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ELEKTRONIK INTELLIGENT CONTROLS

POTENTIOSTATS - WELL USED

From an electronic view, potentiostats are operational amplifiers. Their special features, especially output power, speed, phase stability and extremely high input resistance are a real advantage for many applications beyond electrochemical ones.

The original purpose of a potentiostat is to control the potential between a working electrode WE and a reference electrode RE. Let us start this feature with the potentiostatic control as the regular use of a potentiostat.

1. The Potentiostatic Control of an Electrode

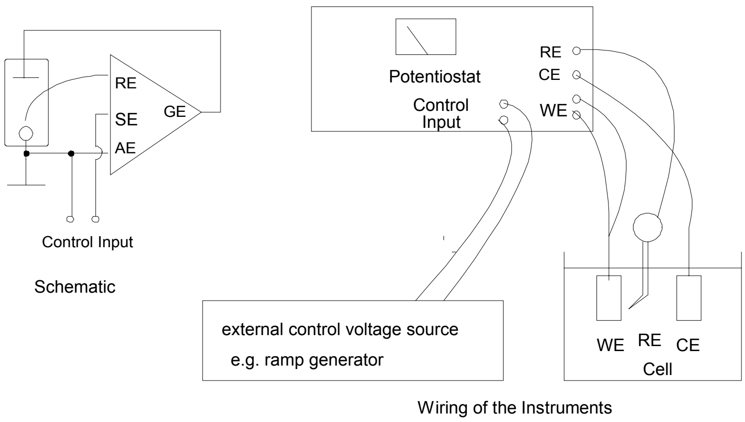


Fig. 1: Schematic of the potentiostatic control loop. RE Reference electrode, WE working electrode, CE counter electrode, CI control input

A control voltage is fed into the control input CI. This control voltage forces a current through the counter electrode exactly as high as to achieve the wanted potential difference between working electrode and reference electrode. The control voltage may be produced by the internal potential control source of the potentiostat, or by an external signal generator, e.g. a ramp generator or a sine wave generator. While for a constant potential the internal potential control source is sufficient, time-dependent signals are to be fed from external sources (except our scanning potentiostats that also have built- in voltage scanners).

2. Potentiostat as controlled Voltage Source

Potentiostats can be used as controlled precision voltage sources. To use this mode, you can - for low voltages - simply connect the counter electrode terminal to the reference electrode terminal. The potential that is fed into the control input (or set by the internal voltage source) now controls directly the voltage of the counter electrode. The maximum current is limited by the set current range, and by the power of the potentiostat, i.e. a 1 - A - Potentiostat can control voltages exactly until 1 A of current are reached. If you want to apply voltages beyond the range of the control voltage, you have to insert a potentioetric divider which increases the voltage amplification of the potentiostat. Fig. 2 shows the correct wiring. The two resistors R1 and R2 are calculated from the ration between maximum control voltage and maximum output voltage. Let the potentiostat’s output voltage be max. 25 V, and the internal control source have max. 1 V, then

$(R1 + R2) / R2 = 25 / 1$

The total resistance should be in the order of some kiloohms to some hundred kiloohms. A value of 24 kOhm for R1 and 1 kOhm for R2 may be a quite convenient pair here. Now, any voltage applied at the control input or set by the internal control source is amplified by 25 and fed to the CE terminal.

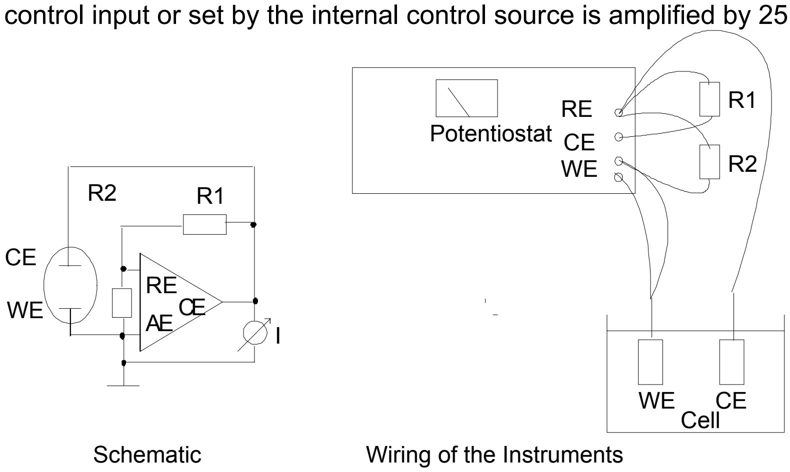


Fig. 2: Potentiostat as controlled voltage source

3. Potentiostat as Controlled Current Source

Each Potentiostat can be used as Galvanostat. For this purpose, instead of the potential of the working electrode a voltage drop E_S across an external resistor R_X is used as feed-back control.. The value of this resistor which is clamped between working electrode terminal of the potentiostat and its reference electrode terminal defines the range of the current: I_C

$$I_C = E_s / R_x$$

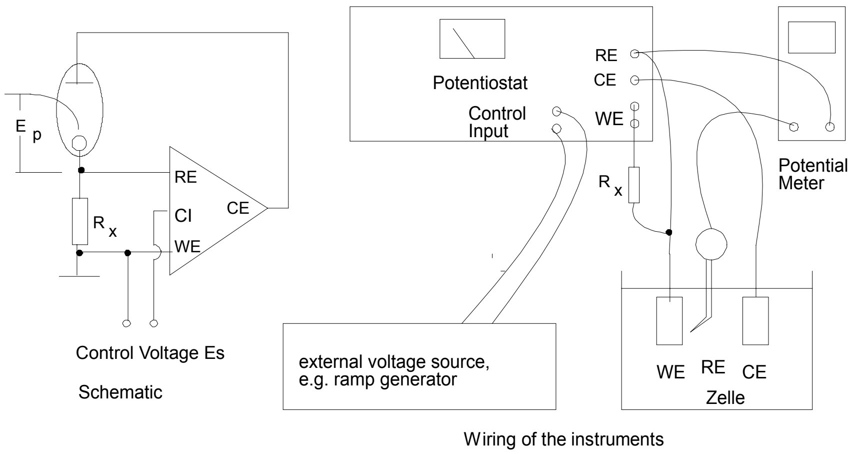


Fig. 3: Potentiostat used as Galvanostat

The current meter shows the actual current..

To measure the potential, an external potential meter must be used, which is connected (floating- i.e. it must not refer to ground!) between the reference electrode and the working electrode, which now not longer is kept on ground potential.

The potential drop across R_x and according the cell current can be controlled either by the internal control source or an external source fed into the control input.

4. Potentiostat as Precision - Amperemeter („Zero-Ohm-Amperemeter“)

A standard current meter, as usually built-in in typical multimeters measures the current as a voltage drop across a shunt resistor. A usual digital 3 ½ digit - voltmeter has a lowest current range of 200 mV, accordingly rises the voltage drop across the internal shunt resistor up to 200 mV when the current corresponds to the full range.

Example: You measure a current of 100 µA in the range 200 µA of the digital voltmeter. Then, the internal shunt is 1 kOhm, across which a voltage of U = R x I = 1000 Ohm x 100 µA = 100 mV now rises.

When measuring the current in usual electronic circuits, this voltage drop may be disregarded. Concerning electrochemical potentials, a drop of 100 mV is nearly enormous: remember that Tafel slopes at ambient temperature may vary by 29 mV per current decade. This example shows drastically that an ammeter for electrochemical measurements should - ideally - have zero ohm internal resistance.

To achieve this, special „zero - ohm - ammeters“, also called active current sinks, are used. Any potentiostat can be used also as such an active current sink, and it is very simple to do so. Connect the counter electrode to the reference electrode, and use the internal range resistor to define the current range. The current is now directly displayed on the built-in current meter, and a corresponding voltage is fed to the current output terminal..

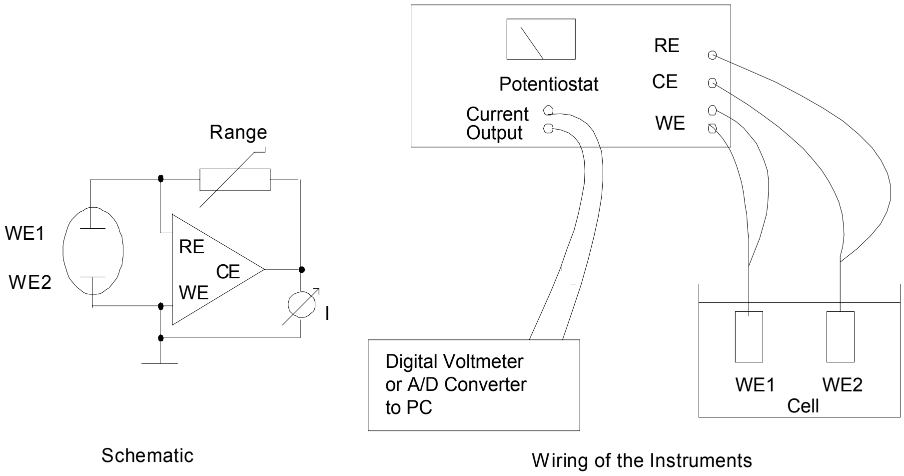


Fig. 4: Potentiostat as Zero - Ohm - Ammeter (Current Sink)

Polarity: The polarity of the current that passes the working electrode is positive if the meter deflects to the right (positive) side.

If the internal range resistor does not give the required resolution, you can introduce an external one (see fig. 4, schematic left side). Then the current is measured as the voltages between CE terminal and ground according to

$I = U / R$

where R is the external range resistor. For R = 1 Mohm, I = U / R = 1 V/µA

A capacitor across the external range resistor will be useful to reduce noise. The time constant of R x C should be in the order of ms for currents down to 1 µA, for lower currents R x C should be in the order of 100 ms up to 1 s. Example: 1 nF x 1000 MOhm = 1 s might be good for measuring currents below 1 nA.

5. A Simple Method to Measure the Polarisation Resistance

The polarisation resistance of a pair of electrodes is defined by the slope of the current - potential curve in the vicinity of the rest potential. If you want to use the polarisation resistance of the working electrode as a measure for the corrosion rate, the polarisation resistance of the counter electrode must be kept small with respect to that of the working electrode. A counter electrode made of gold or platinum which has a large surface compared to the working electrode would be nearly ideal for that purpose (for other possibilities see below).

As a standard procedure, you have to measure the rest potential first. The rest potential is then set potentiostatically, and then the working electrode is gradually polarised, both to the negative and then to the positive direction. The maximum polarisation should be small, some ten millivolts, in order to keep perturbations of the working electrode low.

In some cases, a very simple method is applicable. If the working electrode in the given electrolyte is not prone to local corrosion, it is allowed to use two (to the nearest) identical electrodes as working electrode and as counter electrode. In that case, the potential difference between both electrodes is equal to or near to zero. Connect the first electrode to the working electrode terminals and the other one to the counter electrode terminal, and also to the reference electrode terminal. Now polarise the working electrode, using either the built-in control source of the potentiostat or an external one. If you use the internal control source, you can e.g. set the polarisation to 10 mV, and then switch the source from zero to negative direction, and back, preceding by polarisation to the positive direction, and so on. The schematic is shown in fig. 3. If both electrodes have the same area, the total resistance is the sum of the two (more or less equal) polarisation resistances, that means that this total resistance must be divided by two.

6. Difference Potential Control and Permeation Measurements Using two Potentiostats

Potential differences between two electrodes separated by a membrane are frequently investigated, e.g. to determine the diffusion currents through that membrane: Hydrogen diffusibility is one of the standard applications. This potentiostatic technique requires two potentiostats.

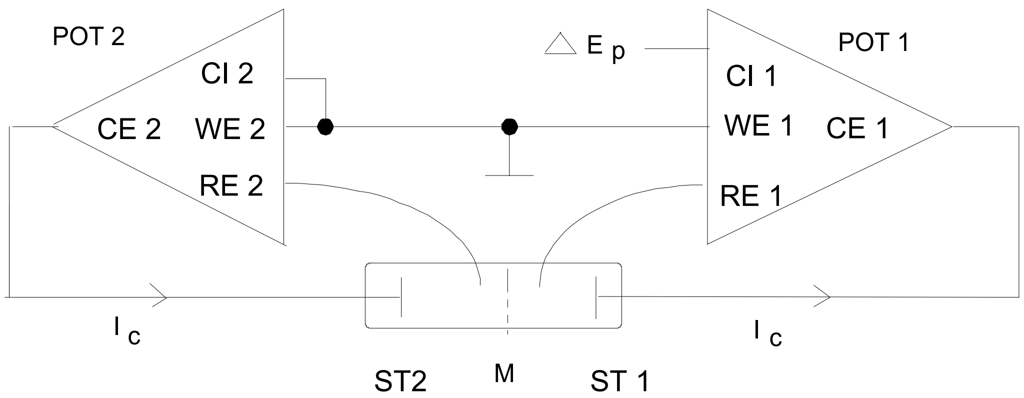
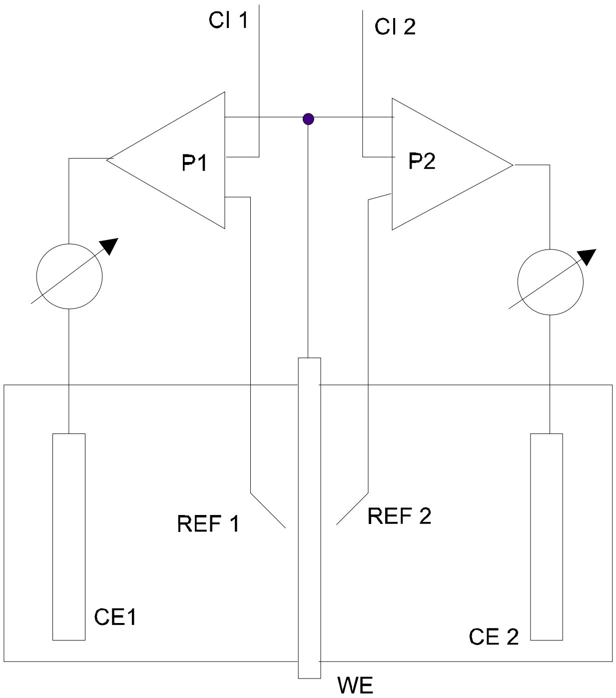


Fig. 4: Difference potential control using two potentiostats. Δ Ep Potential differen-ce, Ic cell current, M membrane

POT 1 controls the reference electrode RE 1 of the cell compartment 1 to virtual ground, as the control input CI 1 of POT 1 is grounded. The current that maintains this potential is delivered by the counter electrode CE 1. POT 2 controls the potential of the reference electrode RE 2 in the second compartment to that potential which is fed into the control input CI 2 of POT 2, resulting in a controlled potential difference between the two faces of the membrane.

The current that maintains the potential difference flows between the two controlling electrodes ST 1 and ST 2, they must be connected to the counter electrode terminals CE 1 and CE 2.

To avoid ring earths, the ground bridge of POT 2 must be removed. Both terminals WE 1 and WE 2 are then connected. For the measurement of small currents it is helpful to screen the cell as well as the cables. Note: When using our „current sink“ potentiostats, LB 95 L, LB 94 AR, or POS 88 (or their predecessors LB 75 L and POS 73), the connection between WE 1 and WE 2 must be connected to ground on either side. In that case, also this connection between WE 1 and WE 2 must be screened. Reason: The working electrode of these potentiostats is not really grounded, but kept to virtual ground.



To measure current - potential curves in this mode, the control input CI 2 of POT 2 must be used. As long as no overload lamp starts to glow, the potential difference is equal to the voltage fed into CI 2.

For permeation experiments, the same setup may be used. Instead of a semipermeable wall, a metal foil or sheet is inserted. If the currents shall be controlled or measured, it is recommended that the current measurement path is in the counter electrode line, and not in the working electrode line: In this case both potentiostas are connected to ground. Using other potentiostatic principles, one potentiostat must be separated from ground.

This setup may be used for either potentiostatic or galvanostatic control of the half cells.

Note: The ground bridge of one of the potentiostats has to be removed, its ground is fixed to the other potentiostat via the WE connection.

7. Measurement of the Redox Potential

If you use a gold electrode or a platinum electrode as counter electrode, there is a very simple way to measure the redox potential. Simply remove the counter electrode terminal from the counter electrode, and connect CE to the working electrode terminals. Then switch the potentiostat to rest potential measurement (operating selector to - Er at our potentiostats). The potential of the noble-metal electrode now is the redox - potential.

8. Using a Potentiostat as HiFi - Amplifier

Last not least a fine idea how to use the potentiostat as an excellent High - Fidelity amplifier. Extreme low noise (20 to 30 µV) and extreme low distortion due to the high slew rate which rarely are obtained from usual HiFi amplifiers will give you a new sensation. If you have a potentiostat which is able to deliver 2 A or more (e.g. our power potentiostats from the HP or STP series), you can use it according to the scheme shown below. The power of the speakers should be in excess of the power of the potentiostat.

The capacitor couple in the CE line to the speaker may be cancelled if you are sure that from the signal source no DC is introduced (may be checked with a voltmeter at the CE terminal). If not morte than some few millivolts DC are fed through, the sound is best when no protection capacitor is used.

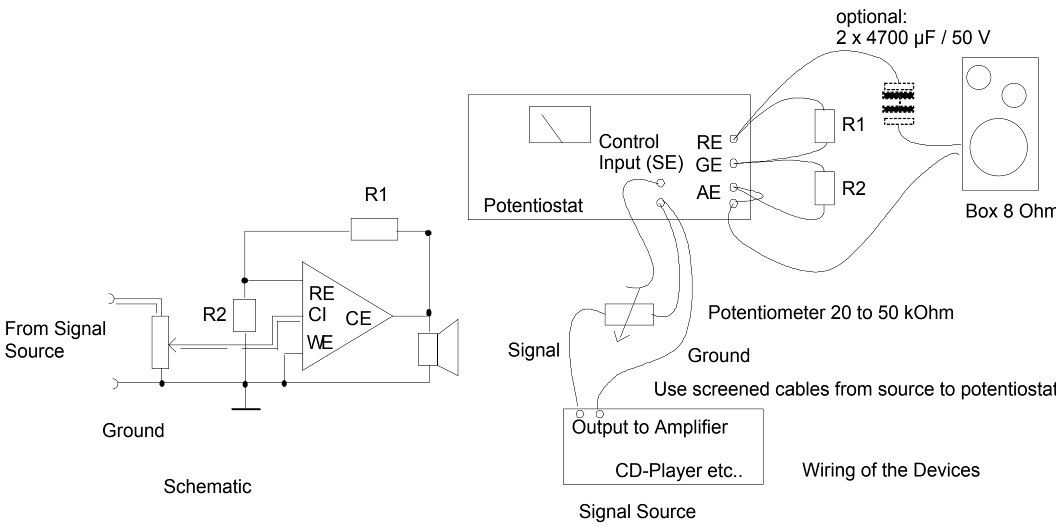


Fig. 6: Potentiostat as HiFi - amplifier

The proper values for R1 and R2 are listed in the table below, calculated for 8 Ohms resistance of the speaker. The currents are the max. currents of the potentiostat. The voltage is calculated to give best results at max. power without distortions. The potentiometer (20 to 50 kOhms) acts as volume control.

Current	Voltage	R1	R2	Power
2 A	16 V	15 kOhm	1 kOhm	32 W
3 A	24 V	24 kOhm	1 kOhm	72 W
5 A	40 V	39 kOhm	1 kOhm	200 W

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