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The area-calibration of mercury electrodes

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Consideration is given to four alternative *in situ* methods of determining the area of a dropping mercury electrode. These methods are particularly relevant to those conditions where ordinary calibration procedures are not possible, for example, in closed systems at elevated pressures and temperatures.

Introduction

For routine and non-routine voltammetric analysis, by far the most satisfactory electrode is the dropping mercury electrode. The constantly renewed surface of high hydrogen overpotential is entirely reproducible and the accurate description of the current-voltage-time characteristics is the basis of polarographic analysis and of other studies of electrode impedance, which lead to values of capacitance, charge-transfer reaction rates and to diffusion coefficients [1, 2].

All of these measurements require that the area of the mercury drop be known at a particular time or as a function of time. This invariably requires a knowledge of m, the rate of flow of mercury (in g/s) down the supporting capillary, which in turn depends on two other factors, namely the capillary characteristics and the head of mercury in the reservoir. At any given time, t, the electrode area, A, is simply given by the expression

$$A = 4\pi\left(\frac{3mt}{4\pi\rho}\right)^{2/3} \text{cm}^2, \qquad (1)$$

where ρ is the density of mercury. This calculation is subject to two small corrections, the first arising from a surface-tension back-pressure term and the second from gravitational distortion of the drop at the end of its life. The first correction can be calculated [3]; it is important only at the beginning of drop life and becomes negligible as the drop grows. The second term can also be calculated and is also for most purposes negligibly small.

The precision with which the area of the dropping mercury electrode is known therefore depends on the knowledge of flow rate and of the time at which the measurement of impedance or current is made. Either the drop life time or the interval of time from the drop birth to the electrode measurement can be easily and accurately measured with an electronic timer and therefore all depends on a precise knowledge of the flow rate of mercury. This itself is readily obtained from an open electrochemical system in which the mercury can be collected over a period of time and weighed.

There are, however, many circumstances in which this is not possible. At high temperatures, at high pressures and indeed in any inaccessible system where the flow rate characteristics may be quite different from those under ambient conditions, it is not easy continuously to calibrate gravimetrically the mercury flow rate and for precise electrochemical work, other procedures are required. This paper sets out to describe other methods of determining electrode areas which were developed of necessity out of studies of electrode impedance, of polarography and of transport numbers at high temperatures and pressures.

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Automatic syphon system

A simple but effective *in situ* measurement of flow rate was achieved by the syphon device shown in Fig. 1. This was constructed from narrow bore glass tubing (i.d. 1·5 mm) such that the internal diameter at the bend B was the same as that at C. In this way differential surface tension effects were minimized. The onset of syphoning was detected by a voltage transient between the bottom mercury pool and an auxiliary electrode. From prior calibration of the device it was possible to determine flow rates with a precision of better than 1 % under conditions of high temperature and pressure. A similar precision is also obtainable from a knowledge of the temperature and pressure coefficients of the characteristics of mercury and the capillary but this information is only of value if the mercury head is constant or known and this is frequently not the case.

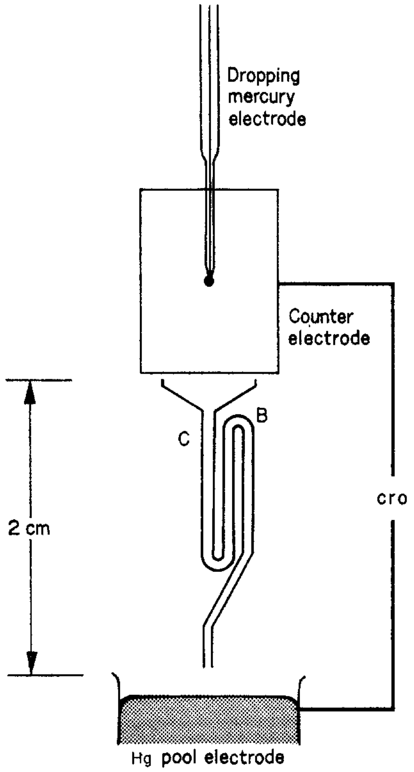

Fig. 1. Syphoning device for calibrating the rate of flow of mercury.

Ohmic resistance calibration

The instantaneous area of a mercury drop may be obtained directly from the corresponding value of the ohmic resistance of the cell in which the mercury drop is one of the electrodes. There are several examples [4, 5] of conductance cells the geometry of which is sufficiently well-defined for the observed resistance, R, to be calculated from the electrode configuration and the specific conductance, κ, of the electrolyte. When both R and κ are independently known then the electrode geometry can be evaluated.

The dropping mercury electrode is invariably generated at the orifice of a slender capillary concentric or co-axial with a much larger surrounding counter electrode. Under these conditions, the effective cell constant, K, is solely a function of the area of the smaller, mercury electrode [6], i.e.

$$R_{\text{cell}} - R_{\text{Hg}} = \frac{1}{\kappa K A} \tag{2}$$

where R_{Hg} is the resistance of the thread of mercury in the capillary. This equation may be derived as follows.

Suppose the mercury drop is suspended from a fine capillary and is therefore unshielded, that its radius be r cm and that the distance d from the counter electrode is much greater than r. Then if the potential of the drop relative to the counter electrode is V volts, the field at the surface of the drop will be given by

$$E = \frac{q}{r^2} = \frac{V}{r}\ \text{V/cm} \tag{3}$$

where q is the charge on the spherical drop. The current, i, distributed evenly over the surface of the sphere will be given by

$$i = 4\pi r^2 E\kappa\ \text{A} \tag{4}$$

and the solution resistance is therefore

$$R_{\text{cell}} - R_{\text{Hg}} = \frac{1}{4\pi r\kappa} = \frac{1}{4\kappa(\pi \text{A})^{\frac{1}{2}}}\ \Omega. \tag{5}$$

If the top surface of the sphere is screened by, for example, a large capillary a different expression obtains, i.e.

$$R_{\text{cell}} - R_{\text{Hg}} = \frac{1}{4\pi r \ln 2}\ \Omega. \tag{6}$$

Where the screening is less marked, then some intermediate expression is indicated [7] and although an exact analytical expression for this might be difficult to find, it is certain that the cell constant is independent of the cell geometry provided only that $r \ll d$. It can therefore be found by some prior calibration experiment which would allow Equation (2) to be used thereafter to calculate A for the given electrode under any circumstances where κ is known.

The only problem then remaining is to resolve the value of R from the observed cell impedance bearing in mind the fact that mercury is seldom a non-polarizable electrode and that its impedance therefore contains contributions from the faradaic impedance, i.e. the resistance corresponding to the electrode reaction, and from the concentration polarization impedance. The analysis of complex impedances is a well-understood procedure and the ohmic resistivity can normally be evaluated from the observed frequency dispersion of the impedance. This is illustrated here in terms of the voltage transient observed in the current-step, galvanostatic technique [2]. At high frequencies, i.e. over short periods of time (1–1,000 μs), the resultant voltage-time transient, recorded oscillographically, has the form shown in Fig. 2. It contains three distinct sections, the almost vertical rise, *a*, due to the ohmic potential, the shallower slope, *b*, corresponding to the charging of the double layer and a still shallower almost imperceptible slope, *c*, corresponding to the slow onset of concentration polarization. There could be complications for electrode reactions with slow rate constants which might require other analytical procedures but the method frequently works well, as in the following example.

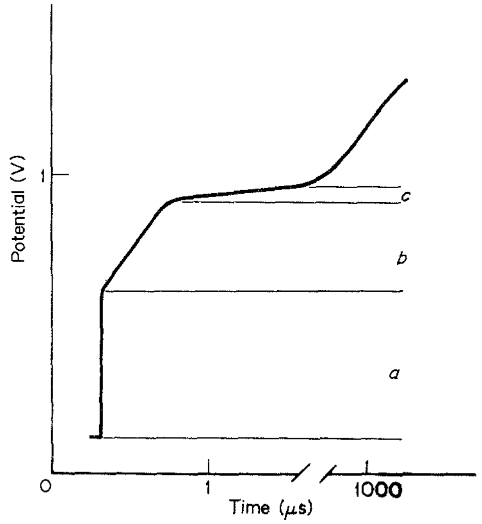

Fig. 2. Voltage-time transient from the current-step method.

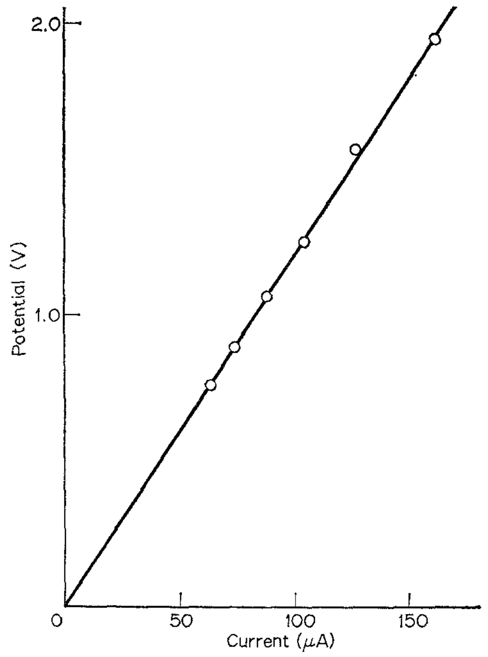

Fig. 3. Ohmic overpotential (region *a* of Fig. 2) as a function of current.

The dropping mercury electrode was used to analyse polarographically a 1 mM thallous chloride in potassium chloride solution in an autoclave operating at 200°C and 1,000 psi. The ohmic part of the observed voltage transient is shown in Fig. 3 as a function of the constant current applied. From the slope of the line and from the known specific conductance of the solution, the electrode area was calculated with a precision of ±1 %. It was subsequently used to evaluate the diffusion coefficient of the thallous ion. Where the specific conductance of the solutions is not known it is easily found from a simultaneous measurement of conductance using two platinum electrodes.

Drop-time method

Perhaps the most important influence on the flow rate of dropping mercury electrodes in autoclaves, pressure vessels and other sealed systems is the variation of hydrostatic head, brought about by buoyancy changes. In two studies [8, 9], carried out in these laboratories, the internal pressure equilibrium did not prevent changes in the effective hydrostatic head caused by changes in the density of the surrounding fluids. From a knowledge of these densities and of the initial flow rate, the new rates can be calculated. It is, however, a tedious process and an alternative method has been proposed [10].

Briefly, the drop time, τ, is a function of the flow rate and the surface tension, γ, i.e.

$$\tau = f(m, \gamma). \tag{7}$$

At constant surface tension, τ is inversely proportional to the flow rate and from measurements of t under prescribed conditions of potential, the variations of flow rate can be found. If the surface tension is also changing, then its variation must be known, although the effect will be small. Once the flow rate is known, then the area at any time t or the average area over the time interval t_2-t_1, can be found.

Stationary mercury electrodes

Another way of defining the area of a mercury electrode is to generate a suspended drop by ejecting from the capillary tip a known volume of mercury. Several examples of so-called hanging mercury drops have been described, most of them manually operated [11–13]. Provided the drop is not left suspended for too long a period, it possesses the desirable properties of a growing drop, as well as many of its own. For example, it is free from the capacity charging current associated with changing area. Moreover, it retains its cathodic product for later stripping analysis.

By far the most sophisticated version of this type of electrode was briefly described by Kinnibrugh [14] who successfully used it in various high pressure vessels up to pressures of 1,500 bars. It is based, as are all other hanging mercury drop electrodes, on a precision syringe containing mercury which is driven out in this case by a steel plunger. The distance travelled by the plunger and therefore the volume of mercury displaced is controlled by the pitch of a micrometer piston. The micrometer is linked via a gear box to a solenoid activated switch, such that a single pulse from a 12 V battery effects a one-twelfth rotation of the solenoid and, through the reduction gears (25:1), a $\frac{1}{300}$th revolution of the micrometer spindle. In terms of the particular area of the syringe plunger used here, it requires ~100 pulses to form and displace a single drop. A block diagram of the system is shown in Fig. 4 and a photograph of the apparatus in Fig. 5 illustrates the extensive degree of miniaturization involved for this whole apparatus to be inserted into a pressure vessel. The finer details of construction and operation are given elsewhere [15].

The volume of mercury, v_{Hg}, displaced by the plunger is readily calculated from the known sensitivity of the micrometer. If this is p cm/turn and if the gear ratio is z, the angular displacement of the solenoid switch is w turns/pulse and the area of the syringe piston is A_p, then

$$v_{\mathrm{Hg}} = wzpA_p \text{ cm}^3 \text{ per pulse.} \tag{8}$$

The corresponding area of the spherical electrode for n pulses will therefore be

$$A_n = 4\pi\left(\frac{(3wzpA_pn)}{4\pi}\right)^{2/3}. \tag{9}$$

All but n are constant for a particular system and thus

$$A = kn^{2/3}. \tag{10}$$

This technique can therefore be used to generate

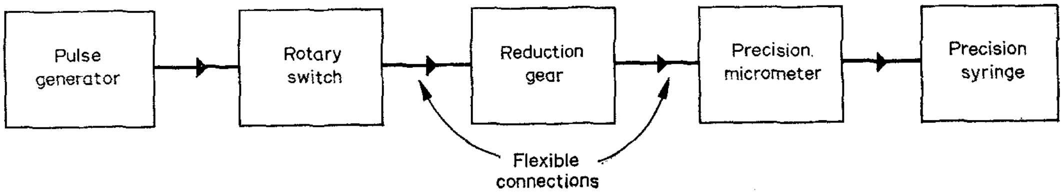

Fig. 4. Block diagram of pulse driven hanging mercury drop.

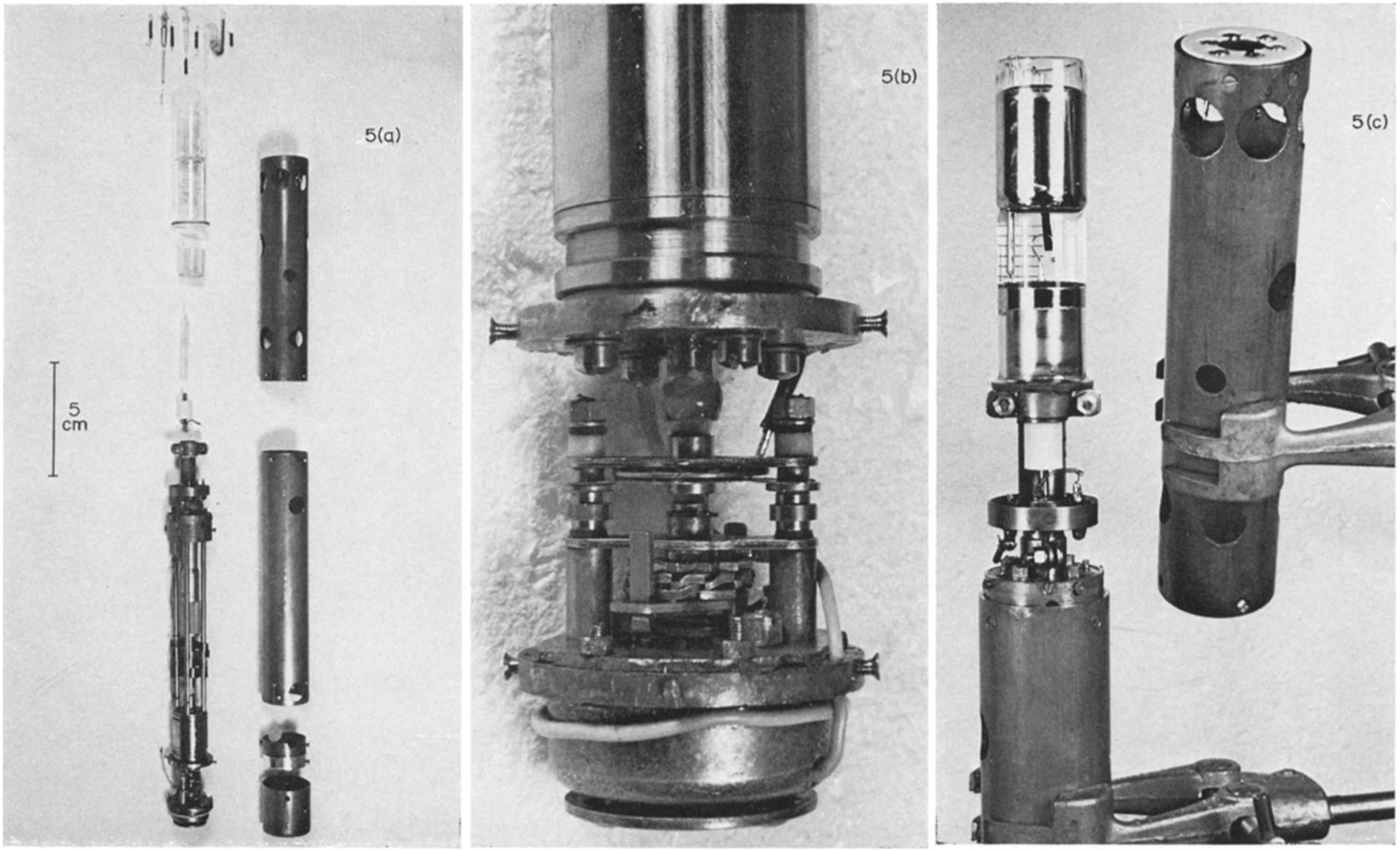

Fig. 5. The pulse driven hanging mercury drop electrode for use at high pressures; (a) the complete assembly; (b) the solenoid switch and gear box, and (c) the electrode compartment.

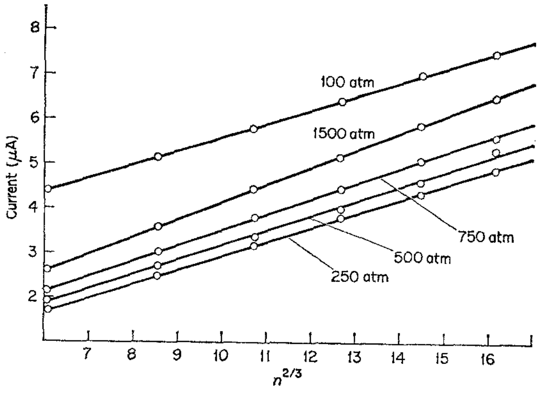

Fig. 6. Cathodic current for the electro-reduction of hydrogen ions, as a function of the number of actuating pulses, at constant overpotential and at various pressures.

an electrode in a succession of small steps. Since the final pulse corresponding to the displacement of a drop is easily monitored, then the size of the new drop is given by Equation (10) where n is the number of succeeding pulses. If there is any doubt concerning the values of k, it can of course be checked by prior gravimetric calibration, as was the case here.

The type of mercury electrode was tested in terms of the cathodic reduction of hydrogen ions at high pressures. The reaction is slow on mercury but is sensitive to pressure and to applied potential. At a particular value of the pressure and of the overpotential, the current is constant, independent of time but directly proportional to electrode area. The validity of Equation (10) was demonstrated by measuring the current as a function of n for a number of different overpotentials and this is illustrated in Fig. 6. In each case $\left(\frac{\partial i}{\partial n^{2/3}}\right)_p$ is strictly linear so that even where the absolute value of A_n might be in doubt, its variation with $n^{2/3}$ will always provide the basis for knowing or eliminating the area term.

Conclusion

We have gathered together here four unusual examples of the use of the mercury electrode in cathodic voltammetry. Their success suggests the possibility of the more widespread use of this electrode as a monitoring system in inaccessible situations. In each case the essential read-out is electronic and these methods could be the basis of more automatic procedures leading to established data acquisition and data processing techniques.

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