

FARADAIC RECTIFICATION: AN AMENDED TREATMENT*

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Abstract—Delahay's graphical treatment of the faradaic rectification technique is critically discussed, taking into account, without approximations, the complete cell impedance as given by Randles' equivalent circuit. As an improvement a numerical approach is proposed, as well as a technique where the frequency is determined at which the rectification signal is zero.

Résumé—Le traitement graphique de Delahay de la technique de rectification faradique est critiqué en tenant compte, sans introduction d'approximations, de l'impédance de la cellule électrochimique complète ainsi qu'elle a été décrite par Randles. Un procédé numérique amélioré est proposé, de même qu'une méthode suivant laquelle on détermine la fréquence nécessaire pour faire disparaître le signal rectifié.

Zusammenfassung—Die graphische Auswertung von Delahay bei der Methode der Faraday-Gleichrichtung wird kritisch diskutiert, indem die vollständige Zellimpedanz, wie sie durch das Äquivalentschema von Randles gegeben ist, ohne Vereinfachung in Betracht gezogen wird. Zur Verbesserung wird eine numerische Methode vorgeschlagen und eine Technik beschrieben, bei der die Frequenz bestimmt wird, wo das Gleichrichtungssignal Null wird.

INTRODUCTION

THE DETERMINATION of the kinetic parameters of an electrode reaction by relaxation methods generally involves three fundamental problems, namely the elimination of ohmic drop, diffusion polarization and double-layer charging current. Unfortunately a successful elimination of one of the three, *eg* diffusion polarization with the aid of fast perturbations, is usually accompanied by a large preponderance of one of the others, *eg* double-layer charging. A useful method, therefore, should provide the best compromise between the circumstances that afford the desired elimination.

The faradaic rectification method has been introduced in this field as a powerful method. The main advantage is the fact that the rectification signal itself represents only the faradaic process, since the influences of the ohmic resistance and double-layer capacitance appear only in the alternating voltage across the interface. Consequently very high frequencies can be applied in order to suppress diffusion polarization to a large extent.

Delahay and co-workers¹⁻³ and Barker⁴ developed the instrumentation of the faradaic rectification method, especially for the application of high frequencies, and outlined an elegant procedure for the evaluation of the rate parameters. They state that rate constants up to 100 cm/s can be determined if frequencies up to 100 MHz are applied. Their treatment, however, is based on two simplifying approximations, which usually are applied without an adequate check to see whether they are justified. Such a check should be performed by calculating the faradaic rectification shift exactly from the obtained cell parameters, preferably as a function of frequency, and comparing this with the experimental results.

In this paper it will be shown that a fitting procedure is also possible without the approximations mentioned. The potentialities of this method will be discussed in relation to the instrumental possibilities.

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THEORY

The basic principle of the method is the appearance of a shift in the dc potential of an electrode, if it is perturbed with a sinusoidally alternating current. If no direct current is allowed to flow, the steady state value of the potential shift ΔE_∞ is given by

$$\frac{\Delta E_\infty}{V_A^2} = \frac{nF}{RT} \left\{ \frac{2\alpha - 1}{4} - \frac{1}{2} \left[\alpha - \frac{C_O^\circ \sqrt{(D_O)}}{C_O^\circ \sqrt{(D_O)} + C_R^\circ \sqrt{(D_R)}} \right] \frac{1 + \cot \Phi}{1 + \cot^2 \Phi} \right\}, \quad (1)$$

in which C_O° and C_R° are the equilibrium concentrations of the electro-active species, V_A is the amplitude of the alternating voltage across the electrode/solution interface, α the transfer coefficient and Φ the phase angle of the faradaic impedance, which depends on α and the rate constant k_{sh} . (1) contains the information on these parameters in a rather intricate way. Moreover, V_A is not directly measurable because a part of the total alternating voltage appears across the ohmic resistance.

Therefore V_A should be expressed in terms of the amplitude i_A of the alternating current passing the cell, and the absolute value $|Y_{el}|$ of the electrode admittance Y_{el} . The latter can be calculated in accordance with Randles' equivalent circuit,^{5,6}

$$|Y_{el}| = (Y_{el}'^2 + Y_{el}''^2)^{1/2}$$

with

$$Y_{el}' = \frac{p + 1}{\sigma \omega^{-1/2} (p^2 + 2p + 2)}, \quad (2a)$$

$$Y_{el}'' = \frac{1}{\sigma \omega^{-1/2} (p^2 + 2p + 2)} + \omega C_d \quad (2b)$$

and

$$p = \theta / \sigma \omega^{-1/2} = p' \omega^{1/2} = \frac{\sqrt{2\omega} \cdot (C_O^\circ)^\alpha \cdot (C_R^\circ)^{(1-\alpha)}}{k_{sh} [C_O^\circ (D_R)^{-1/2} + C_R^\circ (D_O)^{-1/2}]} \quad (3)$$

where C_d is the double-layer capacitance, σ the Warburg coefficient and θ the transfer resistance. Hence,

$$V_A = \frac{i_A}{|Y_{el}|} = \frac{i_A}{\omega C_d} \left[\frac{p^2 + 2p + 2}{(p + 1)^2 + (\sigma^{-1} C_d^{-1} \omega^{-1/2} + 1)^2} \right]^{1/2} \quad (4)$$

and, with $\cot \Phi = p + 1$, (1) can be rewritten as

$$F = \frac{\Delta E_\infty \omega^2 C_d^2}{i_A^2} = \frac{nF}{4RT} \left[\frac{(2\alpha - 1)(p^2 + p) + \frac{C_O^\circ \sqrt{(D_O)} - C_R^\circ \sqrt{(D_R)}}{C_O^\circ \sqrt{(D_O)} + C_R^\circ \sqrt{(D_R)}} (p + 2)}{(p + 1)^2 + (\sigma^{-1} C_d^{-1} \omega^{-1/2} + 1)^2} \right]. \quad (5)$$

If, as usual, the faradaic rectification method is applied to very fast systems, the values of C_d and σ , and thus of the diffusion coefficients, may be obtained with some low-frequency method (eg the complex-plane method⁶ or the oscilloscopic method⁷), for which the system will be entirely diffusion-controlled. Then only the two unknowns α and $p' = \theta/\sigma$ remain to be solved from (5), which must be applied at various frequencies. As is known, the rate constant k_{sh} follows immediately from θ and α .

On the accuracy and correctness of the results some general remarks have to be made. Kooyman *et al*⁸ pointed out that ΔE_∞ should not exceed *ca* 0.2 mV, in order that higher order contributions are less than 5 per cent of the right hand member of (1). If ΔE_∞ does not exceed 0.2 mV, the inaccuracy in the measurements of ΔE_∞ will be about 10 per cent. The inaccuracy in C_d may be estimated to be *ca* 5 per cent. Therefore, the experimental value of $F = \Delta E_\infty \omega^2 C_d^2 / i_A^2$ may contain an error of *ca* 15 per cent.

Fast electrode reactions are most favourably studied at high frequencies. So, the scope of the method depends on the order of magnitude of frequency at which measurements can be performed. Delahay and co-workers claim that frequencies up to 50 or even 100 MHz may be reached, but in our opinion measurements performed above 16 MHz must be considered as very doubtful, because above 16 MHz the rectification signal has been found to be often disturbed by reflexions. Moreover, the output power of the signal generator is at these high frequencies not sufficient to obtain a measurable rectification signal.

In fact, the measurements of Imai and Delahay⁹ on the $\text{Hg}_2^{2+}/\text{Hg}$ electrode at frequencies up to 50 MHz lead to inconsistent results, with respect to both the theory of faradaic rectification and the results of other relaxation methods.¹⁰

Furthermore, it may be noticed that, if p approaches infinity, only the value of α can be determined from (5). This means that the frequency range at which measurements are performed should be adapted to the magnitude of the rate constant.

The accuracy with which both α and p' can be obtained is considerably reduced if

$$(C_O^\circ \sqrt{D_O} - C_R^\circ \sqrt{D_R}) / (C_O^\circ \sqrt{D_O} + C_R^\circ \sqrt{D_R}) \approx 2\alpha - 1.$$

Therefore, measurements preferably should be made with varying ratio $C_O^\circ \sqrt{D_O} / C_R^\circ \sqrt{D_R}$.

Finally, the magnitude of the concentrations proper introduce their influence by means of the term $(\sigma^{-1} C_d^{-1} \omega^{-1/2})$ in the denominator of (5). Delahay¹ pointed out that the total concentration $(C_O^\circ + C_R^\circ)$ should not be below 10^{-3} mole/l, because otherwise the proper value of ΔE_∞ is not reached within the commonly used modulation time. In general the total concentration should not exceed 10^{-2} mole/l, since at higher concentrations a too high output power of the signal generator is needed to obtain a measurable rectification signal. Consequently, if $D_O = D_R \approx 10^{-5} \text{ cm}^2/\text{s}$ and $C_d \approx 20 - 40 \mu\text{F}/\text{cm}^2$, the term $(\sigma^{-1} C_d^{-1} \omega^{-1/2})$ will have a magnitude of 0.1–2 at 1 MHz.

GRAPHICAL EVALUATION OF α AND p'

Delahay and co-workers^{1,2,9} proposed an analysis procedure of faradaic rectification measurements based on a plot of $F = \Delta E_\infty \omega^2 C_d^2 / i_A^2$ against $\omega^{-1/2}$. At sufficiently high frequencies the terms in σ in (4) are negligible (V_A entirely controlled by the double-layer capacitance) and in addition p may be so large that

$$\frac{1 + \cot \Phi}{1 + \cot^2 \Phi} = \frac{p + 2}{p^2 + 2p + 2} \approx \frac{1}{p}.$$

Hence (1) reduces to

$$F = \frac{\Delta E_\infty \omega^2 C_d^2}{i_A^2} = \frac{nF}{4RT} \left\{ 2\alpha - 1 - \left[2\alpha - \frac{2C_O^\circ \sqrt{D_O}}{C_O^\circ \sqrt{D_O} + C_R^\circ \sqrt{D_R}} \right] \frac{\omega^{-1/2}}{p'} \right\}. \quad (6)$$

Consequently the values of α and p' follow from the intercept at $\omega^{-1/2} = 0$ and the slope of the plot.

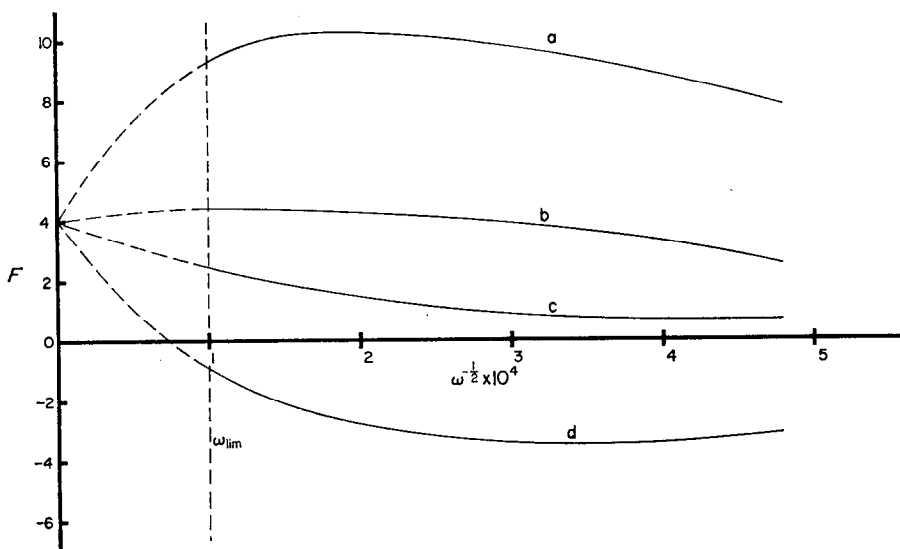


FIG. 1. Calculated plots of F vs $\omega^{-1/2}$.
Fixed values $\sigma = 20 \Omega \text{cm}^2/\text{s}^{1/2}$, $k_{\text{sh}} = 8 \text{ cm/s}$, $\alpha = 0.60$, $n = 2$, $C_d = 30 \mu\text{F cm}^{-2}$;
several values of $C_O^\circ \sqrt{(D_O)}/C_R^\circ \sqrt{(D_R)}$: a, 10.0; b, 1.75; c, 1.0; d, 0.46.

In a comment on the application of this method to the $\text{Hg}_2^{2+}/\text{Hg}$ reaction, two of us¹⁰ pointed out that the results in this case were not consistent with the mentioned approximations and consequently were not correct. Therefore we now discuss the applicability of the procedure in general. In Fig. 1 some curves, calculated from (5), are represented. It is clear that extrapolation of the plots a and d from frequencies below the upper limit ω_{lim} will lead to a large error in α , whereas curves b and c may lead to an acceptable value of α . Thus, Fig. 1 shows clearly the large influence of the Ox/Red ratio in (5) and (6). Therefore it is very important that measurements are performed for various Ox/Red ratios.

Though the curves in Fig. 1 are not exactly straight lines below ω_{lim} , they might appear to be straight, if measured in practice, owing to the large inaccuracy of the measurements. The evaluation of p' from these slopes, according to (6), will, however, lead to largely erroneous results, eg if p' is calculated from the slope of curve c in Fig. 1, which is the best curve for this purpose, there is an error of at least a factor of two.

If the purpose of the method is to determine k_{sh} with an error less than 50 per cent, while the upper frequency limit at which measurements can be performed is about 16 MHz, it seems reasonable to require that the slope of the curve at 4 MHz ($\omega^{-1/2} = 2 \times 10^{-4}$) deviates less than 50 per cent from the slope at infinite frequency. Thus

$$\left| \frac{\left(\frac{dF}{d\omega^{-1/2}} \right)_{\omega^{-1/2}=0} - \left(\frac{dF}{d\omega^{-1/2}} \right)_{\omega^{-1/2}=2 \times 10^{-4}}}{\left(\frac{dF}{d\omega^{-1/2}} \right)_{\omega^{-1/2}=0}} \right| < 0.5. \quad (7)$$

From (5) and (7) the limits of the measurable k_{sh} values can be calculated for different values of α and the Ox/Red ratio, and for reasonable values of σ , n , and C_d . The result is listed in Table 1.

TABLE 1. HIGHEST VALUES OF k_{sh} IN cm/s THAT CAN BE OBTAINED IF ONLY (7) LIMITS THE RANGE.
 $n = 2$, $\sigma = 25 \Omega \text{cm}^2/\text{s}^{1/2}$, $C_d = 30 \mu\text{F}/\text{cm}^2$, concentrations ca 2mM.

$C_O^\circ \sqrt{(D_O)}/C_R^\circ \sqrt{(D_R)}$	$\alpha = 0$	$\alpha = \frac{1}{4}$	$\alpha = \frac{1}{2}$	$\alpha = \frac{3}{4}$	$\alpha = 1$
10	0.9	1.6	1.7	1.5	25
3	1.7	2.6	1.4	—	16
1	5	5	—	5	5
0.33	16	—	1.4	2.6	1.7
0.1	25	1.5	1.7	1.6	0.9

If the results of Table 1 are considered, the conclusion must be that the faradaic rectification method interpreted as described by Delahay *et al* is positively not superior to the other relaxation methods, except for extreme values of α . However, such values are not likely to occur in practice. Therefore, the graphical analysis of measured faradaic rectification data is useful only for an introductory estimation of the kinetic parameters. The values obtained may be used as a starting point for the numerical calculation with the general equation (5). A procedure for this approach is outlined in the following section.

NUMERICAL EVALUATION OF α AND p'

For the numerical evaluation of α and p' it is useful to compare the experimental plot of $F = \Delta E_\infty \omega^2 C_d^2 / i_A^2$ against $\omega^{-1/2}$ with a "reversible plot" calculated from (5) with the experimental values of D_O , D_R , σ and C_d , but with $p' = 0$ (k_{sh} infinite) inserted. The difference between these two curves has to be significant as regards the accuracy of the experimental curve. In general the following condition can be derived,

$$|(F_{\text{exp}})_{\omega_1} - (F_{k_{sh}=\infty})_{\omega_1}| > \Delta F, \quad (8)$$

where ΔF is a constant representative for the experimental accuracy, and ω_1 is a certain value in the frequency range covered sufficiently different from the upper limit ω_{lim} of this range. If (8) is fulfilled, the ordinates F of the smoothed curve at two sufficiently different frequencies are inserted into (5), in order to obtain two equations from which the two unknowns α and p' can be solved. Because of their complex nature, the equations cannot be solved directly, but the solution has to be found by trial and error. For this purpose, the approximate values of α and p' obtained by the graphical evaluation can be of great help.

Since (5) is obtained without any approximations, it is clear that the faradaic rectification method is now limited only by the frequency restrictions and the accuracy of the measurements imposed by the experimental set-up.

An experimental set-up for low frequencies can always be arranged. Therefore, in this paper the lower limit for determining k_{sh} will not be considered.

The potentialities of the numerical method can be calculated with the aid of (8). It has already been pointed out that the inaccuracy in one value of F is 15 per cent. If a smooth curve is constructed through various values of F the accuracy is somewhat better. With this (8) can be rewritten as

$$|(F_{\text{exp}})_{\omega_1} - (F_{k_{sh}=\infty})_{\omega_1}| > 0.1(F_{\text{exp}})_{\omega_1}, \quad (9)$$

where ω_1 may be taken as 10^7 rad/s, if ω_{lim} is 10^8 rad/s (16 MHz). If the purpose is again to determine k_{sh} with an accuracy better than 50 per cent, the general condition is

$$\left| \left(\frac{F}{p'} \right)_{\omega_1} \cdot \left[\left(\frac{dF}{dp'} \right)_{\omega_1} \right]^{-1} \right| < 5. \quad (10)$$

The solution can be found by plotting the left hand part of (10) against p' at constant α . The intersection at 5.0 yields the limiting value of p' , from which the limiting value of k_{sh} is obtained. The results are given in Table 2.

TABLE 2. LIMITS OF RATE CONSTANTS IN cm/s WHICH CAN BE MEASURED WITH LESS THAN 50 PER CENT INACCURACY BY MEANS OF THE NUMERICAL METHOD.
Cell parameters as in Table 1.

$C_O^\circ \sqrt{(D_O)}/C_R^\circ \sqrt{(D_R)}$	$\alpha = 0$	$\alpha = \frac{1}{4}$	$\alpha = \frac{1}{2}$	$\alpha = \frac{3}{4}$	$\alpha = 0$
10	4	5	4	—	30
3	10	9	5	—	25
1	19	9	—	9	19
0.33	25	—	5	9	10
0.1	30	—	4	5	4

If Table 2 is compared with Table 1, the distinct improvement in the potentialities of the faradaic rectification method is apparent. The results listed in Table 2 can still be improved if various measurements for different Ox/Red ratios are combined. A more elegant variation on this method is discussed in the following section.

NUMERICAL EVALUATION OF α AND p' IN THE SPECIAL CASE THAT F IS ZERO

This method is based on measurement of the frequency at which the rectification voltage is zero. The method was first proposed by Imai.¹¹ As Imai stated, its great advantage is that the voltage across the electrode/solution interface, V_A , need not be known. This means that it is not necessary to measure the value of the double-layer capacitance and the amplitude of the alternating current flowing through the cell.

If the rectification voltage is zero, (5) reduces to

$$\frac{(p')^2 \omega + p' \omega^{1/2}}{p' \omega^{1/2} + 2} = - \frac{\frac{C_O^\circ \sqrt{(D_O)} - C_R^\circ \sqrt{(D_R)}}{C_O^\circ \sqrt{(D_O)} + C_R^\circ \sqrt{(D_R)}}}{2\alpha - 1}. \quad (11)$$

Evidently a zero point is obtained only if

$$\frac{C_O^\circ \sqrt{(D_O)} - C_R^\circ \sqrt{(D_R)}}{C_O^\circ \sqrt{(D_O)} + C_R^\circ \sqrt{(D_R)}} / (2\alpha - 1) < 0.$$

This means that if $\alpha < 0.5$ the chosen concentrations have to obey $C_O^\circ \sqrt{(D_O)} > C_R^\circ \sqrt{(D_R)}$ and if $\alpha > 0.5$ the reverse should hold. In order to calculate a rate constant and a transfer coefficient with the aid of (11), it is necessary to measure two zero points, of course for two different Ox/Red ratios. If the two zero points are inserted in (11), they yield two equations with two unknowns (*ie* α and k_{sh}), which can be solved by successive approximation. Note that here k_{sh} enters as an unknown instead p' , since the latter is a function of the Ox/Red ratio (*cf* (3)).

This theory is similar to that given by Imai.¹¹ However, he introduced the same approximations as are needed in the graphical analysis, (6), which may lead to erroneous results¹⁰, if the conditions for the approximations to hold are not met.

As the alternating current as well as the double-layer capacitance and the rectification signal itself do not appear in (11), they do not contribute to the experimental error and consequently to the error in the parameters evaluated by this zero-point method. Instead, an error in the frequency is introduced; *ie*, a small frequency range is observed at which the rectification signal is indistinguishable from zero. This is in fact the most important experimental error. In comparison with the numerical method without the aid of zero points, the latter method leads to far more accurate results.

As a minor disadvantage, an experimental set-up for a wide frequency range (500 Hz–50 MHz) must be available.

CONCLUSION

A striking feature of the faradaic rectification method is the possibility of the determination of transfer coefficients without varying the Ox/Red ratio. This might be advantageous in the study of electrode processes with a potential-dependent rate constant or transfer coefficient (or both), since in all other methods α can be obtained only from measurements at varying Ox/Red ratios.

From Table 2 it follows that the potentialities of the faradaic rectification method, as regards the largest values of measurable rate constants, are an order of magnitude better than other relaxation methods (*eg* impedance⁶ and galvanostatic methods), provided that a favourable Ox/Red ratio is chosen and that the numerical analysis proposed in this paper is applied, at least to check the validity of graphically obtained parameters. If possible the zero-point method for the analysis of experimental data should be preferred, since with this method interference of both the double-layer capacitance and the ohmic resistance is completely eliminated.

We intend to publish experiments supporting these statements in the near future.

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