

## TECHNIQUES FOR THE DETERMINATION OF OHMIC DROP IN HALF-CELLS AND FULL CELLS: A REVIEW

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(Received November 16, 1976; in revised form May 20, 1977)

### Summary

Different methods for the experimental determination of ohmic drop in batteries and half-cells are reviewed. The limitations in use of Luggin capillaries are defined. A novel method for elimination of ohmic error in high-resistance cells is described. This employs a programmable calculator or a minicomputer. By interpretation of the deviations from the log-rate law, values of internal resistance may be determined with some precision. A typical example is given and the results are compared with those obtained by classical oscillographic methods.

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### Introduction

The battery technologist has a strong interest in the ohmic drop (or resistive overpotential as it is sometimes known) as it occurs in every stage of battery development and production. In the early stages of battery development, the main aim of the battery scientist is to obtain polarization data free from resistive overpotential. As the battery development enters the "engineered" phase and passes into production, there is a need to know the value of the internal resistance and indeed this is a parameter which should be sampled as part of the well-designed quality control programme. The range of techniques available for making this sort of measurement is considerable, with some better adapted for half-cell measurements, others more suited to continuous monitoring of production batteries. The published literature describing these methods is sparse and often fails to discuss important facets of a particular technique with the result that these are frequently misapplied, as discussed subsequently. Euler [1] reviewed some of the methods but his

paper has not been published. A recent monograph on primary batteries also contains a valuable section [2] on the measurement of internal resistance, but this treatment is slanted towards applications for fully engineered production batteries and leaves uncovered important aspects of half-cell measurements. Apart from these references and two brief surveys [3, 4] there appears to be no comprehensive and up-to-date review of this important subject. The purpose of the present review is therefore to survey all known techniques, and provide key references while also examining in greater depth those aspects of the subject which are poorly described, or not at all, in the published literature. In this category we include a description of hitherto unpublished work using a programmable calculator to determine with some precision, values of ohmic drop.

### Source of the ohmic error

In the case of a full cell or assembled battery, the concept of ohmic resistance due to the electrolyte (with or without intervening separator) needs no further explanation. Surface films formed on the active masses can also make a further contribution to this term. Where a third electrode is introduced as a reference, either in a full cell or in a half cell, the concept of ohmic error is sometimes misunderstood. This reference electrode is placed at some point on the potential gradient between the two working or counter electrodes and the potential measured will depend on its position in the potential field. The "backmounted" reference electrode, using a capillary entering from the rear of a planar electrode, might be thought to be free from this source of error. However, as Barnartt [5] showed, even in this case, an error remains. The electrical analogue to the reference electrode in a system is the voltage divider network as shown in Fig. 1. The potential difference  $V$  between A and B is, according to Ohm's law, equal to  $iR$  for a current  $i$  flowing in resistance  $R$ . As the slide S moves nearer to A the resistance between A and S,  $R_{AS}$  decreases and, therefore, so does  $V_{AS}$ .

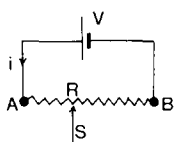


Fig. 1. Voltage divider network.

In an electrochemical cell A and B are the electrodes,  $R$  the resistance and S the reference electrode. The potential difference  $V_{AS}$  is added on to the true potential of A. If this error is to be as low as possible, the reference electrode should be as close as possible to the working electrode. This error due to the resistance between electrodes A and S, is called the " $iR$ ", or "ohmic drop" error. The measurement and correction of this " $iR$ " drop is the subject of the present review.

## Luggin capillaries — uses and misuses

The Luggin capillary, which screens the reference electrode from as much as possible of the potential gradient between the two main electrodes is frequently used. However, even adoption of this device will not always eliminate ohmic error. The authors have often come across examples of gross misuse of the Luggin capillary, as discussed below.

The classical work of Barnartt [5, 6] and Piontelli [7 - 9] on the effect of Luggin placement and geometry appears to have been largely overlooked by younger workers. Barnartt and Piontelli produced electrode potential contour diagrams for Luggin capillaries of different size and of different geometry. Not only did they study the classical glass-tipped capillary facing the electrode, but also the method in which the reference penetrated from the rear of the electrode (simultaneously reported by Milligan [10]) and a further method in which the reference electrode rested on the working electrode and measured its potential through a small orifice in the sidewall.

In the use of the Luggin, the commonest error is, recognizing that the further away it is placed from the electrode surface the greater the error to go to the other extreme and to place it resting on the metal surface. In such a situation “shielding” takes place, and precisely because the Luggin tip obscures the electrode surface, it senses a potential condition there which approximates to a “nil current” condition and which differs from the situation obtaining over the remainder of the electrode surface.

From the work of Barnartt [5, 6] the empirical rule may be laid down that the tip of the probe should not approach closer than  $2d$  from the electrode surface (where  $d$  is the o.d. of the capillary), if shielding errors are to be avoided. While this represents good practice, it is not the total answer to ohmic drop elimination. When higher current densities or more resistive solutions are used, the errors again become unacceptably large. Table 1 shows typical examples, the heavy line demarcating situations embodying the arbitrarily chosen 10 mV or less error and those where the error is greater. Where the electrode reaction is a gas-evolving one, problems may be encountered not only as a result of variable ohmic drops as bubbles form and release on the electrode surface facing the Luggin (and this is discussed below) but also as a result of bubbles actually entering the Luggin capillary. This may be mitigated, if not avoided, either by arranging for the capillary to have a slight upwards slope and/or arranging for a continuous stream of electrolyte from a reservoir to flow out of the capillary into the bulk, thus discouraging entry of bubbles.

## Methods for the elimination, or determination, of internal resistance

The observations above relate solely to the correct use of a Luggin probe. However, as seen in Table 1, there is a wide range of conditions where these precautions alone are not enough. The growing emphasis on energy

TABLE 1

$V_{iR}$  in mV for a capillary tip of diameter 0.02 cm at 0.04 cm from a plane electrode [7]

$i$ (A cm <sup>-2</sup> )	$K(\Omega^{-1} \text{ cm}^{-1})$			
	1	10 <sup>-1</sup>	10 <sup>-2</sup>	10 <sup>-3</sup>
$3 \times 10^{-1}$	10	100	1000	10,000
$3 \times 10^{-2}$	1	10	100	1000
$3 \times 10^{-3}$	0.1	1	10	100
$3 \times 10^{-4}$	0.01	0.1	1	10

conversion devices operating at high current densities as well as the higher current densities (up to 2 A/cm<sup>2</sup>) now being used, for example, in the chlorine industry, forces us to consider other techniques for correct measurement of electrode potential. We can summarize these as follows: (i) micro-meter-mounted Luggin, and extrapolation of electrode potential to value where  $L$  (electrode-Luggin distance) = 0; (ii) use of bridge circuit with compensating resistor (galvanostatic method); (iii) observation of fast transients on an oscilloscope, either single shot or a.c. waveform to determine and subtract the ohmic component; (iv) a.c. bridge; (v) positive feedback techniques (compensation); (vi) mathematical corrections.

Before considering these various methods, whose difficulties and advantages have not previously been compared, some further observations should be made. In the first place, we should not cling too rigorously to the concept of a metal electrode surface with a straightforward ohmic drop in the surrounding solution. The evolution of gas from an electrode surface will create an electrolyte of greater resistance than the gas-free medium as a result of the voidage. In consequence, the measured ohmic drop will likewise increase in such circumstances. At the same time, it is possible, where hydrogen or oxygen are being evolved, for local alkalization or acidification to take place, again with a corresponding change in the resistivity of the medium and thus the measured drop. These two effects, bubbles and pH change, which usually occur simultaneously, are difficult to separate. Tobias [11] has treated the more general problem of electrolyte resistance increase resulting from gas voidage. The resistivity at a given depth  $x$  from the upper surface of solution  $\rho_x$  was found to depend on the volume fraction of the gas  $f_x$  according to the formula  $\rho_x = \rho(1 - f_x)^{-3/2}$  where  $\rho$  is the resistivity of the gas-free electrolyte. Figure 2 shows the effect of this in graphical form, the gas volume fraction being now higher at the top of the electrode than at the bottom so that the effect can be minimized by placing the Luggin capillary close to the bottom of the electrode (though not too close, since "edge" effects operate at the extremities).

It will be appreciated that the resulting variation of the effective " $\rho$ " value from top to bottom of the cell, results in an uneven distribution of current density, this being greatest at the bottom of the cell where fewest bubbles exist. The total situation is thus one of some considerable complexity.

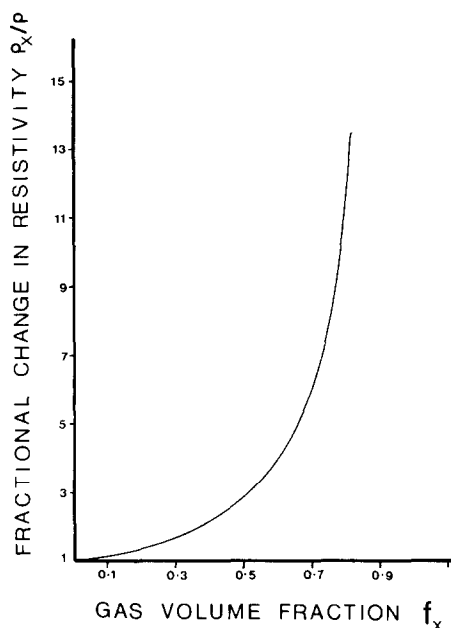


Fig. 2. Dependence of electrolyte resistivity on volume fraction of gas, calculated from the equation  $\rho_x = \rho(1 - f_x)^{-3/2}$  from ref. [11].

In dilute solutions, another source of variable ohmic drop arises from depletion of charge carriers as the diffusion limiting current is approached. There appear to be very few published examples of ohmic drops varying during the course of an experiment. The value of  $R$  can be measured either as the current is switched on ( $R$  corresponds to bulk solution) or as the current is switched off ( $R$  having increased due to bubbles and pH change). Figure 3, obtained in these laboratories, shows that measurements made under these conditions can show substantial differences.

Ohmic drop measurements for composite electrodes such as the  $\text{PbO}_2$ -Ti or  $\text{PbO}_2$ -Ni found in primary batteries can prove difficult to measure with certainty. The difficulty arises because of phenomena which may take place across the basis-metal-coating interface. Thus, just as a metal electrode in solution can be represented by an RC circuit, with its own time constant, a composite electrode may be represented by a pair of these elements in series. The presence of a thin layer of  $\text{TiO}_x$  between the Ti basic metal and the outer  $\text{PbO}_2$  would create such a "double layer" in the solid phase. Without the knowledge of the time constant of this element, it is impossible to state, on the basis of one method alone, what part it plays in the observed measurements. The application of two methods simultaneously — one of them for example being the moveable Luggin capillary, described below — might resolve this.

With these problems in mind, the range of techniques listed above with their inherent characteristics are considered in greater detail.

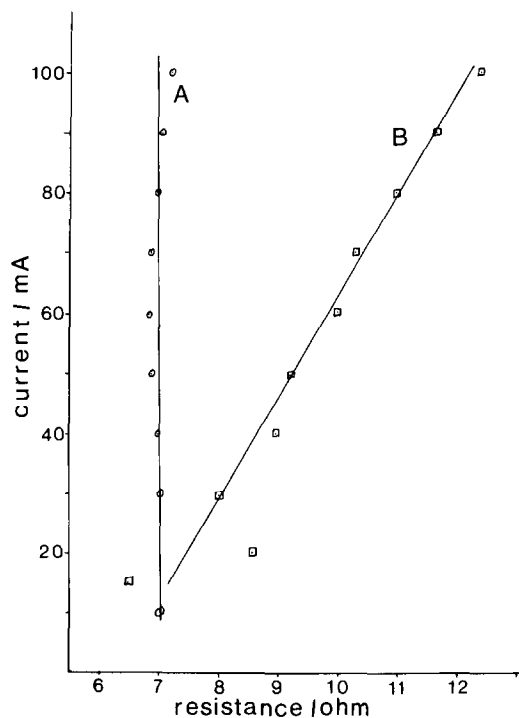


Fig. 3. Resistance measurements obtained during hydrogen evolution on platinum in 2 M NaCl: (A) when the current was switched on; (B) when the current was switched off.

#### *Micrometer-mounted Luggin probe*

By making a series of overvoltage measurements at constant current, and varying the distance of the Luggin tip from the electrode surface, a value of the overvoltage extrapolated to zero distance from the electrode surface can be obtained, but without incurring any of the penalties due to "shielding" which have been referred to above. Because such measurements are by their nature tedious and time consuming, the method is rarely used. In some laboratories, a medical all-glass syringe is adapted for this purpose with a micrometer fitted for precise measurement of the electrode-Luggin gap.

The classic work here is that of Bockris and Azzam [12]. However, Mortimer [13] has criticized this work on the grounds that the capillary tip was less than  $2d$  from the electrode and so the electrode was being shielded. Vetter's suggestion [14] that this technique might be specially useful for separation of solution and film resistive drops is also open to criticism on the grounds that extrapolation to  $l = 0$  of the potential values obtained at different positions of the capillary is valid only for a constant value of  $\rho$ , the specific resistance of the solution, which as we have indicated may not be the case.

### *Compensation (d.c.) bridges*

Berzins and Delahay [15] used a Wheatstone bridge circuit to compensate for the solution resistance in their two-electrode cell. When the solution resistance was compensated, galvanostatic pulses were applied and the cell voltage was measured with an oscilloscope. Jones [16] used a modification of Holler's bridge [17] network in a three-electrode system. They used steady-state galvanostatic polarization to study the corrosion of aluminium alloys in highly resistive solutions of sodium sulphate ( $\rho = 21,000 \Omega \text{ cm}$ ). A bridge resistance of the order of  $1100 \Omega$  was needed to compensate for the ohmic component of the solution, which was determined by an interrupter method. The cell potential was found by balancing the bridge using a potentiometer with an electrometer as null detector. In this method the reference electrode is connected externally to the working electrode by two  $200 \text{ M}\Omega$  resistors. Since the potential difference measured was very small, the current passing through the reference electrode would be of the order of a few nA. However, this system is unsuitable for more general applications where greater electrode polarizations are employed because the current through the reference electrode could easily be around  $10^{-7} \text{ A}$ , which is too high for most commercially available reference electrodes.

Wheatstone bridge networks cannot be used to compensate for resistances below  $1 \Omega$  because the resistance of the connecting wire and terminals becomes significant and cannot be eliminated.

### *Observation of fast transients*

We believe this is not only the most widely used, but also the most widely misused technique. This is because an oscilloscope can be rapidly "hooked up" to obtain a display that looks correct but is in fact wrong. The theory of the method is simple, if the electrode potential is displayed while the current is switched on or off, the ohmic component is the "instantaneous" change in potential. In fact, the situation created by such fast switching takes us into the realm of a.c. theory.

Care needs to be taken in the siting of the measuring equipment, with leads kept as short as possible to minimize pick up of stray capacitances and inductances. All parts of the measuring equipment, whether this be the operational amplifier mounted close to the electrode, as used by Flinn [20], or the oscilloscope on which the data are ultimately recorded, must be of sufficiently high bandwidth to fully record the rapid transients in question. Many oscilloscopes, notably those with differential amplifiers, have bandwidths below  $1 \text{ MHz}$ . Nothing less than  $10 \text{ MHz}$  is acceptable, and the oscilloscope beam intensity too must be sufficient to "write" at the required rate and leave a clearly visible trace.

Another error arises when one in fact measures the decay characteristic of the oscilloscope circuit rather than that of the electrode circuit. The weakness of the whole technique is that inadequate equipment will give an answer but one which may easily be erroneous, indicating too great an ohmic drop.

The Luggin probe that was optimum for simple measurements (as small and thin as possible) is now disadvantageous since its narrow orifice increases

the overall value of  $R$  and hence the decay time for the measurement circuit. Certain tricks have been adopted by various workers to minimize this sort of problem. Fiata *et al.* [18,19] do not simply open circuit their current supply, but switch it to an alternative system. This reduces "ringing". Flinn [20] mounted an operational amplifier immediately above his working electrode to reduce the RC characteristics of that circuit. Ringing can also be removed by replacing the Luggin capillary and reference electrode with a micro wire reference electrode such as palladium/hydrogen or silver/silver chloride [21], or other low-impedance reference electrodes. It is important to use as fast a scan rate on the oscilloscope as possible. Figure 4 shows how too slow a rate prevents discrimination of the ohmic from the subsequent capacitive decay, and makes the recorded data most vulnerable to slow writing speeds of the oscilloscope. Still another error arises when a.c. is present, superimposed on the d.c. electrode potential. If this is not realised, errors will enter as the "break" occurs in or out of phase with the a.c. Triggering of the oscilloscope can be a frustrating problem. The mercury-wetted reed relays which are almost invariably used to "make" or "break" the current, have an "instantaneous" action time. They normally have a 2 - 5 ms time to actuate which in itself need cause no problem if the oscilloscope is fitted with a delay. However, with a standard oscilloscope screen having ten divisions on the time axis, a scan rate of  $20 \mu\text{s}/\text{division}$  means that the complete scan lasts  $200 \mu\text{s}$ . Thus if the trace of the transient is initially positioned in the centre of the screen, the actuation time of the relay needs to be reproducible to within less than  $100 \mu\text{s}$  to ensure capture of the transient on the screen.

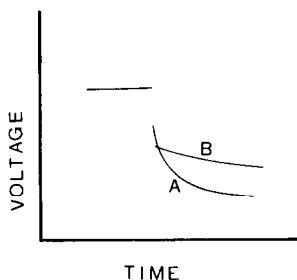


Fig. 4. Oscilloscope trace showing the effect of oscilloscope scan rate. (A) scan rate too low — time intercept is asymptotic, *i.e.* ohmic drop is ill-defined; (B) rate high enough to clearly show ohmic drop, with well-defined intercept.

The electrical circuit may be tested by replacing the electrochemical cell with its electrical analogue using components with known values. This "dummy" cell consists of two resistors in series, one of which has a capacitor connected across it. This circuit allows the measured value of  $R$  to be compared with its true value.

As a further check (with both dummy and electrochemical cells), the ohmic error,  $V_{iR}$ , should be determined at several currents and a graph of  $V_{iR}$  vs.  $i$  plotted. The result should be a straight line with slope  $R$  passing through the origin.



The repetitive “make-and-break”, or interrupter, technique is well known in the battery and fuel cell world [22] and is often referred to as the Kordesch–Marko method [23]. It offers the advantages of a “steady state” oscilloscope display, and a situation where the electrode is switched in such a way that the ratio of “off” and “on” times can be minimal and so the true change in potential of the electrode (after correction) need only be small.

As with the one-shot transient, reproducibility of the switching is important and some form of delay is essential unless very short on/off periods are used. This is because the oscilloscope is usually triggered by the on-(or off-) going transient immediately preceding the off (or on) transient of interest. At  $20 \mu\text{s}/\text{division}$  the interval between these two must be less than  $200 \mu\text{s}$  to be captured on the screen, if no delay is used. This delay may be either internal (*i.e.* part of the oscilloscope) or external. In the latter case the delay unit is triggered either by a transient or a special triggering signal and after a predetermined interval it applies a trigger pulse to the oscilloscope. This method requires a high precision timer — a delay of  $100 \text{ ms} \pm 10 \mu\text{s}$  means a reproducibility of 0.01%.

In this way widely differing on/off ratios may be employed. This is of importance in certain cases where a change in electrolyte composition (*e.g.* pH) occurs close to the electrode when current is flowing, thereby causing a change in resistivity of the electrolyte in the vicinity of the electrode (see Fig. 3). A low on/off ratio should be selected so as to (a) minimize the effect and (b) to allow sufficient time for the electrolyte composition to return to that of the bulk.

A current-interrupter potentiostatic circuit has been used by McIntyre and Peck [24] to monitor the ohmic resistance during an experiment; any variation in  $R$  could thus be detected and allowed for manually.

#### *A.c. bridge techniques*

It might well be said that the introduction of a time-variant function into electrochemical measurement techniques adds a new dimension of complexity and possible error. From the literature it is clear that, of all the methods listed in this paper, the a.c. technique is the most difficult and demanding. Not only is it all too easy, as a result of poor circuit design or construction, to obtain measurements which are artifacts of the system or the circuit, but also it is clear that a considerable degree of expertise is called for in the interpretation of results, even when these are valid in a purely electrical sense. Nevertheless, in the hands of an expert, the method is one of the best available for determination of internal resistance of cells or ohmic error in half cells. In the former case, a good treatment is given in ref. [2] which gives only partial credit to the work of Euler [25, 26] while the books by Thirsk and Harrison [27] and Damaskin [28] describe the application of the method to laboratory-type half-cells. Though the basic principle of the method (obtaining the impedance spectrum) has not changed, modern instruments such as the phase-sensitive detector and auto-balance equipment make measurements much simpler and lend themselves to computer-programmed systems [43].

### Positive-feedback technique

There have been numerous publications on the design of positive feedback systems for potentiostats [29 - 34] and they have been reviewed by Roe [35] and Nicholson [36]. Many modern potentiostats incorporate this feature. However, Bewick [29] has expressed doubts about the value of this technique, showing that it is easy to overcompensate and so produce an error larger than the original ohmic error. Also, Roe [35] has warned that, owing to inadequacies in the design, many published circuits may not necessarily work well in other potentiostat-cell combinations. Most circuits require a knowledge of the ohmic resistance which is then set manually on the potentiostat. Variations in  $R$  may be allowed for by the current-interrupter circuit proposed by Britz and Brocke [37] and the continuous method of Devay *et al.* [38, 39], on which the method of Wabner [42] appears to be based.

### Mathematical methods

#### Graphical

Cannon *et al.* [41] have suggested a mathematical method for the determination of  $R$ , based on the assumption that the reaction under study obeys the modified Tafel equation:

$$\eta = a + b \log i + iR \quad (1)$$

Differentiation produces:

$$\frac{d\eta}{di} = \frac{b}{i} + R$$

$d\eta/di$  is obtained by plotting current-voltage data and drawing tangents to the curve. Then, a plot of  $d\eta/di$  vs.  $1/i$  should be linear with slope  $b$  and intercept  $R$ . The drawing of tangents is susceptible to error and so laborious that it is unrealistic to expect workers to use it on a repetitive basis.

#### Computational

We have found that eqn. (1) can be solved quite easily by regression analysis using a relatively small programmable calculator. The terms  $a$ ,  $b$  and  $R$  are called the regression coefficients. Three simultaneous equations are obtained (eqns. 2, 3 and 4) which can be easily solved to give  $a$ ,  $b$  and  $R$ :

$$an + b\sum \log i + R\sum i = \sum \eta \quad (2)$$

$$a\sum \log i + b\sum (\log i)^2 + R\sum i \log i = \sum \eta \log i \quad (3)$$

$$a\sum i + b\sum i \log i + R\sum i^2 = \sum i\eta \quad (4)$$

where  $n$  is the number of points.

The exchange current density,  $i_0$ , can then be calculated from  $a$  and  $b$ . The authors were able to write a simple program for a programmable calculator using 12 data storage registers and 172 program steps. The program was tested both arithmetically and by comparison with experimental data using the oscillographic method. Figure 5 shows these results. The apparently

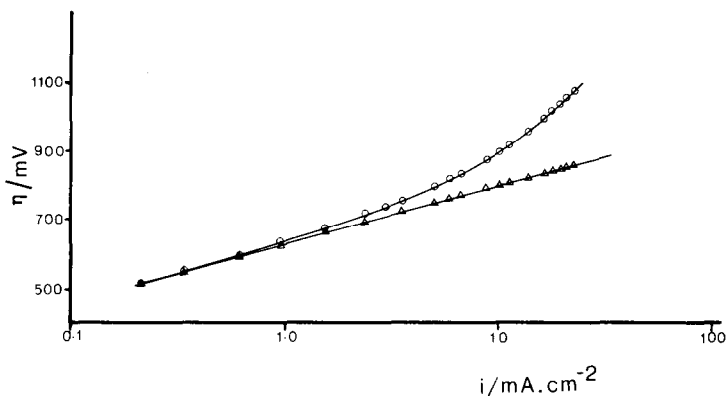


Fig. 5. Chlorine evolution on platinum in 2 M NaCl at 25 °C. Cathodic sweep at 5 mV/s. ○, Experimental points; △, potentials corrected for ohmic drop using  $iR$  program.

successful application of this method calls for a simple statistical evaluation of its worth and this was done by calculating the confidence limits of the regression coefficients. To do this it is first necessary to calculate their variance. Eqns. (2) - (4) can be written in matrix form as below:

$$\begin{pmatrix} n & \Sigma \log i & \Sigma i \\ \Sigma \log i & \Sigma (\log i)^2 & \Sigma i \log i \\ \Sigma i & \Sigma i \log i & \Sigma i^2 \end{pmatrix} \begin{pmatrix} a \\ b \\ R \end{pmatrix} = \begin{pmatrix} \Sigma \eta \\ \Sigma \eta \log i \\ \Sigma i \eta \end{pmatrix}$$

Let the left hand matrix be  $A$ :

$$\text{total sum of squares, } T = \Sigma \eta^2$$

$$\text{sum of squares due to regression, } S, = a\Sigma \eta + b\Sigma \eta \log i + R\Sigma i \eta$$

$$\text{residual sum of squares} = T - S$$

$$\text{let } s^2 = \text{residual s.s.}/(n - 3)$$

then the variance-covariance matrix is  $s^2 A^{-1}$ . The diagonal elements of this matrix are:

$$\begin{pmatrix} \text{Variance of } a & \text{-----} & \text{-----} \\ \text{-----} & \text{variance of } b & \text{-----} \\ \text{-----} & \text{-----} & \text{variance of } R \end{pmatrix}$$

$$\text{where variance of } a = \frac{s^2}{\det A} [\Sigma i^2 \times \Sigma (\log i)^2 - (\Sigma i \log i)^2]$$

$$\text{variance of } b = \frac{s^2}{\det A} [n\Sigma i^2 - (\Sigma i)^2]$$

$$\text{variance of } R = \frac{s^2}{\det A} [n\Sigma (\log i)^2 - (\Sigma \log i)^2]$$

where  $\det A$  (the determinant of matrix  $A$ ) =

$$n[\Sigma i^2 \times \Sigma (\log i)^2 - (\Sigma i \log i)^2] - \Sigma \log i [\Sigma i^2 \times \Sigma \log i - \Sigma i \times \Sigma i \log i] + \Sigma i [\Sigma \log i \times \Sigma i \log i - \Sigma i \times \Sigma (\log i)^2]$$

The confidence limits are  $a \pm t_{n-3} \sqrt{\text{variance of } a}$

$$b \pm t_{n-3} \sqrt{\text{variance of } b}$$

$$R \pm t_{n-3} \sqrt{\text{variance of } R}$$

where  $t_{n-3}$  is obtained from  $t$  tables for  $n - 3$  degrees of freedom.

We were again able to construct a program for this calculation. The original regression program provided all the required summations except for  $\Sigma \eta^2$ , and so was modified accordingly. The total program could still be run on our machine, using 12 data register stores and 360 program steps.

As a check we obtained  $i - \eta$  pairs by assuming suitable values for  $a$ ,  $b$  and  $R$ , and calculating  $\eta$  for various values of  $i$  from eqn. (1). This gave us a set of data that were known to fit eqn. (1). The regression coefficients were calculated several times; (1) with  $\eta$  accurate to 7 decimal places, (2) rounded to 2 d.p., (3) rounded to 1 d.p. (4) zero d.p. The results are shown in Table 2 at the 99% confidence level, *i.e.* to all intents and purposes there is a 99% probability that the confidence interval covers the true regression coefficients.

TABLE 2

Calculation of regression coefficients and confidence intervals for data known to fit the equation  $\eta = a + b \log i + IR$

Number of decimal places	$R$	$b$	$a$	$i_0$
7	4.5000000 $\pm 0.5 \times 10^{-9}$	120.0000000 $\pm 0.07 \times 10^{-7}$	600.0000000 $\pm 0.1 \times 10^{-6}$	$1.0000 \times 10^{-5}$
2	4.5000019 $\pm 0.000011$	119.9999923 $\pm 0.00129$	600.000079 $\pm 0.00208$	$0.9999 \times 10^{-5}$
1	4.4999751 $\pm 0.000086$	120.007008 $\pm 0.010408$	600.010312 $\pm 0.016789$	$1.0004 \times 10^{-5}$
0	4.4999 $\pm 0.00077$	120.0744 $\pm 0.0937$	599.9655 $\pm 0.157$	$1.0079 \times 10^{-5}$
Initial values	4.500000000	120.000000000	600.0000000	$1.000000000 \times 10^{-5}$

Number of points,  $n = 25$ .

$t_{n-3} = 2.819$  for 99% level of confidence.

Figure 5 shows a  $\log i$  vs.  $E$  plot for the chlorine evaluation reaction on platinum in 2  $M$  NaCl. The values calculated by the program were (with confidence intervals at the 99% level):  $-R = 9.5 \pm 0.3 \Omega$ ;  $b = 168.9 \pm 3.6$  mV  $a = 630.0 \pm 1.6$  mV. The value of  $R$  measured by the single-shot-transient method was  $9.2 \pm 1$  ohm.

An extra refinement was the addition of an error-correction program that can be called up to remove points that have been incorrectly inserted into the calculation. This brought the total number of program steps to 415.

For computational convenience we have fitted the regression of  $\eta$  on  $i$ , which means that  $\eta$  is dependent on  $i$ . Experimentally this is achieved during galvanostatic polarization. For potentiostatic operation, where  $\eta$  is fixed and  $i$  allowed to vary, a regression of  $i$  on  $\eta$  would be more appropriate. This is much more complex and is still under study. It is possible for the two methods to give different answers, for both the regression coefficients and the confidence intervals, but if the data are a good fit to eqn. (1) the difference should be quite small.

### *Confidence limits*

The results of this program now enable "confidence limits" to be obtained on the values of  $a$ ,  $b$  and  $R$ . Not only is this in itself a valuable addition, telling us when we are justified in using the approach and when not, but it also leads to another interesting possibility. The situation and equation so far assumed, relate to a "straightforward" activation controlled electrode reaction taking place on a metallic electrode. The error term  $iR$  relates entirely to a solution resistance, and when this is small, as it will be at low current densities, eqn. (1) approximates to the theory-based Tafel equation. However, let us now suppose that the electrode reaction is taking place on a surface which is filmed, perhaps with a layer of anodically formed oxides. Such oxides will have their own resistance and space-charge potentials. In such a case, the equation will be modified to the form:

$$\eta = a + b \log i + i(R + R') + c.f(i) \quad (5)$$

where  $R$  is the solution resistance term and  $R'$  is the film resistance, and  $c.f(i)$  is a non-linear term for space charge potentials. Where  $R$  and  $R'$  remain unchanged through the course of the experiment we have no way of separating them and they will remain lumped together. However, there are a number of situations in which this is not the case. Indeed, usually  $R'$  increases as the anodic potential increases. Alternatively, an electrode system can be first run cathodically, evolving hydrogen for example, when  $R'$  will be zero. Knowing  $R$  from this,  $R'$  can be obtained by subtraction of  $R$  from the lumped term obtained under anodic conditions provided that the  $c.f(i)$  term is negligible compared to  $i(R + R')$ . We can see that, in theory, this program can be used to follow changes in  $R'$ , the film resistance on the surface of an electrode, as the anode potential is increased. However, here, more than previously, statistical treatment is needed to show when attempts are being made to extract  $R$  on the basis of insufficient data points. In certain situations too, changes in  $R$  due to increasing numbers of gas bubbles in solution must be recognized. Of course this method follows these changes just as do the oscillographic methods quoted above.

The ideas given here will enable the user to devise a program best suited to his own needs. Our own preference is for one which produces values at

regular intervals of  $\eta$  with confidence limits, and also enables a cumulative value to be obtained, thereby enabling us to follow changes in the value of  $R$ . Such a program is well within the capability of the Compucorp "Scientist" 327 series machine we have been using.

This approach to ohmic drop determination has now been in use for over twelve months in these laboratories, where a wide range of data including chlorine evolution, hydrogen or oxygen evolution, corrosion kinetics and oxide film growth monitoring have been studied with it. The technique is so simple to apply that it is frequently used to complement some of the other methods which have been earlier discussed, and in view of the known problems which can arise in all of these cases, it frequently offers welcome confirmation. Additionally, it provides a print-out of Tafel slope and (where overvoltage data are fed-in)  $i_0$  all expressed on a statistical error basis (see Fig. 6).

```

{ Current (mA)           0.1000 }
{ Voltage (mV)          880.4000 }
{ "                     0.2000 }
{ "                     916.9200 }
{ "                     0.3000 }
{ "                     938.4500 }
{ "                     0.4000 }
{ "                     953.8500 }
{ "                     0.5000 }
{ "                     965.8800 }
{ "                     0.6000 }
{ "                     975.7800 }
{ "                     0.7000 }
{ "                     984.2100 }
{ "                     0.8000 }
{ "                     991.5700 }

No of pairs             8.0000
of i-V readings        .....
R (ohms)               3.9986
b (slope,mV/decade)   120.0034
a (intercept)         1,000.0017
i0 (mA.cm-2)       0.00000004

Statistical   σR   0.018425967
Data         σb   0.014774829
              σa   0.014462263
              .....

```

Fig. 6. Typical print-out from programmable calculator for ohmic drop program.

Early fears that deviations from rectilinear  $\log i$  vs.  $E$  plots due to concentration polarization might be mistakenly treated by this method to give values of  $R$  have proven unfounded. In practice, when an attempt is made to process  $\log i$  vs.  $E$  data containing an element of concentration polarization, the resulting print-out clearly indicates that the method is being misapplied. Thus, while the printed "R" value or Tafel slope might appear to have a credible value, their associated confidence limits will be abnormally large. In contrast to the typical confidence limits shown in Fig. 6 for a reaction known

to be activation controlled, the mistaken application of diffusion-controlled kinetics data has produced far higher confidence limits such as  $\pm 50$  mV in the Tafel slope figure and the appearance of such error-limits is a clear warning that the results should be treated with extreme caution.

### *Applications to full cells*

The resistance in a full cell may be obtained by this technique, provided the reactions at both electrodes are activation controlled. The system is treated as the sum of the two half cells, the equations being

$$\eta_a = a_a + b_a \log i + iR_a \quad (\text{anodic})$$

$$\eta_c = a_c + b_c \log i + iR_c \quad (\text{cathodic})$$

Addition gives:

$$\eta_a + \eta_c = a_a + a_c + (b_a + b_c) \log i + i(R_a + R_c)$$

since the overpotential  $\eta_i$  at a current density  $i$  is related to the measured potential  $E_i$  by:

$$|\eta_i| = |E_0 - E_i|$$

$$E_{\text{cell}} = A + B \log i + iR$$

where the constants  $A$  and  $B$  have no meaning and  $R$  is the cell resistance. This assumes that all the non-linear components can be approximated under the term  $B \log i$ . A similar suggestion has recently been made elsewhere [40].

### Conclusion

It will be seen that, while several methods exist for determination of the resistive term in electrochemical measurements, all have disadvantages and many of the reported corrections are likely to be at least partly in error. The computational method is only applicable to activation controlled processes. However, with its great simplicity of application, and also the fact that it can be used retrospectively with data obtained from earlier work, the authors feel it offers an attractive alternative in many cases.

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