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REVIEW ARTICLE

Instruments for use in electrode process research

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Abstract The review covers the elementary aspects of construction and use of instruments for electrode process research, dealing with both electrochemical and biological applications where these methodologies overlap. There is a guide to desirable specifications in commercial instrumentation and a list of manufacturers of equipment.

1 Introduction

The review deals with methods for controlling and measuring the electrical parameters of an electrode reaction, concentrating on those aspects which are common to classical electrochemistry and to biological applications. The methods treated include potential, current and charge control and measurement, and small-signal analysis of interfacial impedance by sine-wave techniques. The theory of the design and proper operation of a potentiostat is central to this material, and is outlined in an introductory manner with reference to fuller treatments.

Historically, much research in these areas has been done using 'home-made' equipment, and this approach is emphasised in the review. All of the applications are considered with the operational amplifier as the building block – an approach that has two merits. First, with an understanding of these component parts, cheap but effective special-purpose instruments, equal to or better than general-purpose commercial equipment in performance, can be constructed on the laboratory bench. Secondly, such an understanding will often enable the researcher working with commercial gear to avoid the many pitfalls of connecting chemical and biological systems to electronic equipment.

Finally, there is a general guide to specifications and a summary of the main characteristics of the more readily available commercial equipment.

2 Basics of circuit design

2.1 *Fundamentals of potential control*

A minimum configuration for controlling an electrode potential consists of the working electrode itself (WE) and its electrolyte environment plus a second electrode, the probe or reference electrode (RE). The outside circuit is completed by an electronic control element which measures and regulates the potential. Any current that passes must not disturb the interfacial potential drop between the RE and the solution. An electrode of this kind, which can pass a certain finite current without being affected, is called a non-polarisable electrode.

When currents of more than a few microamperes are drawn by the WE, the RE must be relieved of the function of conducting the current into the solution by the use of a third electrode, the counter-electrode (CE) as shown in figure 1. The only current passed by the RE is that taken by the high-input-impedance voltmeter used to measure the potential difference between the RE and WE. By use of an electrometer amplifier as the input stage of the voltmeter, this current (the bias

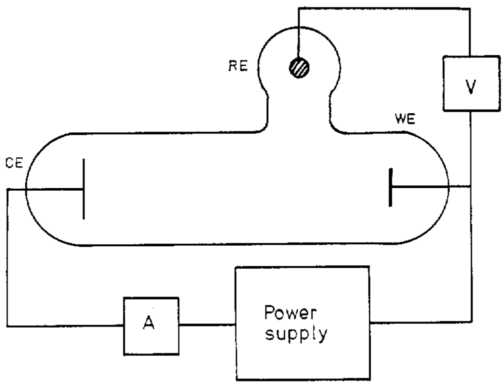

Figure 1 Three-electrode cell with manual control of current.

current of the amplifier) can be made extremely small, and studies are no longer limited to the small currents that can be passed by the RE without falsifying its potential.

Attention must then be given to the question of ohmic drops in the solution. The WE is located in a resistive medium, and any current which it passes necessarily causes a gradient of electrical potential around it. The processes at its surface, however, are controlled by the interfacial potential difference, i.e. the PD between the electrode and the first two or three molecular layers in contact with it. During the passage of a current i, therefore, this PD is different from the desired PD by a quantity iR_u, where R_u is the solution resistance between the WE and the position of the RE.

For an electrode of normal physical size (several millimetres across), R_u will be large and ill-defined, so the expedient is adopted of enclosing the whole RE in a non-conducting envelope (usually glass) which has only a small hole communicating between the electrode inside and the bulk of the working electrolyte. By the drawing out of the RE vessel to a narrow capillary (the Luggin capillary), the tip of which can be positioned suitably close to the WE, R_u can be defined and reduced to a small value (figure 2). An exactly similar

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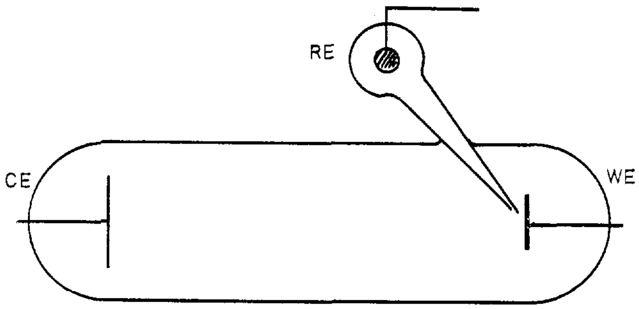

Figure 2 Conventional representation of reference electrode contained within the Luggin capillary.

situation holds when the electrochemical cell is a biological rather than a fabricated structure, except that the capillary then has to be much narrower so as to be able to penetrate a cell with minimum damage. The RE–capillary combination is then usually called a microelectrode.

While the Luggin capillary does in theory allow the resistance R_u to be reduced effectively to zero, in practice R_u can never be exactly zero. The capillary tip would have to be placed so close to the electrode surface as to shield the electrode from the flow of current – the area of the electrode in the shadow of the capillary would then be atypical of the rest of the electrode, and so the PD measured would be erroneous.

These two opposing effects militate against the correct measurement of the potential of the electrode under conditions of high current density, and careful consideration of the design of the system is then necessary, particularly if high precision of PD is needed. The main areas where the effects are serious are thus in the determination of electrochemical kinetics, especially when pulsed currents are measured.

2.2 *Controlling and measuring the potential*

In the arrangement of figure 1, the cell current is varied manually while the potential is observed. To make the system able to follow a preset programme of potential, a self-correcting servo-amplifier must replace the power supply. This will usually be an electronic amplifier, although electro-mechanical devices using a motor-driven generator have been used where slow response is adequate. The only justification for using such a system would be when high currents (more than 100 A) are needed, for example in pilot plant or manufacturing applications.

A generalised control system is shown in figure 3. The control amplifier is labelled OA1, P is the programming potential source, i.e. a waveform generator whose output is the same as the desired variation of WE–RE potential, and M is a current-measuring unit such as a moving-coil meter or digital multimeter.

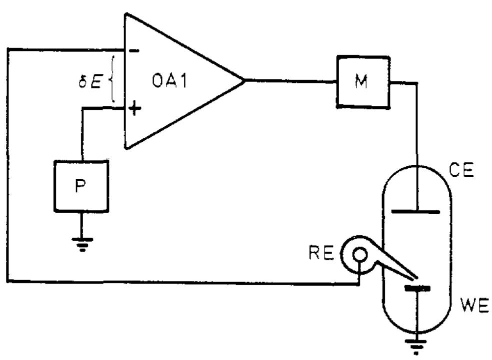

Figure 3 Minimum system for potentiostatic control.

This is a completely general arrangement for following the current–time profile of an electrochemical system, and covers a wide range of applications in electrode process research. There are other important methodologies, in which the current or the charge may be varied under control while the PD is measured (the galvanostatic and coulostatic techniques). These can be carried out using almost the same modules but in a different arrangement. Therefore by achieving a basic understanding of the modules OA1 and M, almost all of the applications in common use are within reach.

2.3 *The operational amplifier*

The operational amplifier (op-amp) is an electronic device designed with characteristics that make it ideally suitable as the active element in self-correcting mechanisms and for carrying out a repertory of operations such as inversion, addition, subtraction, multiplication by a constant, integration and differentiation. Power supplies and voltage offset connections are omitted from the conventional diagram of the op-amp (figure 4(*a*)).

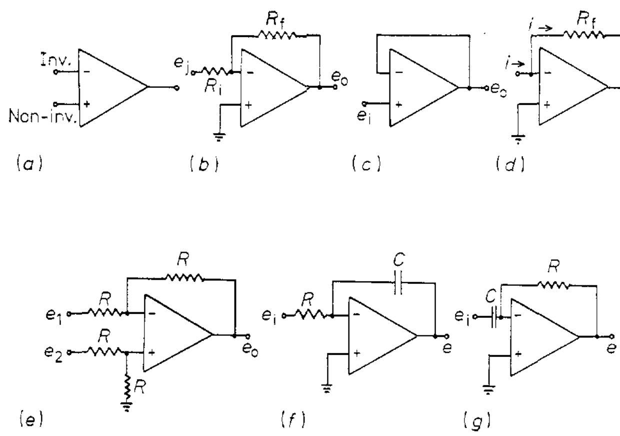

Figure 4 Basic op-amp circuits. (*a*) Open-loop op-amp; (*b*) inverting amplifier: $e_0 = -e_i R_f/R_i$; (*c*) voltage follower: $e_0 = e_i$; (*d*) current follower: $e_0 = -iR_f$; (*e*) differential amplifier: $e_0 = e_2 - e_1$; (*f*) integrator: $e = -(1/RC)\int e_i \mathrm{d}t$; (*g*) differentiator: $e = -RC\, \mathrm{d}e_i/\mathrm{d}t$.

The fundamentals of op-amp circuitry are well described in texts (e.g. Tobey *et al* 1971, Graeme 1975, Clayton 1971, 1975a, b, Kalvoda 1975, Smith 1971, Vassos and Ewing 1972) and in manufacturers' literature. The review by Schroeder (1972) is particularly helpful. The material in §3 requires some basic familiarity with the notation and function of the simple op-amp circuits in figure 4.

3 Practical circuits for various techniques

3.1 *The potentiostat or voltage clamp*

The simplest way of automatically controlling the PD between two electrodes is shown in figure 3. The desired WE–RE PD is programmed by the device P. Any difference δE between this potential and the actual PD is amplified in an inverting sense, and causes a potential to be applied to the CE in the correct direction to minimise the error signal δE. The resulting current is measured on the meter M.

The arrangement works dynamically, i.e. it will respond to a changing value of P, the maximum rate of change being determined by the frequency response of OA1. Clearly the voltage across the cell is limited to the maximum that OA1 can supply, i.e. its voltage compliance, and the current is also limited to the maximum specified for the op-amp.

Figure 3 is not only a simple circuit, it is also a practical one for a certain restricted range of applications. If the current required is small, if the WE impedance is primarily resistive, if the cell voltage is within a ±15 V band, then an economical op-amp will probably work and give the required performance. The op-amp should be of the FET input type (field effect transistor) such as the L155 (National Semiconductor) or the 3140 (RCA) which has very low bias current. With bipolar transistor op-amps (e.g. the ubiquitous 741) the bias currents are about 10^4 times higher (100 nA), so unacceptably high currents are drawn from the RE. Many types of RE, such as the saturated calomel type that makes contact through a sintered glass plug, and all microelectrodes, have a high resistance from about $10^5\ \Omega$ to hundreds of megohms. For an RE of resistance 1 MΩ, a current of 10^{-7} A would thus falsify the measured potential by 0·1 V.

To take care of the problem of bias current, it is possible to use a voltage follower as an isolator or impedance transformer to buffer the reference electrode from the rest of the circuit, as shown in figure 5. This slight extra complication

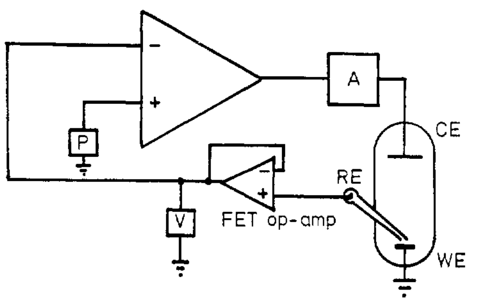

Figure 5 The voltage follower used as an isolator.

confers several important benefits. The output of the FET op-amp is a low-impedance point, so the device used for the potentiostat can be chosen independently of its bias current, thus making a wider range of types available. Moreover, special op-amps that have only one input (inverting), e.g. the high-stability, high-gain, chopper-stabilised types, can also be used for the main amplifier. Other measuring instruments, e.g. oscilloscopes, can be attached to the follower output in order to monitor the RE potential, and it is even possible to use a low-impedance device such as a moving-coil meter for the purpose.

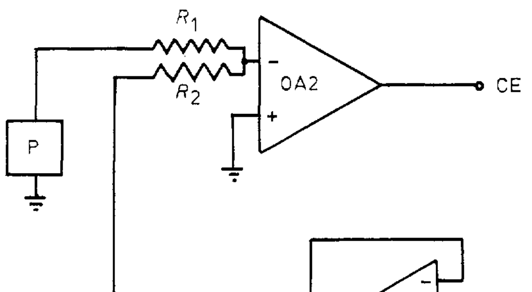

Figure 6 Inverting or summing configuration of the potentiostat amplifier.

When a voltage follower is used, a different arrangement of the main amplifier is possible, i.e. the 'single-ended', inverting or summing configuration (figure 6). The inverting input of OA2 is now a summing junction and a virtual ground, i.e. the sum of all the currents flowing to it is zero; therefore if $R_1 = R_2$, the RE potential must be equal in magnitude but opposite in sign to the programming potential. The provision of the summing junction is useful in forming complex programming waveforms from simpler signals (figure 7).

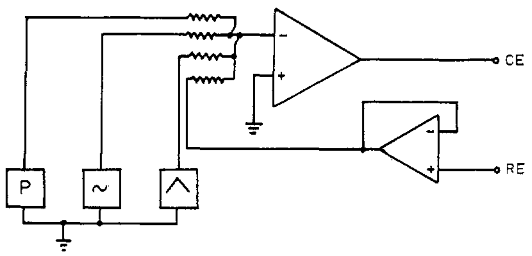

Figure 7 Use of the summing configuration to superimpose a steady bias, plus a small-amplitude sine wave on a slow ramp voltage.

3.2 *Static characteristics of op-amp potentiostats*

Most popular op-amps work from ±15 V power supplies, so the maximum voltage compliance that can be expected is about ±14 V. The current capability is usually not more than about 10 mA. These limitations are often too severe, and a way has to be found to increase the output capability.

The current output of a 15 V op-amp can be raised very easily. Most op-amp manufacturers sell units called boosters (e.g. Burr-Brown 3553 AM – 200 mA at 10 V) which work from 15 V and supply up to 1 A. They are simply connected in series with the op-amp output (figure 8) and generally

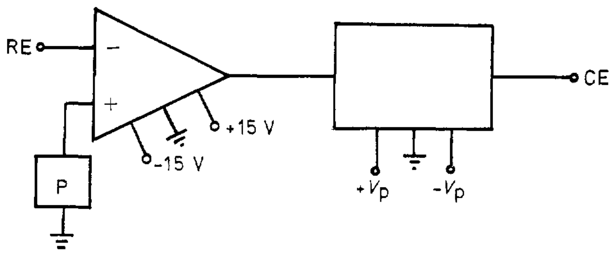

Figure 8 Op-amp with booster, which has its own power supply.

have a beneficial effect on the frequency response of the op-amp, which now has to supply only a small drive current for the booster. Designs for simple add-on booster stages for 15 V op-amps have been published (for example, Woodward *et al* 1973, Hand and Nelson 1976). High-power op-amps are also available with different combinations of maximum voltage and current, e.g. Burr-Brown 3572 AM (±30 V at 5 A) and Analog Devices type 171 (±115 V at 10 mA).

An ingenious method of doubling the cell voltage using 15 V op-amps has been published (Bruckenstein and Miller 1973) in which the cell is driven between two op-amps working in antiphase.

3.3 *Dynamic potentiostat response*

High precision of stabilisation of potential demands that the gain of the potentiostat be high. In measuring pulses and transients, or the response to a sine-wave stimulus over a wide frequency range, therefore, high gain must be preserved to as high a frequency as possible.

Unfortunately the question of frequency response is much more difficult than simply ensuring from the manufacturer's specifications that the gain of the amplifier is sufficient at the highest frequencies of interest. The reason is that, in a feedback system, instabilities and spurious responses are generated if the gain and phase relationships between output and input are uncontrolled between certain limits. A potentiostat can easily become an oscillator! Proper design of the amplifiers and associated circuitry can minimise these dangers, but if it is improperly used, wrong results can still be delivered by a 'perfect' potentiostat.

The theory of the dynamic response of potentiostats has been reviewed in detail (von Fraunhofer and Banks 1972, Harrar and Pomernacki 1973 and references therein). The following is no more than an introduction to these fuller treatments. The theory is complicated by the fact that the behaviour of the system is crucially dependent not only on the potentiostat but also on the impedance of the cell and RE. The special problems of controlling potentials in biological cells have been reviewed by Moore and Cole (1963).

Most op-amps have a frequency response of the type shown in figure 9 (the so called 'compensated' type of

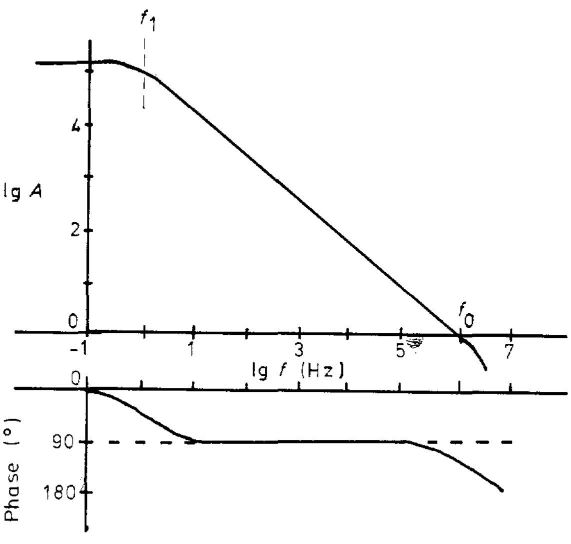

Figure 9 Gain and phase frequency response of a compensated op-amp (Bode plot).

response). 'Uncompensated' op-amps are also available and can be given the correct type of characteristic by adding external components. The open-loop gain of the amplifier (i.e. with no feedback connected) is independent of the frequency from DC up to the 'turnover' frequency f_1, beyond which the gain falls linearly with frequency with a slope of -1 on the log–log plot. The unity-gain crossover point f_0 is an important parameter, and is usually quoted together with the static open-loop gain in op-amp specifications; f_0 is also called the gain–bandwidth product. At some higher frequency the slope changes to -2 and may then increase further.

The phase of the output with respect to the input is also frequency dependent. For the purposes of this simplified discussion, the phase shift can be obtained from the slope of the gain–frequency plot by the rule that a slope of -1 means an additional lag of 90°, -2 means 180° and so on.

An *extra* 180° of phase shift corresponds to the output being *in* phase with signals at the inverting input, instead of exactly out of phase as it is at very low frequencies, so that any feedback from the output to the inverting input will be *positive*, rather than negative, as the proper functioning of any self-regulating device requires. Moreover, if the log of the loop gain (defined below) is positive at the frequency where the additional phase shift is 180° (i.e. the gain is greater than unity) then instability and oscillation will result.

A potentiostat that has a response crossing the unity-gain axis with a slope of -1 is therefore said to have a phase margin of 90°. Unfortunately, an electrochemical cell can use up this margin and exceed it.

The meaning of the term 'loop gain' is illustrated in figure 10. The feedback network is represented by the rectangle,

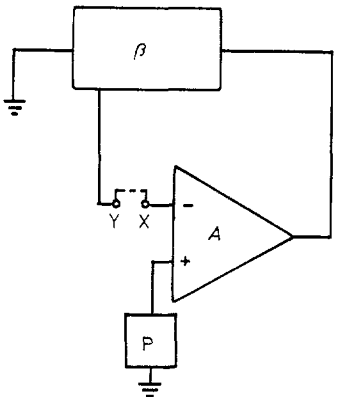

Figure 10 Amplifier with open-loop gain A and feedback network, feedback fraction β.

which signifies the whole of the RE–cell combination, while the triangle represents the amplifier or amplifiers used as the potentiostat. The gain A will have a characteristic (a Bode plot) similar to that presented in figure 9, and the corresponding 'gain' of the feedback network (which will be less than unity, and is hence called the feedback fraction β) can be plotted against frequency in exactly the same way. The loop gain is the product of these two quantities, so on the log plot it is obtained simply by adding the separate values. Thus in figure 10, if the link X–Y were broken and a small signal injected at point X, the signal at Y would be greater by the factor $A\beta$, the loop gain.

The cell impedance can be split into elements: the solution resistance R_s, the uncompensated solution resistance R_u, the reaction resistance R_e and its capacitance C_e, the reference electrode resistance R_{ref}, and its capacitance which can be lumped with the input capacitance of the isolator amplifier and called C_{ref} (figure 11).

The simplest case is when the cell is purely resistive and the time constant $C_{ref}R_{ref}$ is negligible: β is then equal to $(R_e+R_u)/(R_u+R_s+R_e)$ and independent of frequency. No stability problems are created by a cell of this kind. However, the situation is never met in practice because there will always be some interfacial capacitance.

More realistic, but still grossly simplified, cell analogues are given in figures 12(*a*) and (*b*), with their plots of lg β

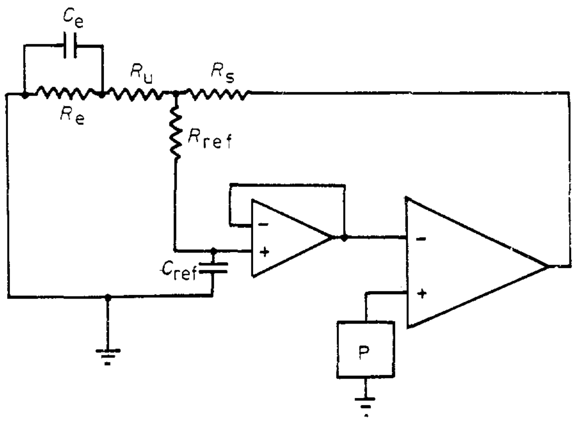

Figure 11 Simplified equivalent circuit of a cell with solution resistance R_s, uncompensated solution resistance R_u, electrode capacitance C_e and resistance R_e, and reference electrode capacitance C_{ref} and resistance R_{ref}.

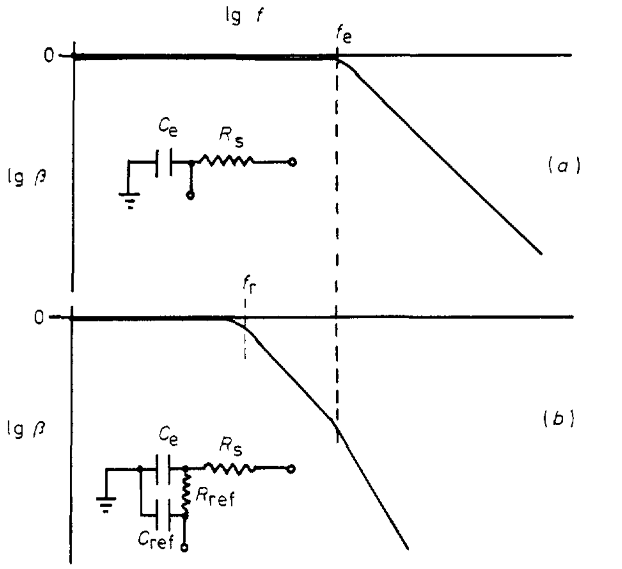

Figure 12 Frequency dependence of feedback fraction for two simple equivalent cells: (*a*) purely capacitive electrode impedance, RE time constant negligible, $f_e=(2\pi C_e R_s)^{-1}$; (*b*) second turnover at $f_r=(2\pi R_{ref} C_{ref})^{-1}$.

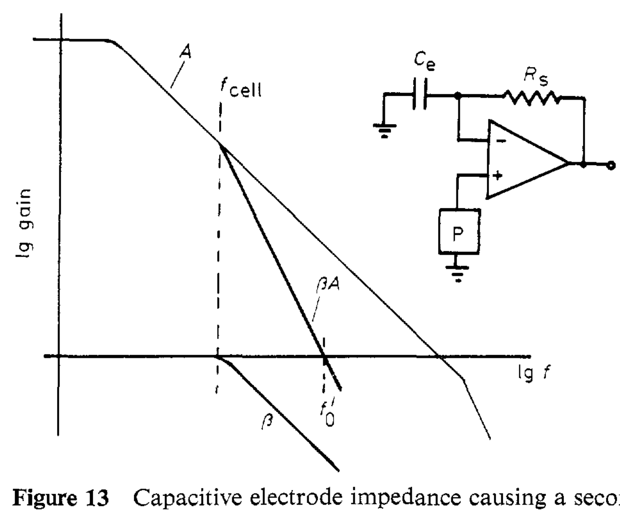

Figure 13 Capacitive electrode impedance causing a second turnover to a slope of -2 at $f_{cell}=(2\pi R_s C_e)^{-1}$.

against lg *f*, from which it is obvious that when these networks are used in the feedback loop, βA will exhibit at least one transition in slope, from -1 to -2. This is shown in figure 13, where the cell crossover frequency f_{cell} is given by $(2\pi R_s C_e)^{-1}$. The zero-crossing slope approaches -2, which means that there is only a small or zero phase margin and the system, although not completely unstable, is said to be underdamped.

The aptness of this description is clear from the 'ringing' response of the system to a pulse input (figure 14(*a*)). Alternatively, if a small-amplitude, sine-wave input of varying frequency is used, the underdamped response is manifest as a peak near f_0 (figure 14(*b*)).

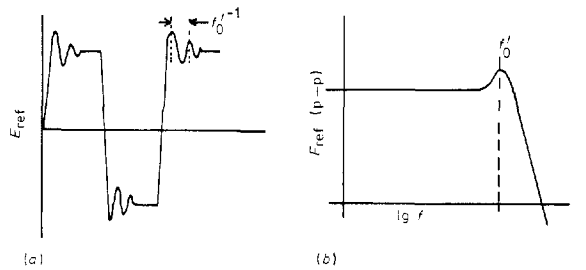

Figure 14 (*a*) 'Ringing' of the RE potential, characteristic of an underdamped system. (*b*) Peak in amplitude of RE signal in response to a constant-amplitude sine wave.

This condition is obviously unhealthy not only because the response generated by the system might be mistaken for interesting chemistry, but also because any further slight increase in the phase shift at f_0 will push the system over into self-sustaining oscillations.

A purely capacitive electrode reaction, i.e. an interface that passes no faradaic current and no ionic migration current (the perfectly polarisable electrode in electrochemist's terms), is clearly a rigorous test of potentiostat performance, particularly if it is coupled with a reference electrode that has a large time constant $R_{ref}C_{ref}$.

3.4 *Optimising potentiostat response*

In seeking a solution to the problem of oscillation or unacceptable ringing, the underlying cause must be re-emphasised; it is a combination of loop gain that is too high with too small a phase margin. While it may not be possible to modify the cell impedance, the *A* term in the loop gain can, however, be changed. One cure, therefore, is just to lower *A* by adding local feedback resistors R_1 and R_2 so that the second cell–potentiostat crossover frequency point is pushed below unity gain (figure 15). The low-frequency gain, equal to R_2/R_1, has a maximum value of $(f_0/f_{cell})^{1/2}$. The safety margin thus achieved has, of course, been obtained at considerable cost: that of drastically lowering the static and low-frequency gain, and with it the accuracy of stabilisation.

One further bit of loop tailoring to alleviate this loss of low-frequency accuracy can be carried out. The local feedback resistor R_2 can be replaced by the series combination R_2C_2, so that the feedback path is not operative at low frequencies. This gives a stepped response to the gain, i.e. at low frequencies the gain has its open-loop value, then there is a turnover to a slope of -1, while at a frequency around $(2\pi R_2 C_2)^{-1}$ the gain becomes flat again at a value of R_2/R_1 (figure 16). An additional way of achieving the objective, by placing an

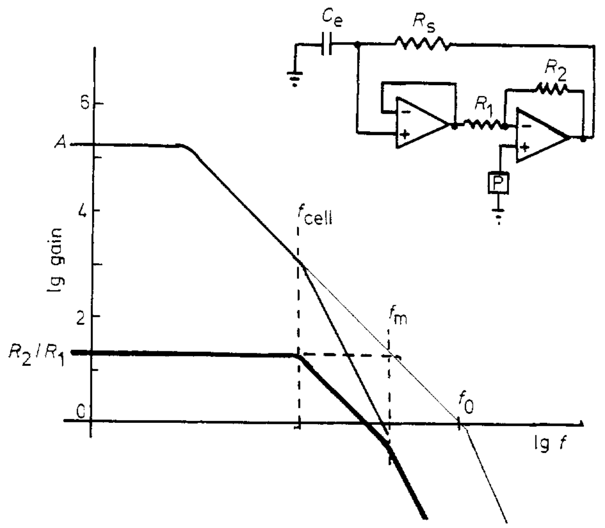

Figure 15 Modified gain (bold line) causes the cell crossover frequency to move from f_{cell} to f_m, and pushes this second turnover below unity gain.

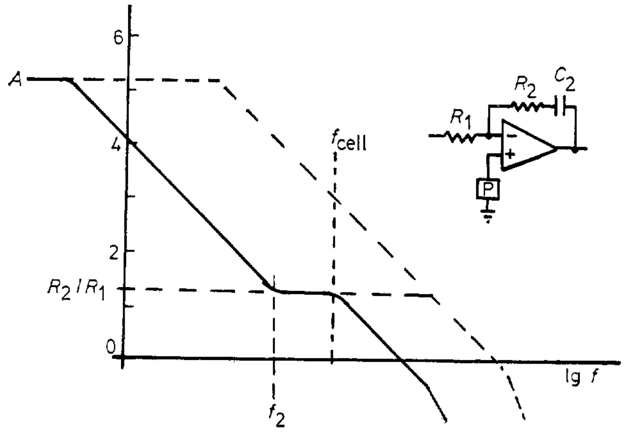

Figure 16 By addition of C_2 in series with R_2, the gain below $f_2=(2\pi R_2C_2)^{-1}$ is allowed to rise to its open-loop value.

active high-pass filter in the reference electrode connection and so compensating the falling open-loop gain with its rising characteristic, has been used by von Fraunhofer and Banks (1972).

Of course such tailoring presupposes that the cell characteristic is known and constant – a rather rare situation, in the absence of which recourse may be had to try-it-and-see pragmatism. In recognition of this, some manufacturers incorporate switched gain controls on their potentiostats, but unfortunately do not usually give particulars of the modified characteristics.

3.4.1 *Minimising input capacitance* The two important sources of loop attenuation and phase shifts that have been identified are the electrode reaction itself with solution resistance, and the RE with its connections to the cell and to the potentiostat. Any reduction in the $C_{ref}R_{ref}$ time constant is advantageous in that a stable system can thereby be maintained over a wider frequency band.

Reference electrodes should therefore be of a highly reversible type (see Ives and Janz 1961 for suitable types), and the Luggin capillary should be as short and as wide as possible. Diffusion barriers such as closed taps or the ceramic plugs often found in commercial reference electrodes generally have a very high resistance that may rule them out for wide-bandwidth applications.

The lead carrying the RE signal to the potentiostat is a 'sensitive' part of the circuit, because noise and mains hum picked up by it cannot be separated from the true signal. It is usual, therefore, to enclose this lead with a grounded shield – a practice that carries with it the danger that excessive capacitance to ground may be introduced. Two ways of reducing this capacitance are available. The first is to place the isolator amplifier very close to the RE, separating it from the box that houses the rest of the electronics. Some commercial instruments provide such a probe or isolator with a separate socket for its power supply. Alternatively, the isolator, consisting simply of an FET voltage follower, may be battery-driven (Aitchison and Brown 1976).

A second solution, which may be combined with the first, is to use a 'driven shield', in which the screening mesh of the RE lead is connected not to ground but to the output of the isolator amplifier. The screen and signal wire are then at virtually the same potential, so their mutual capacitance does not add to the effective input capacitance (figure 17).

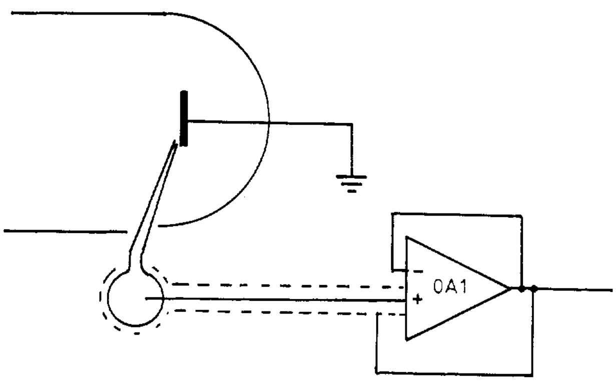

Figure 17 Use of a driven shield to minimise stray capacitance from the reference electrode lead.

In biological applications, input capacitance problems of a much larger order of magnitude are encountered with the glass capillary microelectrode (Ferris 1974, p70). The capacitance is inherent in the electrode design, but it may be possible to compensate electronically for its effects by using as isolator a follower with gain and negative input capacitance (figure 18) – a technique that has some similarities with the positive feedback compensation of resistance

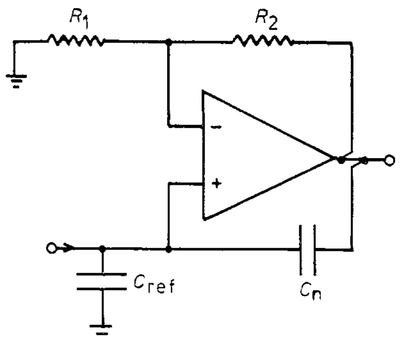

Figure 18 Neutralisation of C_{ref} and input capacitance from all sources with a negative-input-capacitance amplifier. $C_n=C_{ref}R_1/R_2$.

between Luggin tip and WE (§3.6 and Lamy and Herrmann 1975).

The difficulties of measuring the frequency-dependent impedance of a microelectrode are, however, even more severe than those of measuring R_u, so an empirical approach is usually taken to setting the level of compensation correctly. This procedure has been found to be adequate in recording nerve action potentials (Ferris 1974, p 77) but it is not suitable when exact information about the current time profile is essential, as in electrochemical kinetic studies.

3.5 *Current measurement techniques*

To drive transient recorders such as oscilloscopes or pen recorders it is necessary to have some kind of amplifier that will convert a current into a voltage proportional to it. One way of doing this is to use a current follower (figure 4(*d*)). The direct connection between WE and ground is replaced by the virtual ground of the current follower, all of the cell current flowing through *R*. Thus $V_{out} = -iR$.

This arrangement is easy and economical to set up, and convenient to use in that it can be adapted to give good sensitivity over a wide range of currents simply by changing the value of *R*. Because the bias current of the current follower introduces an uncertainty into the measured current, the amplifier should be a low-bias-current type.

There are some limitations and difficulties with the current follower. Because all of the cell current must be drawn through *R* and the output stage, any current boosting that was necessary in the potentiostat circuit will also have to be duplicated in the current follower. Note, however, that only sufficient voltage to drive the recording device (typically 1 V) needs to be supplied by the follower, so the power demand is not as high as that on the potentiostat.

There is also a more subtle limitation that comes from the fact that the input impedance of the current follower is inductive. This arises because the voltage at its input, δE, is given by V_{out}/A where A is the frequency-dependent open-loop gain. In the region where A falls with frequency, δE therefore increases with frequency and the WE sees an inductive impedance. The effects of this are deleterious to the high-frequency accuracy of the current follower, and oscillations may be induced when phase margins are small.

Moreover, the presence of another active device within the feedback loop imposes greater demands upon the quality of the common connections between the cell, potentiostat and recording device if disturbing ground loops are to be avoided.

Use of the current follower therefore can be recommended only for low-frequency applications where stability margins are not critical. The accuracy of the current follower and its effect on the accuracy of the system as a whole have been considered by Pence and Booman (1966).

The second method of measuring current is to place a small resistor in series with the CE and to measure the voltage drop across it with a differential amplifier (figure 19). This simple arrangement will always be inaccurate because the cell is shunted by the R_3–R_4 combination. Two voltage followers therefore have to precede the gain stage (figure 20). With FET followers, *R* may have a value as high as a few megohms.

Of course, some oscilloscopes and recorders have differential amplifiers which could replace the op-amp unit. Care has then to be taken to ensure that the input impedance is high enough to avoid falsifying the measured current. Some pen recorders have an input stage in which one of the differential inputs is connected to the metal chassis with a large capacitor. This can have a spectacularly destabilising effect

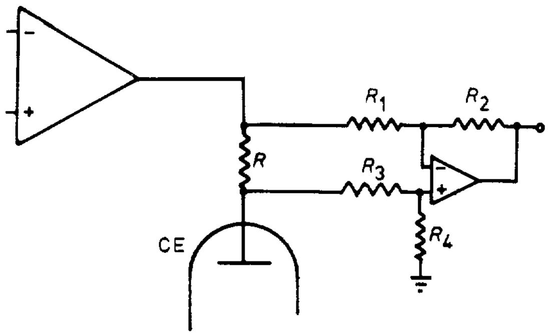

Figure 19 Differential amplifier used to measure the potential drop across the current-measuring resistor *R*. $R_1 = R_3$, $R_2 = R_4$.

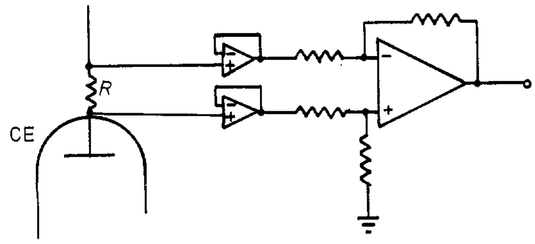

Figure 20 Addition of voltage followers increases dramatically the accuracy of the circuit of figure 19.

on the potentiostat, and is another pitfall of connecting recording gear directly to the current-measuring resistor.

When all the amplifiers needed are of the same voltage type (e.g. 15 V) the arrangement of figure 20 is a very good way of measuring the current. However, if the cell needs high-voltage drive, i.e. the potentiostat is a high-voltage type or is voltage-boosted, the followers and differential amplifier, which in the worst-case condition (disconnected or open-circuited cell) have to take the maximum voltage at their inputs, must also be high-voltage types.

In low-voltage systems, a good alternative for the three-amplifier combination is the so called instrumentation amplifier. These devices are high-input-impedance, fixed-gain systems in a single package, with better performance than that obtainable from separate amplifiers (e.g. Analog Devices AD520, Burr-Brown 3660).

A further type of device for measuring the voltage drop across the current-measuring resistor is the isolation amplifier, particularly useful for high-voltage, low-bandwidth applications. This consists of an input stage, which is an instrumentation amplifier with a floating power supply, that transmits its output to an output stage through an optical coupler or, after modulation, a high-frequency transformer. There is thus complete DC isolation between input and output, so the device is ideally suited for reading small voltage differences across the current-measuring resistor of a high-voltage potentiostat. The frequency range is necessarily rather narrow (e.g. 3·5 kHz for Analog Devices model 285, 10 kHz for Burr-Brown type 3650).

A final example of methods of measuring current is that suggested by Brown (1972) in which a resistor is interposed between ground and the WE so that the current can be measured by a ground-referenced amplifier. The correct degree of positive feedback is then applied to the potentiostat to compensate for the *iR* drop across the resistor (see §3.6).

3.6 *Resistance compensation*

It has been pointed out that while the Luggin capillary allows the gross effects of electrolyte resistance to be eliminated, placing the tip close to the electrode causes shielding effects which are equally as undesirable as uncompensated resistance. An alternative technique has gained popularity in which the Luggin tip is placed far enough away to avoid shielding, while positive feedback is applied to the potentiostat to compensate for the resistance R_u between tip and electrode. The principle is illustrated in figure 21, in which R_s represents

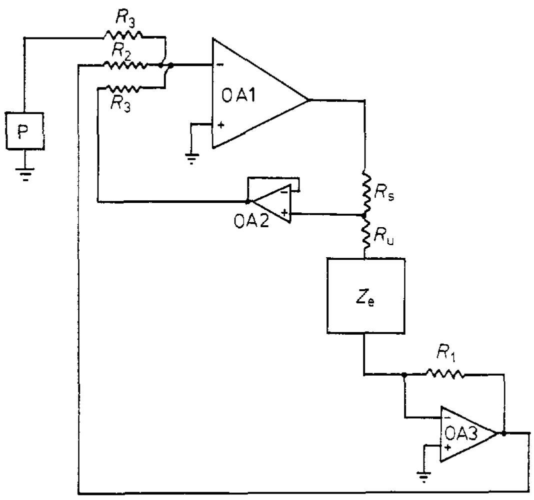

Figure 21 Compensation of the resistance R_u by positive feedback.

solution resistance, Z_e is the impedance of the electrode reaction, and the positive feedback path is from the current follower OA3 to the summing junction of OA1. The gain around this path is controlled by the quotient R_1/R_2, and must be adjusted so that the voltage drop iR_u is exactly compensated. If the relative gain of the compensating signal and the reference signal is unity ($R_2=R_3$) then $R_1=R_u$. Otherwise, the ratios must be adjusted so that $R_u=R_1R_3/R_2$. Compensation can be achieved using adaptations of any of the possible potentiostat-current measurement configurations.

If the gain around the positive feedback path is made too large, overcompensation will occur, leading to instability and oscillation. The criteria which determine the onset of oscillation, and the degree of underdamping and overshoot that precede it, are complicated (Brown *et al* 1966, 1968a, b, Whitson *et al* 1973, Lamy and Herrmann 1975).

A complete analysis of a real cell and electrode system is a study in itself, and would not be practicable in most cases. Nevertheless the technique of *iR* compensation can be usefully applied as long as certain guidelines are observed. First, only known resistances should be compensated – so a method of measuring R_u must be available. Several methods have been advocated, none of them particularly simple (Brown *et al* 1966, Booman and Holbrook 1963, 1965). If, however, R_u *can* be measured, the method of compensation will work satisfactorily (Whitson *et al* 1973, Brown *et al* 1966). Secondly, it is necessary that R_u be constant, which may not be a good approximation if high currents are passing which cause changes in the composition of the solution or in its temperature.

The alternative to measuring R_u is to adjust the degree of positive feedback while the experiment is running, and to 'optimise' the adjustment on the basis of the appearance of the results. This means increasing the compensation gain until oscillation occurs, then retracking until oscillation disappears and overshoot is reduced to an acceptable level. Obviously this procedure is too hit-and-miss for accurate experiments.

3.7 *Charge measurement*

Effective instrumentation for integrating current over a fixed period can again be simply constructed from operational amplifiers. The basic op-amp integrator is shown in figure 4(*f*). The bias current of the amplifier and the offset voltage are integrated as well as the signal, generating errors and a drifting output, so an FET op-amp of high quality is indicated for applications covering a wide range of currents. To the basic circuit must be added means of resetting the output, of running the integration and of holding the final value while it is recorded (Graeme 1975, O'Haver 1971).

Another method is to convert the voltage across the current-measuring resistor *R* to a frequency proportional to it, and then to use a digital counter to accumulate the number of cycles. This method has the advantage that the output, which can be made to read directly in coulombs by proper choice of *R*, does not drift on 'hold'. Earlier designs (Bard and Solon 1962, Phillips and Milner 1969) can be improved upon by using the latest designs of voltage-to-frequency converter (Datel Systems 1976, Phillips *et al* 1977).

3.8 *Programmed current*

Apparatus to cause the current to follow a preset programme (the galvanostatic technique) can be constructed from op-amps if the voltage, current and response time are within their range. Some useful circuits are shown in figure 22. The functioning of (*a*) is most obvious in that the desired current is simply given by the programming voltage E_p divided by *R*.

It is usually necessary in this technique to measure the electrode potential, and this can be done in (*a*) by using a differential amplifier between WE and RE. Alternatively E_{ref} may be obtained by subtracting the known PD across *R* from the potential measured between RE and ground. A circuit in which the WE is at virtual ground is presented in figure 22(*b*). Finally, (*c*) is a circuit (the Howland circuit, see Smith 1971) using positive feedback to generate the constant current. Its advantage is that both the WE and the programming source are grounded.

3.9 *Potentiostatic–galvanostatic mode switching*

It is sometimes necessary to switch at a definite instant from constant potential to constant current control. The similarity between figures 3 and 22(*a*) suggests how this may be done (figure 23). S_1 and S_2 are mercury-wetted relays driven by a pulse generator set to give the correct timing period. Mercury-wetted relays have very fast switching times, but the operate time is imprecise, so it is difficult to synchronise them. Semiconductor switches are not suitable in this circuit because of their high 'on' resistance. An alternative method using diode switches has been suggested (Warner and Schuldiner 1967) and this permits rapid switching. An ingenious though somewhat more complex circuit that permits mode switching with semiconductor switches has been published by Bruckenstein and Miller (1970).

3.10 *Multiple working electrodes*

The necessity sometimes arises, e.g. in rotating disc–ring studies, to control independently the potential of more than one electrode. This can be done by adding separate control loops to the basic potentiostat circuit (Napp *et al* 1967).

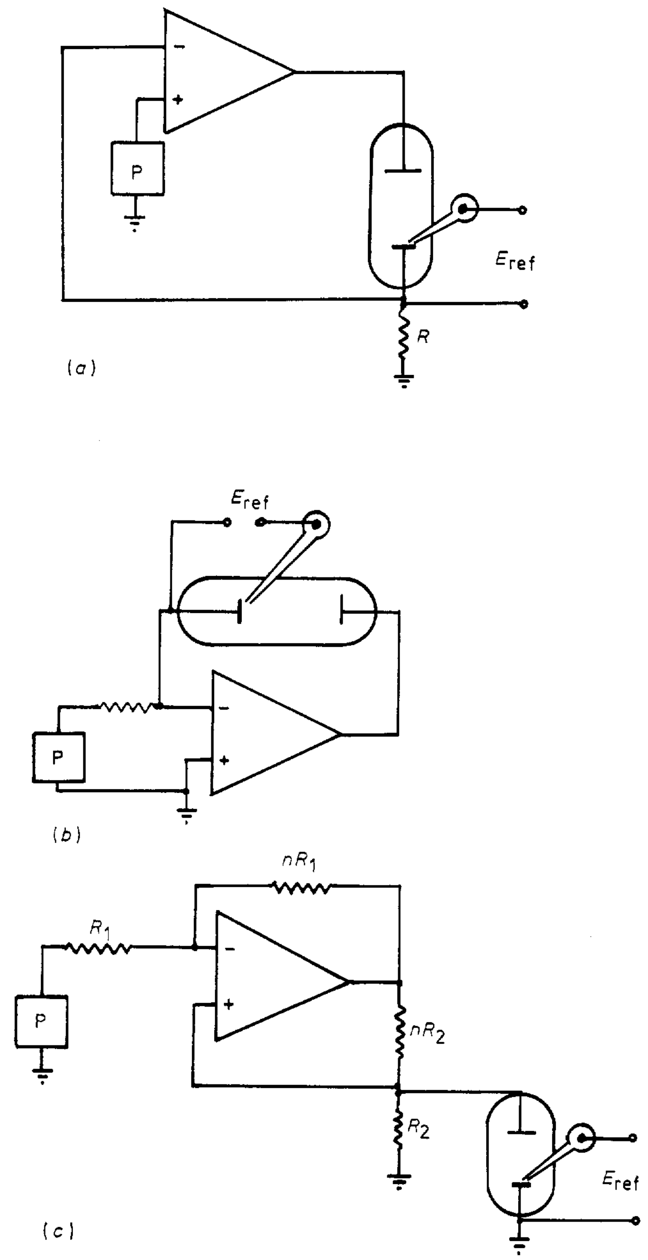

Figure 22 Alternative circuits for programmed current.

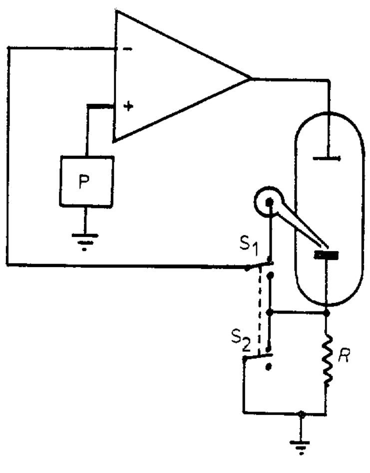

Figure 23 Mode switching between potentiostatic and galvanostatic control.

3.11 *Small-signal* AC *techniques*

In determining the complex impedance of an interface there is a choice between two methods: (*a*) non-stationary, in which the system is excited by an impulse, step or random noise (Pilla 1972); and (*b*) steady state, using small-signal sinusoidal excitation. Method (*a*) is easy to apply, but the results are often difficult to record and analysis may be complicated. The methods have been compared by Creason *et al* (1973) (see de Levie *et al* 1975 for a recent application). This section deals with two different instrumental solutions to method (*b*), both of which yield the frequency-dependent real and imaginary components of impedance with a minimum of calculation (see review by Sluyters-Rehbach and Sluyters 1970).

3.11.1 *Bridge methods* There are many difficulties in obtaining high accuracy from a bridge over a wide range of frequency, e.g. stray impedances and impurity in the standard resistors and capacitors, elimination of harmonics that may be introduced by nonlinearity in the electrode impedance, ground loops and hum pick-up. The necessity to vary the DC bias across the interface without affecting the balance, and the fact that the maximum signal that can be allowed to appear across it is about 10 mV, add greatly to the complication of bridge circuitry. There is at present no commercially available bridge that meets all of these exigencies.

Bridge methods have been reviewed by Armstrong *et al* (1968), who examine the interplay of such factors as electrode size, quality of standard components, cell construction and earthing arrangements on the overall accuracy in various frequency ranges. They advocate different solutions for high and low frequencies. For the audio range up to 10 kHz a 'home-made' Wien bridge with either oscillographic detection of the null point or a system using two phase-sensitive detectors is preferred. Above 10 kHz they suggest a circuit based on a commercial transformer ratio-arm bridge. In measurements on a hanging mercury drop in NaF and HCl solutions the sensitivity was 0·05% from 200 Hz to 400 kHz, the accuracy being limited by the drop area determination rather than by the bridge.

For the specific application of lipid bilayer studies where there is no need to impose a variable bias potential, White and Blessum (1975) have solved many of the problems of stray capacitance by using a simple bridge with the unknown floating, applying the bridge excitation through a photocoupled isolator. The accuracy of measurement was 0·05% from 100 Hz to 10 kHz, and decreased from 0·1 to 4% in the 20–100 kHz range.

3.11.2 *Admittance measurements* Admittance measurements, in which the current is measured directly, should be considered as an alternative to the very cumbersome and time-consuming bridge method when lower accuracy can be tolerated. The method consists of applying a small sinusoidal voltage to the WE with a potentiostat, and analysing the in-phase and quadrature components of the cell current with phase-sensitive detectors. This process lends itself to automation, as has been demonstrated by de Levie and Husovsky (1969) in their circuit for measuring the impedance of a dropping mercury electrode at a timed interval after drop birth. The circuitry uses op-amps for all timing and measurement functions, incorporates positive feedback correction of uncompensated resistance, and permits measurements in the range 10 Hz to 1 kHz. A computerised version of this circuit has been developed by Mohilner *et al* (1976).

Even higher degrees of automation can be achieved with this kind of measurement: the ultimate at the time of writing is the Schlumberger–Solartron frequency response analyser, type 1170 (Armstrong *et al* 1977).

A review of instrumental factors that can reduce accuracy in these methods, together with guidelines on their detection and elimination has been published by Dickinson and Whitfield (1977).

3.12 *Signal generators*

There are many commercial sources of signal generators, but this is another area where the versatility of op-amps coupled to various monolithic semiconductor devices can often be exploited with advantage.

3.12.1 *Pulse, step and ramp sources* The device obtainable from several manufacturers with the type number 555 is a useful source of single pulses (monostable operation), trains of rectangular pulses (astable operation) and step functions (monostable with a long time constant and manual reset). Manufacturers' literature should be consulted for details of performance and the connection diagram for this versatile device.

The output amplitude of the 555 is fixed and depends on the power supply voltage (5–15 V). It can be varied and biased by using resistor networks, and complex trains of pulses can be built up by using several 555s (the twin 555, designated the 556, is useful here) together with an op-amp in summing configuration. The rise time of pulses from the 555 is 100 ns, so a fast-slew-rate op-amp (e.g. Analog Devices type 50, Teledyne Philbrick type 1322) should be used if this rise time is to be preserved at the output of the op-amp. Similar devices are the XR220 (Exar), which needs fewer timing components, and the 553 (Signetics) which consists of a package of four timing devices similar to but less versatile than the 555.

A further monolithic function generator can be mentioned, the 8038 (Intersil). This produces square-, triangle- and sine-wave shapes simultaneously over a wide frequency range (10^{-3} Hz to 1 MHz) all of which can be frequency-modulated by a control voltage. The high harmonic content of the sine wave, however, renders it unsuitable as the excitation signal for AC bridge work. For this purpose, the op-amp oscillator of Smith (1971) can be recommended.

Finally, as a further illustration of the power of op-amp circuitry in conjunction with simple logic ICs, the triangle-wave generator of Britton *et al* (1976) can be cited. The positive and negative ramp slopes are independently variable over a wide range, as are the potential excursions. The initial slope can be selected, and the circuit will give a single ramp, single triangle, or a continuous triangle wave.

3.12.2 *Arbitrary function generators* Sherwood *et al* (1975) have described a generator which, being based on a 16-bit digital-to-analogue converter (DAC), can readily be interfaced to a computer (see, for example, Perone and Jones 1973) and in this way is capable of producing any function. There is, however, enough digital electronics in this design to permit its use as a stand-alone generator of the usual pulse and ramp functions over a wide time range.

There are dangers in seeking to approximate a linear ramp with a DAC which necessarily gives a stepped output rather than a smoothly changing ramp. The response of an electrode is different for the two cases, as has been shown by Zipper and Perone (1973), and mathematical methods for treating responses to 'staircase voltametry' have been developed by Surprenant *et al* (1977). However, if the resolution of the DAC is high enough, its output will emulate a smooth ramp. The 16-bit system of Sherwood *et al* has a resolution of 30 μV for a 2 V full-scale output, and they show cyclic voltammograms which are the same whether produced by a conventional analogue ramp or their DAC generator.

4 Commercially available instruments

4.1 *Potentiostats and galvanostats*

As has been indicated in §3.8 a galvanostat can be constructed from a potentiostat by a simple change of connections, and some manufacturers recognise this by incorporating switches or other means with which to change the function of their instruments.

Commercial instrumentation for controlled potential coulometry has been reviewed by Bard and Santhanam (1970), and a more recent though less complete list of manufacturers is available in the review by Harrar (1975).

In buying an instrument, all of the considerations outlined in §3.3 must be borne in mind. Unfortunately not all firms specify enough parameters, or the right ones, to enable a proper estimate of behaviour with a given cell to be made.

The voltage and current capabilities are always given. While high voltage and current capability is necessary for preparative work and kinetic studies involving pulsed currents, there is no point in purchasing power that cannot be used (e.g. in corrosion studies or biological work). One should also heed the warning that under common fault conditions such as high resistance or disconnected cell, the output voltage will rise to and remain at its maximum, and this may damage associated instruments (including human beings!). Similarly, high currents can damage through overheating or excessive gas evolution.

Circuits are sometimes incorporated to protect the potentiostat from delivering continuously too high a power. Such circuits should reset themselves automatically once the overload is removed.

At least one source of accurate, manually adjustable programming potential should be provided, together with a socket for connecting an external oscillator. The means for switching from one source to another is worthy of note, as mechanical switches have bounce that can cause harmful spikes to appear across the cell. Electronic switching is less likely to introduce transients.

The input (bias) current and input resistance should both be given. FET input stages are now common, giving an input impedance of greater than $10^{10}\ \Omega$ in parallel with no more than 5 pF and with a bias current below 50 pA. This is adequate for all except glass electrodes or biological microelectrodes. The facility for attaching a separate probe amplifier is an advantage, because even for low-resistance electrodes it is possible to reduce pick-up by having a voltage follower amplifier close to the cell. It is desirable to have the probe output available at a terminal for driving recorders. Figures for noise are sometimes given, but are usually not sufficiently detailed to be easy to interpret or compare.

One of the most important specifications, that of frequency response, is the most difficult to assess because manufacturers seem reluctant to publish the full Bode plot for their potentiostats. One is usually left to guess the meaning of their substitute terms such as 'bandwidth', 'response time', etc.

Assurances that the potentiostat 'can never oscillate, even with high capacitance loads' should be treated with scepticism. If systems in which the cell is capacitive and the time constant of the RE is high are to be investigated, the recommendation must be 'try before buy'!

The slew rate (the maximum rate at which the output voltage can change) is an equally important parameter when fast charging of electrode capacitance is necessary. A slew rate of 100 V μs^{-1} can be considered good.

4.2 *Measuring current and charge*
A potentiostat should at the very least have a series of precision current-measuring resistors that can be switched into the CE lead, and terminals at its ends for connection to a differential amplifier. More expensive instruments may have a current follower built in or available as a separate unit.

The specification of current followers should be examined carefully. Because of the difficulties that a current follower creates in achieving a stable system (§3.4) it is usual to give it a lower bandwidth than that of the main amplifier, so this may be a limitation in studies at high frequencies.

Coulometers are available as a free-standing unit or as a plug-in to some systems, and may give an analogue or digital output, or both. Units that use voltage-to-frequency converters are very stable and accurate over long periods, so their main use is in electroanalytical chemistry and corrosion studies. Their rather narrow bandwidth makes them unsuitable for intergrating narrow spikes of charging current. A feature that allows separate integration of positive and negative currents is very valuable.

4.3 iR_u *compensation*
In §3.6 the power and dangers of positive feedback compensation of R_u were mentioned, and it was stressed that only known resistances should be compensated. In commercial instruments, where the trend is for a variable degree of positive feedback to be provided, this control is usually uncalibrated. Therefore calibration with a dummy cell of known resistors is necessary for all but very rough experiments. A turns-counting dial on the feedback control is essential for ease of resetting.

4.4 *Logarithmic current converters*
These are available for some potentiostat systems and can also be bought as a plug-in to recorders. They are essentially slow-speed devices whose principal application is in corrosion testing. Specifications to note are accuracy and temperature stability, and particularly the ability to deal correctly with both positive and negative currents. A wide dynamic range (four or five decades) is an asset when long-term experiments are being run without attention.

5 Commercial equipment

New instruments are constantly appearing, and so rather than attempt to give performance figures for specific models, only the names and addresses of manufacturers most active in the field are included, with a brief note of the scope of their production.

Amel
Fast- rise-time (0·1 μs) potentiostat, with galvanostat, current follower, positive feedback and electronic sequencer. A similar model with ± 200 V output. Multifunction generator.

Apparecchiature di Misura Elettroniche, via Bolzano, 30-20127 Milan, Italy.

Bentham Hi-Tek
Potentiostat with 100 V μs^{-1} slew rate, current follower, positive feedback, probe amplifier, switchable gain and electronically switched programming potential. Digital integrator. Digital signal averager.

Bentham Instruments Ltd, Wick Hill Lane, Wokingham, Berkshire.

Bruker
Low-cost potentiogalvanostat. A more elaborate model with positive feedback. Polarographs.

Bruker Spectrospin Ltd, Unit 3, 209 Torrington Avenue, Coventry CV4 9HN.

Chemical Electronics
Range of potentiostats, some with plug-ins. Versatile function generator. Integrator. Rotating-disc equipment.

Chemical Electronics (Birtley) Ltd, Hutton Close, Washington, Tyne and Wear.

Hermes
Wide range of potentiostats of various powers, some modular. Triangle-, sine-wave and pulse generators. Integrator. Digital transient recorder.

HC Controls (Northumbria) Ltd, Quayside, Newcastle upon Tyne.

MPI
Potentiostat with ± 100 V, $\frac{1}{2}$ A output. General-purpose modular instruments based on plug-in op-amps. Cells for electroanalysis.

McKee–Pedersen Instruments, PO Box 322, Danville, California 94526, USA.

PAR
Modular potentiostat/galvanostat with a ± 100 V, 1 A output, *iR* compensation, probe, electronically switched programme. Log converter, current follower and coulometer available as plug-in or separate instrument. Simplified potentio/galvanostat. Programming unit. Polarographs and computerised polarographs. Digital scan recorder.

Princeton Applied Research Corp., PO Box 2565 Princeton, New Jersey 08540, USA.

Tacussel
Wide range of potentiostats including a very fast-rise-time model, a twin potentiostat, and an electromechanical unit with 20 kW output. Logarithmic converter. Function generators.

Tacussel Electronique, 72–8 rue d'Alsace, 69100 Villeurbanne, France.

H B Thompson and Associates
Compact, low-cost potentiostat, with ± 25 V at 1 A output. Larger units up to 1 kW output.

4, Ravenswood Close, Forest Hall, Newcastle upon Tyne.

Wenking
Potentiostat with alternative output stages, ground-referenced current output. Scanners.

Bank Electronik, Werner-von-Siemans-Strasse 3, 34 Goettingen, West Germany.

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