

Potentiostats

An introduction to the principle of potentiostatic control, including basic potentiostatic circuits, electrochemical applications, and some notes on electrode and cell design

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INTELLIGENT CONTROLS

POTENTIOSTATS

AN INTRODUCTION

Potentiostats are amplifiers used to control a voltage between two electrodes, a working electrode and a reference electrode, to a constant value.

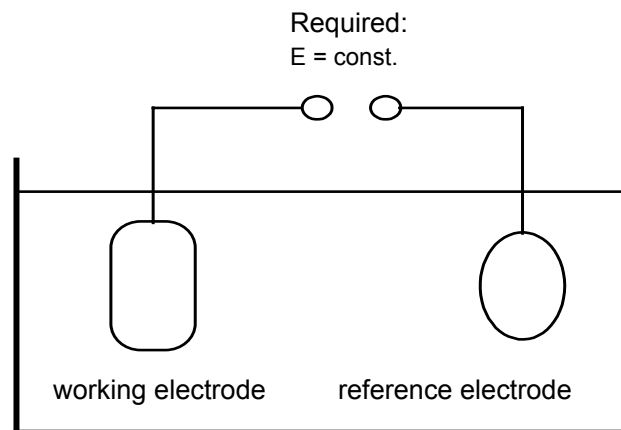


Fig. 1: A simple electrochemical cell

Simple, isn't it?

Let us have a look back into the year 1950. In this period, metallurgists and physico - chemists tried to bring some light into a fascinating electrochemical phenomenon.

If you dip an iron wire (electrochemists say: an iron electrode) into diluted sulphuric acid (which we now will call an electrolyte), it will instantly start to dissolve - it corrodes. If you now insert another electrode, which shall not corrode, e.g. platinum, and connect the iron electrode to the negative pole of a current source, and the platinum wire to the positive pole, the iron dissolution will slow down or even stop, depending on the voltage applied. This phenomenon was detected already in the 17th century by Sir Humphrey Davy.

If you connect the iron electrode to the positive pole, and rise the voltage from very low values to higher ones, the dissolution grows exponentially with rising voltage.

Above a certain current limit, depending on the electrode area and the electrolyte composition and the temperature, you find out that the current suddenly drops to very low values, and the iron electrode stops to dissolve. This phenomenon was detected by Michael Faraday, he called it "passivity". This phenomenon has been object of controverse disputes since then. It could be explained roughly in the fifties of our century. A better understanding was possible after the invention of the potentiostat.

The nature of the phenomenon imposes an electrochemical method to investigate. The idea was to record the characteristical current - voltage curve of the iron dissolution in the electrolyte. However, there was one difficulty: According to the applied method, the results varied strongly.

If you control the current, using an adapted current source, and measure the voltage between the iron electrode and a reference electrode (hence referred to a "potential"), you find, that depending on the direction chosen to record the curve (falling or rising voltage), you will obtain different results.

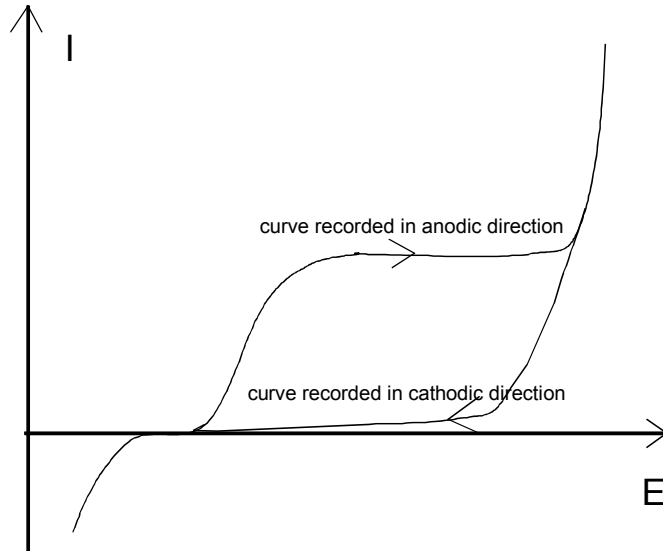


Fig.2: "Galvanostatically" recorded current - potential curve

People tried to go the other way: to control the potential between the reference electrode and the iron electrode, while the current was measured. They used a low - ohmic voltage source to control the potential to a constant value. This method was applicable within certain potential regions. However, between the region of active dissolution and the passive region, oscillations occurred in an interval of some hundred millivolts.

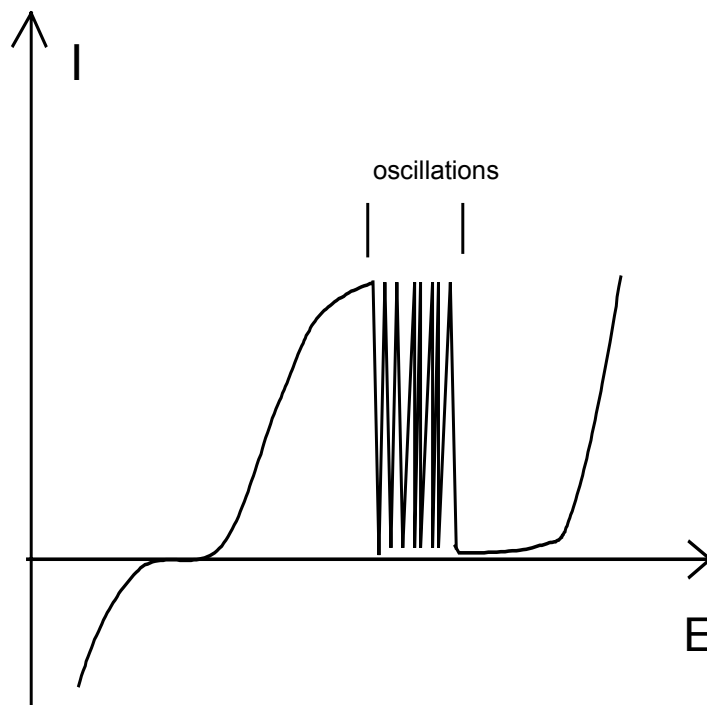


Fig. 3: "potentiostatically" recorded curve with manually controlled potential

The reason for these oscillations could be explained: The current in the active region before onset of passivity is roughly 5 orders of magnitude higher than in the passive region. A low - ohmic voltage source, which may have a source resistivity of 1 Ohm only, produces a potential shift of 100 mV back to the active state when the current is falling from 100 mA to 1 μ A. A stable state cannot be achieved.

So, using manually controlled voltage sources it was impossible to find the true current - potential curve which could help to clarify the mechanisms of passivation. This was the state of knowledge about 1950. D.C. amplifiers promised to bring a solution. Still these amplifiers were equipped with vacuum bulbs, as transistors were not available yet. Disregarding the difficulties of bulb - driven amplifiers which caused stability problems, these amplifiers showed systematic errors.

Let us look at such an amplifier.

The voltage difference between a stable reference - element is formed between the grounded working electrode and a reference electrode. This difference is now amplified and inverted. The resulting current signal drives the counter electrode. Thus, the potential difference is counterbalanced to *nearly* zero. Nearly, because a residual error remains. It is as smaller as higher the amplification is. Such instruments were built in Goettingen, Germany, and at the same time also in Italy, in the UK and the USA.

However, these amplifiers had one systematic problem. Imagine a sine wave fed into the input of the amplifier. It will be amplified and inverted: Inversion means that the phase shift is 180°. But, rising the frequency of the sine wave you find that the phase shift of the amplifier depends on the frequency. As higher the frequency, as higher is the phase shift, until the signal is not longer inverted, but produces an in-phase feedback: That is the feature of an oscillator, and indeed, oscillations are produced.

You may object that we did not intend to feed in a sine wave. But, each sudden voltage rise includes a frequency spectrum, even the intrinsic noise of the instrument, its upper frequency limited by its slope.

Of course, it was possible to use filters limiting the bandwidth of the instrument. But, this would again cause problems: remember above problem of passivating metals. An amplifier, reacting too slow, would again produce oscillations, due to the passivation / activation cycles.

At the time when the first potentiostatic amplifiers had reached this state, an excellent group of physico - chemists worked in Goettingen with professor Bonhoeffer and his assistant Weil. A young physicist, Hans Wenking, joined this group. His task was to manage the institute's scientific instruments. Beyond others, he became familiar with the problems of the electro-chemists. Analysing the available amplifiers, he developed the first potentiostat which worked properly.

It was Wenking's merit to introduce two new features: The difference amplifier and the phase correction. The first potentiostat built by Hans Wenking already showed the features which you find today in a common solid - state operation amplifier. This basic potentiostatic principle is used in many instruments until today.

Let us return to our lecture:

Potentiostats are amplifiers used to control a voltage between two electrodes, a working electrode and a reference electrode, to a constant value.

To achieve this, some conditions have to be matched:

Reference electrodes are electrodes, which maintain a constant voltage referred to the potential of the hydrogen electrode (which is by convention established as the potential reference point). A silver wire, covered with a silver chloride layer, dipping in a chloride solution, is a simple reference electrode. However, as soon as a current passes this electrode, it is polarised, that means its potential varies with the current. Hence, to maintain a stable potential, no current is allowed to pass the reference electrode. Imagine, that any amplifier input has a limited input resistance, and a small current passes this input. A potentiostat must have a very high input resistance to meet this condition, in the range of Gigaohms to Teraohms or even higher.

Now, how can we achieve to maintain a constant potential difference between the reference electrode and the working electrode?

We are forced to introduce a third electrode, which we call counter electrode. A current is forced between working electrode and counter electrode, high enough and in proper polarity to keep the working electrode potential at a constant value with respect to the reference electrode.

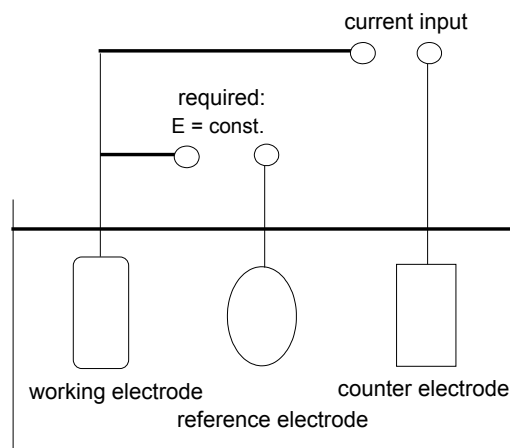


Fig. 4: Principle of a potential - controllable electrochemical cell

The potentiostat has two tasks: To measure the potential difference between working electrode and reference electrode without polarising the reference electrode, and to compare the potential difference to a preset voltage and force a current through the counter electrode towards the working electrode in order to counteract the difference between preset voltage and existing working electrode potential.

How is this to realise?

Use a bipolar operational amplifier (OPA). Such an OPA has two inputs: An inverting input and a non - inverting one, which has following qualities:

If you feed in a voltage into the non - inverting input of an operational amplifier, it will produce an amplified voltage (or current) of same sign. If you feed this voltage into the inverting input, it will produce a voltage (or current) of the same magnitude, but of opposite sign. If we now close the loop between output and input, the voltage difference between the two inputs of the operational amplifier will diminish. Raising the voltage on the inverting input forces a complementary current on the output, which counteracts the input voltage difference.

Let us use the properties of such an operational amplifier. Connect the working electrode to the non - inverting input (+), the reference electrode to the inverting input (-), and the counter electrode to the output.

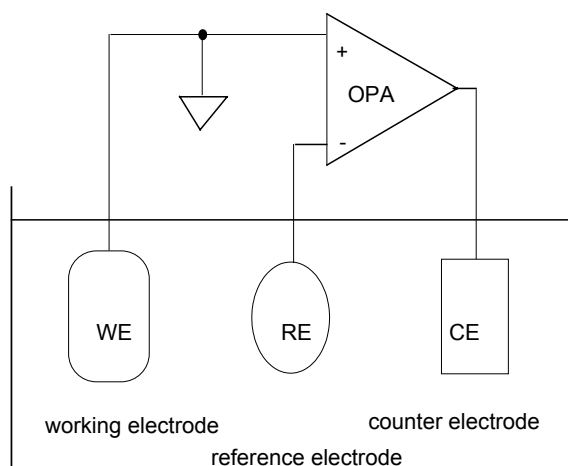


Fig. 5: Using an operational amplifier as potentiostat

The difference between WE and RE will be amplified and inverted by the OPA. A matching current is fed to the counter electrode CE. The control circuit is closed by the cell, where the current passes the electrolyte from the counter electrode to the working electrode. This polarises the working electrode WE exactly so that the difference between the reference electrode input and the working electrode input is set to zero.

Doing so, you can keep the potential of the working electrode exactly on the potential of the reference electrode. If you want to shift the potential of the WE to some other value referring to RE, you only must insert a voltage in series between reference electrode input and the reference electrode. To measure the current through the counter electrode, you must insert a resistor in the counter electrode wiring, across which a voltage can be measured, proportional to the current flowing.

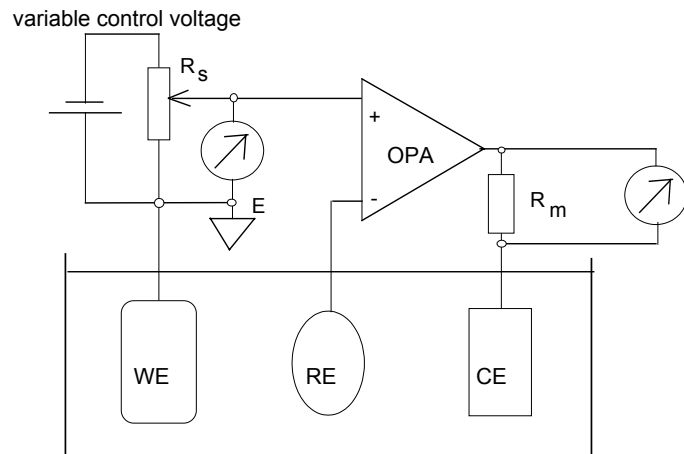


Fig. 6: A potentiostat with potential control

A real potentiostat has some additional elements, which should be mentioned:

The reference electrode input is commonly protected by an input resistor, which prevents the potential amplifier from being destroyed by static high voltage shocks, when the input is open. A phase correction capacitor must be introduced. This capacitor is very important:

The gain of the amplifier decreases with increasing frequency. On the other hand, the phase shift of the amplifier increases with frequency. A sine wave fed into the inverting input is counteracted at the output at low frequencies. At a critical frequency, the internal phase shift of the amplifier reaches 180° , and in consequence, the output signal is in phase with the input signal. The potentiostat then acts as an oscillator, oscillating at full power.

The phase correction capacitor prevents this malfunction, by keeping the phase stable within the destined frequency range.

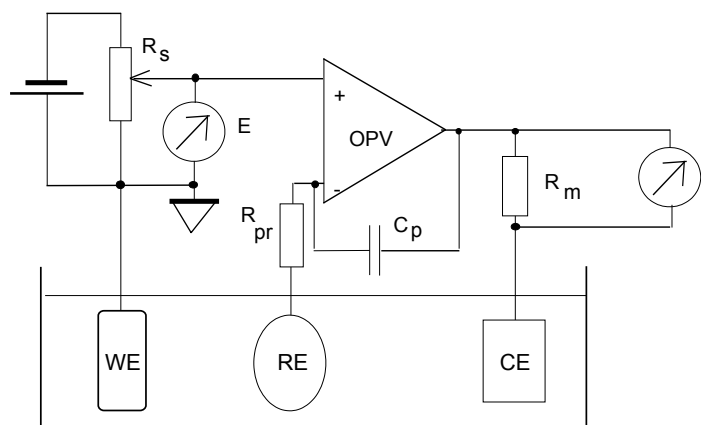


Fig. 7: Complete scheme of a simple potentiostat

These elements are now sufficient to build a potentiostat which is able to control electrochemical cells. If you restrict the interior to this minimum of parts, you get some advantages.

- The electric noise is determined only by the protective resistor in the potential input line, and the intrinsic noise of the operational amplifier, so it can be kept very low.

- the bandwidth is high.
- the working electrode is kept on ground. It does not pick up hum or RF - noise from the environment, so that the cell usually must not be screened.

Drawbacks:

- As the current is measured across a resistor in the counter electrode circuit, it must be measured with a "floating" instrument.
- The potential can be measured only with an electrometer having a very high input resistance.

CHARACTERISTICS OF POTENTIOSTATS

Control speed

Chemical reactions can be very fast. The potentiostat must be able to react at appropriate speed: The speed of a potentiostat is measured in terms of small - signal rise - time, bandwidth and slew rate. The bandwidth depends on the principle of the circuitry and the output power. Usual potentiostats have bandwidths from 10 kHz to some MHz. The slew rate ranges from 10^5 to 10^7 V/s, the small - signal rise - time is in the order of some microseconds or below.

Accuracy

The potentiostat counterbalances voltage difference between set control voltage and existing cell potential only to a good approximation. A residual error remains, which is reciprocal to the open loop gain of the potentiostat: Having an open loop gain of 10^6 , a control voltage of 1 V can be approximated to 1 μ V. However, the total error has other and more influencing sources, e.g. uncompensated cell cable resistances and resistance effects in the cell.

Current range and dynamics

Frequently, high currents are required from the potentiostat. Investigations in material science demand usually some 100 nA to 1 A, for other purposes ten or even hundred amperes are required. On the other hand, very low currents shall be measurable, too. A good laboratory potentiostat may have e.g. an output current of 1 A, and a current resolution of 100 nA or much less. State of the art are one - ampere - potentiostats which are capable to measure less than 1 nA. The relative accuracy of the measurement is better than 1 %, may be less than 0.1%. The usable span of current between full range and the lowest detectable current in the same range is called the dynamic. The dynamic of a good potentiostat reaches 5 decades. The overall span from the highest current range to the lowest threshold current covers 9 or more decades.

Please compare: A good laboratory balance measures weights of 200 grams to 0.1 mg, that means a range of $2 \cdot 10^6 : 1$. Potentiostats cover a much wider span!

Noise

Electronic noise is the sum of all statistic current fluctuations produced in a circuitry. Most of the noise is produced by thermal effects in resistors, another main part in semiconductors. In potentiostats, the most sensitive circuit is the input stage, producing noise in the input resistor and the first amplifier stage. Good potentiostats are equipped with low-noise amplifiers. However: There is a discrepancy. Low - noise operational amplifiers usually do not possess high input resistivity, or they have a restricted frequency range. It is essential to choose the input stage amplifier according to the main purpose of the potentiostat.

Stability

A potentiostat used for a wide variety of electrochemical tests has to show good stability, as the electrodes act in the control circuit, with all their variety of capacities, resistances, and frequency - dependent impedances. You may test a potentiostat, by feeding a 1 kHz - rectangle wave of e.g. 100 mV amplitude into the control input. Connect a dummy cell with different capacitors to the potentiostat, and an oscilloscope to the potential output. The rectangle wave should be

transferred to this output with a) a high slew rate and b) oscillations caused by high capacities should be properly damped.

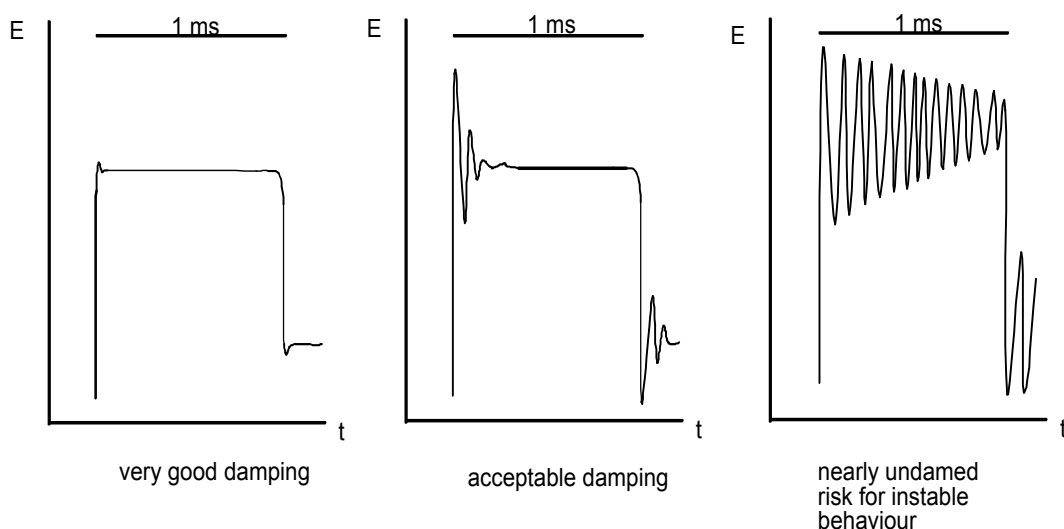


Fig. 8: Examples for good and bad damping of rectangle pulses on a dummy load with $1 \mu\text{F}$ between working electrode and reference electrode. The counter electrode is connected to the reference electrode. This a rather hard test for a potentiostat!

Phase correction

Connecting a dummy cell with pure ohmic load, current and potential should be in phase as near to the theoretic limits as possible. Otherwise certain experiments (e.g. measurement of a.c. impedance) produce wrong results.

You see:

A potentiostat, which is both extreme fast and produces extreme low noise and controls currents from femtoamperes to kiloamperes is physically impossible. If the potentiostat is very fast, we have to accept a certain amount of noise. If we want a high - power potentiostat, there is no point to measure extreme small currents with it. But within the limits shown above, potentiostats are very versatile instruments.

THE INTERIOR OF A POTENTIOSTAT

The most simple potentiostat has already been introduced in fig. 7, and you already know its advantages (fast, low - noise) and drawbacks (floating current measurement only, no output for the measurement of the existing potential). In addition, the output voltage at the counter electrode is limited to 15 V, and the output current of the shown circuit is limited to a few milliamperes.

To overcome these limitations, we have to add some additional amplifier stages.

The Power Stage

The power stage usually is a simple booster, similar to the power stage in your stereo amplifier. Equipped with a separate power supply, it can deliver both high currents and high voltages. The

total output power can be raised up to the range of several hundred watts or even kilowatts. Usually, it is protected against short circuit of the electrodes.

The components vary greatly: Either Darlington or Power-MOS-FET transistors are arranged to form a bipolar, symmetric amplifier. The maximum power dissipation is equal to the rated output power. According to the size of the housing, power stages up to 80 Watts can be cooled by natural convection. Above this limit, cooling fans are used to keep the temperatures within tolerable limits. When comparing the potentiostat to your stereo amplifier, which may have a rated output power of 200 Watts, don't forget that the full output power there is required only during very short periods. If you try to feed in a sine wave of e.g. 1000 Hz to your stereo amplifier and let it work at full power for hours, you will either find out that it has a proper working thermal fuse, or otherwise some repair might be necessary. Just a remark: good laboratory power - potentiostats can be used as "High End" audio amplifiers of superior quality.

All our power stages are equipped with truly oversized power-MOS-FETs, the design temperature of the cooling units is as low as 60°C, so our power stages survive decades.

High Voltage Power Stages

There is a practical limit for the compliance voltage of high - voltage potentiostats. The power transistors must resist twice the compliance voltage. A variety of N - type transistors is available which operate up to 1000 V, or even above, but to build a very good power stage, N - P - pairs are required. The available P - type transistors do not tolerate more than 400 V. This restricts the compliance voltage of high - precision, fast potentiostats to 200 V.

High Current Power Stages

There is no theoretical limit for the current of an analogue controlled power stage. However, cooling problems restrict the current to some ten, perhaps 100 amperes for laboratory potentiostats which should withstand also short - circuit conditions.

Design Details

An interesting feature may be the coupling between the potentiostatic amplifier VA and the power stage. In the traditional type of coupling the output voltage of the potentiostatic amplifier (VA) operates on a power stage which itself shows the same construction details as an operational amplifier, therefore it has a rather complex circuitry. A more simple way is possible using the power supplied to the potentiostatic preamplifier to drive directly the gates of MOS - FET power transistors. These "directly coupled" power stages have extended bandwidth, however this technique is restricted to compliance voltages below about 40 V.

The Potential Buffer

In most potentiostats, the signal from the reference electrode input is fed through an impedance transformer. This is an amplifier which is wired as buffer, which amplifies the input current, while the voltage remains changed. Doing so, the reference electrode is charged with extreme small currents only, and the output is able to feed appreciable loads. The input resistor R_p protects the buffer input from static loads, and the capacitor C_i reduces the intrinsic noise of R_p .

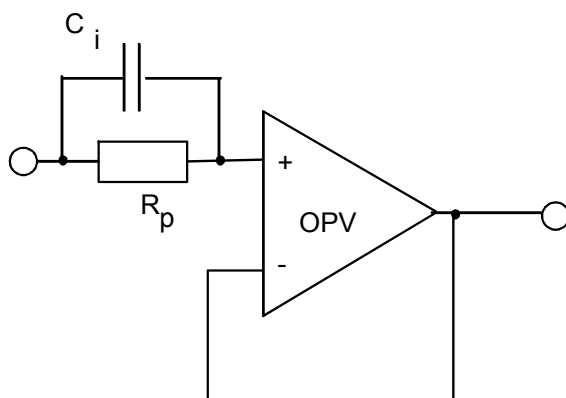


Fig. 9: Typical buffer circuit

Usually BIFET operational amplifiers are used for this stage, having an extreme high input resistance, accordingly low input currents are required. The input resistance is in the order of 10^{11} to 10^{14} Ohms or higher, the input bias current some pA or less, and the noise is typically below $20 \text{ nV}/\sqrt{\text{Hz}}$. In the further text, this kind of amplifier circuitry is abbreviated as BUF.

For very extreme conditions, it may be useful to have the buffer circuit separated from the potentiostat's housing, coupled directly to the reference electrode at very short distance. This can be done, if required, with practically any potentiostat.

The Potentiostatic Amplifier (VA)

This stage is the potentiostat's core, and quite similar to the simple potentiostatic circuits. The requirements are:

- high open - loop gain (typically more than 100.000).

This stage is responsible for the main part of the total amplification.

- high input resistance

In spite of the use of a buffer, high input resistance is wanted because we want to use the input as summing point for both control signals and feedback signals. The higher the input resistivity, the smaller are errors due to ohmic load of the control voltage source. Typically, the input resistivity of this stage is about 10^9 Ohms.

- high common - mode rejection: This prevents noise signals, which are injected simultaneously at both inputs of the operational amplifier, from being amplified.

Different wiring principles are used:

- a) The non-inverting input is kept on ground, and connected to the working electrode. In this case the inverting input is the summing point (also called starpoint) for both the existing potential from the reference electrode input and any control voltages. The adding is done by adding resistors. The higher they are, the lower is the input current required from the control sources.

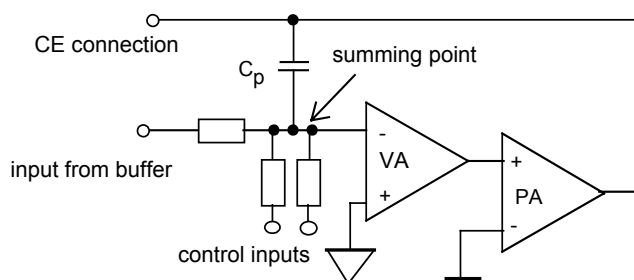


Fig. 10: Summation at the inverting input of the OPA

b) the inverting input is kept on ground, and the potential is fed to the non - inverting input. In this case, the inversion must be done in the power stage amplifier.

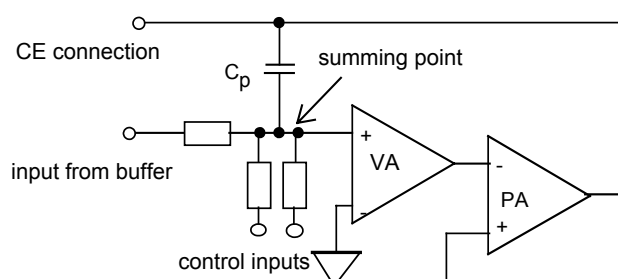


Fig. 11: Summation at the non - inverting input of the OPA. Here the PA stage inverts the signal.

Current Measurement Circuits

The basic circuit consists simply of a range resistor in the counter electrode line, across which a voltage develops proportional to the current passing this resistor. While this resistor is in the CE circuit, the working electrode remains on true ground, and the cell set-up is very insensible to noise pickup. Of course, the current - proportional voltage does not refer to ground. That was no lack in former times when the current was read from an analogue meter on the front panel only, but any data recording instruments connected to these terminals required floating (non - grounded) inputs.

It is of course possible to pick up the current - proportional voltage across the range resistor and use a difference amplifier (instrumentation amplifier) to transfer the "floating" current signal to a ground - referred one. This is possible, but if the CE voltage is too high, this method has some drawbacks with respect to noise and bandwidth which restrict its use to potentiostats having CE voltages of less than some 20 volts.

There are some alternatives to this concept:

The "Floating Supply" Concept

The idea is to have two separate grounds, the signal ground, to which the working electrode is connected, and a separate power ground, i.e. the ground of the current supply. The range resistor is connected between these two grounds. As any current from the working electrode has to flow to the power ground, it passes the range resistor. The zero point of the power stage now must be kept on the working electrode potential, but without galvanic coupling. This is done by creating a "virtual zero", using a separate buffer stage ZBUF.

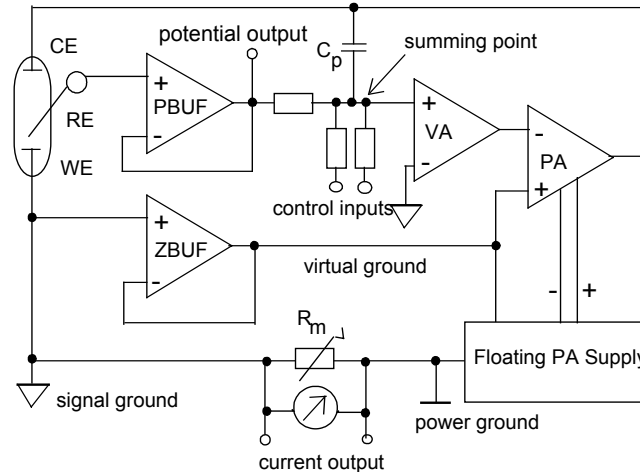


Fig. 12: Principal scheme of a "floating power supply" potentiostat

Advantages are:

- due to the grounded working electrode, is insensitive to noise - pickup
- the recorder outputs of both potential and current refer to ground

Drawbacks:

In practice, anti - parallel diodes are wired in parallel to the range resistor R_m , protecting the resistor from being burnt as soon as over - range conditions are met during unattended measurements. As soon as critical limits of the current (and consequently a critical voltage) are exceeded, they form a parallel current path. On the other hand, these diodes have a small leakage current, which limit the measurement of low currents to the order of some nA.

The main part of the total noise is determined by the protection resistor R_s , by the adding resistor which connects the potential buffer to the adding point, and the intrinsic noise of both operational amplifiers PBUF and PS. The total noise is given by

$$U_R = \sqrt{U^2_{R_s} + U^2_{Rad} + R^2_{PBUF} + R^2_{PS}}$$

Example: Let us assume a bandwidth of 200 kHz. Let both the adding resistor and the protective resistor have a value of 200 kOhms, and the intrinsic noise of the amplifiers may be 18 μ V eff within the bandwidth. This results in an effective noise of 27 μ V.

Current Measurement by Passive Shunt

The next possibility for measurement of the current is to place the range resistor R_m between ground and working electrode. The current passing the range resistor produces a voltage drop across it. In consequence, the potential drop measured between reference electrode and ground is not longer the potential of the working electrode! To obtain this, the voltage drop across R_m must be measured separately and fed back to the potential input of the potentiostat amplifier. This is done by a current - buffer CBUF which picks up this voltage drop, inverts it and feeds it back to the adding point. Due to the inversion, it will be subtracted there from the total voltage measured

between ground and the reference electrode. In effect, the voltage at the adding point again is identical to the voltage between working electrode and reference electrode. On the other hand, the voltage drop across R_m is the current - proportional signal fed out to the current recorder output.

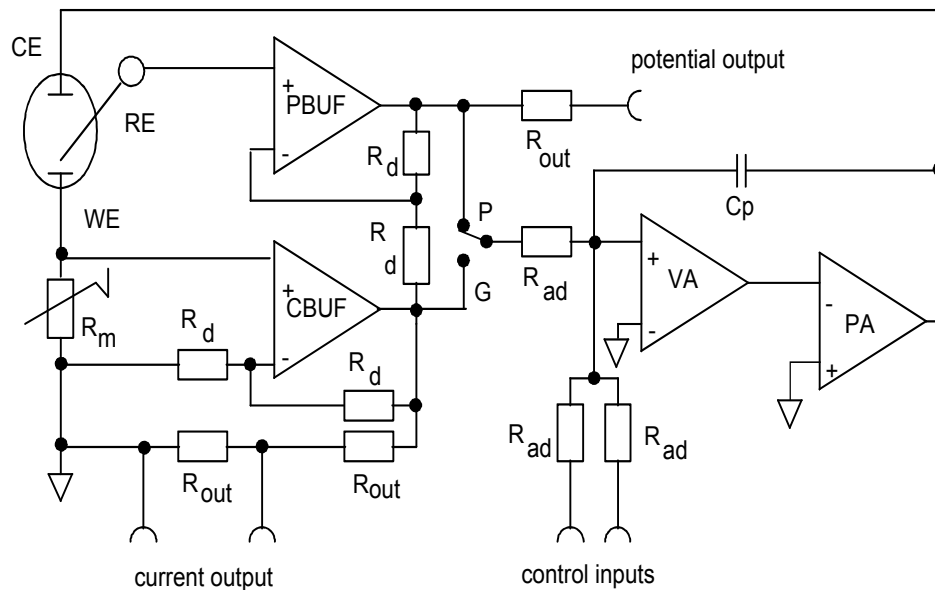


Fig. 13: A potentiostat with input - difference former CBUF for separation of current and potential signal. The working electrode now is not grounded, but coupled "tight" to ground potential by the relatively low - ohmic resistor R_m . The switch P/G allows simple change from potentiostatic to galvanostatic mode.

This circuit is technically much more complex compared to the "floating supply" principle, but it has some interesting advantages:

- This principle makes it very easy to switch from the potentiostatic to the galvanostatic operation mode. In the galvanostatic mode, the potential buffer is further on measuring the existing potential.
- the current signal measured across R_{out} gives the possibility to measure very low currents, in other word, the dynamic is increased.
- both potential and current outputs refer to ground

Drawbacks:

- the circuitry is complex, much more parts are required
- noise picked up at the working electrode passes the range resistor, as the working electrode is not longer grounded. This requires better screening than a set-up using a "floating supply" does.

The reference electrode potential is measured from the difference between WE and REF input using a difference amplifier. The potential accuracy therefore is limited to the order of 0.2%, in contrary to all other systems measuring the exact potential.

- more elements contribute to the total noise: a second protective resistor in the input circuit of CBUF and the current buffer CBUF itself.

- the bandwidth is smaller compared to a "floating supply" potentiostat if equipped with the same operational amplifiers.

- for convenient IR - drop compensation, an additional inverter has to be spent at the current recorder output.

Active Shunt: The Current Sink Principle - "Zero Resistance Ammeter"

A current sink is a current - to voltage converter, which measures the current passing a shunt (i.e. the range resistor R_m) free of load, i.e. the voltage drop across it is compensated. In consequence, very high - ohmic resistors can be employed, so very low currents can be measured very precise. The circuitry is complex, in addition to the current buffer CS-VA a second power stage CS-PA is demanded, which has to feed the same current passing the working electrode in order to keep the working electrode at ground potential.

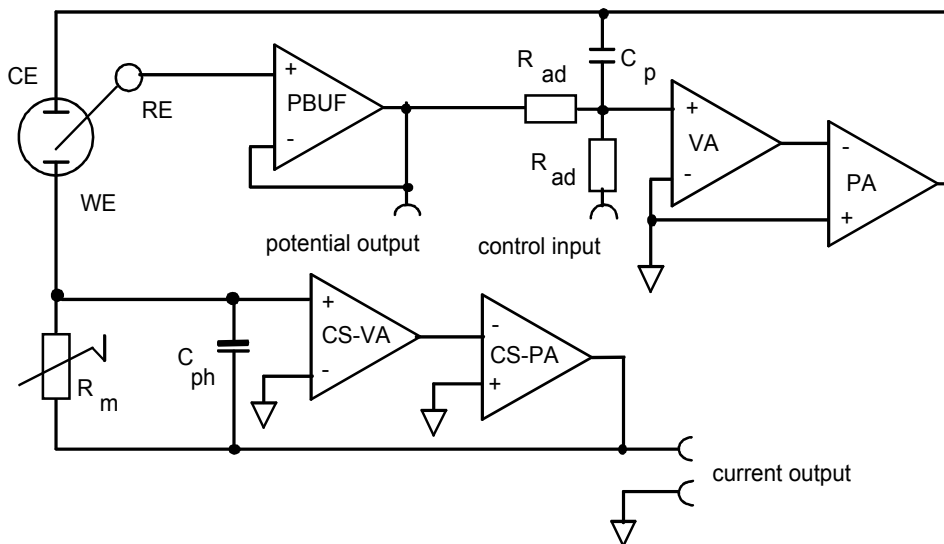


Fig. 14: The current passing the working electrode is measured across a resistor R_m , and compensated by the current sink CS. The working electrode is kept on virtual ground.

Advantages:

- extreme small currents can be measured
- different basic potentiostat designs can be employed
- both potential and current are measured referring to ground
- very high range dynamics are achieved (120 dB and more, corresponding to 5 ... 6 decades)

Drawbacks:

- as the working electrode is not grounded (but kept virtually on ground potential), noise pickup of the working electrode requires good screening of the electrochemical cell and cables. This is essential, as this principle is used mostly for the measurement of small currents, using high - ohmic range resistors, which result in high amplification of the input signals.

- noise in the high - frequency band is enhanced compared to simpler principles, as the bandwidth determining capacitor must not exceed certain limits to preserve the total stability. Note that low - frequency noise is not tackled.

ADDITIONAL CIRCUITRY

Potentiostat - Galvanostat Conversion

Potentiostats which do not have a switch to change from potentiostatic to galvanostatic operation mode can be converted to galvanostats in a most simple way.

The reference electrode is removed from the reference electrode input, and an external resistor R_x is wired between the reference electrode input and the working electrode input. The working electrode is then connected to the reference electrode input.

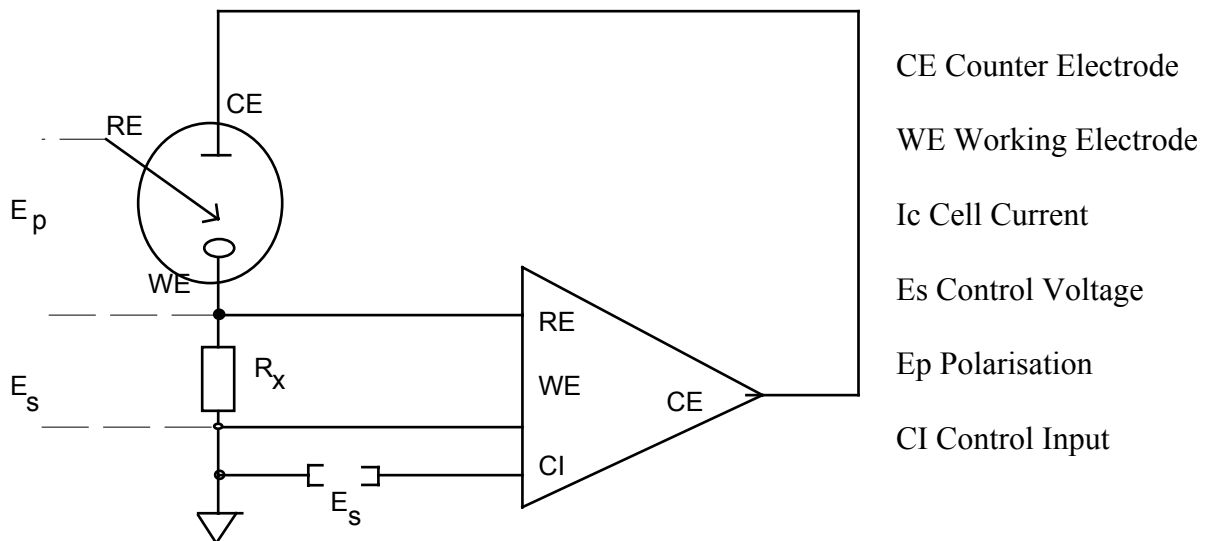


Fig 15: Galvanostatic control using a potentiostat

The current passing the resistor R_x produces a voltage drop across R_x given by

$$I_c = E_s / R_x$$

where E_s is the voltage fed into the control input CI. The maximum load of the resistor for a given current range is given by

$$P = I_c^2 * R_x$$

Example: If the maximum current shall be 10 A, the input voltage 1 V to obtain full range current, then $R_x = E_s / I_c = 0,1$ Ohms, and the power is $10^2 * 0,1 = 10$ Watts. The range resistor for the 10 A - range thus has a heat dissipation of 10 Watts.

If you want to measure the potential, an external potential meter must be employed, which is connected to the reference electrode and the working electrode. It shall have a floating (not grounded) input, as the potential now does not refer to ground, but is kept "high" according to the voltage drop across R_x .

The set current can be controlled either by the potentiostats internal control source, or any external source at CI.

IR - DROP ERROR AND ITS COMPENSATION

There are mechanical reasons why the capillary of the reference electrode cannot protrude into the plane containing the double layer of the working electrode. Owing to this unavoidable fact there is a potential drop from the plane where the capillary ends, to the working electrode boundary layer in which the potential has to be controlled. This potential drop is proportional to the current density and varies in inverse proportion to the electrolyte conductivity. It becomes important only when the current density is high or where the electrolyte has a very low conductivity.

In simple cases it is possible to describe this potential drop as a fairly constant electrolyte resistance R multiplied by the cell current I . A constant electrolytic series resistance before the boundary layer of the working electrode can of course be compensated by feedback to the input of a voltage drop proportional to the input of a voltage drop proportional to the current. But accurate determination of the magnitude of such a resistance raises serious experimental problems. In most cases there is no certainty that this measured electrolyte resistance remains constant when the potential is changed, when the current varies, when chemical reactions take place in the boundary layer, when the temperature alters, or even when the capillary tip moves relatively to the working electrode boundary. Methods for determining this electrolytic series resistance have been described for certain special applications and their discussion would go beyond the scope of these notes.

Most of our potentiostats permit simple IR drop compensation provided the precondition of the method, an approximately constant electrolytic resistance, is fulfilled. The current output terminals give a voltage drop to ground which is proportional to the cell current. After reduction in a voltage divider, a small part of this voltage is fed back into one of the control inputs to be superimposed on the internal control voltage. A positive feedback proportional to current increases the control voltage by an amount which is proportional to the resistance inserted by the range selector switch and to the cell current. With an external voltage divider only part of the resistance affects the current feedback.

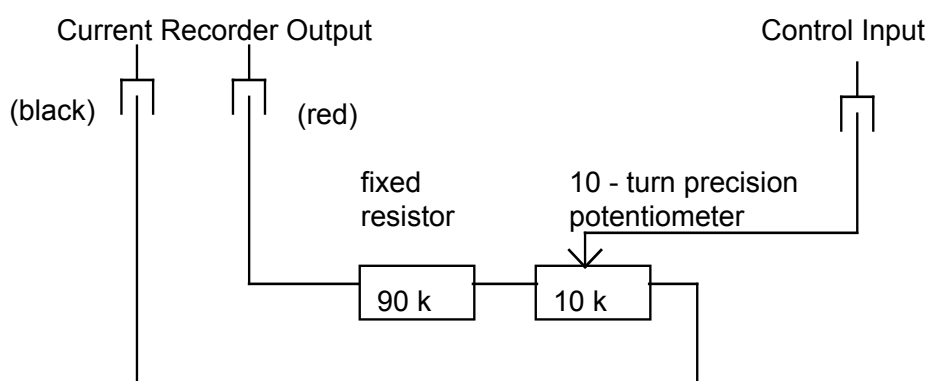


Fig. 16: Current signal feed - back for IR - drop compensation. The 90 k resistor is only required if no special IR - drop - input is available

The resistances introduced by the sensitivity steps of the range switch vary from 100 kOhm to 1 Ohm for current ranges from 0.01 mA to 1 A. Resistances of this order greatly exceed the range in which IR drop compensation would normally be applicable, and it is necessary to provide a large measure of voltage division. The external feedback potentiometer (Suggested value 10 kOhm to 1 k) has to have a series resistance (suggested values 100 k to 1 M) in order to reduce

the IR voltage for compensation. With a 100 : 1 voltage divider it is possible to compensate IR drops up to 1% of the voltage at the current output terminal. For compensation of higher IR - drops, a 10:1 divider will do it.

A rough approximation to IR drop compensation can be obtained by observing the step response on an oscilloscope, without actually measuring the electrolytic series resistance. A square - wave signal of approx. 10 mV amplitude is injected in one of the control inputs, thus added to the control voltage. Then vary the positive feedback, starting from zero, turning the feedback dial until step response of the potential (observed on the oscilloscope) exhibits appreciable overshoot. At this stage at least the major part of the electrolytic series resistance has been compensated. It is assumed that there is a double layer capacity in the boundary layer of the working electrode; this will be the case in most applications.

The problems of IR drop compensation can only be discussed briefly within this text. It should be mentioned, however, that in contrast to the opinion expressed repeatedly in various publications, it is possible to overcompensate the IR drop up to a factor 2 without rendering the control circuit unstable. Unstability only occurs when the entire resistance of the control circuit is compensated, and the potentiostat then shifts to full output; this causes rapid destruction of the carefully prepared specimen. Experiments involving IR drop compensation should only be undertaken by experienced workers with a full understanding of the phenomena involved.

It is advisable to investigate in each case whether suitable design of the cell can keep the IR drop small enough to be negligible in evaluating the specimen characteristics.

Caution: An overcompensation of the IR-drop of more than 200 % will lead to a hazardous instability of the potentiostat which may cause damage to the potentiostat as full-power oscillations may occur at maximum frequency. IR - drop compensation can lead to instability, depending on the cell's properties.

IR - drop compensation should always be conducted by trained personnel being aware of the risks.

FURTHER ELECTRONIC EQUIPMENT USED WITH POTENTIOSTATS

Signal Generators

As a rule, you will not restrict your measurements simply to keep the potential at a constant value. Usually, you will vary the potential with time. This variation of the potential with time can be linearly, then the graph of the potential - time function is a ramp, or, reversing the direction of the potential variation, a triangle. Others may vary the potential stepwise, or impress sine waves, or use electrical noise.

All these potential variations are controlled by a voltage source, which we now call function generators or signal generators. Signal generators are used widely in electronic laboratories. For the use with potentiostats, the signal generator should fulfil some special qualities.

The voltage generated to control a potentiostat should be 'clean', that means, undesired noise shall be as low as possible. That is the reason why cheap D / A converter boards which are simply put into a personal computer usually are not qualified to control a potentiostat. Their

output signal is not clean enough with respect to digital noise, or glitch pulses. These pulses may be very short, not detectable for usual oscilloscopes, but have rather high peak voltages. In electrochemical terms, some ten millivolts are really high. Such noise influences the mean potential, which is different from the displayed set potential.

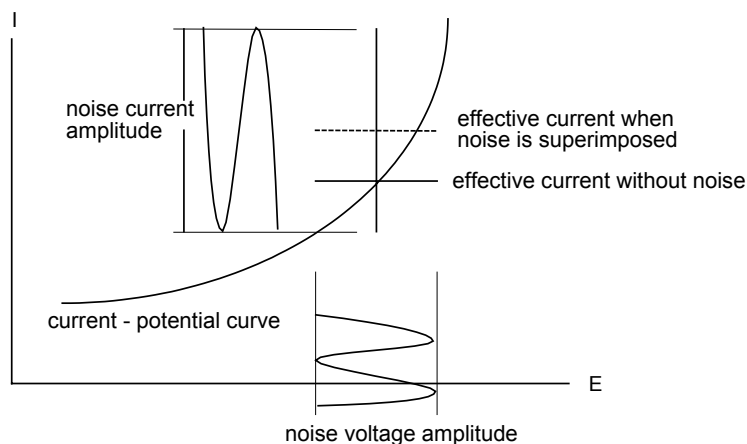


Fig. 17: Influence of AC noise

Especially critical are these signals when the working electrode is kept in a potential range where undesired voltage variations invoke another reaction at the electrode.

Signal generators for electrochemical use are therefore especially adapted. Linear voltage ramps are conventionally produced using analogue ramp generators. Pulses are produced by square wave pulse generators which have the ability to set the pulse height very exactly within a few microseconds or fractions of a microsecond, and which have the ability to join two or more different pulses together as single pulse sequences or periodically.

Advanced computer - controlled D/A converters may also be qualified. Usually they are not put into a personal computer, but act externally, using a current supply separated from the computer. They have, in addition, anti - glitch - filters which eliminate disturbing voltage peaks.

Some potentiostat manufacturers offer potentiostats with built - in signal generators. These instruments are compact, usually less costly than separate potentiostat and signal generator sets. In some few cases, the performance of such potentiostat / signal generator units is superior to separate combinations.

Potential Meters

Sometimes you want to measure only the potential between different electrodes. Some simpler potentiostats do not provide a potential output. If you want to measure the existing potential, you have to use a potential meter. If you use a usual potentiostat as galvanostat, you are mostly forced to use a separate potential meter, too.

In all these cases, a potential meter is required. If the potential variations are slow and the potentials do not exceed 2 volts, you can use a laboratory pH - meter. Its input resistance usually exceeds 10^{12} Ohms, high enough for potential measurements. It works slow, as the frequency is limited to keep noise low. The input voltage range is restricted to ± 2 V because pH measurements do not exceed this range.

In other cases, either when fast potential variations are to be measured, or the potential exceeds 2 V, or the potential meter must have an extreme low - noise performance, special designed potential meters are required.

Current Sinks

Current sinks are ampere meters which do not influence the measurement (or much more less than usual ammeters). They are used to measure currents down to very low ranges of nano-amperes or even picoamperes, having input resistances of milliohms or few ohms. They are commonly used when galvanic currents are to be measured between two different electrodes, where an ohmic drop caused by the ampere meter would badly influence the result. Using current sinks, nice circuits are possible: the control of independent working electrodes within one cell, or the measurement of very low currents using a conventional potentiostat.

Integrators

Integrators are used to measure electric charges. Remember that the Ampere was once defined by the electric charge required to deposit a defined mass of silver. Integrators are simply coupled to the current output of a potentiostat, to measure the charge required for completion of a certain reaction. That is e.g. a simple way to determine the thickness of galvanic coatings, or to determine the capacity of batteries.

WHAT IS THE BEST POTENTIOSTAT FOR YOUR LABORATORY

There is a variety of potentiostat models for a variety of applications fields. As the development of the instrumentation overruns the "design - lifetime" of this brochure, we cut out this chapter and ask you to read our brochure *Which potentiostat for which purpose*.

CELLS AND ELECTRODES

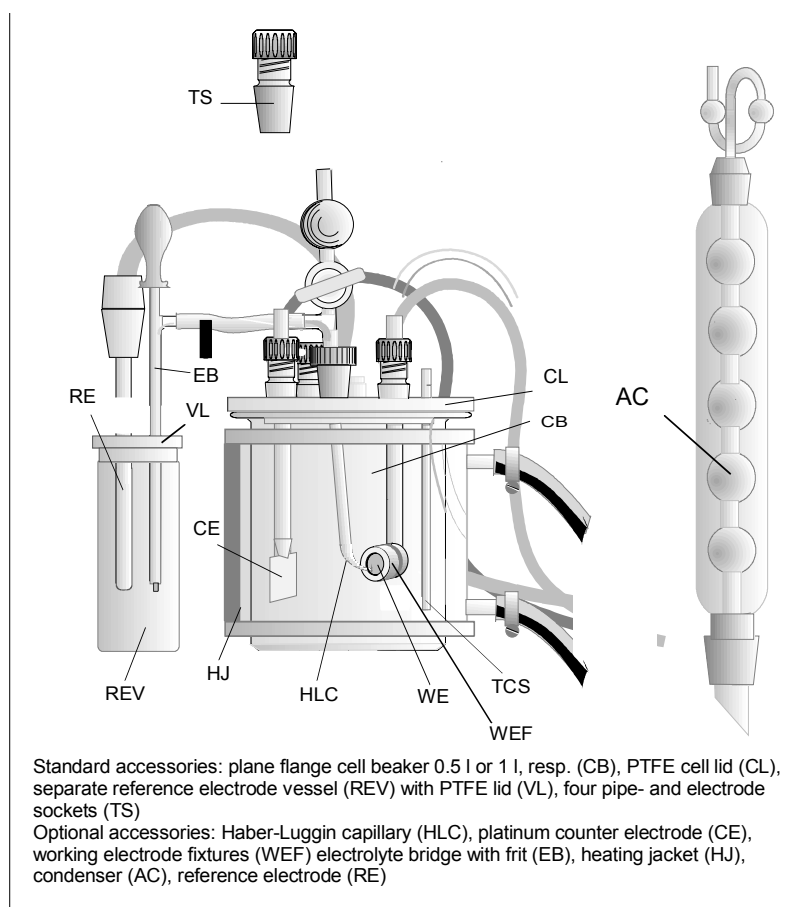


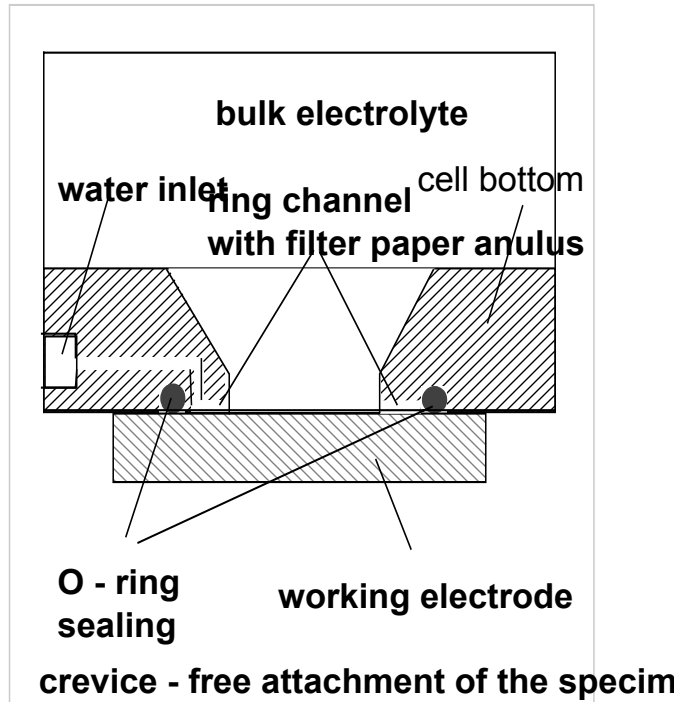
Fig. 18: Universal cell for corrosion testing

Cells

The size and construction details of an electrochemical cell are determined by its purpose. Any cell design is adapted for some more or less special methods and will not deliver very satisfying results when using other methods. The aim of the measurement so far defines the cell.

With respect to a rather common size of electrodes - let's say 1 to 10 cm², and typically medium to high conductive electrolytes, there are standard cell designs. The volume ranges from 100 ml to a few litres and, for the sake of universality, a wide flange should be used to insert a lid which takes up the electrodes, and in addition gas pipes for electrolyte conditioning, perhaps a reflow-cooler, a thermometer and other auxiliary equipment like e.g. pH - electrodes.

Cells for Pitting Corrosion Testing



If you have to investigate pitting corrosion, you always have to cope with crevice corrosion affecting your results. To avoid crevice corrosion, one method is to keep the crevice area free of chlorides. In the so-called "Avesta - Cell" developed by Rolf Quarfort, a paper anulus which covers the border of the specimen is purged with water at very low rates.

Fig. 19: WE - attachment in the Avesta Cell

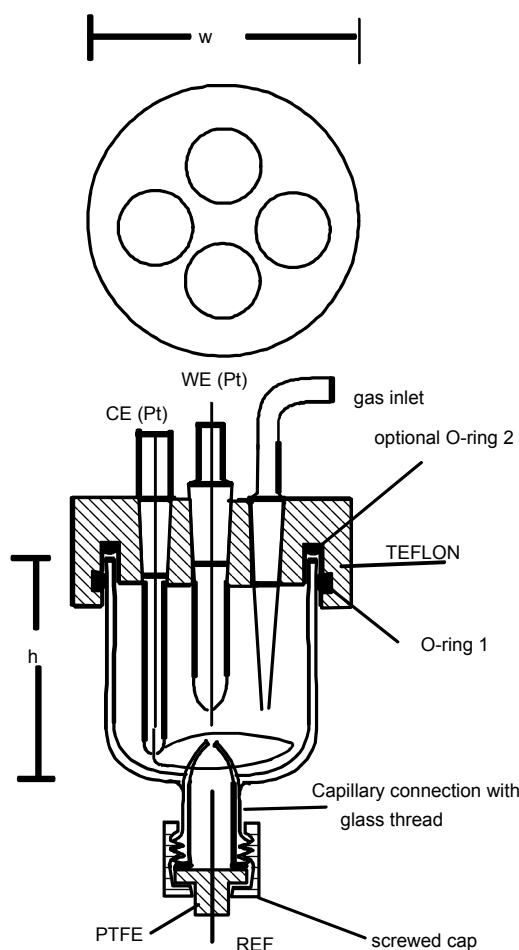
Applying high currents, it may be essential to keep an eye on the geometry of working electrode and counter electrode to obtain uniform current densities across the working electrode surface. One method is to use

parallel electrodes of the same size, another method is the use of concentrically arranged electrodes: where the working electrode is in the centre and the counter electrode around it.

If reactions occur at the counter electrode and the products are not allowed to enter the bulk electrolyte, the counter electrode is to be separated by a frit.

A fast - response - cell arrangement requires short distances, and usually short distances between working electrode and counter electrode. In those cases it is essential to use a fast - response counter electrode instead of a highly stable calomel electrode. In chloride containing solutions, a silver wire will be an ideal reference, forming a silver/silver chloride reference electrode.

Cells for Cyclovoltammetry



A typical example is the cell design for cyclovoltammetric measurements with a small volume and a good electrode geometry. Only the required electrodes and two pipes for gas inlet and outlet are fed through. The diameter (w) may vary from 30 to 60 mm, the height may vary from 25 to 50 mm.

Cells for analytical purposes are also rather small in order to keep the volume to be analysed as small as possible. In such cases, it is helpful to insert a separate small beaker into an existing cell.

Fig. 21: Small cell for voltammetric measurements

Notes on the design of electrochemical cells

The dimension and the shape of the electrochemical cell for potentiostatic experiments is determined by electrochemical requirements of the intended investigations.

The arrangement of the counter and working electrode should be such that the actual form of these electrodes ensures a uniform current density at the surface of the working electrode. With a rod-shaped working electrode, for example, the counter electrode should be in the form of a ring surrounding the rod electrode. When using a flat surface the preferred shape of the counter electrode is a flat surface parallel to the working electrode. When both faces of the working electrode are used as two parallel surfaces two counter electrodes on both sides of the working electrode, equally shaped and spaced, should be used and connected together.

In various experiments it is essential for electrochemical reasons to separate the anode and cathode spaces in the cell by placing a membrane or frit between the working and counter electrode. Among the various possibilities it is always preferable to choose the arrangement with the better electrical conductivity. The use of the potentiostat to the limit of maximum current always presumes that the output voltage remains within the overall voltage range of the potentiostat.

A number of different arrangements of the reference electrode with capillary relative to the working electrode have been reported in the literature. Each of the extremely varied applications

in which potentiostatic control is used will make a particular arrangement appear especially favourable. It would go too far in this context to discuss the different special arrangements in detail. It sometimes happens that insufficient protection is provided against the entry of gas bubbles into the capillary. Such gas bubbles may stop the potential transfer through the capillary and thereby interrupt the sensing section of the control loop. The potentiostat will then operate at full output in either direction. Long-term tests may in this way become useless within a short time interval.

In order to prevent diffusion of foreign ions into the electrolyte space of the cell or into the reference electrode it is sometimes necessary to provide an effective separation between the electrolyte space of the reference electrode and that of the working electrode.

It might appear reasonable to achieve this separation through the use of high -resistance frits or capillaries. There are, however, definite limitations in this direction which are determined by the fact that the transfer time constant of the capillary - reference electrode system must remain small compared with the time constant of the potentiostat itself. For this reason the a. c. impedance of the arrangement should preferably remain below a rate of 10 k Ω . The requirement of avoiding the diffusion can also be met by using relatively low resistance frits and providing a sufficiently large electrolyte space for the reference electrode which is separated by a siphon.

The capillary of the reference electrode must not cover the surface element of the working electrode against which the potential difference is determined, otherwise the potential at this point may be different relative to the remaining surface of the working electrode especially at high current - densities. Fluctuations in electrolyte density, gas bubbles passing through the space between capillary and working electrode, reaction products which are not removed from the boundary electrolyte working electrode surface by a sufficiently powerful flow of the electrolyte, all give rise to potential fluctuations which the potentiostat compensates through current changes.

ELECTRODES

When the material of the working electrode itself is object under test, the surface usually is determined in before and cannot be changed into any shape. Frequently, only part of the surface is the test object, all other parts have to be electrically insulated. For this purpose, different methods are used:

- insulation by resins

A high - quality resin layer usually is sufficient to insulate those parts of the surface which shall be excluded from the measurement. The demands are: good insulation, resistance against water diffusion, resistance against formation of crevices between it and the substrate, and, last not least, it should not release monomers or other chemicals into the electrolyte. Only a few commercially available resins do have such properties. You will find them mostly within the group of two - component epoxy resins.

Similar problems occur when the electrode is insulated by embedding in compact resin in. To avoid crevice formation, it is essential that the resin does not shrink during hardening, but extend. In addition, hardening usually deliberates heat, which rises the temperature. Fast

hardening rises the temperature by 40°C or more, and in consequence crevices start to form when the mould is cooling again.

Embedding in PTFE

It is a rather good practice to use PTFE insulation for cylindrical electrodes, when the face of the cylinder is to be exposed to the electrolyte. This method is advantageous when working at room temperature or little above. To achieve a crevice - free fit of the electrode, make a drill in the PTFE block slightly narrower than the outer diameter of the electrode is. Heat the PTFE block to 150°C (approximately), and put in the electrode. The thermal expansion of PTFE is much higher than that of any metal, so it will fit quite tight after cooling. Some, in addition, press a ring of corrosion resistant metal above the PTFE after cooling.

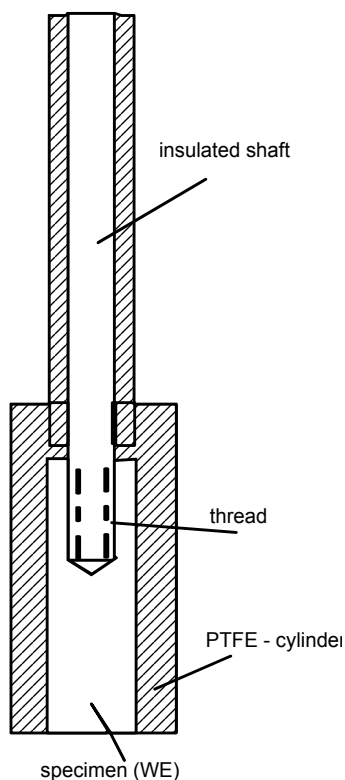


Fig. 22: PTFE - insulated fixture for cylindrical working electrodes

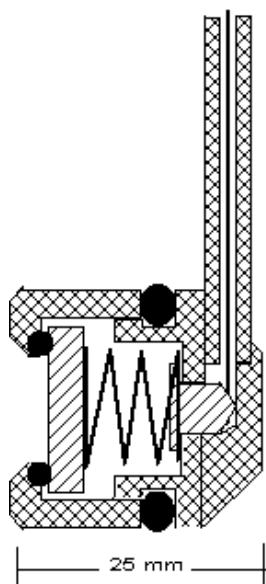
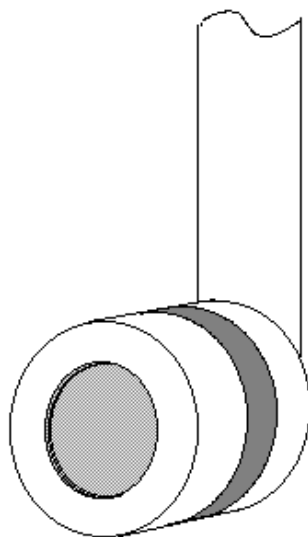
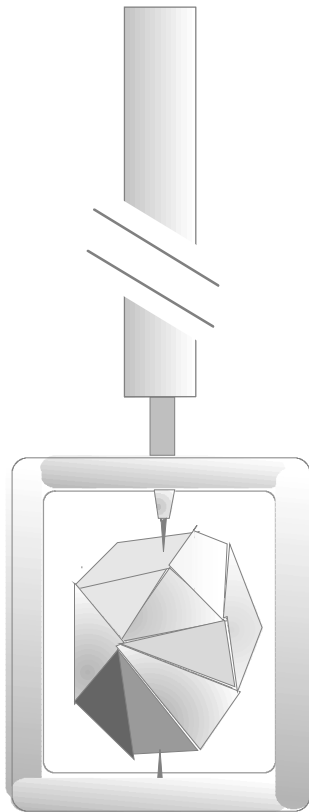


Fig. 23: Easy - to - change electrode fixture



Working Electrode Fixtures for Easy Change of the Specimen

If numbers of sheet specimens have to be measured, a specimen holder may be fine which allows easy change of the specimens. Such holders are made of resin, preferentially perspex glass for temperatures up to 60°C, PVDF or PEEK for use at temperatures above 100°C. This method is not recommended for long - term measurements of passive metals, but well adapted for stripping of platings or similar tasks.



If all faces of the working electrode may be exposed to the electrolyte, you can contact it with a platinum wire. However, when cathodic currents shall be measured, be aware that the cathodic reactions as e.g. hydrogen formation run much faster on platinum surfaces than on other metals. To avoid this, the platinum area should be as small as possible. There are electrode holder designs using two very small tips of platinum or another inert metal, fixing and contacting the electrode.

Fig. 24: Platinum - tip - contacted electrode fixture

Rotating electrodes

Rotating electrodes are used to

- establish controlled flow conditions along the electrode surface
- investigate reaction kinetics: transport reactions

Rotating electrodes are expected to run without flutter. The contacts should transfer the currents and potential signals without noise. High - precision rotating electrodes therefore use mercury contacts.

The rotating disk electrode - RDE

Main advantage of the RDE is the laminar flow of the electrolyte in parallel to the disk surface up to very high flow rates. So, diffusion layers down to the order of micrometers can be obtained.

The rotating ring - disk - electrode RRDE

This design consists of a disk electrode with an insulated, concentrically ring electrode around it. The distance between disk and ring is small, less than 1 mm. This design is used to determine the lifetime of intermediates produced at the disk electrode. A wide variety of special designs have been developed from this base design, using either splitted rings (where the two or more parts of the rings are kept at different potentials), or even optical quartz rings for product analysis.

Rotating cylinder electrodes

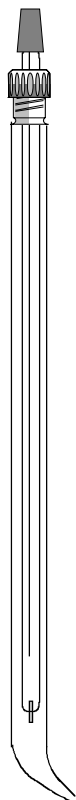
Rotating cylinder electrodes are advantageous when turbulence effects shall be studied, or rather large electrode areas have to be controlled. Moreover, it is possible to insert heaters or coolers into such electrodes to study the effect of heat transfer across the electrode surface.

REFERENCE ELECTRODES

A reference electrode is an electrode, where an element (usually a metal) is in balance with its reaction product in a certain environment. The hydrogen electrode with the balance $H_2 \leftrightarrow 2 H^+$ is by convention the origin of the electrochemical potential scale. However, the hydrogen electrode is somewhat inconvenient to use, therefore other metal / ion systems are used. The most used ones in laboratories are the calomel electrode, and the silver / silver chloride electrode. To avoid problems by electrode contamination, for some purposes also mercury sulphate or mercury oxide electrodes are used. In industrial applications, where some drift may be neglected, also copper - based references are used.

What is the use of a Haber - Luggin Capillary?

To keep the reference electrode system clean and free of contamination from the cell electrolyte, it is usually kept in a separate beaker. A liquid bridge transfers the potentials from the cell to that beaker. Now, when a current flows between counter electrode and working electrode, there is a voltage drop between these two electrodes. As the potential of the working electrode is the interesting one, the point of potential measurement should be as near to the working electrode surface as possible. In practice, the liquid bridge is formed by glass tube. In front of the working electrode the glass tube is narrowed to a capillary tip. The tip is essential to avoid "potential shadowing" effects. It is a good practice to keep 0.5 to 1 mm distance from the working electrode, and the capillary should have an inner diameter of 0.2 to 0.5 mm.



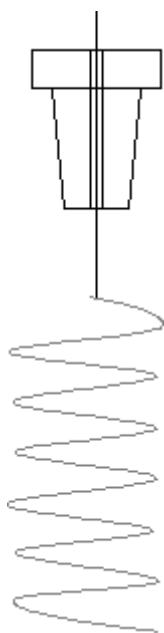
Nevertheless, there is a residual potential drop between the capillary tip and the working electrode, due to the voltage drop from the current passing along this distance between counter electrode and working electrode. It is not possible to reduce this voltage drop (usually called IR - drop, because it arises from a current I passing along the electrolyte of a resistance R) to zero. A correction of this error is possible, if the potentiostat has the possibility of IR - drop compensation.

Some try to make the Haber - Luggin - capillary as thin as possible to reduce the electrolyte contamination. This is not a good practice, because the increasing electric resistance within the capillary makes the system prone to noise - pickup. In case of contamination risks it is better to use a gel filling of the bridge. Most problems arise from the formation of gas bubbles within the capillary. To avoid this, a cotton thread inside the tube may help to avoid a total interruption of the liquid bridge. Other measures are careful design of the bridge tube: It is helpful to keep the inner diameter of the tube as wide as possible, only the capillary tip should be small. A bulb reservoir at the highest point of the bridge will be helpful to trap bubbles which form due to temperature drop effects between the cell and the separate electrode.

Figure left: Slim reference electrode mounted inside the Haber - Luggin - capillary

There are other designs, including a forced circulation of the bridge electrolyte to achieve high reliability over extended periods. Very good properties show reference electrodes kept within a slim glass pipe inside the cell. The glass pipe itself then acts as Haber - Luggin - capillary. A certain drawback of this method is the risk of contamination of cell electrolyte and reference electrolyte. But this is only of interest when highest purity of the electrolyte is required.

COUNTER ELECTRODES



Disregarding cells where the counter electrode itself is wanted to participate chemically in the reaction, the counter electrode material usually shall not participate in the electrochemical reaction, or, at least, its reaction products should not influence the measurement. Redox reactions shall be fast there. Therefore, platinum is the most used material for counter electrodes. On the other hand, platinum is expensive, and for large counter electrode areas it is too expensive. So, counter electrodes made from nickel base alloys, or carbon, may do it. Remember that nickel base alloys may passivate, and carbon will be oxidised at high potentials of the CE. Therefore those materials should have sufficient areas to avoid strong polarisation. Platinised titanium has become a good choice when larger counter electrode areas are required. Platinised titanium is produced either in form of sheets or even grid. Grids have always fine properties: large active area compared to the geometric area, and the electrolyte may flow through the counter electrode, in addition.

Also at the counter electrode, a voltage drop occurs across the metal / electrolyte interface. To reduce this drop, it may be useful to use platinum covered with platinum black to increase the active surface.

Fig. 25: A platinum wire as a simple counter electrode

POTENTIOSTATIC MEASUREMENTS: CELL CONNECTION

The correct connection of the cell is essential for error - free operation of an electrochemical system. Lack of information and / or laziness lead to troubles.

It is essential, that the current leading wires are connected carefully, to avoid voltage drops across the connection. Especially the working electrode should have a good connection, otherwise the voltage drop across it directly will produce a potential error. Crocodiles are not always sufficient for that purpose.

Some rules:

Counter electrode connection:

The counter electrode connection is the least critical point. This line is not prone to noise - pickup, so it is no need to shield this line. Shielding of this line might increase parasitic capacitance which affect the dynamic response of the potentiostat. Shielding there might be required if other instrumentation in the neighbourhood is affected by RF produced when highly dynamic signals - as e.g. rectangular pulses - are used. In this case it is necessary to keep the

cable as short as possible. RF cables of type RG 58 or power - RF antenna cables are better than other shielded cables.

If banana connectors are used, gold- or silver - plated bunch plugs are best. Prefer soldered connectors to screwed ones, because the screwed ones will corrode inside, and the contacts decrease.

As soon as the counter electrode voltage of a potentiostat exceeds 40 V, the voltage may become hazardous to your health. In those cases all connections should be designed secure, it should not be possible to touch the counter electrode connection. Before disconnecting the cell, set the potentiostat to the stand - by - mode, and connect the reference electrode plug to that of the counter electrode. Then, no high voltage can arise at the counter electrode also if it happens that the potentiostat is set to the potentiostatic mode.

Working electrode connection

Most potentiostats keep the working electrode on ground potential. However, the working electrode is not in any case connected to ground: it is virtually kept on ground potential. In these cases, the working electrode is prone to noise pickup and should be shielded. Please read the manual of your potentiostat carefully to find out whether this cable has to be shielded or not.

As the working electrode cable itself has some resistance, potential errors may occur due to the potential drop in the working electrode cable. It is therefore good practice to have two connections at the potentiostat: One for the working electrode potential cable, and another for the current cable. As long as the currents remain below some few milliamperes, both terminals may be connected at the potentiostat, and only a single wire is used to connect the working electrode. At currents above 100 mA it is recommended to use two separate cables, and the potential line should be connected as near to the working electrode as possible. In the potential sense cable, no current is flowing, therefore this separate line transfers the working electrode potential without ohmic drop error.

Example: The cable resistance of the working electrode may be 20 mOhms, and the contact resistances across the terminals 10 mOhms at either end. If a current of 2.5 A is passed through the cable, a potential drop of 100 mV would occur!

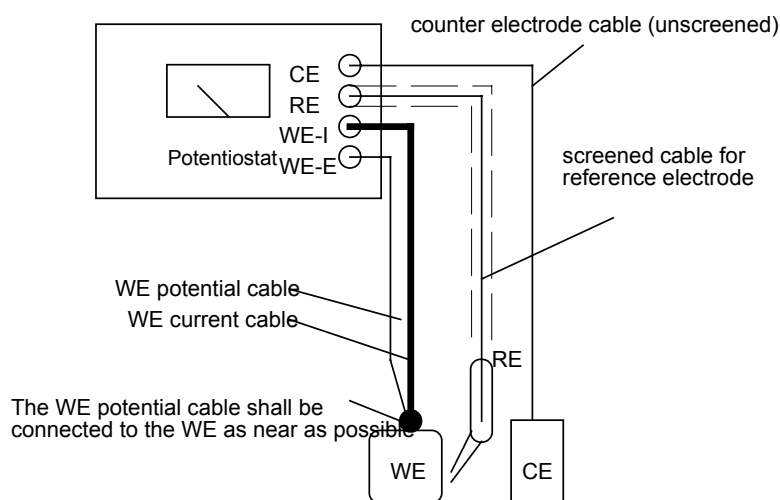


Fig. 26: Correct connection of the working electrode using two separate cables

If potentiostats do have two separate terminals for working electrode current and working electrode potential, always both terminals must be connected to the working electrode. If only the current terminal is connected, appreciable potential errors will occur, and worse: you do not see them, because the error occurs outside the potentiostat! If only the potential sense cable is connected, current flowing in this line may even produce damages.

Note: If the potentiostat uses a current sink or (equivalent) zero-resistance - ammeter, the working electrode lines may be shielded, too. Depending on the potentiostat's internal control mode, the working electrode is kept on ground potential and correspondingly the shield is connected to ground. There exist other types where the reference electrode is kept on ground potential, and the current sink is polarised. In that case, the working electrode shield is kept on the potential of the polarised working electrode. If your manual is lost, you find the shielding method by measuring the shield potential versus ground, when the potentiostat is set to e.g. 1V.

Reference Electrode Connection

Reference electrodes have a high source resistance. That means, that currents passing the reference electrode will produce appreciable potential drops. From this reason, the reference electrode input of the potentiostat always must have a high input resistance, usually above 10^{10} Ohms. So, the current through the reference electrode never exceeds some picoamperes.

On the other hand, such high input resistances make the input very prone to noise pick - up, from line hum to RF frequencies. It must be shielded. It is quite common to use terminals which give a good RF shielding, as e.g. BNC. Again, a type RG 58 cable is a good choice for reference electrode connection. If the current through the reference electrode must be kept extremely small, let us say in the range of some femtoamperes (the potentiostat is supposed to have correspondingly high input resistance), PTFE - insulated reference electrode cables give the best results.

Remember, that the shield of this cable usually is not connected to ground, but instead kept virtually on the reference electrode potential. Reason for this practice is to avoid capacitive loads between the reference electrode cable and its shield. So, never connect this shield to ground. Otherwise you may find funny potential errors.

Keep an eye on your reference electrode cable! Replace old cables as soon as corrosion products are visible at the plugs. Even the cable itself loses its good properties with time.

General rules for cell installation and wiring

Using our potentiostats, it is wise to place the cell at the right side of the potentiostat (ref. front view). The transformers inside are on the left side, so the stray fields will have least effect. Use short cell cables. Longer cables affect the dynamic response of the system. Our laboratory potentiostats usually are delivered with a cell cable which is optimised with respect to stray capacitance, insulation resistance and inductivity.

The colour code of the plugs helps to avoid connection errors.

Electrode	plug colour
-----------	-------------

Reference	green (blue if Schott system plug is used)
Counter Electrode	yellow
Working Electrode	Black (both current and potential line plugs)
Shield	grey

Electrical Noise and How to Minimise its Effects

It is NOT true that shielded cables always are the best choice to suppress electrical noise. To find the proper method, it is necessary to understand the sources of noise and the transport mechanisms.

The designation "noise" is the badly defined sum of all undesired signals trapped by your measurement set-up. We have to distinguish between real noise and other signals which are undesired as well, but not noise in electronic understanding. For our purpose, the designation "noise" may be sufficient as well. But we have to sum up all types here for better understanding.

Low Frequency Noise: Drifting below 1 Hz

Low frequency noise in this frequency range is no external effect, but occurs inside the instruments due to thermal drift. This is the reason why high precision measurements require constant ambient temperature on one hand, and warmed up instruments on the other hand. If this is a problem, you may be forced to install all instruments along with your cell in a thermostated cabinet.

Audio and Subsonic Frequency Range (10 Hz to 100 kHz)

The hardest impact in this frequency range comes from your power line. Its 50 Hz (or 60 Hz) as well as other frequencies generated by railway power lines or - near motors - the frequency - controlled power sources are well defined "signals" rather than "noise" in the electrical sense. The power lines act as transmitters, and the cell and its wiring act as receivers. The superior part of the electrical energy is transmitted by inductive coupling. Only a minor part of the energy is transported by capacitive coupling.

Inductive coupling means, that increasing the distance between transmitters (power cables etc.) and your cell and the cell cables is the most effective method to decrease the 50 Hz pickup. Next to it you should know, that lines arranged in parallel are most effective coupling (remember a transformer!), whereas lines crossing at 90° have only little inductive coupling.

Faradayic cages have some reducing effect on the audio frequency stray fields if they consist of magnetic screening material. Mu -metal is best, but costly. Low-alloyed steel sheets having one or several mm thickness do a good job. But also aluminium will do it if the walls are thick enough: 3 mm or more is sufficient to reduce magnetic fields y stray current induction in thick sheets of good conductivity. Aluminium is mentioned because its conductivity - to - weight ratio is best.

Capacitive coupling of audio frequencies is done e.g. by power transformers. They are of course inductive couplers, but there exists also a capacitance between primary and secondary coil. When a couple of instruments are working together, the capacitive currents have to pass the earth line from one instrument to the other. That is the reason why earth lines shall be reasonably

thick, wires having 1 mm² or more are usually sufficient, but the thin wires of computer ribbon cables usually are not.

RF Frequencies

RF frequencies are caused by radio stations, radar towers and similar sources. If you are close to such a station, you will be forced to do better shielding jobs than usually is required. When I did my military service, I learned that the radar beam of the tower up-hill was strong enough to leave "hiccups" on my music cassettes while I played them. The beam waves passed the (obviously badly shielded) plastic housing of my player, and passed consequently through the pickup - head coil having enough energy to leave exact time stamps every three seconds on the tape.

Radio stations may act over distances of several kilometres. Inside concrete walls which are armed with iron there is usually no problem, unless the installation of the power cables is done unwisely. In our laboratory, we are able to pick up different radio stations which are about 8 km apart, just by operating the electrochemical cell with a long salt bridge near a window facing the radio station.

Pulses produced by the start switches of fluorescent lamps are another most common source of RF frequencies. They may be regarded as RF pulses, having also a strong inductive field.

RF signals are transmitted as electromagnetic waves. RF - shielded cables and in addition a Faradayic cage around your cell is quite sufficient to avoid any problem.

Receivers for Undesired Noise

Any metal part, which is isolated from ground, acts as antenna and field concentrator of any electromagnetic field. So, keep metal parts at distance or connect them to ground.

All unshielded wires are also receivers. The impact is harmless as long as the cables are fed by low - ohmic sources.

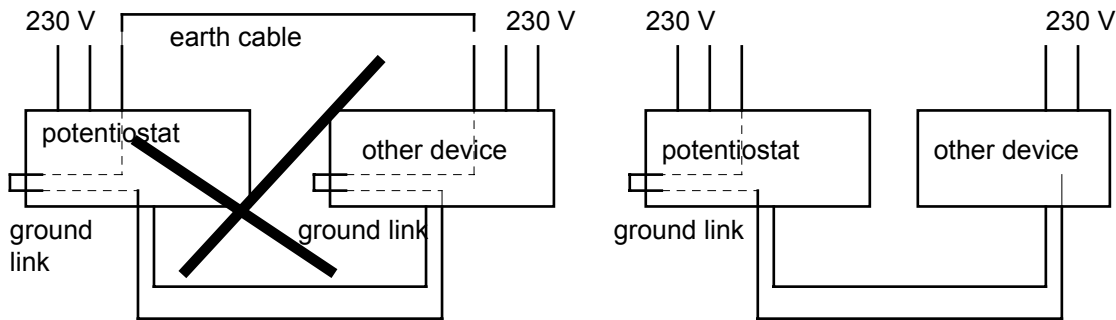
Output terminals of common instruments, including potentiostats, which have less than some kOhms source resistance may be regarded as sufficiently "hard" not to be troubled by RF or AF waves. Nevertheless you should not place them straight along power cables.

Input terminals which are designed to have high input resistance, on the other hand, are prone to pick up any wave from the environment. So, if both your signal source and the amplifier input have high impedance (or resistance), you are bound to shield the transmission line as good as possible. reference electrodes and their connections belong to this group, as well as the salt bridge between bulk electrolyte and reference electrode. The cell itself is also a source having high resistance if the electrolyte has low conductivity.

Grounding: Some Essentials

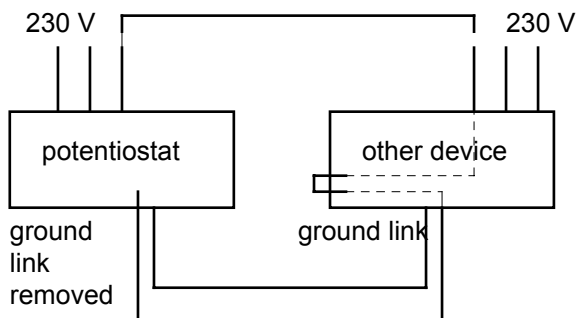
One of the most common sources leading to heavy 50 Hz noise are ground loops. When a ground line is connected from instrument A to instrument B, from B to C and from C back to A, you have produced a ground loop. This loop acts as one coil of a transformer, and any power line in the vicinity acts as primary "coil". You wouldn't do that willingly, but sometimes the ground connections are hidden, e.g. when instrument A and instrument B both have their ground

connected internally to protective ground. Personal computers and oscilloscopes usually have such a forced marriage between measurement ground and protection ground. You are not allowed to change this from security reasons. Just keep in mind that such a pair, when used in the same test rig, have to be wired cautiously. You may e.g. leave the ground line of the oscilloscope open, which leads also to poor results. The better way is frequently to risk a ground loop, but keep it as short as possible, having the shielded signal cables close to the power cables of both instruments. That reads crazy and in contradiction to everything I told above, but there are cases where this is better than other methods.



Bad circuit: an earth ring is produced along the dashed line

Good circuit: other device has plastic housing



Good circuit: one ground link is removed, earth connected to other device

Fig. 28: Good and bad ground connections

Ground loops produce a lot of problems, from noise up to quite appreciable voltages which in cases may lead to damage of the instruments. To avoid such ground loops, our instruments have the possibility to disconnect the internal ground from protection earth.

Other Cable - Related Problems

Not a noise problem, but related to it is the fact, that in most houses the power line is split up into the three phases delivered from the power station. The common reason for this is to keep the power balanced over all three phases. However, leakage currents, induction and capacitive pickup create differences between the protection ground lines. You may find appreciable potential differences between them, depending on the quality of the electrical power installation and the power you consume from the different phases. It is always a good practice to hang all

instruments forming a measurement stand to the same phase, while motors, lamps and all other consumers may be connected freely.

Shielding Measures

Use cables with shield for protection against RF noise. They help a little against audio frequency impact, too. The better way to reduce audio frequency impact is to drill each pair of signal line and ground line. Drilled lines do not pick up magnetic stray fields.

A Faradayic cage must be of thick sheets of either steel (do NOT use chromium-nickel stainless steels!) or aluminium if it shall help against magnetic fields also. Cheaper, and simple to handle is a U - bend sheet of 3 mm aluminium, wide and enough to enclose the cell and the reference electrode container. When the opening of the U is towards you, and all power cables behind it, it is nearly as good as a professional Faradayic cabinet.

Summary

Use a Faradayic cage if

- very small currents are to be measured
- the electrolyte has low conductivity
- the reference electrode system has high source resistance

A simple shield is formed by an iron sheet, bent to an "U", connected to ground. It should cover the cell together with the reference electrode.

Other helpful measures

- Remove all metal parts in the vicinity of the cell which are not required. They may concentrate stray fields and focus it to the cell.
- If it is not possible to remove these metal parts, connect them to ground.
- Use short cables for the ground lines.
- Mark one single point as the central point for grounding to avoid ring earths.
- Keep in mind: It is easy to shield the cell against electromagnetic stray fields.
- It is more difficult to protect the cell from inductive (magnetic) stray fields. Keep distance from the source of troubles. If distance cannot be increased enough, thick iron walls or even special (and expensive) shielding alloys as e.g. mu - metal have to be used.
- If no cell cable combination is used, but single wires, keep the counter electrode line and the working electrode lines close to one another to avoid induction loops.

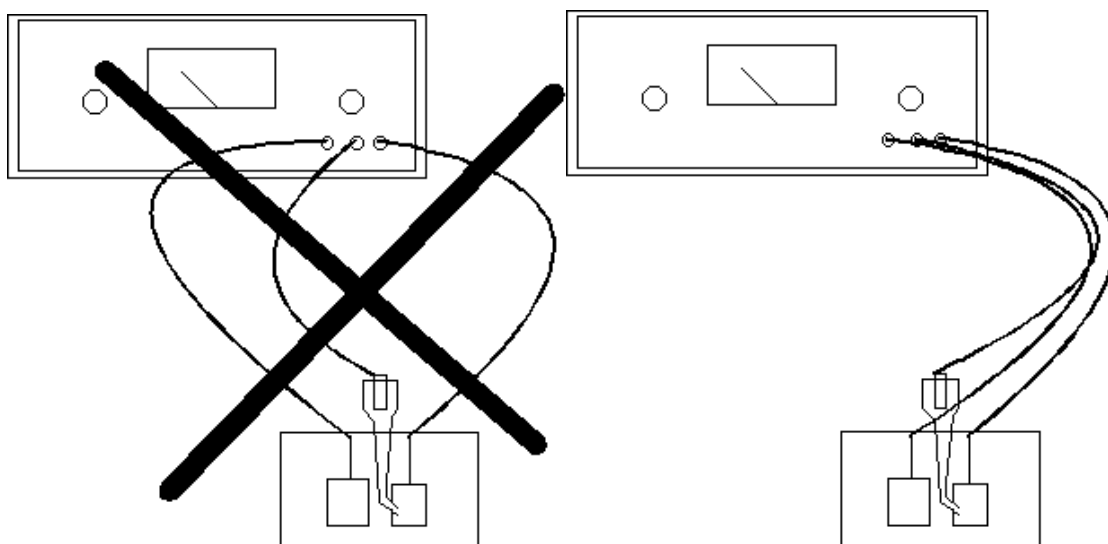


Fig. 27: Avoid loose cable loops, keep them close together!

If no cable combination is used, please avoid to spread the cables as shown left. Open loops are formed, which are prone to noise pick - up.

Don't's:

Don't produce ring earths

Don't connect the reference electrode shield instead of the ground line to the faradayic cage.

Don't place computers, especially computer screens, in the neighbourhood of the cell.

Don't place line cables in parallel to and in vicinity of the cell cable or any other cable feeding control voltages into the potentiostat.

Connection of data recorders

The analogue recording outputs have low source impedance. For this reason, the connection of data recorders does not make troubles. Only remember that the input resistance of a data recorder should have a resistance which is 1000 times the output resistance of the source to keep the transfer error at 0.1% of the signal.

One speciality should be kept in mind: Usually, the working electrode is kept on ground. That implies, that the potential of the reference electrode is measured with respect to ground - i.e. the working electrode. Hence, the sign of the potential is reversed, as electrochemists commonly look at the potential of the working electrode with respect to the reference electrode. To produce a correct sign of the potential, we should have now an inverting amplifier at the potential recording output. This is neither impossible nor expensive, but it always decreases the accuracy of the potential reading and, worse, introduces a certain phase shift. We (and some other potentiostat manufacturers) therefore do not invert the potential output.

Current Recorder Output

Remember that the simplest potentiostatic principle uses a resistor in the counter electrode circuit to measure the current. These outputs do not refer to ground, and data recorders need to have floating inputs. In all modern laboratory potentiostats, the current recorder output is referred to ground.

COMPUTER - BASED MEASUREMENTS

Using advanced hardware for data conversion, there are little problems arising from digital noise, if the cabling is done in a proper manner. On the other hand, there are indeed some differences between a pure analogue instrumentation and a mixed analogue / digital one.

Remember that a D / A converter never is able to produce a smooth voltage - time curve. Instead, the voltage is changed in increments of some tenths of a millivolt, maybe somewhat below. Anyhow, you will find staircases instead of a ramp or a curve. The cell will react, if the potential is changed stepwise, by producing transients. These transients may be appreciably high.

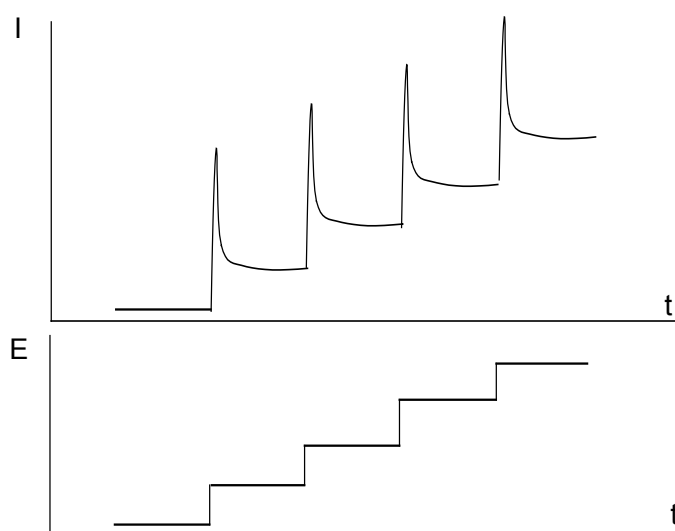


Fig. 29: A "ramp", produced by a D / A - converter, always produces transients as the control voltage is changed stepwise.

It is quite clear that this behaviour might lead to measurement errors as long as there is poor synchronisation between the steps of a D / A output and the data recording.

Another source of errors is the fact that many D / A - converters show a certain feed - through of digital signals (so - called digital noise). As the characteristic of current - potential curves usually is non - linear, transients and other noise signals will shift the mean current also when the cell capacity cares for a good filtering of the digital noise. For the effect of these glitches on the measurement see also fig. 17.

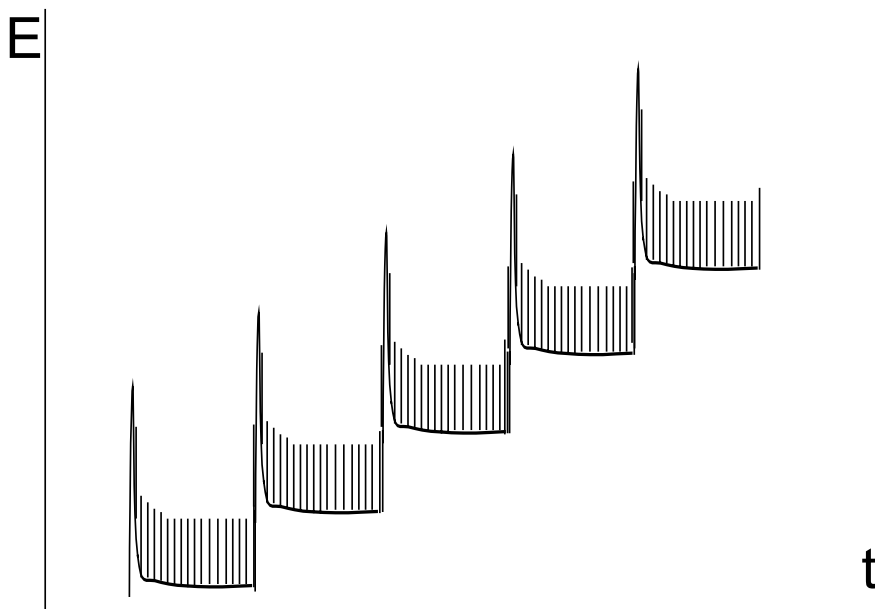


Fig. 30: Glitches and feed - through of digital signals

While, as shown, the digital production of control voltages may introduce errors, the conversion of analogue signals to digital numbers does not make problems. Only keep in mind that, usually, the least significant bits of the conversion are not quite reliable. A 12 - bit A / D converter so far produces a resolution of 1 in 1000, and a 16 bit converter may be reliable for a resolution of 1 in 10,000. The potentiostat itself has a current recording threshold which goes down to five decades below the applied current range or even lower. So, a certain loss of resolution will be unavoidable.

A simple system which produces reliable results consists of a potentiostat, an analogue controlled signal source (signal generator) and an A / D converter card inside a personal computer. These cards are available with rather fast data sampling up to more than 100,000 measurements per second, enough even to record transients. Smooth ramps are produced by the analogue signal generator, for step functions the D / A converter on the card will be sufficient.

Fast transients require both fast rising pulses and correspondingly fast recording. In those cases it is recommended to use digital oscilloscopes (or special transient recorders) to obtain best results. PC - boards having such qualities are available, but the good ones still have their price. For good quality of the control signal, a special pulse generator usually produces better pulse shapes than a D / A - converter. However, in most cases a sampling rate of 2 to 5 microseconds will be sufficient for most electrochemical transients.

For "stationary" current - potential curves, fast data recording is not desired, a few data points per second or per minute will be more than enough. For those applications, a slow system voltmeter having a resolution of 4 1/2 decades or even higher is best choice. Some electronic

distributors sell boxes, coupled to the computer by the serial line, the printer port or USB port which produce good results at moderate price.

SOME TYPICAL APPLICATIONS

Potentiostatic control of the working electrode

After connecting the cell according to the rules given above, some checks should be done:

Check the control voltage (and its sign) before switching to the potentiostatic mode. Some potentiostats have the possibility for such checks, operating on an internal dummy load. If your potentiostat has not, use the lowest current range when switching on: that keeps the current low and avoids destruction of your electrodes when wiring errors have occurred or a too high control voltage is applied.

Recording current - potential curves

Different methods are used to record current - potential curves. The standard method is the continuous or perhaps the stepwise variation of the potential from a start value to an end value. The start value can be the rest potential, or (usually) a cathodic potential where the working electrode does not dissolve. Whether smooth voltage ramps or steps are used for potential variation depends on the purpose. Stepwise variation of the potential may give additional information if e.g. pitting corrosion tests are performed, as the current decay within each single potential step helps to find the most negative pitting potential. In other cases, continuous potential variation is more desired, because the data processing is easier.

Measurement of the Polarisation Resistance

The measurement of the polarisation resistance requires the polarisation within a few millivolts in the vicinity of the rest potential. It is convenient to use galvanostatic polarisation for this purpose, because the rest potential establishes as soon as no current is applied. On the other hand, varying electrode processes may cause appreciable changes in the polarisation resistance, leading to undesired polarisation voltages. Then, potentiostatic polarisation is advantageous. Before starting the polarisation, the rest potential shall be allowed to achieve a stable value. Then the working electrode is polarised a few mV from the rest potential. Doing this cyclically and checking the rest potential in intervals, continuous changes in the R_p can be measured.

Measurement of the rest potential

The rest potential can be obtained by feeding an equal voltage (of opposite sign) to the control input of the potentiostat. This method of compensation, cited in some books, is now obsolete. Most potentiostats have a separate operation mode for this task. As the reference electrode inputs now have extreme high input resistances, errors due to parasitic currents through the reference electrode are to be disregarded in all practical cases.

On the other hand, it may be of interest to do such compensation also in the rest potential measurement mode of the potentiostat. Doing so, the current is zero when the potentiostat is switched to the potentiostatic mode and curve recording starts in the currentless state. If you want to use this method, please contact us.

Galvanostatic Measurements

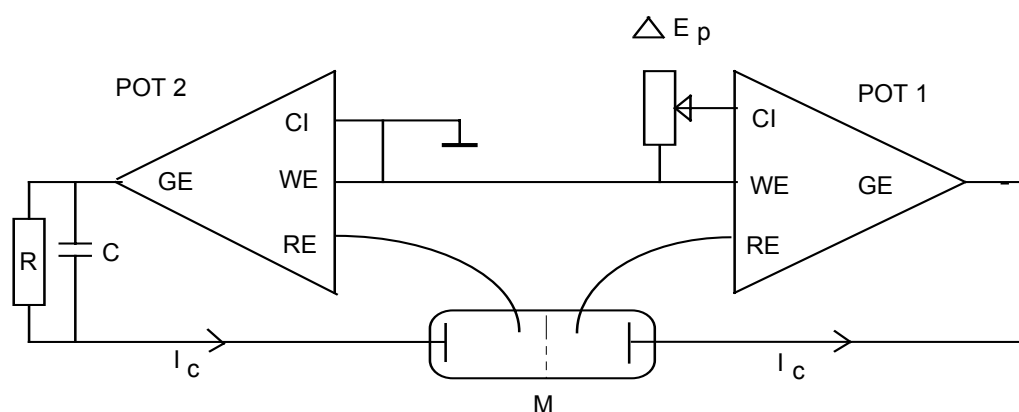
Any potentiostat can act as galvanostat, too. To convert a potentiostat into a galvanostat, only a simple resistor is required. See chapter "Additional circuitry". However, when converting a

potentiostat into a galvanostat, you lose the potential signal at the potential output. If you are interested in the actual potential, you have to use a separate potential meter. The main advantage of using the potentiostat as galvanostat is its very fast and "clean" response on pulses.

Otherwise, it is much more convenient to use potentiostats which have a built - in galvanostatic mode.

MEASUREMENTS USING SEVERAL POTENTIOSTATS

Difference potential control



ΔE_p	Difference potential	RE	Reference electrode	WE	Working electrode
I_c	Cell current	CE	Counter electrode	CI	Control input
M	Membrane				

Fig. 31: Differential potential control

The potentiostatic control of the potential difference between two faces of a membrane requires two potentiostats. POT 1 controls the potential of the reference electrode REF1 to virtual ground, as the control input of POT 1 is kept on ground. The necessary current is provided by the counter electrode CE1. POT 2 controls the potential of the reference electrode REF 2 to a voltage which is fed into its control input, referring to ground. As result, POT 2 forms the difference potential. The current which is required to keep the potential difference flows between the two counter electrodes CE1 and CE 2. The two working electrode inputs of the potentiostats are connected to one another. To avoid ring earths, POT 2 should be disconnected from ground. For this purpose, our potentiostats have a ground bridge connector, which can be simply removed. If small currents are to be measured, all electrode cables must be shielded.

are quite independent of the electronic instrument and determined solely by the processes in the electrochemical cell.

The capillary of the reference electrode senses the potential against the working electrode only over a limited area of the surface. Local variations over the boundary layer of the working electrode from the potential sensing point increase as the current density increases and the differences in the spatial current density distribution become larger. Irregular and large surfaces are favourable to the development of such potential variations. Localised electrochemical attack of the surface (pitting corrosion, crack formation) will also produce non - uniform potential distributions over the surface of the working electrode.

The tip of the capillary cannot reach the boundary layer of the working electrode. In favourable cases it has a distance of some tenths of millimetres from the boundary layer. Between the plane where the potential is sensed, and the boundary layer in which the potential is to be controlled, there is a potential drop which depends on current -density and which may become excessively large, especially with poorly conducting electrolytes. Although the suggestions made in Section 2.5 offer means for reducing this error (IR-drop), it seems unlikely that it can be excluded completely since complete compensation may give rise to over - compensation and instability as a result of slight changes in the electrolyte at the surface of the working electrode.

The supply of the boundary layer with fresh electrolyte and the removal of reaction products from this boundary layer at high current densities represents a problem which cannot be solved completely, at least as long as common stirring devices are used.

The potential between working electrode and reference electrode depends on temperature. Large electric power losses in the cell may result to an appreciable increase in temperature, which then influence the potential.

The sources of error which finally limit all useful potentiostatic investigations, can be taken to increase with:

- the size of the working electrode,
- surface irregularities in this surface,
- current density variations over the surface,
- decrease in electrolytic conductivity,
- increase in current density
- increase in total current
- increase in the electric power converted in the cell.

FAILURE DETECTION

If errors occur and you try to find the source of the error please remember:

Usually the potentiostat is not defect. Typical errors are:

- Wrong wiring
- Bad contacts
- Broken cables
- Gas bubbles in the reference electrode bridge

To check this, a first test may be to set the potentiostat to the check mode (some of our potentiostats have this mode, called E_c). Set the range to 1 to 10 mA (depending on the available range settings) and set the internal control source to any voltage between 100 mV and 1 V. A corresponding current should flow across the internal dummy load.

It is sometimes more informative to use an external dummy load, because then the cabling also is tested. If the potentiostat has no check mode, you are bound to use an external dummy cell anyhow.

The following test circuit is useful for a fast test:

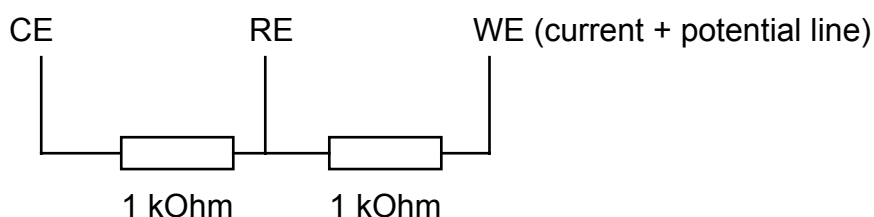


Fig. 34: A simple dummy load cell

Turn the control voltage to 1 V, set the current range to 1 mA.
Turn the operation mode switch to position "I" or potentiostatic control.

The meter shall show full scale deflection (or 1 mA if the ranges are arranged in another scale).
Turning the potential to lower values, the meter shall follow the setting.

If this works, but the cell does not work, replace the reference electrode by a copper wire dipping directly into the cell (without Haber-Luggin-capillary and other bridges). You should be able to control the potential when setting the operation mode switch to "I" - whatever the potential meter means now. If not, the bug lies within the cell cable. Check the connections according to the list given above, bending the cables violently during testing to find possibly broken lines (2 persons may be necessary to perform this test).

If the cables are in good order, but the dummy cell test does not work, consider the potentiostat to be wrong.

Change to another current range and repeat the testing. If things are working properly (keep in mind the dummy cell will show other values depending of the set current range), a range resistor may have been burnt out in the range tried previously. It may be helpful to use a few different dummy loads equipped with resistors for both higher or lower current ranges.

Proper resistor arrangements are

1 A	1 Ohm (2 Watt)
100 mA	10 Ohm
10 mA	100 Ohm
1 mA	1 kOhm
100 μ A	10 kOhm
10 μ A	100 kOhm
1 μ A	1 MOhm

If all these tests show bad results, take into consideration that the potentiostat might be wrong. If the error occurs only within one range, or perhaps two ranges, the range resistor or the range switch contacts may be wrong. If the error occurs in all ranges, the potentiostat has some internal defect which can be detected and repaired by trained personnel only.

BASIC THEORY OF POTENTIAL CONTROL

Electronic potentiostats are used for controlling the potential in an electrochemical cell. The current in the cell from a counter electrode to a working electrode is controlled by means of the potentiostat so that the actual potential of the current - carrying working electrode relative to a current - free reference electrode follows a predetermined control voltage and is held constant at its instantaneous value irrespective of electrochemical processes.

The ideal potential controller has an infinite gain and operates so that the difference between actual and control voltage disappears without any noise or disturbance being introduced. The control action takes place in a negligibly short time.

A practical control action is determined by the technical characteristics of the potentiostat, and by the electrical replacement circuit of the electrochemical cell. The fundamental principle of this type of control will be discussed below.

Potentiostats in their electronic action are identical with difference operational amplifiers whose power output provides voltage and current for the cell in the feedback loop. Unlike the usual application of operational amplifiers in which the feedback loop is determined by separate electrical components, potential control by potentiostats includes an electrochemical cell in the control loop whose impedance varies greatly with potential and time. Both the conductivity and the double layer capacitance of the boundary layer where the potential is being controlled, vary over many decades as the potential changes. Information on the electrical replacement circuit of the control loop is often available only after experimental results with controlled potential have been obtained. It is essential therefore, that the potentiostat provides sufficiently accurate and stable control of the cell potential over an extremely wide range of cell currents for extensive variations in the usual complex feedback circuit and in addition operates within a sufficiently short interval of time.

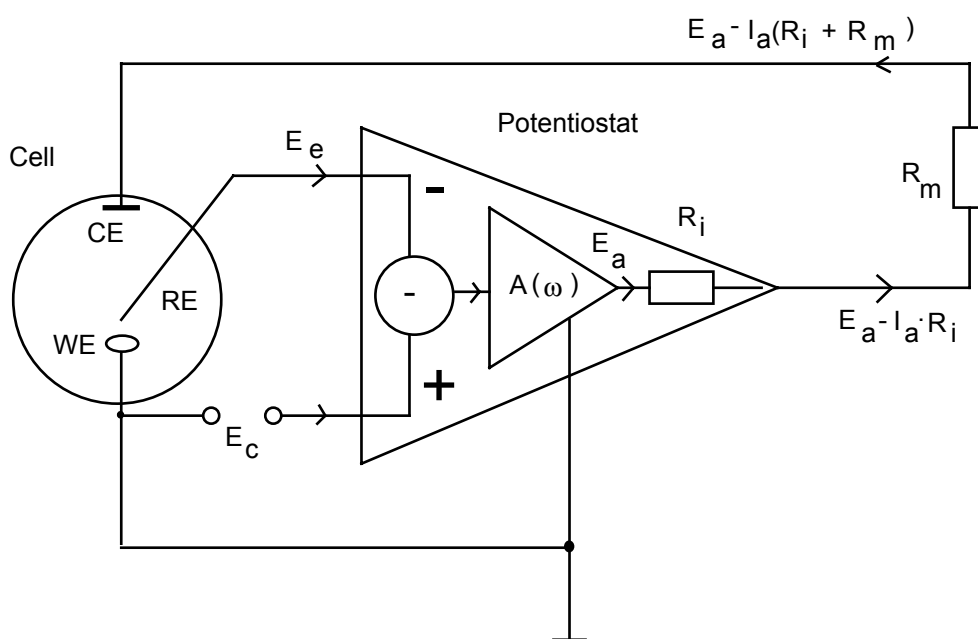


Fig. A1 Schematic diagram of potential control

The input difference stage forms the difference $\Delta E = E_c - E_e$ between the control potential fed in at the non - inverting input (+) of the potentiostat, and the actual potential E_e between reference

electrode RE and electrode RE and working electrode WE. This difference ΔE is amplified with the open - loop gain $A(\omega)$ to $\Delta E * A(\omega)$. The internal resistance of the power output stage R_i reduces the amplified open - loop voltage of the output by the amount $I_a * R_j$ if the output is loaded by the cell current I_a .

The relationship between the deviation of the actual controlled voltage, referred to the control voltage ΔE , and the open - loop output voltage is given by

$$\Delta E * A(\omega) = E_a \quad (1)$$

The open - loop output voltage equals the amplified input difference voltage

$$dE = E_c - E_e \quad (2)$$

The actual voltage E_e is itself part of the open - loop output voltage. E_a . It is determined by the feedback factor β which represents the voltage division in the output circuit:

$$\beta(\omega) = \frac{E_e}{E_a} = \frac{R_e}{R_i + R_m + R_z + R_e} \quad (3)$$

Here R_j is the internal resistance of the output stage
 R_m is The resistance of a current measuring device
 R_z is the cell resistance from the counter electrode to the boundary layer
 R_e is the boundary layer impedance; the drop across it is E_e .

The relative deviation of the actual controlled voltage, referred to the control voltage, is given by

$$\frac{\Delta E}{E_c} = \frac{\Delta E}{E_e + \Delta E} \quad (4)$$

Substituting Equations 1 and 3 into 4 gives the frequency transfer function of the relative deviation

$$\Delta F(\omega) = \frac{\Delta E}{E_c} = \frac{1}{1 + \beta(\omega)A(\omega)} \quad (5)$$

The transfer function of the actual controlled voltage is obtained as

$$F(\omega) = \frac{E_e}{E_c} = \frac{1}{1 + \frac{1}{1 + \beta(\omega)A(\omega)}} \quad (6)$$

Both transfer functions have a pole at $\beta(\omega) = -1$. Here control loop becomes unstable.

In principle it is possible for the product $\beta(\omega)$ to reach a value of -1 since both terms are generally complex. The control circuit becomes unstable, for example, if at a frequency ω the phase angle of the feedback $\beta(\omega)$ as well as the phase angle between input difference voltage and output voltage of the potentiostat becomes equal to or greater than 90° , so that their sum is equal

to or greater than 180° , before the product $\beta(\omega) * A(\omega)$ has dropped below 1 (unity gain crossover frequency).

Since the feedback factor $\beta(\omega)$ in an electrochemical cell is a complex operator and can vary greatly, it is necessary that at least the potentiostat itself is phase - compensated, i. e. that its internal phase angle does not exceed 90° . When the internal resistance of the output power stage also remains in phase up to about the unity gain crossover limit, an additional 90° phase margin is left for the feedback loop before the instability limit is reached and oscillations are produced.

There is, therefore, no point in extending the bandwidth of potentiostats to values for the unity gain cross-over limit at which the internal phase angle exceeds 90° and the internal impedance of the power output stage develops an appreciable component, in order to suggest shorter response times to the user. Within the range up to the unity gain crossover limit of the potentiostat it is necessary to allow for a 90° phase angle between the voltage at the counter electrode and the part voltage at the reference electrode. For a potentiostat without phase compensation the system then reaches the instability limit. Oscillations are excited which may increase up to the output limit of the potentiostat. Under these conditions the potentiostat becomes incapable of controlling the potential.

A phase compensated potentiostat has a gain within the frequency range from zero to the unity gain cross-over limit (which will be referred to below as the transit frequency ω_t which falls off from a corner frequency ω_o at the rate of 20 dB per frequency decade. The phase angle reaches 45° at ω_o and increases to 90° at ω_t . In theory it approaches 90° asymptotically without quite reaching it.

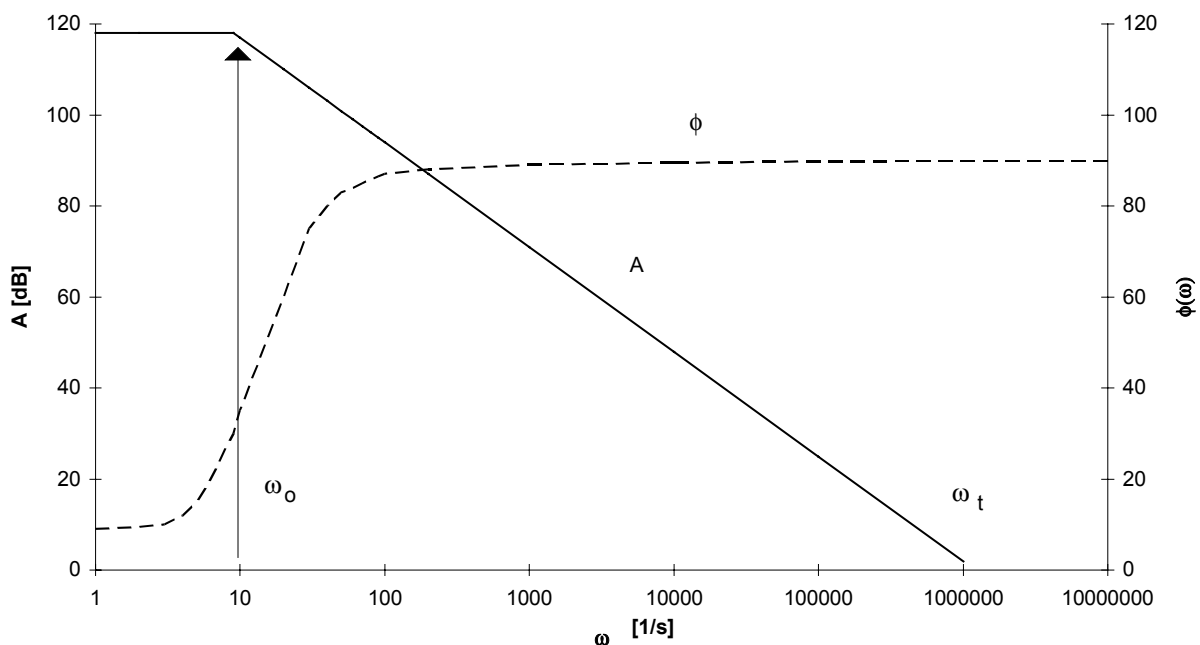


Fig. A2: Variation of gain and phase angle with frequency for a phase compensated potentiostat ST 88

The phase - compensated open loop gain $A(\omega)$ is given by the following equation within the interval

$$0 \leq \omega \leq \omega_t :$$

$$A(\omega) = A_o \frac{1}{1 + j \frac{\omega}{\omega_o}} = \frac{A_o}{\sqrt{1 + \left(\frac{\omega}{\omega_o}\right)^2}} \exp(-j * \arctan \frac{\omega}{\omega_o}) \quad (7)$$

In the interval $\omega > \omega_o$ this equation can be replaced by the approximation

$$A(\omega) = A_o \frac{\omega_o}{\omega} \exp(-j * \arctan \frac{\omega}{\omega_o}) \quad (8)$$

in which $A_o \omega_o = \omega_t$ is the transit frequency, also referred to as the gain - bandwidth product.

For $\omega > \omega_o$ this approximation can be replaced by

$$A(\omega) = A_o \frac{\omega_o}{\omega} \exp(-j90^\circ) = -jA_o \frac{\omega_o}{\omega} \quad (9)$$

This approximation also takes account of the fact that technical systems not only approach the 90° phase angle, but in fact reach it even when phase compensation is good.

We shall now extend the analysis to include practical cell replacement circuits and the corresponding feedback factors. The control circuit is first evaluated for its stability.

In the equivalent circuit alongside the symbols have the following significance:

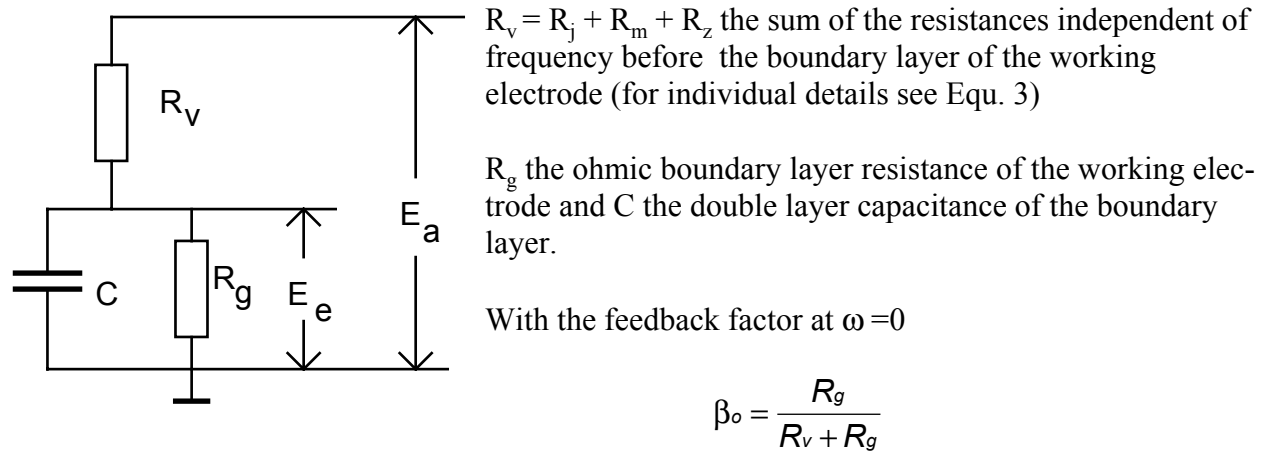


Fig. A3: Special case of a cell replacement circuit

and the 3 dB bandwidth for the feedback factor

$$\omega_p = \frac{1}{R_p * C}$$

where R_p represents the resistance due to R_v and R_g in parallel

$$R_p = \frac{R_v * R_g}{R_v + R_g}$$

the feedback factor as a function of frequency is given by

$$\beta(\omega) = \beta_o \frac{1}{1 + j \frac{\omega}{\omega_p}} = \frac{\beta_o}{\sqrt{1 + \left(\frac{\omega}{\omega_p}\right)^2}} \exp(-j * \arctan(\frac{\omega}{\omega_p})) \quad (10)$$

For the range $\omega_p < \omega < \omega_t$ this equation can be replaced by the approximation

$$\beta(\omega) = \beta_o \frac{\omega_p}{\omega} \exp(-j * \arctan(\frac{\omega}{\omega_p})) \quad (11)$$

The stability analysis can be limited to this interval since the values of the phase angle $\tan^{-1} \frac{\omega}{\omega_r}$ are only appreciable within this range

Stability is ensured if the value of $A(\omega) * \beta(\omega)$ has fallen below 1 before the phase angle reaches 180° , as was indicated by Equations 5 and 6.

We have

$$A(\omega)\beta(\omega) = A_o \beta_o \frac{\omega_o \omega_p}{\omega^2} \exp(-j(\arctan(\frac{\omega}{\omega_o}) + \arctan(\frac{\omega}{\omega_p}))) \quad (12)$$

Even when $A_o \beta_o$ is very large, the value of $A(\omega) \beta(\omega)$ for increasing ω becomes smaller than 1 before the phase angle

$$\varphi = \arctan \frac{\omega}{\omega_o} + \arctan \frac{\omega}{\omega_p} \quad \text{reaches } 180^\circ, \text{ when } \omega \rightarrow \infty.$$

The control loop just remains stable. The pole in Equations 5 and 6 is just not being reached.

The considerations on the phase angle are modified if the potential transfer from the boundary layer to the potentiostat input within the interval $0 \leq \omega \leq \omega_t$ becomes variable with frequency. In the cell replacement circuit shown alongside

R_k is the ohmic resistance of the reference electrode / capillary system

C_k is the input capacitance of the reference electrode input of the potentiostat together with the cable capacitance.

If the 3 dB limit of this RC circuit

$$\omega_k = \frac{1}{R_k * C_k}$$

becomes smaller than the transit frequency of the potentiostat it is necessary to take it into account.

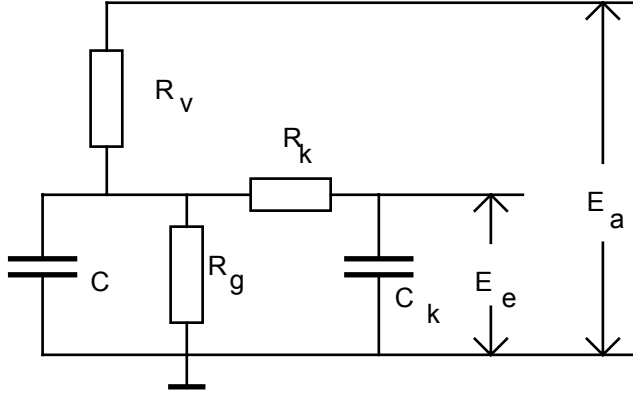


Fig. A4: Cell replacement circuit 2 with time constant

For $R_k \gg R_p$ we have in that case

$$\beta(\omega) = \beta_o \frac{1}{1 + j \frac{\omega}{\omega_p}} * \frac{1}{1 + j \frac{\omega}{\omega_k}}$$

or, after separation into magnitude and phase:

$$\beta(\omega) = \beta_o \frac{1}{\sqrt{1 + (j \frac{\omega}{\omega_p})^2}} * \frac{1}{\sqrt{1 + (j \frac{\omega}{\omega_k})^2}} \exp(-j(\arctan \frac{\omega}{\omega_p} + \arctan \frac{\omega}{\omega_k})) \quad (14.)$$

For the range $\omega > \omega_p$

this equations can be replaced by the approximate expression

$$\beta(\omega) = \beta_o \frac{\omega}{\omega_o} * \frac{1}{\sqrt{1 + (j \frac{\omega}{\omega_k})^2}} \exp(-j(\arctan \frac{\omega}{\omega_p} + \arctan \frac{\omega}{\omega_k})) \quad (15)$$

The product $A * \beta$ which is decisive for stability for $\omega \gg \omega$ is given by

$$A(\omega) * \beta(\omega) = \frac{\omega_o A_o \beta_o}{\omega} \frac{1}{\sqrt{1 + (j \frac{\omega}{\omega_p})^2}} * \frac{1}{\sqrt{1 + (j \frac{\omega}{\omega_k})^2}} \exp(-j(90^\circ + \arctan \frac{\omega}{\omega_p} + \arctan \frac{\omega}{\omega_k})) \quad (16)$$

The instability limit is reached when the phase angel

$$\arctan \frac{\omega}{\omega_p} + \arctan \frac{\omega}{\omega_k} = 90^\circ$$

and the magnitude

$$\beta_o \frac{\omega}{\omega} \frac{1}{\sqrt{1 + (j \frac{\omega}{\omega_p})^2}} * \frac{1}{\sqrt{1 + (j \frac{\omega}{\omega_k})^2}} \geq 1$$

The phase angle becomes 90° at

$$\omega = \sqrt{\omega_p * \omega_k}$$

and the magnitude becomes ≥ 1 when $\omega_p + \omega_k \leq \beta_o \omega_t$

Instability is certain to be avoided when $\omega_k > \omega_t \beta_o$ or, indefinite β_o , when $\omega_k > \omega_t$.

The somewhat critical feedback loop configurations shown in Fig. 3 or the still more critical one according to Fig. 4 does not occur in this form in practical circuits. A loss - free capacitor in the

boundary layer of the working electrode cannot be achieved in practice. If a loss resistance R_s is assumed in series with the double layer capacitance, the phase angle of the feedback factor does not reach the critical angle of 90° . After reaching a maximum phase angle between 45° and 90° it decreases again with increasing ω .

With the simplifying combinations β_0 feedback factor at $\omega = 0$ and

R_p total resistance R_v and R_g in parallel (see Equ. 10)
and the 3 dB limit $\omega_g = \frac{1}{(R_p + R_s) * C}$

Fig. % Replacement circuit with loss resistance

the feedback factor is obtained as

$$\beta(\omega) = \frac{1 + \omega R_s C}{1 + j\omega(R_p + R_s) * C} * \beta_0 \quad (17)$$

With $\omega_s = \omega_s = \frac{1}{R_s C}$ which because of the definition above is always greater than ω_g we obtain, after

separating into magnitude phase:

$$\beta(\omega) = \beta_0 \frac{\sqrt{1 + (j \frac{\omega}{\omega_s})^2}}{\sqrt{1 + (j \frac{\omega}{\omega_p})^2}} \exp(-j(\arctan \frac{\omega}{\omega_g} - \arctan \frac{\omega}{\omega_s})) \quad (18)$$

The phase angle has a maximum at the point $\omega = \sqrt{\omega_g * \omega_s}$, which can readily be confirmed by differentiation.

The phase angle can no longer approach 90° asymptotically. From the maximum phase angle it decreases towards 0 as ω increases.

The stability criteria for Equ. 12 can therefore, be applied without approaching the critical limits so closely. The phase angle remains smaller as R_s approaches R_p . For $R_s = R_p$ we have $\omega_s = 2\omega_g$ and the maximum phase angle remains below 20° . For $R_p = 10 \cdot R_s$ the phase angle remains below 55° ; it only approaches 80° at $R_p = 100 \cdot R_s$.

We shall now determine the transfer function for this replacement circuit which is close to the actual conditions, and show it as a graph. It is assumed that the time constant of the reference electrode / capillary system is negligible with $\omega_k > \omega_t$; this assumption can always be realised in practice (see details under 5.1)

The transfer function of the actual voltage, referred to the control voltage, is according to Equ. 6:

$$F(\omega) = \frac{E_e}{E_c} = \frac{1}{1 + \frac{1}{1 + \beta(\omega)A(\omega)}}$$

that is an operator of the form

$$F(\omega) = \frac{1}{1 + K * \exp(j * \varphi)}$$

with K within the range $0 < \omega < \omega_t$

$$K(\omega) = \frac{\sqrt{1 + \left(\frac{\omega}{\omega_o}\right)^2} * \sqrt{1 + \left(\frac{\omega}{\omega_g}\right)^2}}{A_o \beta_o * \sqrt{1 + \left(\frac{\omega}{\omega_{2s}}\right)^2}}$$

and
$$\varphi(\omega) = \arctan\left(\frac{\omega}{\omega_o}\right) + \arctan\left(\frac{\omega}{\omega_g}\right) - \arctan\left(\frac{\omega}{\omega_s}\right)$$

After separating amplitude and phase we have

$$F(\omega) = \frac{1}{\sqrt{1 + 2K \cos \varphi + K^2}} * \exp(-j * \arctan\left(\frac{K \sin \varphi}{1 + K \cos \varphi}\right)) \quad (19)$$

Within the interval $0 < \omega < \omega_g$ K is very small compared with 1 and φ is close to 90° .

The transfer function is obtained using the practical values $\omega_t = 2 \cdot 10^6 \text{ s}^{-1}$ and $\omega_t = 100 \omega_g$ and $\omega_t = 10 \omega_s$ with $\beta_o = 0.5$.

At the point $\omega = \omega_s$ we have $K = \frac{\omega_s^2}{\omega_o \omega_g \beta_o}$ and $\varphi = 135^\circ$

$$F(\omega) = \sqrt{2} \exp(-j * 45^\circ),$$

a rise of + 3 dB.

At the point $K = 1$ the phase angle is again about $\varphi = 90^\circ$

and
$$F(\omega) = \frac{1}{\sqrt{2}} \exp(-j * 45^\circ)$$

the - 3 dB limit.

The overall characteristic is shown in Fig. A5

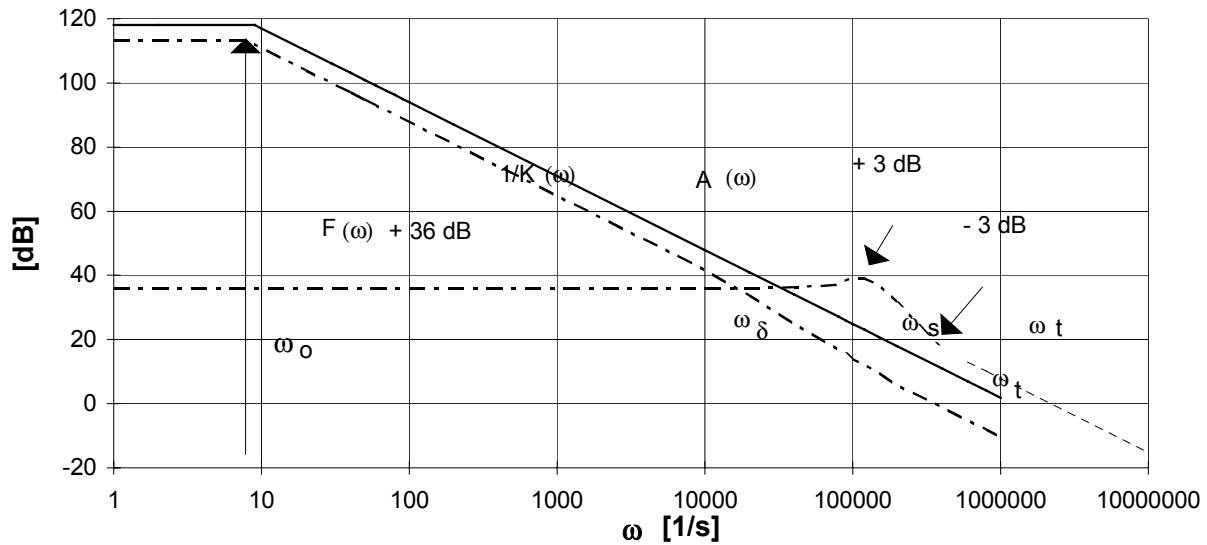


Fig A5: Frequency transfer function with cell replacement circuit

It has been adopted to include the rise time or time constant among the technical data of potentiostats. It is only sensible to quote a rise time or time constant for the closed control loop of the potentiostat (output connected to inverting input), and again only if the potentiostat is phase- compensated.

A phase - compensated potentiostat on full feedback with $\beta(\omega) = 1$ has for all $\omega > \omega_0$ a transfer function

$$F(\omega) = \frac{1}{\sqrt{1 + \left(j\frac{\omega}{\omega_t}\right)^2}} \exp(-j(\arctan \frac{\omega}{\omega_t}))$$

This function is identical with a low - pass filter consisting of R and C which has a time constant

$$T = RC = \frac{1}{\omega_t} = \frac{1}{2\pi f_t}$$

This time constant indicates the time when the output has approached its final value to within an amount 1/e following the application of a step function to the input.

After $t = 2.5 T$ the output has exceeded the level of 10 % below the final value; at $t = 5 T$ the deviation from the final value is less than 1 %. This is the value quoted as the rise time in our technical data.

The rise time in the control loop of the potentiostat with an electrochemical cell depends to a decisive extent on β_0 and the position of ω_g and ω_s . It is, therefore, in no way determined by the transit frequency or any rise time calculated from it. If there is any rise in the transfer function $F(\omega)$ the response of the control loop to a step input includes overshoot. With a considerable rise this may develop into an oscillation whose decay time is determined largely by the position of ω_g and ω_s , i.e. is independent of the potentiostat. In such a case there is little point in quoting figures on a rise time to within 10 % or 1 % of the final value.

Summary:

1. In order to ensure stable potential control of an electrochemical cell with a double layer capacitance in the boundary layer it is essential to have a potentiostat with phase compensation. The internal phase angle of the potentiostat must not exceed 90° up to about the transit frequency.
2. For similar reasons it is necessary that the internal resistance of the power output stage should not produce additional phase shift up to about the transit frequency.
3. The time constant of the reference electrode /capillary system $T_k = R_k C_k$ should be kept small compared with the rise time constant of the potentiostat $T = 1/\omega_t$.
4. The cell resistance R_z and the resistance R_m and R_j should be made as small as possible in order to achieve a large bandwidth.
5. If ω_g is smaller than $\beta_o \omega_t$ there is a rise in the frequency characteristic which increases when ω_g and $\beta_c \omega_t$ are further apart and when the difference between R_p and R_s increases. This rise causes an overshoot in the response to a step input and produces damped oscillations as the difference between the two values increases.

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