^{-1}]^{-1}$
a_{2m}	$p_{2m}/(2\omega_m R_{ct} C_d)$	

 k_f = forward rate constant, $\alpha = -d(\ln k_f)/d\varphi$, $\alpha' = d\alpha/d\varphi$.

$A_m^{(0)}$	$\frac{R_{ct}}{4R'_{ct}} + \frac{nF\lambda'_f}{RT2\lambda p_m^2 + 2p_m + 2} + \frac{\lambda'_c}{2\lambda^2 R_{ct} p_m^2 + 2p_m + 2}$	1
$A_m^{(2)}$	$\frac{R_{ct}}{R'_{ct}} - \frac{nF\lambda'_f}{RT2\lambda p_m^2 + 2p_m + 2} - \frac{\lambda'_c}{\lambda^2 R_{ct}(p_m^2 + 2p_m + 2)^2}$	$\frac{p_m + 1}{p_m^2 + 2p_m}$
$B_m^{(2)}$	$-\frac{nF\lambda'_f}{RT2\lambda p_m^2 + 2p_m + 2} - \frac{\lambda'_c}{4\lambda^2 R_{ct}(p_m^2 + 2p_m + 2)^2}$	
$C_m^{(0)}$	$\frac{1}{C_d} \frac{dC_d}{dE}$	
$C_m^{(2)}$	$\frac{1}{C_d} \frac{dC_d}{dE}$	

Now the first step is to solve $\Delta j_{F,1}$ and $\tilde{\gamma}_{O,1}$ from eqn. (25), with, as proposed in eqn. (24), $\Delta E_1 = E_m \sin \omega_m t$. Of course, because of the linear relation the solution (in the so-called stationary state) will be of the form

$$\Delta j_{F,1} = [a_m^{(1)} \sin \omega_m t + b_m^{(1)} \cos \omega_m t] E_m \quad (31)$$

An attractive way to determine $a_m^{(1)}$ and $b_m^{(1)}$ is to make use of the *complex impedance* or *admittance* concept:

$$\left[\frac{\Delta j_{F,1}(s)}{\Delta E_1(s)} \right]_{s=i\omega} = Z_F(i\omega)^{-1} = \left[\frac{\omega a_m^{(1)} + s b_m^{(1)}}{\omega} \right]_{s=i\omega} = a_m^{(1)} + i b_m^{(1)} \quad (32)$$

Relating this equation to eqn. (29) gives for the current

$$\Delta j_{F,1} = \frac{p_m (p_m + 1) \sin \omega_m t + \cos \omega_m t}{R_{ct} p_m^2 + 2p_m + 2} E_m \quad (33)$$

with $p_m = (2\omega_m)^{1/2} \lambda^{-1}$ (see Table 4). In a similar way eqn. (28) can now be used with $s = i\omega$ to find $\tilde{\gamma}_{O,1}$. The result is

$$\begin{aligned} -\lambda \tilde{\gamma}_{O,1} &= p_m^{-1} [(a_m^{(1)} + b_m^{(1)}) \sin \omega_m t + (b_m^{(1)} - a_m^{(1)}) \cos \omega_m t] E_m \\ &= \frac{1}{R_{ct}} \frac{(p_m + 2) \sin \omega_m t - p_m \cos \omega_m t}{p_m^2 + 2p_m + 2} E_m \end{aligned} \quad (34)$$

This relation is necessary to elaborate the second order relationship, eqn. (26), which contains terms in ΔE_1^2 , $\tilde{\gamma}_{O,1} \Delta E_1$ and $\tilde{\gamma}_{O,1}^2$ and thus terms in $\sin^2 \omega_m t$, $\cos^2 \omega_m t$ and $\sin \omega_m t \cos \omega_m t$. In view of the trigonometric relations like $\sin^2 \omega_m t = 1 - \cos 2\omega_m t$ etc., it must be anticipated that both $\Delta j_{F,2}$ and ΔE_2 , if different from zero, will contain terms in $\sin 2\omega_m t \cos 2\omega_m t$ (second harmonics) as well as a d.c. component (faradaic rectification). Expressions for current and/or potential must be deduced from the right-hand side of eqn. (26), i.e.

$$-S_F = [A_m^{(0)} + A_m^{(2)} \cos 2\omega_m t + B_m^{(2)} \sin 2\omega_m t] E_m^2 \quad (35)$$

with specifications of $A_m^{(0)}$, etc. as in Table 4. These specifications are derived by equating eqns. (35) and (27) with proper substitution for ΔE_1 and $\tilde{\gamma}_{O,1}$. Four theoretical cases will be treated next.

(i) *No shunting of the faradaic branch.* In this case the second order current is prevented from flowing, i.e. $\Delta j_{F,2} = 0$, $\tilde{\gamma}_{O,2} = 0$, so that ΔE_2 equals S_F .

(ii) *Shunting by a zero-impedance lead.* In this case the second order interfacial potential must be zero, and the current that flows is maximal. Since S_F is specified, eqn. (26), with $\Delta E_2 = 0$, can be solved in the same way as eqn. (25), i.e. via Laplace transformation:

$$\frac{\Delta j_{F,2}(s)}{S_F(s)} = -Z_F(s)^{-1}$$

Reverse transformation (with real s for the rectification term, and $s = i\omega$ for the sinusoidal terms) leads to

$$\begin{aligned} \Delta j_{F,2} &= R_{ct}^{-1} [A_m^{(0)} \exp(\lambda^2 t) \operatorname{erfc}(\lambda t^{1/2})] E_m^2 \\ &+ \frac{p_{2m} (p_{2m} + 1) B_m^{(2)} - A_m^{(2)}}{R_{ct} p_{2m}^2 + 2p_{2m} + 2} E_m^2 \sin 2\omega_m t \end{aligned}$$

$$+ \frac{p_{2m} B_m^{(2)} + (p_{2m} + 1) A_m^{(2)}}{R_{ct} p_{2m}^2 + 2p_{2m} + 2} E_m^2 \cos 2\omega_m t \quad (36)$$

with $p_{2m} = (4\omega_m)^{1/2}/\lambda$ (see Table 4).

(iii) *Shunting by the double layer at open circuit.* In this case there will be no external current, but the two "voltage sources" S_F and S_C may produce a net internal current $\Delta j_{2,int} = \Delta j_{F,2} = -\Delta j_{C,2}$, while there is also a finite interfacial potential ΔE_2 . Following eqn. (22) we can derive

$$\frac{\overline{\Delta j_{2,int}(s)}}{\overline{S_C(s)} - \overline{S_F(s)}} = [Z_F(s) + Z_C(s)]^{-1} \quad (37)$$

$$\overline{\Delta E_2(s)} = \frac{Z_F(s)\overline{S_C(s)} + Z_C(s)\overline{S_F(s)}}{Z_F(s) + Z_C(s)} \quad (38)$$

which evidently requires specification of S_C , cf. eqn. (20):

$$-S_C = [C_m^{(0)} + C_m^{(2)} \cos 2\omega_m t] E_m^2 \quad (39)$$

with $C_m^{(0)} = -C_m^{(2)} = (d \ln C_d/dE)/4$ [Table 4].

The reverse transformation with real s is somewhat tedious but feasible. It delivers the rectification component in a form similar to that derived by Delahay et al. [3]:

$$\begin{aligned} \Delta E_2^{(0)} &= A_m^{(0)} E_m^2 \\ &- \frac{A_m^{(0)} - C_m^{(0)}}{R_{ct} C_d (H - G)} \left[\frac{1}{G} \exp(G^2 t) \operatorname{erfc}(Gt^{1/2}) - \frac{1}{H} \exp(H^2 t) \operatorname{erfc}(Ht^{1/2}) \right] \end{aligned} \quad (40)$$

with

$$G, H = \frac{1}{2} [\lambda \pm (\lambda^2 - 4R_{ct}^{-1}C_d^{-1})^{1/2}]$$

Again the second harmonic components are found from eqn. (38) by taking s imaginary, say $s = i2\omega$, analogously to the procedure around eqn. (32). After separation of the real and imaginary part we find for the interfacial potential:

$$\begin{aligned} \Delta E_2 &= \left[a_{2m} \frac{(p_{2m} + 1)(A_m^{(2)} - C_m^{(2)}) + (a_{2m} + 1)B_m^{(2)}}{(p_{2m} + 1)^2 + (a_{2m} + 1)^2} \right] E_m^2 \sin 2\omega_m t \\ &+ \left[a_{2m} \frac{(a_{2m} + 1)(A_m^{(2)} - C_m^{(2)}) - (p_{2m} + 1)B_m^{(2)}}{(p_{2m} + 1)^2 + (a_{2m} + 1)^2} + C_m^{(2)} \right] E_m^2 \cos 2\omega_m t \end{aligned} \quad (41)$$

where $a_{2m} = p_{2m}/(2\omega_m R_{ct} C_d)$ [Table 4].

(iv) *Faradaic + capacitive branch shunted by a zero-impedance lead.* If the sum of ohmic resistance and external resistance is negligible with respect to the interfacial impedance, ΔE_2 will approach zero, so that an external current $\Delta j_{2,ext}$ flows, equal to $\Delta j_{F,2} + \Delta j_{C,2}$. From eqn. (22)

$$\overline{\Delta j_{2,ext}(s)} = -\frac{\overline{S_F(s)}}{Z_F(s)} - \frac{\overline{S_C(s)}}{Z_C(s)} \quad (42)$$

Similar arguments as in case (ii) are applicable, and evidently eqn. (36) has to be extended by the double layer contribution. This contribution appears to consist of a charge impulse $\Delta q_2 = C_d C_m^{(0)} E_m^2$ at $t = 0$ and a stationary second

harmonic current:

$$\Delta j_{c,2} = 2\omega_m C_d C_m^{(2)} E_m^2 \sin 2\omega_m t \quad (43)$$

(7) EXTENSION TO OTHER PERTURBATION WAVE-FORMS

The more complex input wave-forms summarized in Table 1 are either summations or products of sinusoidal functions. Their treatment can, however, be generalized by recalling that a product of two sine waves can always be decomposed according to

$$\begin{aligned} 2 \sin \omega_H t \sin \omega_L t &= \cos(\omega_H - \omega_L)t - \cos(\omega_H + \omega_L)t \\ &= \sin \omega_m t + \sin \omega_n t \end{aligned} \quad (44)$$

where evidently $\omega_m t = (\omega_H - \omega_L)t + \pi/2$, and $\omega_n t = (\omega_H + \omega_L)t - \pi/2$.

The first order term of the interfacial potential, cf. eqn. (3c) can therefore be supposed to be of the form

$$\Delta E_1 = \sum_{m=1}^N E_m \sin(\omega_m t + \theta_m) \quad (45)$$

where θ_m refers the phase shift of each term to the corresponding term in a similar series representing the real input signal (current or voltage), much the same as for the single frequency input waveform, cf. Table 3.

The procedure to find the second order responses involves the same steps as in section (6), only requiring careful elaboration of the trigonometric relations. We will not go into detail but as an example give the result for S_F and S_C assuming $\theta_m = 0$ (potentiostatic control with ideal resistance compensation):

$$\begin{aligned} S_F &= \sum_{m=1}^N [A_m^{(0)} + A_m^{(2)} \cos 2\omega_m t + B_m^{(2)} \sin 2\omega_m t] E_m^2 \\ &+ \sum_{m=1}^{N-1} \sum_{n=m+1}^N (A_m^{(2)} + A_n^{(2)}) [\cos(\omega_m + \omega_n)t - \cos(\omega_m - \omega_n)t] E_m E_n \\ &+ \sum_{m=1}^{N-1} \sum_{n=m+1}^N [(B_m^{(2)} + B_n^{(2)}) \sin(\omega_m + \omega_n)t - (B_m^{(2)} - B_n^{(2)}) \sin(\omega_m - \omega_n)t] E_m E_n \end{aligned} \quad (46)$$

and

$$\begin{aligned} S_C &= \sum_{m=1}^N [C_m^{(0)} + C_m^{(2)} \cos 2\omega_m t] E_m^2 \\ &+ \sum_{m=1}^{N-1} \sum_{n=m+1}^N 2C_m^{(2)} [\cos(\omega_m - \omega_n)t - \cos(\omega_m + \omega_n)t] E_m E_n \end{aligned} \quad (47)$$

The coefficients $A_m^{(0)}$, $A_n^{(0)}$, etc. can be derived from Table 4, after insertion of the proper frequency.

This general formulation is applicable to all the techniques mentioned in Table 1.

(8) DISCUSSION

With the theory presented above surveyable expressions have been obtained which are applicable to all second order techniques. The basic equations are both eqns. (10) and (11) for the faradaic process and both eqns. (16) and (17) for the double layer charging process. These equations show the striking similarity between the first order and the second order current-potential relation, when the origin of the second order responses are conceived as internal voltage sources (S_F and S_C) with magnitudes entirely determined by first order quantities as variables and second order partial derivatives as parameters. In a way, this approach "linearizes" the second order effects, and enables to calculate the second order response of a cell with the aid of the (operational) impedance concept. In some respects, a few additional remarks can be made.

(i) *Comparison with existing theories.* The theory of faradaic rectification, as developed by Delahay and coworkers [3] and later refined by de Leeuwe et al. [4] most closely resembles the formalism presented here. It is easily verified that their faradaic rectification voltage is equal in nature to the first term in eqn. (35), $A_m^{(0)} E_m^2$, while the total rectification, including the double layer, is identical in form to eqn. (40). This result holds of course, for a galvanostatic performance, which is usually applied. An equation for the faradaic rectification current, similar to the first term of eqn. (36), has also been derived [27].

As for the second harmonic distortion effect, only an expression for the second harmonic a.c. polarographic current (i.e. potentiostatic performance) has been derived by McCord and Smith [13–15]. This expression is written in terms of current amplitude and phase angle, instead of the notation preferred by us in terms of two orthogonal components. However, it can be shown that McCord's expression is in fact identical to the a.c. part of eqn. (36). The second harmonic charging current is neglected by these authors, because they use to work with a twin-cell construction, by which the charging current is eliminated [28]. In our opinion one should be careful in using this method for kinetic studies, since it puts high demands on both the ohmic drop compensation and the actual subtraction of Δj_{C2} . To our knowledge, expressions for a second harmonic potential response, similar to eqn. (35) or (41) never have been published.

Comparing these both responses to a single harmonic perturbation, the second harmonic technique has been developed as a typical low-frequency technique, whereas the rectification technique (with square-wave modulation) appears to be a powerful method for high-frequency studies. In this sense they are more or less complementary. It could be that the alternative way of modulation by a sine-wave, in casu the demodulation technique, provides the possibility to cover both high and low frequency ranges. In part I of this series [7] we discussed the galvanostatic performance with a low-frequency modulated high frequency current, especially with regard to the analogy with the rectification techniques. The potentiostatic performance has been discussed by Brocke [11] but this treatment is incorrect because a Taylor expansion is applied to the

components of the interfacial admittance instead of the original current-potential-concentration relation. Moreover it is restricted to infinitely fast electron transfer. Another treatment has been given by Zheletsov [12], unfortunately resulting in very complex equations, which in view of our results seems not to be necessary. We intend to deal with a general treatment of the demodulation technique and the intermodulation techniques, for which to our knowledge no theory has been presented, in the near future.

(ii) *The parameters.* As mentioned in section (2, vi) nearly all specific treatments published thus far have been started with an a priori definition of the equation describing charge transfer [i.e. our eqn. (6)], in particular by means of the BVT equation. As we preferred not to do this, it is interesting to examine what kind of information about charge transfer kinetics may be obtained from our expressions. Naturally it is only possible to obtain — by means of a fitting procedure — a number of *operational parameters* defining the frequency dependence of the eventual cell response.

(a) *First order parameters.* Equation (33) and also eqn. (29) reveal that there are two first order parameters, viz. R_{ct} and λ . R_{ct} is known as the "charge transfer resistance" and may be seen as representative for an "operational exchange current density" $I_0 = (nF/RT)R_{ct}^{-1}$. The parameter λ is related to the "irreversibility quotient" p' introduced in our earlier work: $p' = 2^{1/2}/\lambda$. It may be noted that these two parameters do not necessarily provide twofold information, because Reinmuth has shown [16] that under equilibrium conditions (no d.c. current flowing) the two are related; in our notation:

$$\lambda R_{ct} = \frac{n^2 F^2}{RT} [\bar{C}_O^{-1} D_O^{-1/2} + \bar{C}_R^{-1} D_R^{-1/2}] \quad (48)$$

In the presence of a d.c. current, however, λ and R_{ct} need not to be coupled in this sense.

(b) *Second order parameters.* The second order response being determined by the identity of S_F , cf. eqn. (35), it follows from Table 4 that there are three additional second order parameters, R'_{ct} , λ'_t and λ'_c , occurring in combination with the first order parameters as coefficients of frequency-dependent terms. Of course the meaning of λ , λ'_t and λ'_c , comprising the partial derivatives \bar{O} and \bar{R} , $\bar{O}F$ and $\bar{R}F$, etc. is a consequence of the chosen mode of mass transfer. So, it cannot be excluded that in other cases there may be more parameters of the λ -type. The total number of parameters, however, appears to be limited by the number of partial derivatives in the Taylor expansion, i.e. six, according to Table 2.

(iii) *The study of charge transfer kinetics.* Though the use of operational parameters is most helpful in keeping formulae simple, the interpretation in terms of system parameters like k_{sh} , α , etc. requires the postulation of a model and translation of this model into analytical expressions for R_{ct} , λ , etc. As an example we did this in Table 4 for the classical BVT equation, written in its most general form:

$$j_F = nFk_t[C_R \exp \varphi - C_O] \quad (49)$$

Some other examples have been collected and discussed by Van der Pol et al. [5]. Evidently there are at most three kinetic parameters, k_t , α and α' , which

can be solved from the operational parameters. It seems that even an internal check on the validity of the model is possible, especially if measurements are made at varying d.c. potential.

Because eqn. (49) is linear in C_O and C_R , λ'_c becomes zero in BVT. It is evident that any non-linearity in the participating concentrations in a more complex rate equation could only be detected by invoking a second order technique. Reinmuth has even established that it is necessary to combine first and second order techniques for this purpose [16]. The possibility of detecting λ'_c in a relatively simple way distinguishes our formalism from that of Rangarajan [17,18], which is more general as an "operator formalism", but assumes a linear current-concentration relation.

(iv) *Conclusion.* It can be stated that the formulae developed in this paper offer an attractive starting-point for analysis procedures of second order responses. Separation of mass transfer from charge transfer, as well as accounting for double-layer effects and ohmic loss are relatively easy to be executed. Also the derivations are suitable for modification with regard to more complex situations, e.g. interference of homogeneous kinetics, reactant adsorption, etc. which as yet are almost exclusively incorporated only in first order impedance theories.

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