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**Short communication**

# ON THE MEANING OF THE IMPEDANCE CONCEPT IN THE CASE OF AN OBJECT THAT VARIES WITH TIME AND IN THE CASE OF A SWEPT F FREQUENCY

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ABSTRACT

Expressions are derived that describe the behaviour of a condenser the capacity of which varies linearly with time under potentiostatic and galvanostatic a.c. conditions. The "impedances" are found to be different. Application to the dropping mercury electrode is indicated. Also the behaviour of a constant capacitor subject to a frequency swept a.c. potential or current is calculated. The admittance of the capacitor is found to have increased in the latter two cases.

## INTRODUCTION

Recently we communicated on the instrumental artefacts that as a consequence of slow response of a detector can mar impedance measurements performed on time-dependent objects [1]. However, also the concept of impedance itself sometimes becomes more complex in such a case. We wish to show this complication on a pure capacitor the capacitance of which varies linearly with times:

$$C = at \tag{1}$$

By definition the charge on the condenser is related to the voltage across it by

$$Q = CV \tag{2}$$

In case of a sinusoidally varying voltage

$$V = V_m \sin \omega t \tag{3}$$

(1), (2), and (3) lead to

$$Q = atV_m \sin \omega t \tag{4}$$

whence, for the current $i = dQ/dt$ one obtains

$$i = aV_m \sin \omega t + \omega\, atV_m \cos \omega t \tag{5}$$

Evidently in addition to the term to be expected, $at\omega V_m \cos \omega t$, an in-phase component $aV_m \sin \omega t$ is obtained. In other words, in case of this time-dependent capacitor the observed admittance $Y$ is complex instead of being imaginary:

$$Y = a + j\omega at = a + j\omega C(t) \tag{6a}$$

and its reciprocal, the impedance $Z$ is:

$$Z = \frac{1}{a(1+\omega^2 t^2)} - \mathrm{j}\frac{\omega t}{a(1+\omega^2 t^2)} \qquad (6b)$$

instead of $Z = -\mathrm{j}/\omega C(t)$.

If similar reasonings are applied to a time dependent resistor no complication is met, because only in cases where the derivation involves differentiation with respect to $t$ an extra term arises.

Thus far the experiment was supposed to be conducted potentiostatically (cf. eqn. 3) and one may wonder how a time-dependent condenser behaves under galvanostatic conditions, i.e.

$$i = i_m \sin \omega t \qquad (7)$$

Combination of eqns. (1), (2), and (7) leads to

$$Q = \int i_m \sin \omega t \, \mathrm{d}t = -\frac{i_m}{\omega} \cos \omega t = atV$$

Whence

$$V = -\frac{i_m}{\omega a t} \cos \omega t \qquad (8)$$

Comparing eqns. (7) and (8) it is evident that under galvanostatic conditions the condenser presents the characteristics expected from its impedance

$$Z = -\frac{1}{\mathrm{j}\omega C} \qquad (9)$$

irrespective whether $C$ is a function of time or not.

From the foregoing it must be concluded that the concept of impedance should be applied with care to time-dependent objects: the impedance measured will be dependent on the way the experiment is conducted.

Because in a bridge the object conducts electric current neither under potentiostatic nor under galvanostatic conditions its behaviour cannot easily be predicted.

In case of a time-dependent self inductance it can be shown in an analogous way that the object behaves normal under potentiostatic conditions and presents a real component under galvanostatic conditions.

## APPLICATION TO A DROPPING MERCURY ELECTRODE

It easily can be shown that also for this object the galvanostatic experiment gives no special effect. Therefore we confine to the potentiostatic experiment and for the sake of simplicity in this Section we restrict to a theoretical electrode without faradaic process and without series resistance. The double layer capacity of this electrode will be proportional to the electrode surface area, so on the assumption of constant mercury flow

$$C = at^{2/3} \qquad (10)$$

Then with (3) following the same reasoning as before we find an expression for the cell current

$$i = aV_m(\tfrac{2}{3}t^{-1/3}\sin\omega t + \omega t^{2/3}\cos\omega t) \qquad (11)$$

Again, in addition to the "normal" response $V_m\omega C(t)\cos\omega t$, the current contains an in-phase component, $2/3aV_mt^{-1/3}\sin\omega t$. Evidently, in this case of the dropping mercury electrode, this term extinguishes slowly. It is interesting to calculate on which condition the "error" is negligible.

An acceptable error in the phase angle is 0.2 degree, which corresponds with $\mathrm{tg}\varphi < 0.0035$.

From eqn. (11) it follows $\mathrm{tg}\varphi = 2/3\omega t$, whence $\omega t > 200$. For a drop life of three seconds the lowest allowed frequency is henceforth found to be about 10 Hz. However, if one intends to apply the so-called rapid a.c. polarography technique as proposed by Zatka [2], Bond et al. [3,4] and Canterford [5], the small time values involved ($t = 0.16$ s), require a frequency limit $f > 200$ Hz.

## APPLICATION TO MORE COMPLEX EQUIVALENT CIRCUITS

Calculation of the current response of an $RC$ series combination where both $R$ and $C$ are functions of time requires solving the differential equation

$$\frac{\mathrm{d}i}{\mathrm{d}t} + \left[\frac{\mathrm{d}\ln R(t)C(t)}{\mathrm{d}t} + \frac{1}{R(t)C(t)}\right]i - \frac{V_m}{R(t)}\left[\frac{\mathrm{d}\ln C(t)}{\mathrm{d}t}\sin\omega t + \cos\omega t\right] = 0 \qquad (12)$$

in which for a practical dropping mercury electrode $C(t) = at^{2/3}$ and $R(t) = R_{hom} + bt^{-1/3}$. As yet no analytical solution of this differential equation could be found.

## SWEPT FREQUENCY IMPEDANCE MEASUREMENTS

Now that voltage controlled oscillators and phase locked detectors are available it is tempting to construct a network analysing system that automatically measures the cell impedance or admittance at a continuously varying frequency. Again the general feeling will be that the rate of change of the frequency should be low compared to the frequency applied. We believe it is interesting to know more quantitatively the errors involved and also to known the nature of the error, viz. whether something happens to the in-phase component or the quadrature. Again we treat the problem independently of the effects of non-zero time constants discussed in ref. 1.

For the sake of simplicity we restrict this discussion to a capacitor with a time-independent capacity.

If the frequency is swept linearly with time

$$\omega = a + bt$$

a potentiostatic perturbation applied (cf. eqn. 3) becomes

$$V = V_m\sin(at + bt^2) \qquad (13)$$

whence with $i = C\mathrm{d}V/\mathrm{d}t$

$$i = (a + 2bt)CV_m\cos(at + bt^2) \qquad (14)$$

Comparison of eqns. (13) and (14) leads to the conclusion that the "impedance" of the capacitor is

$$Z(t) = \frac{1}{\mathrm{j}(a + 2bt)C} \tag{15}$$

while neglect of the fact that the frequency is being swept leads to

$$Z = \frac{1}{\mathrm{j}\omega C} = \frac{1}{\mathrm{j}(a + bt)C} \tag{16}$$

Comparing eqns. (15) and (16) we can conclude that the admittance $Y = 1/Z$ observed in a swept frequency experiment is larger than the admittance that would have been observed at a certain constant frequency, the difference being equal to $\mathrm{j}btC = \mathrm{j}(\omega - \omega_{t=0})C$. Of course $b$ also can be chosen negative, in which case the admittance will be found smaller. An analogous calculation can be made with a linearly frequency swept a.c. current

$$i = i_{\mathrm{m}} \sin(at + bt^2) \tag{17}$$

with the intent to see what happens to the admittance of a constant capacitor in that case. Evaluation of the voltage across the capacitor requires solution of the integral

$$V(t) = \frac{i_{\mathrm{m}}}{C} \int_0^t \sin(at + bt^2)\mathrm{d}t \tag{18}$$

An alternative formulation of this integral is [6]

$$V(t) = \frac{i_{\mathrm{m}}}{C}\frac{\pi}{2b}\left\{\cos\left(\frac{a^2}{4b}\right)\mathcal{S}\left[\frac{1}{\sqrt{2\pi b}}(a + 2bt)\right] - \sin\left(\frac{a^2}{4b}\right)\mathcal{C}\left[\frac{1}{\sqrt{2\pi b}}(a + 2bt)\right]\right\} \tag{19}$$

in which $\mathcal{S}(x)$ and $\mathcal{C}(x)$ stand for the sine and cosine Fresnel integral, respectively. Numerical values of these integrals have been tabulated [7]. For $x = (2\pi b)^{-1/2}(2bt + a) > 5$ they can be approximated by analytical expressions, yielding for $V(t)$:

$$V(t) = \frac{i_{\mathrm{m}}}{2C}\sqrt{\frac{\pi}{2b}}\left[\cos\left(\frac{a^2}{4b}\right) - \sin\left(\frac{a^2}{4b}\right)\right] - \frac{0.318\pi i_{\mathrm{m}}}{C(a + 2bt)}\cos(at + bt^2) \tag{20}$$

As $0.318\pi$ equals 0.99997 the a.c. term in eqn. (20) leads to nearly the same conclusion as in the potentiostatic case, i.e. that towards a linearly frequency swept current a capacitor exhibits a changed admittance, the difference as compared to a constant frequency experiment being equal to $\mathrm{j}btC = \mathrm{j}(\omega - \omega_{t=0})C$.

The condition for (20) to be valid appears to be fulfilled in realistic practical cases. For example it is met already at $t = 0$ for a swept frequency starting at 26 Hz swept with a rate of 26 Hz $\mathrm{s}^{-1}$.

## CONCLUSIONS

From the foregoing discussion it can be concluded that under normal practical conditions the determination of the double layer at a dropping mercury electrode will not be complicated by its time dependency. The in-phase component of the capacitance of the double layer can be calculated from eqn. (10) with

$$a = 4\pi C_d \left(\frac{3m}{4\pi 13.6}\right)^{2/3}$$

always to be much smaller than the ohmic resistance of the cell.

In the study of electrode kinetics, however, the ohmic resistance is subtracted before the analysis and moreover the analysis is most sensitive to errors in the phase angle. Therefore under unfavourable conditions like small drop time and very reversible electrode reaction the effect described could influence the result. Unfortunately a quantitiative study based on an equivalent circuit comprising a faradaic process looks impossible due to mathematical complexity.

Measurements with frequency swept a.c. voltage or current lead to an error in the double layer capacitance that can be calculated easily. The allowed sweep rate can be calculated and its value will also serve as a guide in more complex equivalent circuits.

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