INTRODUCTION

Electrochemistry has developed into a key science in many areas currently under development. To take just a few of the most recent examples, we might mention hydrogen technology, microelectronics, nanotechnologies and sensor elements.

Suitable professionally manufactured instruments are available nowadays for a wide spectrum of electrochemical methods of investigation - from simple, static measurements of potential through to the analysis of electrochemical noise. Modern devices allow high precision measurements to be made conveniently. It has now become the exception to find home-made, customised electronics being used for these purposes in laboratories. This is because an in-house construction capable of the precision and reliability of professional instruments calls for high level of detailed understanding along with a high level of commitment for its manufacture, and this resource may well be lost from the project itself.

However the brave new world of experimentation also has its downside. The notorious "black box" stands between the object of interest and the experimental result. Just what happens on the way from the electrical contacts at the measuring cell to the solid-looking digital display of a numerical value? Does this number, or this pretty graph in the printed document, truly represent the property that was looked for, or is it just an answer to a question that was never actually asked?

The fact is that modern instrumentation distances the scientist from the measurement process itself. A certain measure of understanding of how the measured data is acquired and what goes on within the black box is necessary if the capacity to be critical of the results is to be recreated.

It is for this reason that the present chapter takes on the task of reminding the reader of the fundamentals of electrochemical instrumentation. The principles underlying measurement set-ups for the most popular electrochemical methods are then further discussed. Significant emphasis is placed there on the recognition of parasitic effects. This should help us to avoid the artefacts of the measurement process, which would dramatically decrease the great meaning of correctly measured electrochemical information.

I. A REFRESHER: NECESSARY BASIC PRINCIPLES OF ELECTRICAL THEORY

Anyone who feels comfortable with terms such as "electrical resistance", "complex impedance", "parallel circuit", "series circuit ", "capacitance" and "inductance" can confidently skip the following section, and go straight on to section II. Those who read on will be introduced briefly to those fundamental principles of electrical theory that are necessary for understanding electrochemical measurement procedures.

Electromagnetism is one of the fundamental forces of nature, along with gravity and the nuclear forces [1]. Its components, electricity and magnetism, are linked to one another through Maxwell's equations, while its force is transmitted by photons. When considering electrochemical processes it is possible to leave the relationship between electromagnetism and the other natural forces safely to one side.

The time-scale of electrochemical processes is usually long, and rapidly changing electrical and magnetic fields rarely occur. For the same reason, wave aspects are negligible. It is usually therefore sufficient, for electrochemical purposes, to focus on electricity in isolation.

The elementary force associated with electricity is electric potential. For different locations in space, r, it assigns different potential energies, $E(r)$, adopted by bodies within that field, depending on their charge, Q.
The potential defines the "electrical tension", V, between two positions in spacewith the dimension "Volt" [V].

$$V = \Delta E / Q \quad [V] \tag{1}$$

When a charge, Q, moves between two such spatial elements within a time, t, this process is referred to as an "electrical current"

$$I = Q/t \quad [A] \tag{2}$$

having the unit "Ampere" [A]. If the spatial elements differ in voltage by ΔV, then the energy

$$\Delta E = \Delta V \cdot I \cdot t \ \ [VAs] \tag{3}$$

is released. The above processes can be more easily grasped if we restrict ourselves to their effects on precisely two spatial positions, the "poles", in a closed system. A full electrical description of such a "two-pole" comprises the voltage, V(t), between the poles and the current, I(t), that flows between the two poles.

Some special cases of V(t) and I(t) characterise particular electrical material classes. In particular, I=0 at constant V≠0 applies to insulators, V=0 at constant I≠0 describes superconductors, while $V \propto I$ [1] applies to Ohmic conductors.
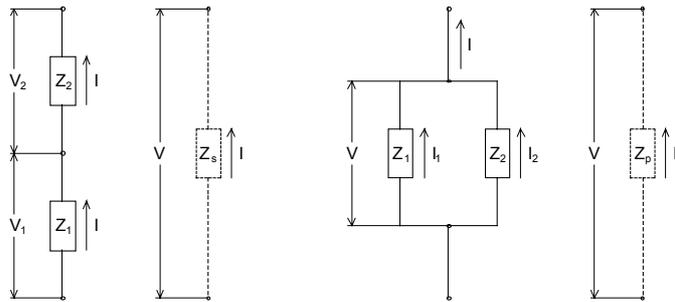

Fig. 1. Serial and parallel connection of two-poles Z_i with corresponding voltage V and current I.

If two two-poles are connected together at one end of each (series connection, Fig. 1, left), then the voltages add to form the total voltage at the open pole ends. The same current flows through both two-poles. If the two two-poles are connected at both ends (parallel circuit, Fig. 1, right), then those two two-poles have the same voltage. The total current through the joint pole is the sum of the partial currents in the individual two-poles.

$$Z_s = Z_1 + Z_2 \tag{4}$$

$$1/Z_p = 1/Z_1 + 1/Z_2 \tag{5}$$

The diagram moves straight on to illustrate the rules for the property of "impedance", Z=V/I, for two-poles (equations 4 and 5). These rules for serial and parallel connection can be extended to describe combinations of a number of two-poles to form a "network" (Fig. 2, equations 6 and 7) [2]. Kirchhoff's laws state that the sum of all potentials along a closed path within a network is zero, just like all the differences of altitude occurring during a walk in the mountains add up to zero if you return to your starting point. They state further that the sum of all the currents at a node is also zero. This is quite easy to understand, if we think of the node as a point with zero dimensions having one-dimensional inflows and outflows: what flows in must also flow out.
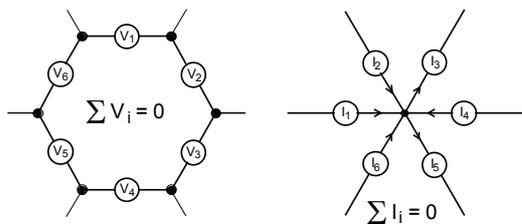

Fig. 2. Kirchhoff's law: Voltage and current in network meshes and nodes.

$$\sum_{i=1}^{n} V_i = 0 \tag{6}$$

$$\sum_{i=1}^{n} I_i = 0 \tag{7}$$

Two-poles such as Ohmic conductors whose behaviour is independent of time can be completely electrically described by curves relating voltage and current, either of the form V = f(I), or expressed as I = g(V). The most elementary representatives of this class are Ohmic conductors themselves, in which the function f(I) is simply (k · I) where k is a constant; in other words the relationship is one of direct proportionality.

The proportionality factor is the electrical resistance, R, and its unit is the Ohm [Ω]. The relationship $V \propto I$ is "Ohm's law" (Eq. 8).

$$V = R \cdot I \ \ [V] \tag{8}$$

---

[1] In the following the symbol ∝ is used to indicate proportionality between two magnitudes.

Ohmic relationships occur frequently in electrochemistry. Metallic and ionic conductors are the most frequent representatives of this group.
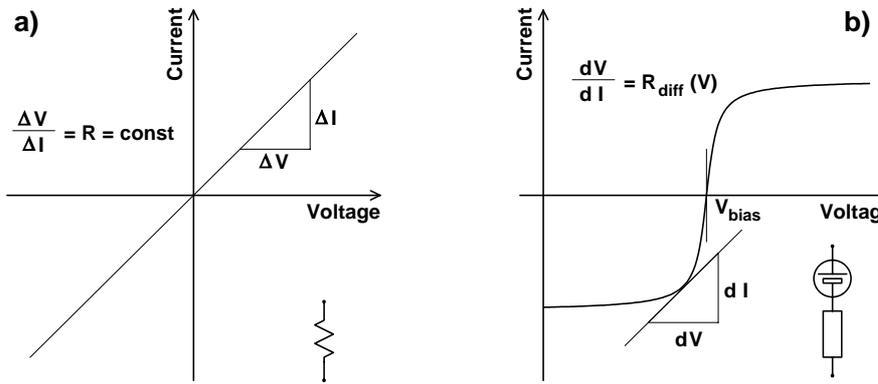

Fig. 3. Symbol and current-voltage-curve of an Ohmic resistance (a) and a non-linear two-pole including a potential source (b).

Current-voltage curves (Fig. 3a) for Ohmic resistors are straight lines through the origin at V=0 and I=0. Two-poles, such as resistors, that exhibit zero current at constant V=0 are referred to as "passive". An "active" two-pole results from connecting a passive two-pole in series with a voltage source. The voltage source symbolises a special two-pole with a constant potential difference that is independent of the current flowing. An example of the current-voltage curve for this sort of object is shown in Fig. 3b. It is found to be useful to generalise the concept of resistance to non-linear, active two-poles. Such a combination provides, for instance, a usable electrical model for the behaviour of fuel cells or batteries when operating close to their nominal voltage. A non-linear differential resistance is therefore defined

$$R_{diff} = (dV / dI)_V \qquad (9)$$

for selected sections of a current-voltage curve at constant V. Both linear and non-linear conductivity occur widely. Something approaching linearity (where R_{diff} is constant) is most often found when the potential between the poles under consideration affects the velocity with which charge is transported but does not have a significant effect on the number of charge carriers available for that transport. This is most often the case when the total potential difference is distributed more or less evenly over the space between the poles. If, on the other hand, high field strengths occur locally, as can happen when the conductivity mechanisms change at phase boundaries, this can form active charge carrier. The activation processes lead to an exponential dependence of conductivity on the potential difference. The resulting current-voltage curve often has the form

$$I = I_1 \cdot \left(e^{\frac{(V-V_1)}{b_1 \cdot V_T}} - 1 \right) + I_2 \cdot \left(e^{\frac{(V-V_2)}{b_2 \cdot V_T}} - 1 \right) \ ...$$

$$(10)$$

$$I = \sum_{i=1}^{n} I_i \cdot \left(e^{\frac{(V-V_i)}{b_i \cdot V_T}} - 1 \right)$$

where b_i represents the characteristic constants, I_i the current, V_i the activation potential and V_T is the "temperature voltage". The magnitude V_T has a value of approx. 26mV at room temperature, and is composed only of physical constants and the temperature:

$$V_T = R \cdot T / F \qquad (11)$$

Here R represents the general gas constant, F the Faraday constant and T the absolute temperature. Common examples of current-voltage curves described by Eq. 10 are the characteristic curves of semiconductor barrier layers ("diode curves") and the electrochemical transfer reaction (the "Butler-Volmer" curve). Differentiating Eq. 10 shows that the differential resistance of such a current-voltage curve in the simplest case of n=1 takes the value

$$R_{diff} = b \cdot V_T / (I+I_1) \qquad (12)$$

We can now gain a glimpse of the usefulness of the concept of differential resistance:

- The coefficients, b, can easily be determined from the curve of R_{diff} against current. Generally they are around $b \approx z$, where z is the effective number of the charge carriers responsible for the current flow. In this way they reveal something about the mechanism of the current-carrying processes.
- At the point where I=0 it is possible to determine the "exchange currents", I_i, leading us, for example, to reaction rates.
- The temperature dependency of R_{diff} allows us to determine band gaps in semiconductors and activation energies $E_i = V_i \cdot Q_e$ (where Q_e is the elementary electron charge) for electrochemical processes.

VOLTAGE, CURRENT AND TIME: THE ROLE OF TIME

So far we have restricted ourselves to cases in which the effect of time can be ignored, and in which the two-pole can be characterised by an unambiguous current-voltage curve. In fact, nature seldom approximates to this limiting case. The simple idea that "everything changes" is only one reason for this. Even in the absence of ageing effects, in order to observe time-independent laws it is necessary first of all for temporal changes to entirely subside. The following example will illustrate this.

Metals are typical Ohmic conductors. However the resistance of metals is, to a first approximation, proportional to temperature. The current-voltage curve of the tungsten filament of a conventional light bulb exhibits Ohmic resistance at small currents. If the curve is, however, traced at higher currents, the electrical power dissipated

$$N = V \cdot I \tag{13}$$

leads over time to a noticeable rise in temperature through electrical heating. A very rapid recording of the curve does not give the filament time to heat up, and illustrates the linear current-voltage relationship of the "cold resistance". If, on the other hand, the measurement is taken sufficiently slowly for the electrical power and the radiated heat to reach approximate equilibrium, then a significantly bent "steady state" current-voltage curve (Fig. 4) is obtained.
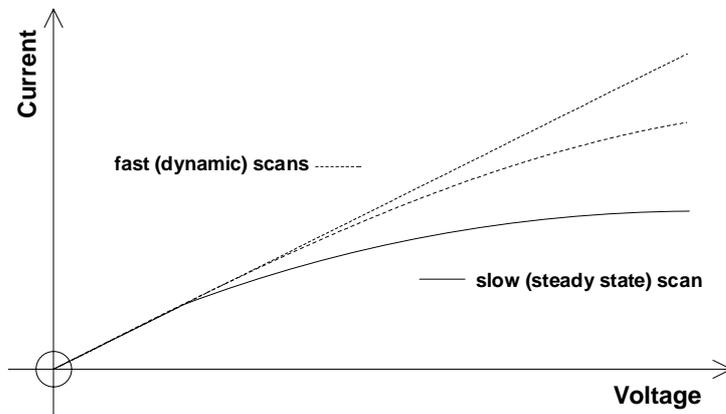
Two-poles such as incandescent bulbs therefore exhibit an "electrical memory". Both voltage and the current have an effect on the two-pole, so that the current no longer depends purely on the instantaneous value of the voltage at time t_1, but also on what has previously happened during $t < t_1$ (equations 14 and 15). Similar considerations apply to the dependence of the voltage on current.

Fig. 4. Fast "dynamic" (dotted lines) and slow "steady state" (solid line) current voltage curves of a light bulb.

$$I(t_1) = f[V(t \leq t_1)] \tag{14}$$

$$V(t_1) = f[I(t \leq t_1)] \tag{15}$$

Objects with electrical memory can be described by time-dependent differential equations such as equations 16 or 17:

$$I(t) = a_0 \cdot V + a_1 \cdot dV/dt + a_2 \cdot d^2V/dt^2 + \ldots \tag{16}$$

$$V(t) = b_0 \cdot I + b_1 \cdot dI/dt + b_2 \cdot d^2I/dt^2 + \ldots \tag{17}$$

The most elementary representatives of such two-poles are, on the one hand, the capacitor and on the other hand, as an example of objects that behave inductively, the coil. Capacitors are electrical components in which the voltage, V, between the terminals is proportional to the electrical charge, Q, that has passed through the terminals (Eq. 18). The quotient, C, is known as the capacitance

$$V = Q/C \tag{18}$$

The current, I, which is the charge, Q, flowing in unit time (Eq. 19), leads to the time law

$$I = dQ/dt \tag{19}$$

for the capacitor in differential form (Eq. 20), where the symbol for the time derivative of X, dX/dt is $\overset{\bullet}{X}$.

$$I = C \cdot \frac{dV}{dt} = C \cdot \overset{\bullet}{V} \tag{20}$$

If Eq. 20 is solved for V (Eq. 21), then the electrical memory (Eq. 15) can be immediately seen at the limits of the integral.

$$V(t_1) = \frac{1}{C} \cdot \int_{t=0}^{t=t_1} I \cdot dt \tag{21}$$

The electrical properties of a capacitor can be illustrated by interpreting equations 20 and 21: When the voltage at the terminals is constant, no current flows. If the voltage changes, the current at the terminals is proportional to the rate of change in the voltage, dV/dt and to the capacitance, C. The voltage, V, across the capacitor is proportional to the current that has flown over time, and therefore to the charge, Q, and inversely proportional to the capacitance. Let us avoid one widespread misconception by making it clear that a capacitor does not "store" any net charge. Just as in the case of resistors or of any other two-pole, the same amount of charge that flows into one pole emerges from the other – see Kirchhoff's law. The big difference between a capacitor and a resistor is the energetic reversibility. The electrical energy, $V \cdot I \cdot t$, which is dissipated to the environment by a resistor, is stored reversibly in a capacitor.
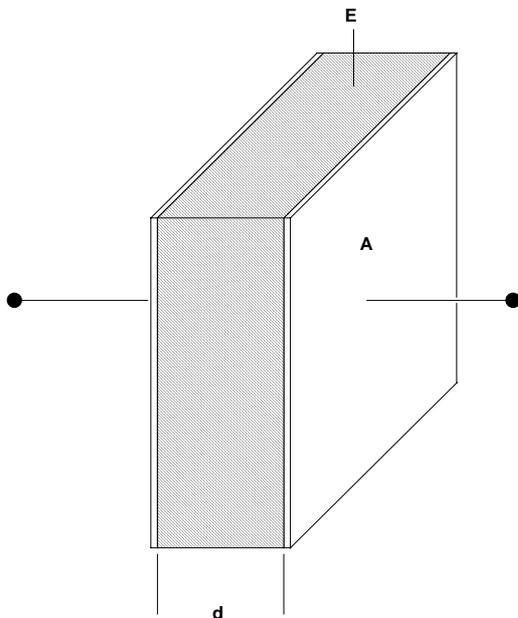

Fig. 5 Plate capacitor with metal plates of area A and distance d, filled with a dielectric medium E.

From the physical point of view, capacitive behaviour is as elementary as is resistive behaviour. The most common form of capacitance is the plate capacitor (Fig. 5). The energy is stored by holding the difference in charge through an electrical field on two facing conductive surfaces such as two sheets of metal foil. The capacitance of a plate capacitor, C_{pc} (Eq. 22) is proportional to the area of the plates, A, and to the dielectric constant, ε, of the material between the plates, known as the dielectric, E. It also increases as the distance between the plates, d, is reduced.

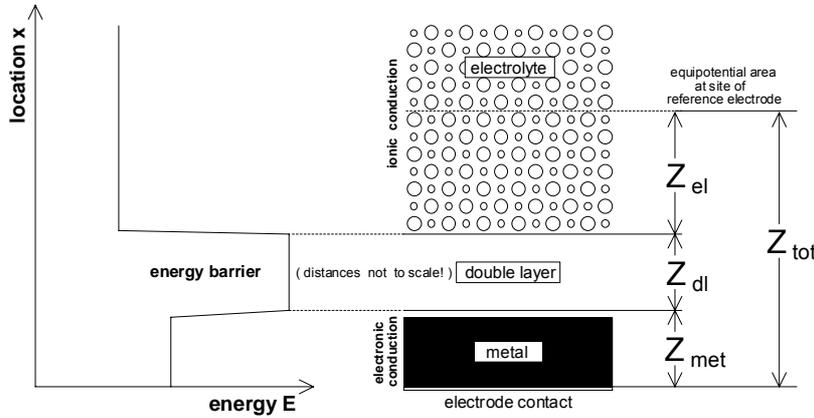$$C_{pc} = \frac{\varepsilon \cdot \varepsilon_0 \cdot A}{d} \tag{22}$$

The dielectric constant ε_0 of vacuum is about $8.85 \cdot 10^{-12}$ [As/Vm]. Capacitances are often seen from their negative side in electrochemical applications: it is not just plate capacitors, but any other conductor extending through space that has a capacitance. The electrical leads to an object being measured are exclusively intended to transfer information between the object and the measuring instrument – but this information can, unfortunately, be corrupted by the "stray capacitance".

Structures analogous to plate capacitors also play a useful role in electrochemistry [4]. Coating systems or other layers on the surfaces of metals form, together with the electrolytes, plate capacitor structures. Eq. 22 shows that if the magnitudes C, ε and A are known, it is possible to determine the layer thickness, d, which is useful in the study of coatings.

The capacitance of the electrochemical double layer (Fig. 6) is also created by a "plate capacitor" consisting of electrolyte and electrode. The role of dielectric is performed here by the – more or less – insulating energy barrier at the location of the transition between ion conduction and electron conduction (the "electrochemical double layer"). In contrast to a dielectric, the tiny "thickness" of the double layer in coating layers easily causes high field-strengths to develop – with the consequential dependency of physical behaviour on potential.

Capacitance of adsorption and crystallisation, and the capacitance of the blocked finite diffusion are typical examples of another type of capacitance which will be discussed in more detail in the chapter on Electrochemical Impedance Spectroscopy EIS. Charge transport is linked here to the transport of material. It is not the effect of the quantity of charge on the electrical field that leads to capacitive behaviour in accordance with Eq. 21, but rather the electrochemical activity associated with the material concentration. In accordance with the Nernst equation (Eq. 23) it is possible to assign different potentials to charged species with different activities, a_i, in different regions of space (phases), so assigning one voltage, V, to two phases. The factors V_T and b have the significance explained above.

$$V_{2,1} = b \cdot V_T \cdot \ln\left(\frac{a_2}{a_1}\right)$$ (23)

Eq. 23 illustrates one of the great strengths of electrical methods applied to chemistry: if the activities, a_i, represent the concentrations, c_i, then concentration relationships can easily be determined from V. This provides the key to a whole range of electro-analytic methods.

Let us now discuss a second form of electrical memory:

Inductive behaviour is displayed by electrical components in which the voltage, V, between the terminals is proportional to the rate of change of the current flowing in it, dI/dt. The physical properties follow the time-dependency law for inductance, L:

$$V = L \cdot \frac{dI}{dt} = L \cdot \dot{I}$$ (24)

If Eq. 24 is solved for I (Eq. 25), then the electrical memory (Eq. 14) of the inductance can be seen again in the limits of the integral, as it was in the case of capacitance.

$$I(t_1) = \frac{1}{L} \cdot \int_{t=0}^{t=t_1} V \cdot dt$$ (25)

The behaviour of inductance is complementary to that of capacitance: equations 20 and 21 can be converted into equations 24 and 25 by swapping the roles of voltage and current. An interpretation of equations 24 and 25 shows that the voltage is zero when the current is constant in an inductive two-pole. If the current changes, the voltage at the terminals is proportional to the rate of change of current, dI/dt, and to the inductance, L. Like those associated with capacitance, the electrical processes in an inductance are reversible – inductors store electrical energy. Inductance is most

typically found in an inductor constructed as a coil. The energy here, $V \cdot I \cdot t$ is stored as the difference in the "electrical impulse" $\Delta V \cdot t$ in the associated magnetic field. Inductances most usually show an unpleasant aspect in electrochemical applications: every conductor that extends through space shows the same kind of inductive behaviour as a coil. Like the stray capacitance of electrical leads, their "stray inductance" can also lead to errors in the information provided about the measured object. In the section on constructional tips for electrical cells, the consequences of stray effects will be examined in more detail.

Similarly to the capacitor-like behaviour, inductive behaviour is not linked to the appearance of magnetic fields. Eq. 25 shows that for su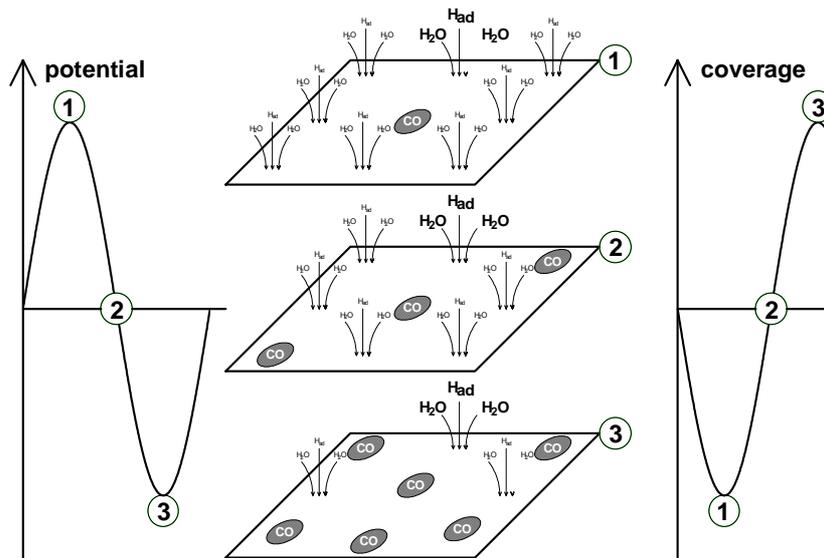ch a system, the current depends on the history of the potential. If a flow of mass is required, so that an electrochemical system can follow the potential curve by adopting a new current ("relaxation"), time-dependent laws similar to Eq. 25 may apply. The same is true if the conductivity of a system rises significantly with the temperature, but the current corresponding to the electrical heating settles with some delay due to the system's thermal inertia.

Relaxation inductances can be seen in a system in which activation and re-passivation processes take place corresponding to the changing potential – as is often the case in corrosion processes or in the CO poisoning of fuel cell anodes (Fig. 7).

Fig. 7 The potential dependency of the share of electrochemical active surface may lead to inductive appearance. In this example of a PEM fuel cell, carbon monoxide blocks the active surface for the main electrochemical reaction, the hydrogen oxidation. Three states of coverage are sketched, beginning with the most anodic state. The coverage will follow the potential with a certain delay in time what will cause "relaxation inductance".

Inductance due to thermal relaxation occurs as soon as electrical heating plays a noticeable part in electrolytes – fuel cells and electrolysis cells are examples of this.

FROM DIFFERENTIAL RESISTANCE TO IMPEDANCE

We have seen that two-poles are generally described electrically by time-dependent differential equations for voltage and current. In the case of the elementary two-poles, capacitance, inductance, and particularly resistance, these time-dependent laws are manageable and easily understood. If, however, we imagine a network composed of these components it is soon found that a mathematical treatment of the resulting system of differential equations easily becomes difficult. If, in addition to these fundamental elements, more complicated, non-linear descriptions of electrochemical processes are also found, analysis in the "time domain" becomes nothing but an exercise in mathematics.

There is, however, another approach available. As a first step the signal (preferably the voltage) is divided into a stationary component and a dynamic component. In the stationary case, i.e. the time-independent case, the system of differential equations simplifies itself to expressions similar to Eq. 10. They determine the "working point" (bias) on the stationary current-voltage curve. The dynamic component is investigated in a second step. The key here is to – provisionally – restrict the analysis to periodic sinusoidal time signals of voltage and current. Sinusoidal signals have the convenient property that all the functions of the signals in linear systems are, in turn, sinusoidal and have the same period – regardless of how complicated the time-dependent system of differential equations is. This is of course due to the fact that all derivatives of sinusoidal signals and their linear combinations are also sinusoidal.

Finally, a simple trick makes it possible to model non-linear systems: in cases where the signal V(t) consists of a constant, stationary component V_{bias} onto which a very small dynamic component, $V_\sim$ (Fig. 8, Eq. 26) is superimposed, non-linear time-dependent laws can be developed as a power series, and truncated after the linear term.
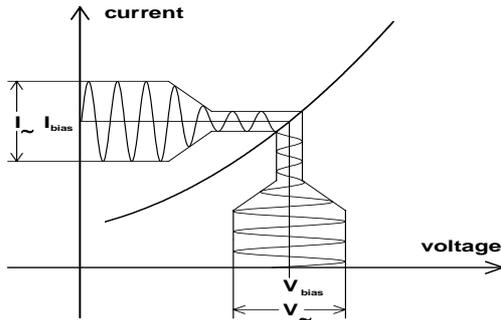
$$V(t) = V_{bias} + V_\sim \tag{26}$$

Like the voltage, the resulting current can be split into a stationary component, I_{bias}, and a dynamic component, $I_\sim$ (Eq. 27).

$$I(t) = I_{bias} + I_\sim \tag{27}$$

Fig. 8 Modulation of the steady state current voltage curve at a certain bias by a small sinusoidal voltage results in a sinusoidal current. AC voltage and current exhibit the same periodicity with a constant phase shift.

Sinusoidal time signals, $V_\sim(t)$, are usefully expressed using Euler's relation [5], Eq. 28, in complex notation. In this way cosine and sine components can conveniently be combined into one "periodicity factor", $e^{j\omega t}$, and separated from the peak value, $V_\wedge$, otherwise known as the amplitude, as in Eq. 29, where j is the imaginary unit and $\omega = 2 \cdot \pi \cdot f$ represents the angular frequency.

$$e^{jx} = \cos x + j \cdot \sin x \tag{28}$$

$$V_\sim = V_\wedge \cdot e^{j\omega t} \tag{29}$$

$$I_\sim = I_\wedge \cdot e^{j(\omega t + \varphi)} = \quad I_\wedge \cdot e^{j\omega t} \cdot e^{j\varphi} \tag{30}$$

Making the assumption, mentioned above, of a small value of $V_\sim$, the current associated with Eq. 29 follows from Eq. 30. The periodicity factor for $I_\sim$ is extended with a "phase shift" between the voltage and the current characteristic for the two-pole system with a value $-\pi \leq \varphi \leq +\pi$. The particular advantage of this procedure is that an "alternating current" analogue to the differential resistance, R_{diff}, can be found. If the small components $V_\sim$ and $I_\sim$ are divided, analogously to the derivation of R_{diff}, the periodicity factors reduce to the component that represents the phase shift. We obtain the complex analogue to R_{diff}, namely the AC "impedance" Z of the two-pole:

$$Z(f) = \frac{V_\sim}{I_\sim} = \frac{V_\wedge}{I_\wedge} \cdot e^{-j\varphi} \tag{31}$$

Like the magnitudes $V_\sim$ and $I_\sim$, Z generally depends on the frequency, f, in a way characteristic for the two-pole. It is now possible to understand where the strength of the impedance concept lies as compared with stationary methods: if a number of Ohmic 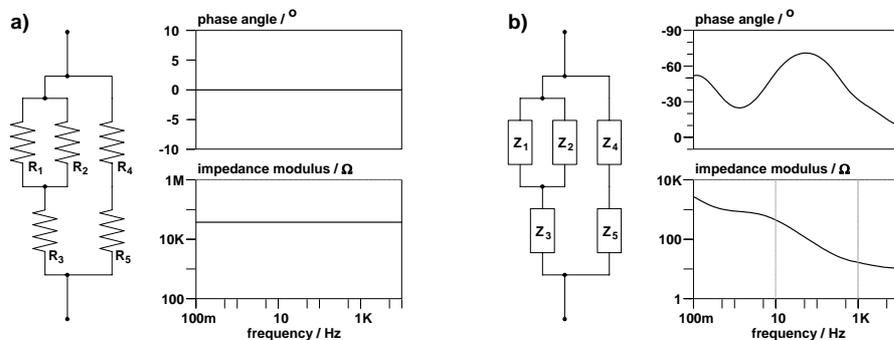resistances are combined into any kind of network with two poles (Fig. 9), the values of the individual resistances can not be determined from the total resistance of the two-pole. The case of frequency-dependent impedances is, however, different: if the frequency response of the individual components is

Fig. 9 Two-poles built from resistance networks (a) and impedance networks (b) with typical impedance spectra (Bode diagrams, see Eq. 37).

significantly different, it is possible in favourable cases to determine the full set of parameters, if the network is examined at a sufficiently large number of different frequencies.

As has already been explained, characteristic impedances can be assigned to electrochemical processes. In electrochemical impedance spectroscopy (EIS) the impedance of an electrochemical cell is investigated over a very wide range of frequencies. An impedance spectrum, or an impedance transfer function, is measured. The network data decoded from this can be used to derive chemical and kinetic parameters, mechanisms and electrode topologies.

So far, the route from the general time-dependent law (equations 16 and 17) to the impedance transfer function (Eq. 31) has only been presented in a brief and abstract form. The principles of the method for the simplest cases can be understood in the following derivation of the impedance for capacitance and inductance.

We begin with the time-dependent law for the capacitor in differential form (Eq. 20)

$$I = C \cdot \frac{dV}{dt} = C \cdot \dot{V}$$

and expand the voltage function for the small, sinusoidal test function, (Eq. 29.)

$$V_\sim = V_\wedge \cdot e^{j\omega t}$$

$$dV/dt = \dot{V} = V_\wedge \cdot e^{j\omega t} \cdot j\omega = V_\sim \cdot j\omega \tag{32}$$

Differentiating Eq. 29, we obtain the expression in Eq. 32 for the time derivative of the sinusoidal voltage, dV/dt.

The impedance Z_C is then easily obtained by inserting the result into Eq. 20 (equations 33 and 34).

$$I_\sim = C \cdot \dot{V}_\sim = C \cdot V_\sim \cdot j\omega \tag{33}$$

$$Z_C(f) = \frac{V_\sim}{I_\sim} = \frac{1}{2\pi f C} \cdot \frac{1}{j} \qquad [\Omega] \tag{34}$$

The inductance behaves in a manner complementary to the capacitance – if the places of voltage and current are swapped in the above derivation, the impedance Z_L^* of the inductance (Eq. 35) is obtained in a manner similar to that of Eq. 34.

$$Z_L(f) = \frac{V_\sim}{I_\sim} = 2\pi f L j \qquad [\Omega] \tag{35}$$

In principle, we have inserted the operator $e^{j\omega t}$ into the time law of the capacitor, which is a function of the three variables voltage, current and time, converting it into a function of frequency, Z. Its origin as a function of several variables is indicated by the complex character of Z: instead of the original function of three variables, we now have obtained two functions of one variable, namely the functions for the real and imaginary components of Z. Real functions of one variable can be meaningfully represented in one plane. Generally speaking, two methods of graphical representation have become accepted for the complex function Z. In the "Nyquist diagram" or the "complex plane plot", the real and imaginary parts are plotted on linear axes against one another in one plane (Fig. 10, Eq. 36). The frequency variable does not appear directly. If the logarithm of the complex impedance is formed, then the components of the complex logarithm (Eq. 37) can be plotted on a plane diagram of the two components against the logarithm of frequency (a Bode diagram).

$$x = \text{Re}\{ Z(f) \}, \qquad y = \text{Im}\{ Z(f) \} \tag{36}$$

$$x = \ln f / \text{Hz}, \qquad y_{|Z|} = \text{Re}\{ \ln(Z(f) \} \qquad y_\varphi = \text{Im}\{ \ln(Z(f) \} \tag{37}$$

A wide range of methods for representing the frequency dependency of magnitudes directly derived from the impedance is in common use. Capacitance, inductance, the complex dielectric constant, the dielectric modulus, complex refractive index and so forth may be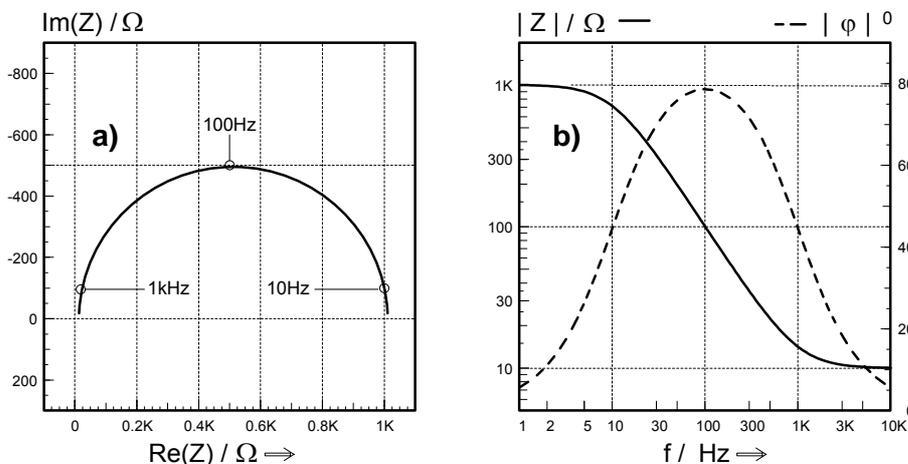 displayed. What they all have in common is that, in contrast to the elementary approach above, specifice models are hypothesised as to how the observed electrical impedance arises. We do not need to pursue these considerations any further here but keep in mind the principle of AC impedance – many aspects of electrochemical instrumentation can be more easily

Fig. 10 Typical plot of an impedance transfer function: Complex Plane Plot (a) and Bode Diagram (b).

understood with their aid.

This excursion into fundamental electrical principles has prepared us sufficiently to follow those who are more advanced into the next chapter.

II. FUNDAMENTALS OF ELECTROCHEMICAL INSTRUMENTATION: MEASUREMENT OF POTENTIAL AND CURRENT IN ELECTROCHEMICAL CELLS

Electrochemistry is the chemistry of redox processes. When the anodic part of the reaction (Eq. 38, oxidation of a reduction agent) takes place in a separate site from the cathodic part of the reaction (Eq. 39, reduction of an oxidation agent), then an electron exchange current is not immediately possible between the reaction partners.
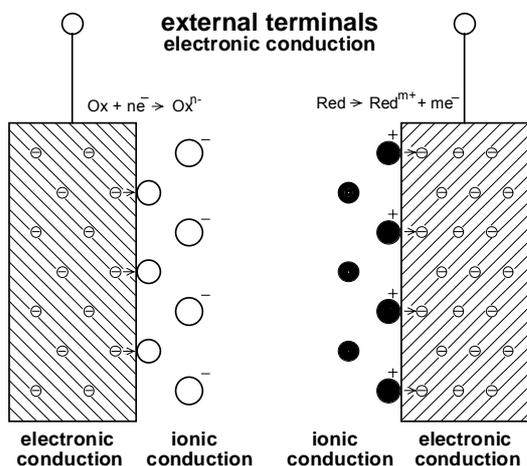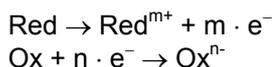

Fig. 11 Two electrodes, connected by ionic conducting media, build an electrochemical „full cell" arrangement. The indicated reactions will take place, if current flow between the external terminals is enabled.

$$Red \rightarrow Red^{m+} + m \cdot e^-$$
$$Ox + n \cdot e^- \rightarrow Ox^{n-}$$

In order to maintain charge neutrality, the electrons must take the route through an additional electron conductor that electrically joins the anode and cathode sites. If the connection is accessible outside the electrochemical system, the exchange currents can be monitored in the external part of the electrical circuit. The sequence of electron conductor and ion conductor, and again of ion conductor and electron conductor thus represents a full cell (two-electrode cells, Fig. 11; arrangements with additional potential probes, and cells with three or four electrodes are discussed further below).

Two elementary limiting cases must be distinguished in the two-electrode experiment:

1. The external electrical circuit is completely interrupted at a certain point (Fig.12a). At the phase boundaries between ionic conductors and electron conductors potential differences develop, and these precisely oppose the thermodynamic driving force of the partial reaction. Both anodic and cathodic forward and reverse reactions reach equilibrium. The net electrochemical reaction is thus inhibited, and no external current flows. As in any other

electrical circuit, the sum of all the partial potentials in the loop is zero (Kirchhoff's law, Eq. 40).

$$\sum_{i=1}^{k} V_i = 0 \qquad (40)$$

In the simplest case, shown in the sketch, only the partial potentials of the anode and the cathode need to be considered. This means that, apart from the arithmetic sign, the potential found at the terminals of the circuit interruption is equal to the sum of the anode and cathode potentials. The observable electrical magnitude is a voltage (the full cell's OCP), the current being zero.

1. The external electrical circuit is completed by a load at the open ends. In the example shown, this is an Ohmic resistance (Fig. 12b). If the potential relationships from limiting case 1 are transferred to limiting case 2, a current given by

$$I_r = \frac{OCP}{R} \qquad (41)$$

should flow through the resistance (Eq. 41), in accordance with Ohm's law.

Both anodic and cathodic forward and reverse reactions lose their equilibrium. The net electrochemical reaction begins. The electrical current loading and the chemical reactions, however, both develop additional inhibiting potential differences at the phase boundaries (e.g. charge transfer polarisation and diffusion over-potential) the nature of which is described extensively in other chapters.
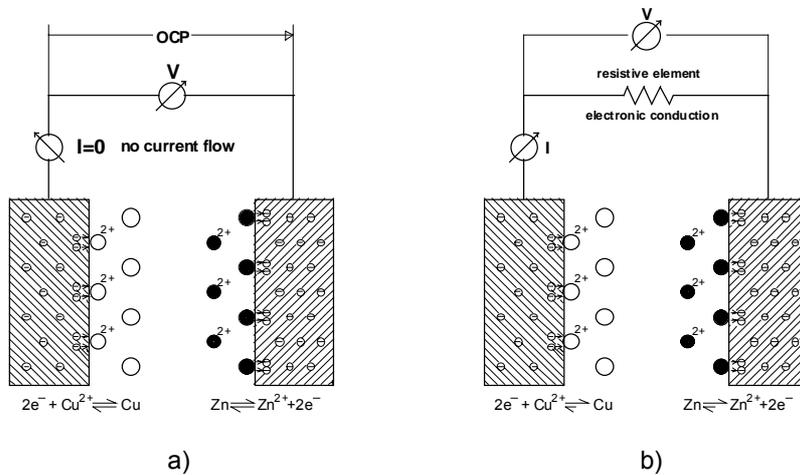
Consequently the current, I_r, cannot flow continuously. Instead, a time-dependent current $|I(t)| < |I_r|$, which can become stable after a certain time, arises. The observable physical magnitudes are the voltage at the resistor and the current in the electrical circuit.

Fig. 12 Two limiting cases for an electrochemical full cell: The electrochemical net reaction is inhibited due to an inhibited external current flow (a). The Open Circuit Potential OCP appears at the terminals. In case of an enabled external current flow (b) an electrochemical net reaction takes place according to the difference in the free energy.

THE IDEAL MEASUREMENT

Fundamentally, any measurement has an effect on the measured object – this is in fact a necessary consequence of the quantum nature of the world. In the classical, limiting case it is still nevertheless possible to come close to the ideal of a measurement without influence.

In other words, an ideal instrument behaves as if it were not actually part of the system. Putting it more precisely, if undesirable side-effects to be avoided, the instrument must not remove any energy from the system under investigation ("zero-power measurement").

In the case of measuring potential as shown in Fig. 12a it is easy to see that an ideal measuring instrument connected between the terminals of the interruption in the circuit must not cause any current to flow. Otherwise, the instrument itself has an effect similar to the load resistor in arrangement 12b, causing the potential, V(t), to differ from the OCP.

MEASURING POTENTIAL – AN EASY JOB?

Technical solutions for potential measuring instruments are not perfect. Fig. 13 expresses the non-ideal properties relevant to this case for a voltmeter in the form of an equivalent circuit diagram. Components are connected in parallel with the ideal virtual instrument here, resulting in the flow of parasitic current.
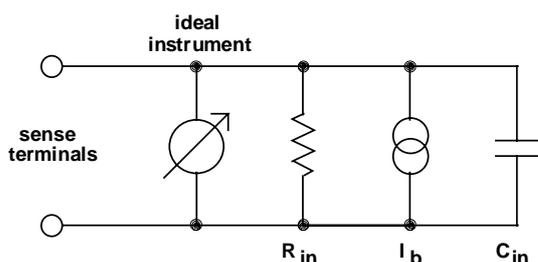
Fig. 13 Input resistance, input capacitance and bias current characterises a technical voltmeter.

The symbol for the resistor R_{in} stands for the unwanted component in the current that is proportional to a constant measured potential in accordance with Ohm's law. The current source I_b, on the other hand, represents a component in the current that is independent of the measured potential (bias - or leakage current).

In addition to the most important characteristics of the input resistance and leakage current, the input capacitance C_{in} is also significant. A reminder: capacitors are electrical components in which the voltage, V, between the terminals is proportional to the stored electrical charge, Q (see also chapter I. Eq. 18-20).

On the other hand the current through the capacitor, I, is proportional to the rate of change of charge, dQ/dt. From this we can conclude that the input capacitance of a voltmeter is of no concern to us provided the voltage being measured is constant. We can assume that in the case of typical "DC" method[2] only the instrument input resistance and its leakage current need to be considered.

The following example, however, illustrates how complex an apparently simple measurement of equilibrium potential can be. The equilibrium potential of a metal plate (with an area of about 20 cm^2) protected from corrosion by an organic polymer (with a thickness of about 100 μm) is to be measured. The counter electrode is to be a low resistance reference electrode, such as a silver mesh coated with AgCl in a chloride electrolyte, whose contribution to the total potential (V_{ref}) is assumed to be constant and known (Fig. 14).
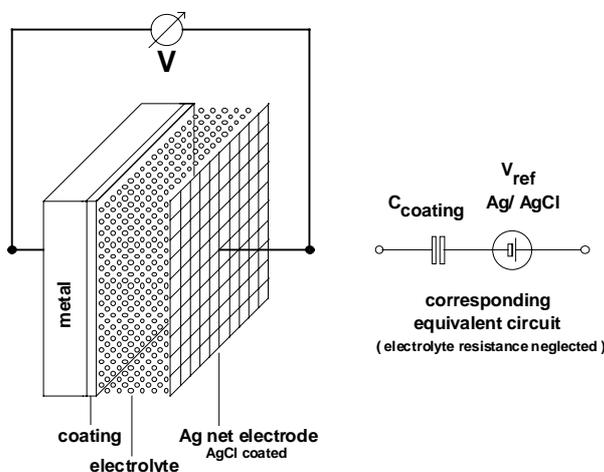

Fig. 14 Potential measurement at a coated metal electrode (left). At first approximation the electrode appears as the circuit sketched at the right hand side.

The metal-polymer-electrolyte phase sequence itself behaves in a manner similar to a capacitor; the contributions from reactions expressed in equations 38 and 39 are assumed to be negligible. In order to describe the object being measured in a simplified way we make use of an equivalent circuit diagram, similar to the way in which we characterised a voltmeter. A description that includes a voltage source and a capacitor is sufficient for the sketched case.

We assume that there is no charge on the capacitor, C_e, before the measuring instrument is connected. If we could measure without side-effects, the cell voltage would be given by V=V_{ref}. If, however, our instrument has a small input capacitance, C_m, not negligible in comparison with the capacitance of the electrode, then after connection of the voltmeter a charge of

$$Q = V_{ref} \cdot C_{ser} \quad \text{where} \quad C_{ser} = (1/C_m + 1/C_e)^{-1}$$

is distributed over the series network, C_{ser}, consisting of the capacitances of the electrode and the measuring instrument. Only a fraction $V_{ref} = C_e/(C_m+C_e)$ is then measured. If the input capacitance of the measuring instrument is about 50 pF (a typical input capacitance for a broad band voltmeter between the working and reference electrode terminals), the measurement of the equilibrium potential of the film electrode (with an electrode capacitance of approx. 1 nF) is already distorted by about 5%.

---

[2] In what follows, "DC" methods refer to standard electrochemical methods in which the measured magnitudes only change slowly in comparison with the reaction times of the system under investigation ("stationary" or "quasi-stationary" methods).

If, in the expectation of a better absolute precision, one uses a commercial 6½-digit multimeter (with an input capacitance of approx. 1 nF), then only half the value of V_{ref} is measured!

The above example does not just demonstrate pitfalls of apparently simple measurement tasks, it was also selected in order to illustrate the problems associated with the concept of equilibrium potential: Because the measurement of potential with no side-effects is in fact an illusion, the determination of equilibrium potential is only meaningful when redox reactions following Eq. 38 and 39 are proceeding at the boundaries between the phases. Their equilibrium may only be lightly disturbed by the unavoidable injection of charge involved in the measurement. Material reserves of the reagents in Eq. 38 and 39 must therefore exist for buffering. If processes that can stabilise the potential are entirely absent, such as would be the case on an electrode with a perfect layer of insulation, then measurement of the equilibrium potential is not possible.

REQUIREMENTS OF AN INSTRUMENT FOR MEASURING POTENTIAL

We can now summarise our experience with the measurement of potential:

- A good voltmeter should not cause any additional current flow as a result of its presence in the measured circuit.
- Input resistance, leakage current and input capacitance are the most important characteristics of a voltmeter.
- The input resistance should be large in comparison with the internal resistance of the measured object.
- The leakage current should be negligibly small in comparison with the electrochemical exchange current in the object.
- The dynamic current component resulting from the input capacitance when the potential changes over time must also be negligibly small in comparison with the exchange current. For this reason, the input capacitance must be particularly small when fast measurements are being taken.
- If these rules are not followed, such as would be the case when no potential stabilizing electrochemical reaction is taking place, the measurement of potential is irrelevant.

Tab.1.: Typical source impedance, R_{src}, of the electrochemical system, acceptable measuring instrument input resistance R_{in}, with input capacitance, and acceptable leakage current I_b

Application of potential measurement	R_{src}	R_{in}, C_{in}	I_b
Cell voltage of batteries and fuel cells.	10^{-4}-10 Ω	10^4 Ω // 10^{-9} F	µA - mA
Single electrode potentials in batteries and fuel cells, corrosion in auto-passive systems	10^2-10^6 Ω	10^8 Ω // 10^{-9} F	nA - µA
Corrosion under paints and coatings, potential measurement on micro-electrodes and electrochemical sensors	10^4-10^9 Ω	10^{12} Ω // 10^{-10} F	fA - pA
SECM and other nano electrodes	10^4-10^9 Ω	10^{12} Ω // 10^{-12} F	fA - pA
Electrochemical potential noise	10^2-10^9 Ω	10^{12} Ω // 10^{-10} F	fA - pA

The suitability of the instrument depends heavily, of course, on the system being investigated. The parasitic properties of a simple hand multimeter ($\approx$10 MΩ input resistance, $\approx$1 nF input capacitance, leakage current < 100pA) do not make any noticeable contribution to the measuring error when measuring the cell voltage of batteries or fuel cells. However the same instrument will yield grossly incorrect measurements when measuring a pH value using a glass electrode. Table 1 provides a general overview of the requirements of voltmeters for particular applications.

MEASURING THE CELL UNDER LOAD: MEASURING CURRENT

So far we have only been concerned with measuring potential. Now let us consider the measurement of current. We recall limiting case 2, sketched above, in which the electrical circuit is completed by a load connected between the open terminals.
The current that flows is our second most important source of information about the system being investigated. Whereas the potential provides us in the first place with information about the thermodynamic driving forces of the reactions involved, the current is associated through Faraday's law directly with the net progress of the reactions. It thus also provides us with kinetic information.

If current is to be measured, an appropriate instrument must be inserted into the circuit. The requirements for suitable instruments are complementary to the requirements for measuring potential. An additional partial potential across the current measuring instrument is included in the zero sum of the potentials in the circuit. This therefore changes the partial potentials at the other locations. This means that the current flowing in the circuit is different from that which flows when the current is not being measured. In order to minimise the effect of the measurement on the state of the system, the partial potential across the instrument should be a minimum. An "ideal" instrument for measuring current therefore is effectively a short circuit and, analogously to the ideal measurement of potential, absorbs no power from the system.

Fig. 15 indicates the relevant non-ideal properties of a measuring instrument for the current measuring case in the form of an equivalent circuit diagram. Component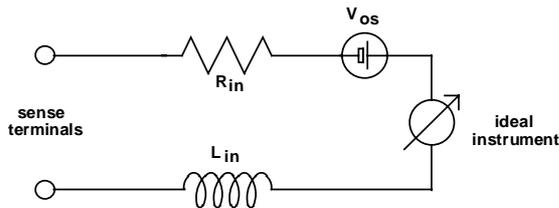s are connected in series with the ideal virtual instrument here, resulting in the development of parasitic potentials. The series resistor represents the direct current internal resistance developing an error voltage proportional to the current. The voltage source represents an error voltage (offset voltage) independent of the measured current. In addition to the most important characteristics of series resistance and offset voltage, the series inductance may also be significant if the currents change in time at a significant rate. A reminder: an inductor is an electrical component in which the voltage, V, between the terminals is proportional to the rate of change of the current flowing in it, dI/dt (see also chapter I, Eq. 24). It follows that this inductance is of no significance for DC measurements. It can, however, make a significant contribution to errors in dynamic measurements.

Fig. 15 Series input resistance, series input inductance and offset voltage mainly characterise a real world current meter.

Table 2 provides a general overview of the requirements of current measuring instruments for particular applications.

Tab. 2 Typical source potential V, typical currents I, acceptable series impedance, Z_{ser}, in the measuring instrument and acceptable offset voltage V_{offs} in current measurements

Current measurement application	Typical source potential	Typical currents	Acceptable measuring instrument series impedance	Acceptable offset voltage
Load current in batteries and fuel cells.	1 V	$10^{-1} – 10^{3}$ A	10 μΩ ~ 1 nH	1 mV
Corrosion in auto-passive systems	0.1V - 1 V	$10^{-10} – 10^{-6}$ A	1KΩ ~ 10 μH	1 mV
Corrosion under paints and coatings, current measurement on micro-electrodes and electrochemical sensors	0.1V - 1 V	$10^{-13} – 10^{-8}$ A	10 KΩ ~ 100 μH	1 mV
SECM and other nano electrodes	1mV - 1 V	$10^{-13} – 10^{-9}$ A	10 KΩ ~ 1 μH	0.1 mV
Electrochemical current noise	1mV – 0.1 V	$10^{-14} – 10^{-6}$ A	1Ω ~ 1 μH	0.1 mV

Voltmeters are available that approach perfection, at least for slow measurements. Near-perfect current measuring instruments, however, are a great deal more difficult to implement, even for direct current. The reason for this is that the most accurate measurement principle is based on the generation and acquisition of a voltage signal proportional to the current. Accurate current measurement therefore is usually the measurement of the potential difference across a measuring resistor inserted into the circuit (the "load voltage" across a "shunt"). It is not difficult to guess that this kind of current measurement can be quite problematic in a number of application fields.

 The following example demonstrates this in the case of measuring the current in a battery (Fig. 16). A battery is intended to supply a current of 1 A to a defined load. The resulting terminal voltage at the battery is to be 1 V. An additional shunt resistance of 1 mΩ in the circuit whose current is being

measured will create a potential between its terminals of approx. 1 mV. This will lower the current in the circuit by something of the order of 0.1%. This generates a corresponding systematic measurement error. In addition to this there is a stochastic measurement error with a similar order of magnitude created, for instance, by thermal error voltages present when measuring the already small load voltage of approximately 1 mV. Simply reducing the magnitude of the shunt resistance does not, therefore, result in an improvement of the overall precision.
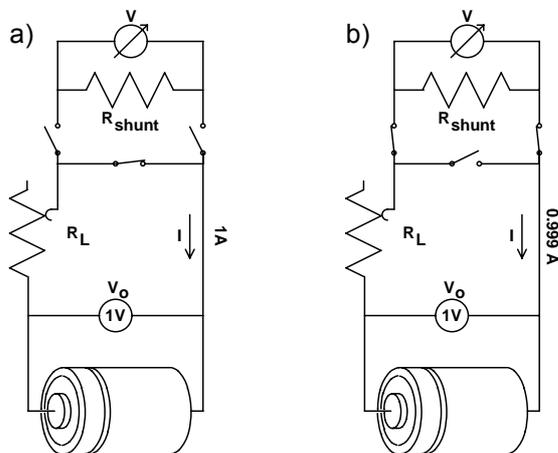

Fig. 16 Introducing a shunt type current meter influences the measuring object: The resulting current (b) is less than without current measurement (a).

The solution to the problem is found to lie in the application of active instrumentation amplifiers operating according to the current-voltage converter principle (ZRA). The way these devices work will be considered in detail later. For the moment, let it just be said that they are not the magic bullet. It calls for an electronic component (an operational amplifier) to handle the entire measured current, and to pass it via a diversion from the first measurement terminal to the second. This is just about practicable for measured currents less than 1 A. ZRAs that are suitable for batteries or fuel cells are, however, not commercially standard.

Conventional ammeters, such as those found in multimeters, are mostly based on the shunt principle. When used for electrochemical measurements, it is essential that their load voltage (terminal voltage), which is liable to be between 0.1 V and 1 V (!!!) when the measuring scale is being fully exploited, is taken into account: better use a less sensitive measurement range to minimise the resulting error.

"CLEAR RELATIONSHIPS" – ACTIVE CONTROL OF THE STATE OF THE CELL SYSTEM

Describing the state of an electrochemical system on the basis of measurements obtained passively is often inadequate. It is often desirable to actively create certain conditions in the system, and in some cases to vary them.

In the example shown in Fig. 16 it is possible to adjust the current roughly to around 1 A by carefully choosing the load, and then to check it with an ammeter. Instead of now using a time-consuming process of trial and error to repeatedly vary the load in order to approach the exact desired value of 1 A it is much more attractive to delegate the cycle of adjustment, comparison and further adjustment to an automatic system. An automated system that adjusts the desired current in a circuit including the system under investigation is known in electrochemistry as a "galvanostat" (Fig. 17a). The effect of the galvanostat on the circuit is the same as a constant current source. In a system under galvanostatic control, the current is the command variable, and the potentials are the response variables.
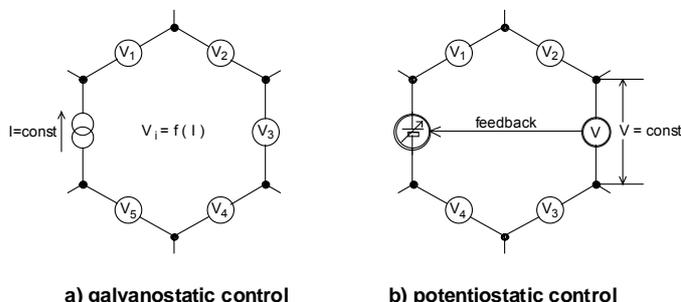

a) galvanostatic control   **b) potentiostatic control**

Fig. 17 Controlling the conditions in an electric circuit. Current control (a) and voltage control (b).

Instead of forcing a specific current in a system, it is also possible, with an appropriate regulation device, to specify a fixed potential between two points in the circuit (Fig. 17b). This kind of "potentiostat" has the effect of a constant voltage source. In a system under potentiostatic control, the potential is the command variable, and the current is the response variable.

There are, furthermore, particularly elegant solutions for potentiostats and galvanostats to the problem of the load voltage when measuring current.

Before we consider these techniques and the associated methods of electrochemical cell construction more closely, it will be worthwhile recapitulating the principles of operational amplifiers.

III. ELECTRONIC AIDS FOR THE ELECTROCHEMICAL ENGINEER

Potentiostats, galvanostats, operational amplifiers... a considerable number of active aids have already been mentioned. Sometimes it is not enough simply to be aware of the function and the purpose of our electronic helpers. If we want accurate measurements, and if we want to be able to interpret them reliably, it is also important to understand the way in which these devices work.

THE PRINCIPLES OF OPERATIONAL AMPLIFIERS

Generally speaking, amplifiers are used to create large effects out of small causes. In instrumentation technology they can help us to come closer to the ideal of measurements with no side-effects extracting power. Many amplifiers are designed as closed systems, in which the user can only indirectly, if at all, have any effect on their basic properties. Parameters such as the "amplification factor" or the "frequency range" are determined within the closed system. One example of this would be the amplification of the radio signals received by a mobile telephone as they pass from the antenna to become outputs for the ear-piece and for the display.

In many scientific applications, however, it is useful if the experimenter himself has a large measure of control over the function and properties of amplifiers. For this reason operational amplifiers (OPAs) were developed in the 1960s, stimulated by applications in analog computing. OPAs are amplifiers for electrical voltage with properties that come close to the ideal. The nature of the amplification can be specified over an enormous range through the connection of additional, external circuitry [6].
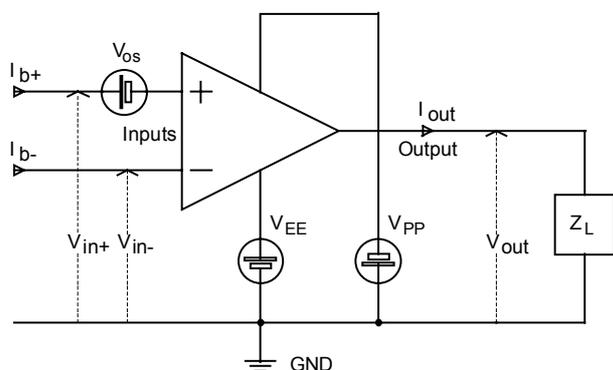
Through appropriately selected circuitry, a variety of basic functions can be implemented such as voltage followers, inverting and non-inverting amplifiers, adders, integrators… It is then possible to use these basic functions to construct devices useful for electrochemistry, such as instrumentation amplifiers, potentiostats and galvanostats.

Fig. 18 Operational amplifier symbol with the characteristic input- and output voltages V_{in} and V_{out}, the supply voltages V_{EE} and V_{PP}, the output load current flowing through the load Z_L, and the parasitic input bias currents I_{b+} and I_{b-}.

Fig. 18 illustrates the circuit symbol for an OPA, together with the input and output signals, the symbols for power supply (the voltage supplies V_{EE} and V_{PP}) and the most important parasitic magnitudes. The power supply and the parasitic magnitudes will in most cases not be included in the sketches below for simplicity. The reader should nevertheless not forget that there are deviations from the ideal. The current that comes out of the amplifier, moreover, must ultimately derive from the power supply.

$$V_{out} = (V_{in+} - V_{in-}) \cdot A_{ol} \qquad (42)$$

The "magic formula", responsible for all the practical things that can be done with OPAs, (Eq. 42) is quick to explain:

- The OPA's output voltage, V_{out}, is proportional to the difference between the input voltages V_{in+} at the non-inverting input and V_{in-} at the inverting input.
- The proportionality factor is the OPA's open-circuit amplification, A_{ol}, and can be assumed to be close to ∞, independently of the output current, I_{out}, resulting from the load, Z_L.

- The parasitic magnitudes of the input leakage current I_{b+}, I_{b-} and the input offset voltage, V_{os}, are assumed to be negligibly small.

A USEFUL HELPER FOR POTENTIAL MEASUREMENTS: THE VOLTAGE FOLLOWER

The simplest basic configuration of an OPA is the voltage follower (Fig. 19).

Eq. 42 shows that even a small difference in the inputs (V_{in+} - V_{in-}) is sufficient to cause a large output voltage, V_{out}. If the output voltage is fed back unmodified to the inverting input, the output potential becomes $V_{out} \approx V_{in+} \cdot (1 - 1/A_{ol})$. In other words, the output voltage "follows" the input voltage, apart from the tiny difference V_{in+}/A_{ol}. V_{out} is an image of the input voltage regardless the load Z_L and the output current I_{out}. The output terminal of the OPA can be connected to subsequent signal processing electronics without having any loading effect on the signal source.
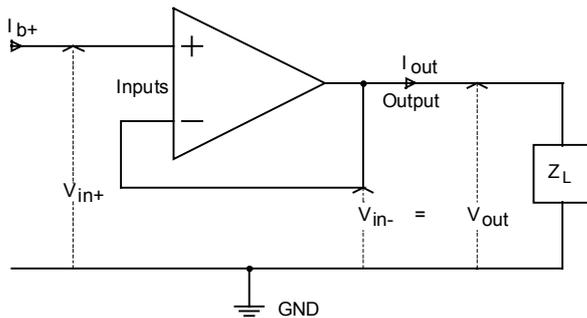

If the load Z_L is our multi-purpose measuring instrument with an input resistance of 10 MΩ, it can be seen that the combination of voltage follower and multimeter is quite suitable for acquiring the voltage of a glass electrode – provided that the absolute value of the OPA's input leakage current, I_{b+}, and its input offset voltage, V_{os}, are small enough. The capability to decouple the current in a load circuit from a potential source also suggests the main application of a voltage follower: the acquisition and buffering of potentials from high-impedance sources (a buffer amplifier) at the input of the operational amplifier. A buffer is often required as an element in analog signal conditioning, for instance when voltage dividers, filters and so forth cause significant source resistance, but the potential that develops must be further processed with as little modification as possible.

Fig. 19 An OPA configured as a voltage follower. The output voltage V_{out} is near the input voltage V_{in+}, in spite of the load current I_{out} flowing through Z_L. A good voltage follower exhibits low input leakage current I_{b+}.

"ACTIVE SHIELDING" WITH A VOLTAGE FOLLOWER – A PATENT SOLUTION FOR INTERFERENCE?

One variation of the buffer amplifier helps to defuse a general problem that arises when taking measurements on high-impedance test 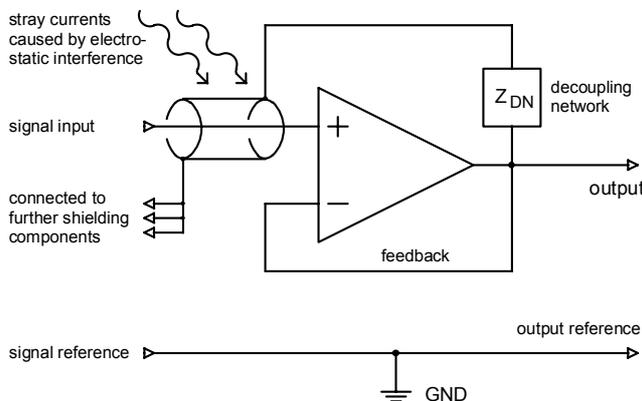pieces. The potential at high-impedance sources is not just disturbed by the measurement process, but is also affected by interfering currents arising from electric fields in the neighbourhood of the source. Stray capacitances lead to dynamic potential errors, while static errors can also be caused by incomplete insulation. The usual counter measure, electrostatic screening, will be discussed in more detail later. At this point it is necessary to explain that any type of screening itself leads to an increase in the stray capacitance, unless the potential of the screen is simultaneously raised to the signal potential. This is exactly what a buffer amplifier can do, if the screen is connected to the amplifier output. Fig. 20 shows schematically how stray currents created by external fields are absorbed

by the active screen and diverted to the output of the OPA. Provided the stray currents are small, the potential differences they will cause in the decoupling network, DN, between the signal lead and the

Fig. 20 The output of a voltage follower can drive active shielding. Almost no additional load appears at the signal input line, due to a minimal voltage difference between signal and shielding.

screen will remain negligibly small. The field strength is therefore zero in the neighbourhood of the signal lead, and the signal remains unaffected.

An examination of the circuit in Fig. 20 may raise the question of why we do not omit the network DN when constructing an "ideal" active screen, since it does restrict the effectiveness of the circuit. Unfortunately, the non-ideal dynamic properties of OPAs prevent the arrangement from working without the DN (although a simple resistor may be all that is necessary). The imperfections of OPAs in the AC domain plays an important role in the practical aspects of using potentiostats and galvanostats. This will have to be considered in more detail later.

"INVERTING AMPLIFIERS" – HELP WITH THE MEASUREMENT OF CURRENT

So far we have considered OPA circuits in which the non-inverting input (abbreviated to In+ below) is used as the signal input. Signals can also be fed to the inverting input (abbreviated below to In-). A number of useful circuits can be implemented in this way.
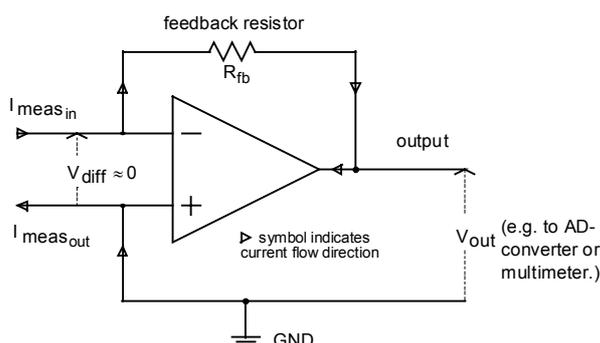
The principle can be demonstrated through a current-voltage converter or ZRA (Fig. 21). In this case In+ is connected to the reference potential. In- is connected to the output via a resistor, R_{fb}. When idle (input current zero) the reference potential also appears at the output, so that the output voltage is zero. If a current I_{meas} is fed into the input (e.g. the current to be measured when the application is that of a current/voltage converter) then a potential given by $V_{out}= - I_{meas} \cdot R_{fb}$ develops at the OPA's output. The full input current flows through the resistor, R_{fb}, to the output of the OPA, and the difference in the input voltages is once again minimal. Because a significant voltage does not develop between the input and the output of the current (which is why the configuration is called a zero resistance amplifier, or ZRA), the current-voltage converter can be used as an almost ideal method of measuring currents.

Fig. 21 When a current I_{meas} is fed into the inverting input of an OPA, a current proportional output voltage V_{out} can be measured. This type of current-to-voltage converter is called Zero Resistance Amplifier (ZRA) due to diminishing voltage drop V_{diff} between the current inlet and outlet.

The inverting amplifier, or IA, (Fig. 22) is only one step beyond the ZRA. The ZRA at the current input is combined with the simplest form of voltage-to-current converter, i.e. a resistor (R_{in}): R_{in} generates the current $I_{meas}=V_{in}/R_{in}$ at the input. This yields the IA's transfer function, g, where the output voltage is given by $V_{out}= - I_{meas} \cdot R_{fb}$:
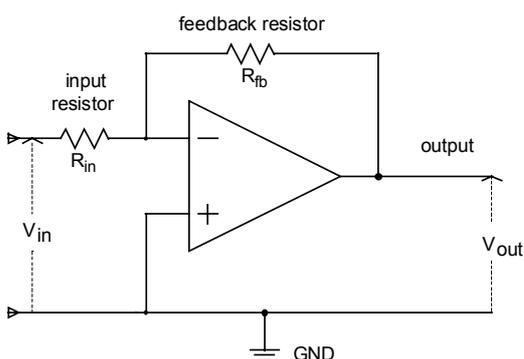
$$g = \frac{V_{out}}{V_{in}} = -\frac{R_{fb}}{R_{in}} \tag{43}$$

Example: To build an IA with an amplification factor of ten (g=-10), R_{fb} must be ten times larger than R_{in}, so that, for instance $R_{in} = 100\ \Omega$ could be used with $R_{fb} = 1000\ \Omega$.

Fig. 22 An Inverting Amplifier IA is built from a ZRA plus an input resistor as voltage to current converter.

A LITTLE SECRET: COMPONENT DIMENSIONING FOR OPA CIRCUITS

It is not the intention of this chapter to enter the details of OPA dimensioning. A few hints as to why in the example above 1000 Ω was recommended for R_{fb} rather than 1 MΩ or 1 Ω (with the corresponding choice for R_{in}) will, however, help us later to manage some of the difficulties of dynamic electrochemical measurements. The dimensions are, of course, chosen so that the circuit satisfies the

user's requirements as best as possible. A low-resistance design offers a number of advantages here over high-resistance dimensioning.

1. Leakage currents are less significant. If, for example, an OPA has an input bias current, I_b, of ± 100 nA (typical for precision OPAs with medium bandwidth), I_b causes an additional voltage error $V_e = R_{in} \cdot I_b$.
   With the dimensioning above this yields just 10 μV – this is in the same range as other small potential measurement errors such as V_{os}, and much smaller than, for instance, the potential tolerance of a commercially available reference electrode.

2. The energy distribution of the conductive electrons in resistors results in a noise voltage (observed as standard deviation of the nominal voltage), characteristic for the absolute temperature, T, the value of the resistance, R, and the frequency bandwidth, Δf (Eq. 44).

$$V_r = \sqrt{4 \cdot k \cdot T \cdot R \cdot \Delta f} \tag{44}$$

3. The noise contribution of the OPA's input leakage current ΔI_b adds to the total input bias current. It causes a voltage noise which increases with the resistor value. Low-resistance dimensioning reduces the effects of these unwanted potential variations on the signal being measured.

4. The electrostatic and magnetic properties of space and of any material that fills it cause pervasive, but usually undesirable, capacitive and inductive elements in the behaviour of electronic components and circuits. Strictly speaking, a resistor only behaves as an Ohmic conductor when the voltage is constant. As the frequency of AC signals rises, its behaviour is determined more and more by its stray capacitance and stray inductance. Down to a value of a few 100 Ω this is primarily noticeable, in the usual physical structures, as the stray capacitance which, together with the stray capacitances of the OPA and of the circuit itself, typically amounts to a value of around 10 pF. At a frequency of 1 kHz a capacitance of this size has the same admittance as a 15 MΩ resistor. The total impedance of the effective feedback network is dominated almost completely by the 1 KΩ resistor, suggested for R_{fb}. A nearly vanishing 0.007% error appears at this frequency.

These considerations all favour low-resistance dimensioning. There are, on the other hand, at least two arguments that represent a lower limit for the choice of resistance:

1. The stray inductance becomes significant when AC signals are present in resistors with less than 10 Ω.

2. Low values of resistance require high currents. A typical precision OPA can supply about 10 mA of output current. This limits the minimum value for R_{fb} to about 1 KΩ, if we assume that we plan to operate in a range of ± 10 V, appropriate to electrochemistry. Generally speaking, low-resistance dimensioning has a disadvantageous effect on the current requirement of a circuit, and this must be considered particularly for battery operated constructions.

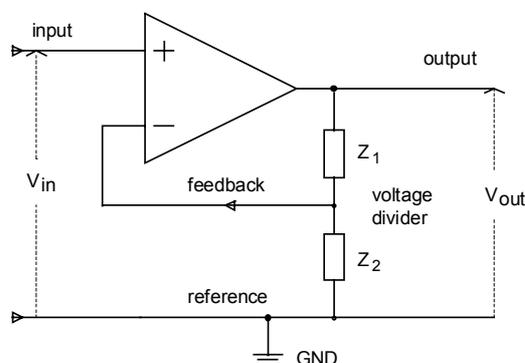## THE NON-INVERTING AMPLIFIER, OR NIA

Fig. 23 The Non-Inverting Amplifier NIA uses a voltage divider for the feedback signal.

The step from the buffer amplifier to the non-inverting amplifier (NIA) is as easy as the step from the ZRA to the IA. Not the entire output signal is fed back to the input of the OPA as was the case with the buffer. Instead of this, a voltage divider consisting of Z_1 and Z_2 is used to generate a fraction, b, of the output voltage V_{out}. This fraction b is used for feedback (Fig. 23). In order to minimise the voltage difference at its inputs, the OPA then adopts a voltage of $V_{out} \approx V_{in} \cdot (1+1/b)$ at its output.

In order for the voltage divider ratio, b, to be real and to be nearly independent of frequency, the partial impedances Z_1 and Z_2 must have the same frequency characteristic. This is most easily achieved with two resistors (Eq. 45).

$$b = R_2 / R_1 \tag{45}$$

This yields the simple relationship of Eq. 46 for the amplification of the NIA:

$$g \equiv V_{out} / V_{in} = 1 + R_1/R_2 \tag{46}$$

Like the IA, the NIA is most often used for adapting levels, e.g. to adapt an input signal to the useful range of an A/D converter. In contrast to the IA its amplification is positive, $g \geq 1$, and it has an almost infinite input resistance (at In_+). The IA and NIA play complementary roles in analog signal processing.

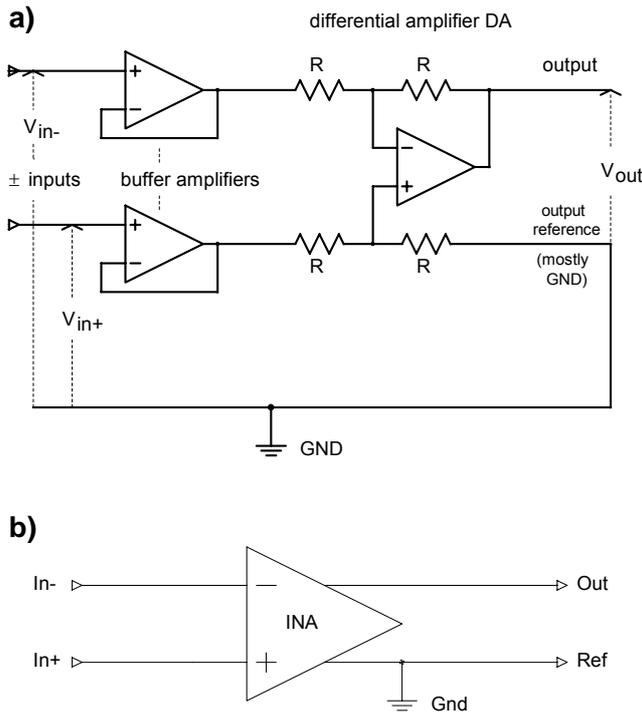<h2 style="text-align:center">THE INSTRUMENTATION AMPLIFIER – A "JACK-OF-ALL-TRADES"</h2>

Fig. 24 Instrumentation Amplifier INA. A, detailed circuit, b, INA symbol. An OPA based INA contains a Differential Amplifier DA structure.

The properties of both amplifier types are combined in the "instrumentation amplifier", INA. The disadvantage of the most simple form of construction, shown as a "difference amplifier", DA, in Fig. 24, is the low input resistance resulting from the resistors $R_1 – R_4$. Preceeding it by two buffer amplifiers allows the DA to be extended to form an INA with a nearly infinite input resistance.

INAs are versatile modules, because voltage differences can be acquired and converted to relate to a new reference point such as GND. This makes it possible, for instance, to measure partial potentials in multi-phase systems, or to use shunt measuring techniques to determine currents at any location within a circuit. Figure 25 shows how the potential difference between the two sides of a membrane in an electrolyte through which current is flowing can be measured with the aid of an INA.

Fig. 25 also illustrates the special feature of a good INA: the output voltage V_{out}, should depend only on the difference in voltages between the two potential probes (the differential signal), and should be as little influenced as possible by their mean potential in comparison with the GND reference, the common mode signal $V_{cm} = (V_{in+} + V_{in-}) / 2$.
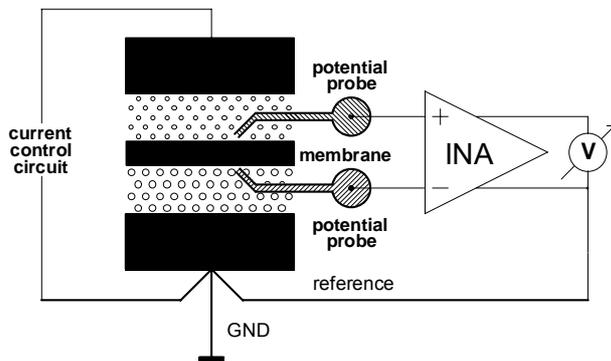

Fig. 25 Measuring potentials floating to GND by means of an INA.

The parameter that serves as a figure of merit for his feature is the common mode rejection ratio, CMRR (Eq. 47). It indicates the factor by which the desired amplification, g, of the meaningful signal at the output is greater than the unwanted amplification, G, of the common-mode signal V_{cm}.

$$CMRR = \frac{g}{G} \quad \text{where}$$

$$g = \frac{V_{out}}{V_{in+} - V_{in-}} \quad \text{and} \quad G = \frac{2 \cdot V_{out}}{V_{in+} + V_{in-}} \tag{47}$$
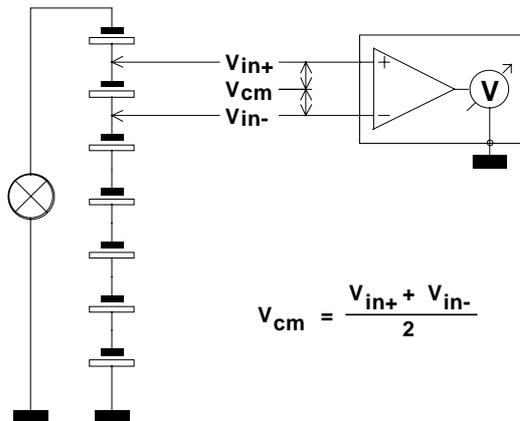
Fig. 26 The nature of the common mode interference illustrated by the potential measurement in a fuel cell stack.

$$V_{cm} = \frac{V_{in+} + V_{in-}}{2}$$

Fig. 26 explains the role of the common mode rejection in the context of the task of measuring the single- cell potentials in a battery of cells (e.g. a stack of fuel cells).

THE 3-ELECTRODE CELL AND THE POTENTIOSTAT

The most important task of OPA technology in electrochemistry has to be the implementation of potentiostats for the operation of 3-electrode cells. It is clearly very useful if, rather than merely passively measuring the potential at any one time in an electrode-electrolyte system (a half-cell), it is possible to actively control it. The potential measurement of the half-cell can indeed easily be implemented by means of a second electrode serving as a reference electrode (RE). In order to set up conditions other than those associated with the equilibrium position at the electrode under investigation (the working electrode, WE), it is however necessary to use another electrode (the counter electrode, CE). This allows the potential and the current in the working electrode to be controlled, while the reference electrode continues not to draw current. This makes the contribution of the reference electrode in the measurement of the total potential constant; changes in the potential can be assigned entirely to the working electrode. Fig. 27 shows schematically the structure of a 3-electrode cell with the characteristic measurement and control parameters.
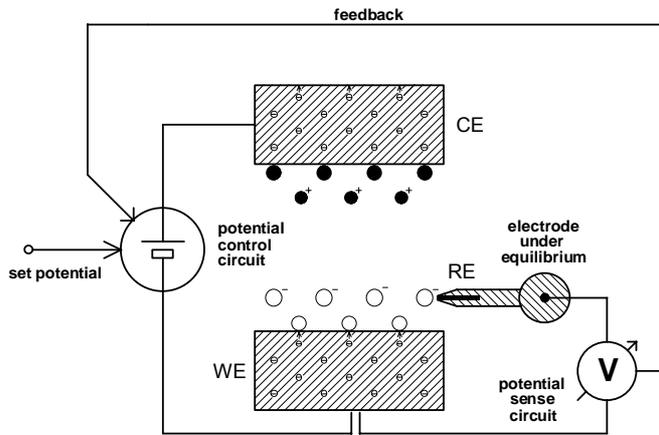

Fig. 27 Potentiostatic control of an electrochemical cell. The voltage measured at the equipotential plane by means of a Reference Electrode RE in front of the Working Electrode WE is used as a feedback signal to control the Counter Electrode CE.

The information obtained, without drawing current, about the actual potential difference between the working electrode and the reference electrode by using the potential measurement circuit serves as "negative feedback" for the control loop: the difference between the desired potential and the measured potential is highly amplified, and is used to adjust the potential and the current in the circuit between the working electrode and the counter electrode until the stage is reached where this difference is minimised.

THE SIMPLEST POSSIBLE POTENTIOSTAT: A MODIFIED NON-INVERTING AMPLIFIER

We can see that this task can easily be performed by an NIA (Figs. 28 and 23): the potential, GND, on which all voltages are referred, is connected to the working electrode, the OPA In+ input to the set potential, In- to the reference electrode, and the OPA output to the counter electrode. The tap between the impedances Z1 and Z2 in Fig. 23 is formed by the equipotential plane at the opening of the reference electrode capillaries. Other than in Fig. 23 the lead to In- is seen to contain the potential offset, V_{ref}, caused by the reference electrode. Impedance Z1 is formed by the region of material

between the counter electrode and the equipotential plane, while impedance Z2 is formed by the region between the equipotential plane and the working electrode.

The (not directly accessible) potential, V_{equ}, of the equipotential surface in front of the electrode under investigation adopts the value given by Eq. 48:
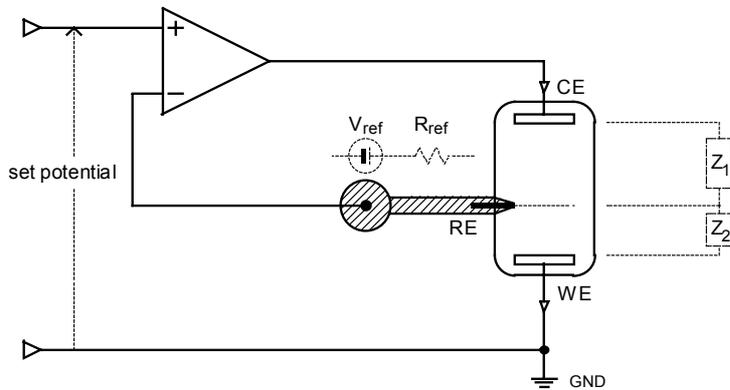

Fig. 28 A NIA Working as a Basic Potentiostat Circuit

$$V_{equ} \approx (V_+ - V_{ref}) \cdot \left(1 - \frac{Z_1 + Z_2}{Z_2 \cdot A_{ol}}\right)$$

$$V_{equ} \approx V_+ - V_{ref}$$

(48)

Eq. 48 tells us that an OPA does indeed work as a potentiostat, and that, apart from the offset potential of the reference electrode, fixes at In_ the set potential desired for the working electrode (Eq. 48). More precisely, the term $(Z_1 + Z_2) / (Z_2 \cdot A_{ol})$ in Eq.48 must remain negligibly small. This is only the case when the open circuit gain factor, A_{ol}, is large in comparison with the ratio of Z_1 / Z_2.

Let us consider the very important practical consequences of this:

- The ratio of the impedance of the counter electrode, Z_1, and of the working electrode, Z_2, determines whether the potentiostat can perform its function!

When constructing 3-electrode cells, many electrochemical engineers attempt to place the opening of the reference electrode capillary as close as possible in front of the working electrode. This is intended to minimise the influence of the column of electrolyte located above the electrode (the "Ohmic drop" $R_{el} \cdot I$).

If this is overdone, however, the result, instead of being more precise, may get unpredictible. Due to the double layer capacity the impedance at high frequencies of an electrode is dominated by R_{el}. As the total impedance of the counter electrode, Z_1, even rises when minimising R_{el}, the impedance of the working electrode, Z_2, becomes very small, and the ratio Z_1/Z_2 then becomes dangerously large – the potentiostat no longer operates properly! These kind of errors have particularly dramatic effects on "fast" measurements such as those required for impedance spectroscopy. Because of its fundamental significance, this aspect of the construction of measurements cells will be considered in more detail later. In the meantime, bearing the following rules of thumb in mind can give us general protection from unpleasant surprises of the above type:

- The position of the capillary opening should not be closer to the working electrode than one tenth of the distance between the working electrode and the counter electrode.
- The area of the counter electrode should not be significantly smaller than the area of the working electrode.

A further aspect of the Z_1/Z_2 ratio should also be considered: if, as might happen with polarisation measurements, we want to set a potential of $V_{equ} = \pm 1V$ at the equipotential surface in front of the working electrode, the potentiostat must provide a voltage of $V_{out} \approx V_{equ} \cdot Z_1/Z_2$ at the terminal of the counter electrode. If we stay within the above rules, this can just about be managed by a standard precision OPA operating from $\pm 15V$ supply rails. Failing to observe this problem, e.g. when the ratio $Z_1/Z_2 \approx 20$, will mean that the desired range for V_{equ} of $\pm 1V$ can no longer be covered.

One obvious possibility would be to seek a solution through raising the available output voltage range (the "compliance voltage") of the potentiostat. It is indeed true that there are some tasks required in electrochemistry, such as the measurement of cell stacks, that can only be handled with an extended voltage range. Apart from the unavoidable loss in precision of the electronics used[3] in high-voltage

---

[3] Electrical components cannot be optimised equally well in respect of every important parameter. In particular, very high voltage or current requirements in amplifiers are incompatible with simultaneous requirements for low noise, low error voltages, small leakage currents or fast response. Precision amplifiers for DC work best with $\pm 15V$ power supplies and with output currents of up to $\pm 10mA$. When maximum speed (slew rate, settling time and bandwidth) are important, supply

potentiostats, high values of the ratio Z_1/Z_2 cause the errors resulting from leakage currents flowing between the counter electrode to the reference electrode and ground to become large. This is particularly noticeable in AC measurements on high-resistance electrolytes. Measurements involving high-resistance electrolytes do not necessarily require a higher output voltage, V_{out}, because as the resistance of the electrolyte columns increase, Z_1 and Z_2 are affected equally. The corresponding rise in the resistance from the capillary to the reference electrode is a bigger problem. The high source resistance of the potential probe (R_{ref} in Fig. 28) turns out to be particularly problematic:

Ideally, no current should flow in the lead from the reference electrode to In.. In that case, R_{ref} would not impair the precision of the measurements. In fact, leakage currents from this lead to the counter electrode and GND (significant for bulky reference electrodes) and in In. can play a fatal role. The effects can, in particular, be dramatic in AC measurements when the ratio Z_1/Z_2 is unfavourable. The following points should therefore be taken to heart:

- Reduction of the potential probe's source resistance and leakage current. Reference electrodes should be small, while electrolyte paths within the probe should be short and have large cross section.
- If a high source resistance is unavoidable, then a buffer amplifier (Fig. 20) should be inserted into the lead from the potential probe to In. as close as possible to the location of the electrode.

THE "CATCH" IN THE 3-ELECTRODE ARRANGEMENT

In our "minimal potentiostat", one side of the power supply in the potentiostatic control circuit and one side in the potential measurement circuit have a joint connection: the working electrode is connected to the joint GND reference for bot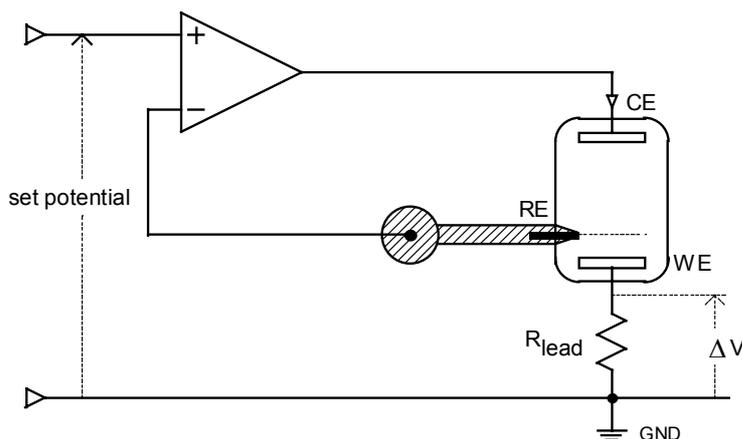h circuits. This can lead to difficulties. A membrane cell, such as that sketched in Fig. 25, or other similar arrangements of solid bodies fitted with entirely separate potential sensing circuits, cannot be operated successfully with the minimal potentiostat. There are also strict limits on measurements in conventional three-electrode cells: they only function with sufficient precision if the influence of the common lead to the working electrode is negligibly small. From its electrical role, the material of which the metallic lead is made belongs to the working electrode. If current in the control circuit leads to significant voltage differences along the lead, the actual potential will differ from what is wanted (Fig. 29).

Fig. 29 A potentiostatic three-electrode arrangement cannot avoid a difference ΔV between set voltage and actual voltage at the equipotential plane of the cell. It is due to the Ohmic drop in the working electrode to GND connection line with the resistance R_{lead}.

A cure is to entirely separate the current control circuit and the potential measuring circuit, representing a change to the 4-electrode arrangement, also known as the Kelvin scheme, as shown in Figure. 25. The potentiostat must, of course, also be capable of handling the two circuits separately. This is achieved by inserting an INA into the minimal potentiostat's potential measuring circuit in order to shift the reference of the measured potential to GND (Fig. 30).

---

voltages of $\pm$ 5V are optimum, and output currents of up to $\pm$ 100 mA are possible. Because the parameters that are most important for electrochemical applications are scarcely satisfied by components available on the market, the manufacturers of potentiostats generally have to develop their own constructions.
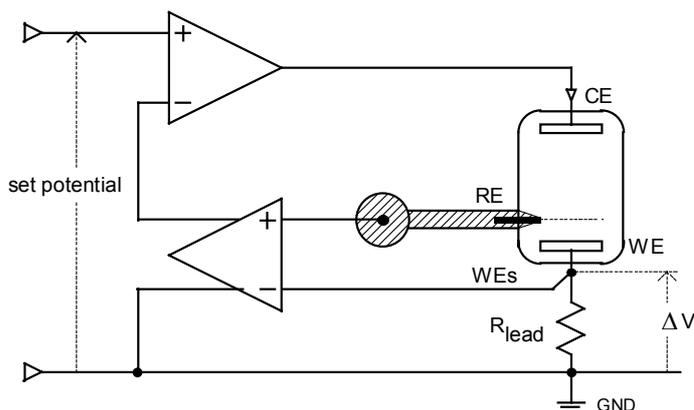
Fig. 30 A potentiostatic four-electrode set-up adjusts the set potential precisely in spite of Ohmic drop ΔV across the resistance R_{lead} of the working electrode feeding line by means of an additional sensing line WEs.

There are only a few kinds of electrochemical measurement that can be taken with a 3-electrode arrangement at the potentiostat without any further thought. In typical DC methods, and when the currents in the control circuit do not exceed a few mA, the errors resulting from the small potential differences in the common working electrode lead are negligible. In the presence of rapidly changing signals and high frequencies, this lead may acquire an easily noticed, even dominating, influence over the potential of the working electrode, and it is essential that the following is borne in mind:

- Whenever possible, only use potentiostats that fully support the four electrode arrangement.

- Even three-electrode cells should be connected according to the four-electrode scheme by providing separate leads for the working electrode to the current control circuit input and the potential measurement circuit input.

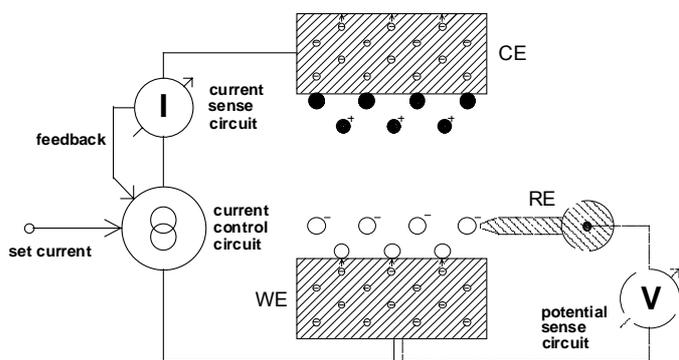THE GALVANOSTAT – THE COMPLEMENT TO THE POTENTIOSTAT

Fig. 31 In a galvanostatic arrangement a current control unit feeds in a set current into an electrochemical full cell circuit. The potential sense circuit is optional.

Like potentiostats, galvanostats are systems with feedback. The information used by the control circuit for regulation purposes, however, does not originate from a potential measured at a particular location, but from the current flowing in the control circuit itself (Fig. 31).

An NIA can help again when it is planned to make a specified current flow in a control circuit. Fig. 32 illustrates how a minimal galvanostat can be constructed using a single OPA in the NIA configuration.

It functions according to a simple principle: Because the NIA generates almost exactly the potential V_{in+} specified at In+ at the common node of Z_1 and Z_2, it is only necessary to substitute an Ohmic resistor, R_{meas}, for Z_2. The current in the

Fig. 32 A simple galvanostat circuit based on an OPA in NIA configuration. The set current is adjusted by V_{set} and R_{meas}.

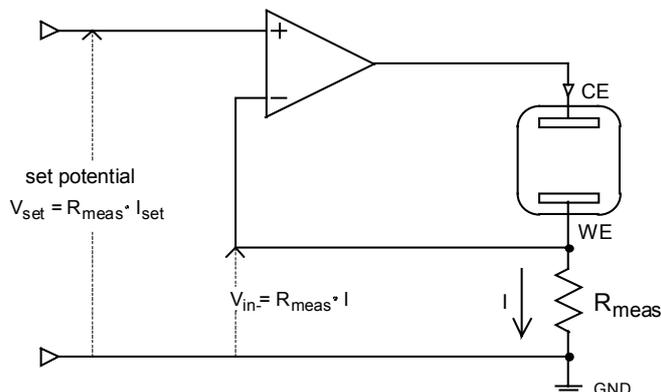circuit between the OPA output through the series circuit represented by Z_1 and R_{meas} to GND is then given by $I \propto V_{in+} / R_{meas}$. The electrochemical cell is inserted in the place of Z_1. It is therefore clear that with a little skill, a potentiostat can also be used as a galvanostat, even if the device manufacturer had not planned this:

Simply connect the working electrode at the input for the reference electrode, and connect this point through a measuring resistor, R_{meas} (e.g. from a resistor decade box) to the

potentiostat's working electrode output. The set value, once again, is a voltage. In order to create a specific current, I_{set}, specify a potential of $V_{set} = I_{set} \cdot R_{meas}$.

The problem of three or four electrode connection does not apply to a galvanostat, because the current is inserted through just two connections. Regulating to the set value does not require any potential to be measured. In order, however, for the experiment to sense the resulting potentials precisely, the same point applies as was explained above for the potentiostat: current-carrying and potential-measuring leads should always be separate.

A large number of electrochemical workstations offer the facility of choosing between the function of a potentiostat and of a galvanostat. The two methods of operation are equally fundamental for a large number of electrochemical techniques.

THE "BEST" IS JUST GOOD ENOUGH – BUT WHAT IS THE "BEST"?

Just what is a "good" potentiostat or galvanostat, and what is a "bad" one? There is no simple answer to this question.

There is, of course, a whole string of trivial criteria: the device should, for instance, be electrically safe, easy to operate, reliable, have a long service life and be economical. Most of these properties are not very easy to judge solely from the manufacturer's brochure, and the question of value for money can only be answered when the other criteria, together with the performance data, are considered along with the price.

For the technical data there are no binding standards governing which specifications are to be provided or how they are to be presented. Moreover it is often the application that determines whether "more" or "less" of a particular property means that the device is "better" or "worse": what might, for instance, appear indispensable when cycling rechargeable batteries may turn out to be a problem for sensitive methods such as the measurement of electrochemical noise.

As in the chapter on the measurement of voltage and current, some transparency to frequently cited general properties and technical data relevant to potentiostats, galvanostats and other electrochemical instruments will be provided. This will also involve a discussion of aspects of the coupling of instruments to computers (A/D-D/A conversion, interfaces etc.) that are so common nowadays.

After that a brief explanation of the principles of frequently applied electrochemical techniques will be provided, without making too many inroads into the comprehensive articles in other chapters of this book. The key point is to outline the method-specific requirements of the relevant instrumentation technology.

THE ROLE OF THE EARTH POTENTIAL

When we consider a particular experiment we tend to estimate our chances of success or failure on the basis, on the one hand, of the properties of the object being measured and, on the other hand, on the quality of the measuring instrument. This would indeed be enough, if only the experiment took place in a closed mini-universe. Unfortunately, however, the main cause of potential problems, namely the environment in which the measurements are taken, is then ignored. A few key words – screening, grounding, galvanic isolation, antenna effect – are enough to suggest that a small book could be written on the topic of "avoiding external influences" alone. If we wish to make a at least realistic estimate of the effect of sources of error, then we must also consider the environment of the experimental set up, and we must form a usable model of it. The term "ground" (GND) has often been used above as the notional reference point, used as the zero in a measuring set-up. It is helpful to specify an electrical

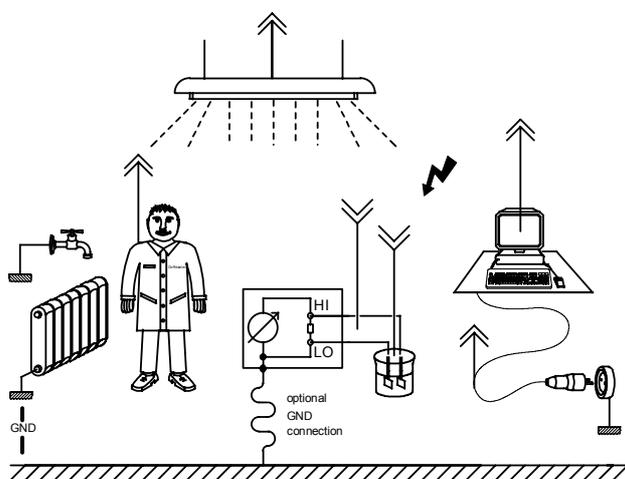**Fig. 33** The role of the electric environment within an electrochemical experiment. The interference symbol is the flash. Interference sources and receivers are symbolised by antennas accordingly. Grounded objects are indicated by a GND symbol.

zero level to which all the voltages in the system are related.

The potential of the earth's surface is an obvious reference to take for this purpose when modelling the environment in which measurements are taken. It can also be considered to be constant enough over a wide surrounding area. All conductors that are joined to this "ground potential", such as water pipes, heating systems, the housing of earthed electrical devices or protective earth contacts in the power supply itself are assigned a potential of zero in this simple model. These conductors are all included under the label "GND" in Fig. 33. All other conductors not belonging to the item being measured, such as mains power conductors, lamp housings, the screen and the observer of the experiment, have potentials unequal to zero. Commonly, these are also subject to variations over time: mains-operated devices demonstrate systematic oscillations at mains frequency, data display devices at the screen refresh frequency, while gas discharge lamps adopt a variety of often chaotic frequencies.

The pervasive potential variations at mains frequency are also transferred to the human body. Moving around in the area of an experiment, a human being will often also become electrostatically charged, undergoing a slow, but large change in potential. All these conductors are indicated in Fig. 33, for the sake of simplicity, as "transmitting antennae", because they fill the space around the experiment with disturbances to the electrical field. Then there is the experiment itself, including the leads to the measuring instrument: the conductors used here function as "receiving antennae" for the polluting field.

The possible potential difference between the reference potential of the measuring set-up (the "LO" reference)[4] and the ground or earth potential, GND, does not just have an effect on the influence of the different sources of interference, but is also used to classify various types of measuring set-up. If there is a conductive connection (the GND path in Fig. 33) between LO and GND, then we speak of a "grounded" or of a "non-floating" arrangement. If there is no earth conductor, we speak of electrical isolation (a "floating" arrangement).

Misunderstandings of the significance of electrical isolation and grounding when constructing experimental set-ups are often causes of experimenters' headaches. Before we can list a number of clear pointers for construction, we need to understand the causes of interference from the measuring environment rather better.

As is usually the case with interference, the problem lies in the competition between the wanted and the unwanted electrical effects (signals and interference). For the important case of measuring small currents, Fig. 33 illustrates that the flow of energy from the "transmitting" to the "receiving" antennae leads to unwanted interfering currents that compete with the signal current. It does not help much to attempt to interrupt the circuit of the interfering current by removing the earth conductor. The measuring set-up itself will act as an antenna, causing interference currents to flow as a result of radiation even in the absence of a ground conductor. The most effective method of countering interference arising from electric fields is to capture the currents that are created by means of "screens" in front of the measuring circuit's "receiving antennae", and to divert them to the ground potential before they affect the signals (Fig. 34).
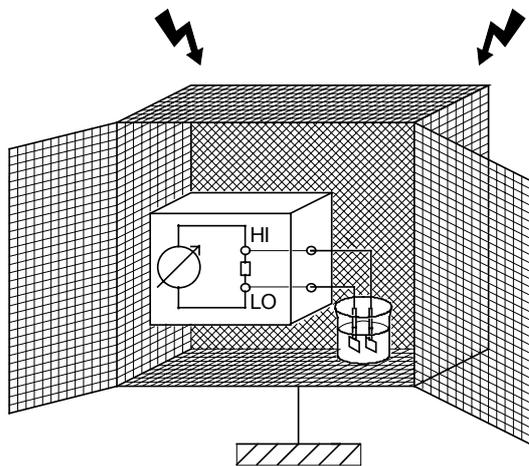

Fig. 34 A shield of conductive material acts as a bypass for the disturbing currents caused by an electrostatic noisy environment.

If a ground connection is present it is easier to omit additional screening, since none of the conductors connected to ground have an interfering effect. When a measuring set-up is grounded, an observer can easily be changed from an "interferer" to a "suppressor" simply by touching something at ground potential such as the earthed housing of the measuring instrument.

One thing is clear now: an earth connection is "good". But are more connections better?

---

[4] Frequently the structure of the signal inputs to an instrumentation circuit for voltage or current is, other than with an ideal INA, asymmetric in respect of the circuit's reference potential. The input that is "closer" to the reference potential (i.e. is not different from that of the reference, or has only a small difference) is referred to as the LO input, or the "cold terminal". The other input is referred to as the HI input, or the "hot terminal".

It can, in practice, often happen that there is already an earth connection in an electrochemical system being investigated. Picture, for instance, corrosion investigations on a pipeline or in the cooling circuit of a power plant.

Fig. 35 illustrates what happens when an earthed instrument is used in such a system to measure the potential between a water pipe and a reference electrode that has been inserted. In the worst case, shown in Fig. 35a, the grounded LO input of the instrument is connected to the reference electrode, while the HI input is connected to the pipe. It is easy to see that this causes the potential of the reference electrode to be short-circuited via the ground connection of the LO input. It is obvious that this cannot work.
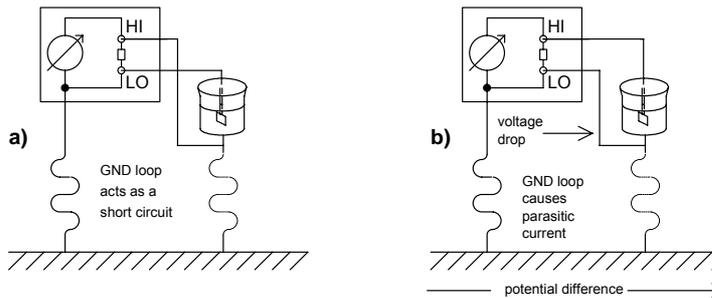

Fig. 35 Two ways to connect a grounded meter to a grounded object: The bad one (a) and still not so nice (b) The metal beaker with the electrode and electrolyte inside symbolises a segment of a water pipe.

But the inverse case in Fig. 35b still has its problems. In this case, the ground connections of the LO input on the one side and of the pipe on the other form a closed conductive path (an "earth loop"). If even slight differences in potential arise between the two earths, such as might be caused by the electrochemical potential differences of different materials, the low resistance of the loop can easily cause large currents to flow. This in turn means that noticeable potential differences arise in the connecting path between the LO input and the pipe, leading again to measurement errors.

In order to take precise measurements in such a system, the instrument itself must not have its own earth connection – in other words it must be electrically isolated.

At this point we can formulate a few rules, to which more comments will be added below:

- For sensitive electrochemical measurements, the reference potential of the measurement set-up should be connected to earth at just one point.
- If the object being measured does not have its own earth connection, the simplest technique is to use an earthed instrument. If an electrically isolated instrument is nevertheless used, an additional earth connection should be made.
- On the other hand, if the object being measured is connected to earth at some point, then an electrically isolated instrument *must* be used.
- If possible, whichever part of the object being measured is likely to function most powerfully as an antenna should be connected to the instrument's LO input.
- If extensive screening is necessary, the instrument's LO input is connected to the screening, such as the Faraday cage.
- If an earthed instrument is used for the measurements, all the conductors at earth potential in the region around the measuring location contribute to the avoidance of interference. Conductors that are not earthed, however, function as transmitters of interference. Workstation supports, stands, screening cages and any observers should therefore also be grounded.

These tips are first of all oriented to the frequently occurring situation in which electrostatic interference limits the accuracy of experimental measurements. This is typical for electrochemical measurements on coating layers, micro-electrodes, or when pH electrodes are used, as well as generally when the typical currents are less than the order of magnitude of a μA.

They should also help to avoid incorrect measurements of potential resulting from ground loops, which unfortunately also have effects when the typical currents are in the higher ranges, which otherwise are not problematic.

If the above rules are taken seriously, then it is usually possible to avoid the inconvenience of using a Faraday cage. As an example, when measuring the corrosion potential of the coated inner wall of a beverage can, it is necessary for the measuring arrangement to be protected very effectively from electrostatic interference. A reference electrode is placed for this purpose inside the can. If, following typical electrochemical practice, the reference electrode is connected to the LO input of the earthed
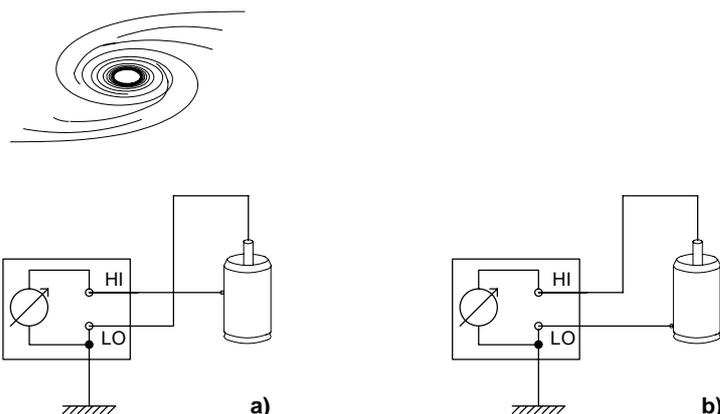
Fig. 36 Two ways to measure the corrosion potential of the protective layer inside a beverage can: in arrangement a the potential is disturbed by the electric fields of the environment. If one connect the can to ground (b) much less interference will arise.

measuring instrument, the body of the can act as an antenna for interference (Fig. 36a). If the body of the can is connected as the working electrode to the LO input, the can acts as a perfect screen for the reference electrode inside, connected to the HI input (Fig. 36b).

Deciding on the optimum design for the measurement set-up is not always as easy as it is for a simple measurement of potential. In potentiostatic experiments we begin by thinking about four leads instead of just two. If there are additional signals (e.g. in disc-ring experiments) or more sophisticated methods (such as fast pulse and impedance measurements) it becomes even more complicated. The points made above remain just as important. Optimum design of the measuring set-up, however, sometimes requires additional knowledge about the instruments being used and how they are connected or isolated from ground.

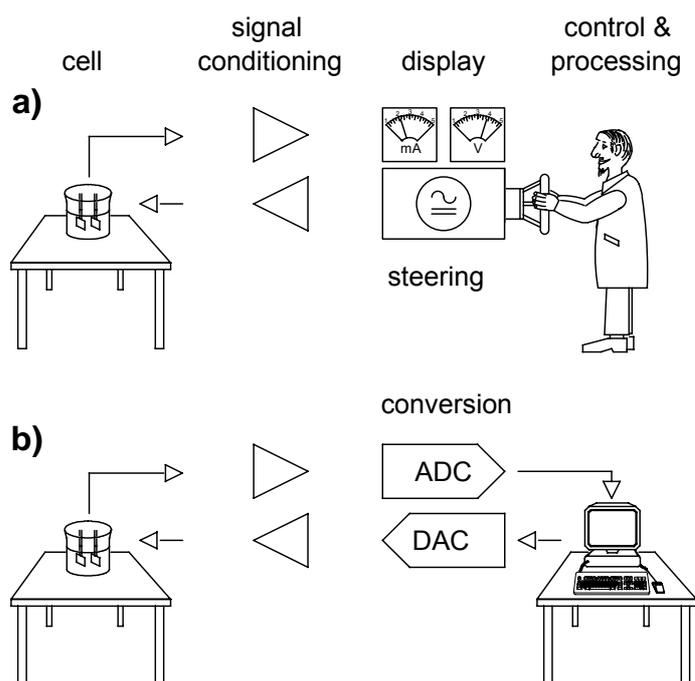<p align="center">THE COMPUTER AS A MEASUREMENT SLAVE</p>

Fig. 37 Traditional (a) and computerised (b) electrochemical experiment.

At the information output of most of the circuits processing analog signals discussed above one or more symbols for measuring instruments have generally been drawn.
In our considerations so far, the function and method of operation of the modules has been our primary focus. We have therefore ignored the fact that in modern laboratories a large part of the information has, for a long time, not been passed directly from a display instrument to the observer's eye (Fig. 37).

The signals that have been created are instead first digitised, and then further processed by a microprocessor. Although a PC is at the end of the line of measurement processing, an entire hierarchy of processors can sometimes be involved. Required signals such as the value and the modifications over time of the set potential and set current of the potentiostat or galvanostat are no longer simply controlled by manually adjustable voltage sources and function generators. The set magnitudes are instead specified by microprocessors as digital values, and are fed through digital/analog converters to provide analog electrical signals for controlling the equipment.

The crucial steps here are the conversion of the analog measurements into digital values – the Analog/Digital conversion A/D – and the inverse process of Digital/Analog conversion D/A, [7]. Analog measurements represent physical magnitudes. As such, and leaving aside quantum effects, they can be "resolved" to any degree, just like real numbers. In digital calculators, on the other hand, data has only a limited resolution. The resolution is usually indicated by the data's word length. This is the number of independent binary information units, or bits, in one data word. Eight such bits, each of

which can adopt precisely two states, are known as one byte, a data word that therefore can adopt 2^8 = 256 discrete states. One straightforward way of representing these states is to number them with integers from 0 to 255.

It is now easy to picture the digitisation process. What is necessary is to distribute the expected range[5] of a measured physical magnitude in an appropriate way over the number of discrete states in a data word. One byte could be used to represent voltages from 0 to 255 V in steps of 1 V. If the zero point and the range of values is adapted rather more appropriately for typical electrochemical values, the voltage range from -1.28 V to +1.27 V could be represented with a resolution of 10 mV. Smaller or larger values than the chosen interval can, of course, not be represented, and lead to an underflow or overflow situation. The expected range represents a segment of the series of real numbers, while the range of the digital states is a segment from the series of integers. It is therefore also possible to formally understand the digitisation process as a linear mapping of an interval within the series of real numbers onto an interval within the series of integers (see also Fig. 38).

This is a severe loss of information – or so it might appear. Lengthening the data word brings an improvement. If we represent the range of measurements discussed above, from -1.28 V to 1.27 V, by means of two bytes instead of one, then we require a 16-bit A/D converter. This gives us the digital result with a resolution of 2.56 V / 2^{16}. The resulting steps are then about 40 μV wide – it is hardly possible to determine an electrochemical potential more precisely than this.

The problem of D/A conversion is quite similar. In this case, the desired output range for the specified magnitude is represented by the interval of the discrete states of the data word that describes it. An 8-bit D/A converter scaled as above can therefore provide an output for the set value of a potentiostat over the range from -1.28 V to +1.27 V with a resolution of 10 mV, while steps of about 40 μV are provided by a 16-bit D/A converter.

So – do we want more resolution, according to the slogan "a lot helps a lot"? No other isolated parameter related to digital measurement acquisition is so misleading as the number of bits in A/D and D/A converters, since the word length only indicates how many states are, in principle, available – how accurately occupied they are in fact remains quite open. The user can get a much clearer representation of the precision of an instrument from the traditional error specification. The manufacturer here quotes an absolute uncertainty along with a value-dependent relative uncertainty, and whichever is the larger will apply. The controlled output voltage of the potentiostat mentioned above, could, for instance, be specified as follows:

Output voltage: resolution 16 bit, uncertainty $\pm$ 0.5 mV absolute, $\pm$ 0.05% of the set value.

This would be quite a respectable specification for an electrochemical device – it is seldom for the output voltage of a potentiostat to really be more precise. The permissible error here is, as is usual when long word lengths are quoted, about an order of magnitude greater than suggested by the bit-resolution.

A/D AND D/A CONVERTER FAMILIES, FUNCTIONAL PRINCIPLES, INTENDED APPLICATIONS AND CONVERSION PARAMETERS

If we pay attention to the traditional methods of quoting errors, then we are quite well protected from nasty surprises. If the reader finds this enough, he can skip the chapter that follows.

A more detailed consideration of the properties of A/D and D/A converters (in the following short ADC and DAC) is necessary if we want to orient ourselves reliably in the jungle of computer-controlled instrument specifications. The most important static specifications (i.e. relevant in the time average) of absolute and relative errors, as explained above, can easily be understood through the diagram of the representation process (Fig. 38). On one side is a segment from the series of real numbers corresponding to the range of set or expected values. In the above example of the 8-bit DAC this extends from -1.280000... to +1.270000..... On the other side is the range of integers that indicates the available states of the digital word.

---

[5] The literature often refers to the expected range of a physical magnitude as its dynamic range. Although an attempt is made in this chapter of the book to restrict the use of the adjective "dynamic" to processes that vary in time, the term "dynamic range" will be used below in its accepted meaning of the expected range.

If the converter operates perfectly, the two ranges fit together precisely (Fig. 38a). If the two segments are displaced with respect to one another, then the difference from the ideal value is a fixed amount, the offset error (Fig. 38b. In addition to this, the length of the analog segment can differ from the intended value, leading to an error proportional to the analog value, the gain error (Fig. 38c).

Both the offset error and the gain error make significant contributions to the total error. With word lengths of 13 bits or more, they usually dominate any digitisation error associated with the resolution. The static precision of a converter can also be impaired by errors in the linearity of the mapping. Figures on linearity, however, appear to be the poor relation of manufacturers' specifications. Nevertheless, they are enormously important for digitally generated control signals in the majority of
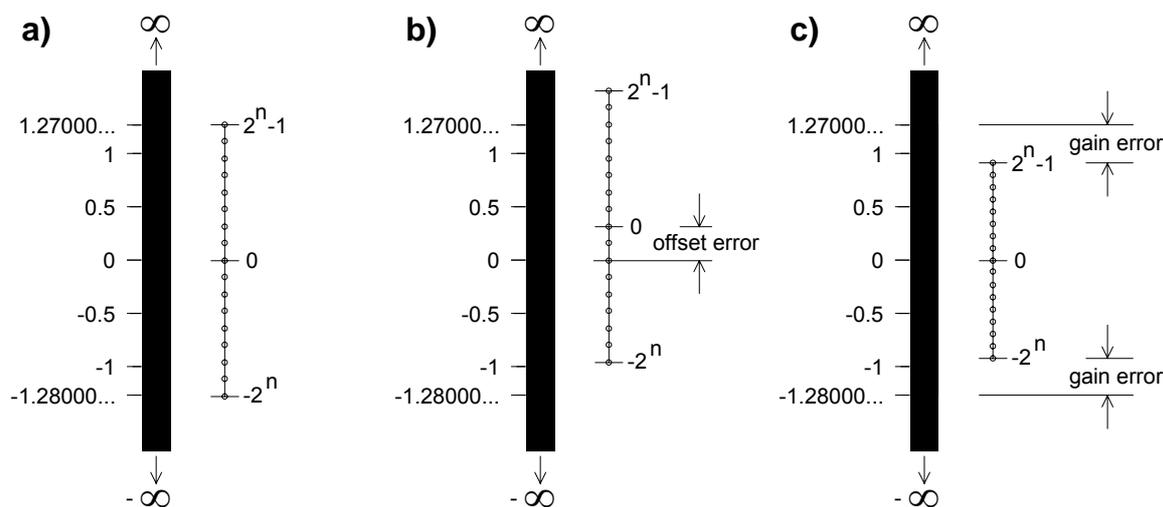
Fig. 38 Proper conversion (a), conversion affected by offset error (b) and gain error (c).

dynamic measurements.

Fig. 39 differs from the principle of Fig. 38 primarily in that the association between an analog value and a digital code is represented on X and Y co-ordinates. An ideal converter is illustrated by a straight staircase function. It passes through the scaling points defined by the initial and final values of the intervals. Converters with offset or gain errors miss these points (Fig. 39, left). Fig. 39, right, shows the characteristic curve of a converter with linearity errors. A bend in the staircase results in "integral non linearity, INL", while deviations from the constant step height result in "differential non linearity, DNL".
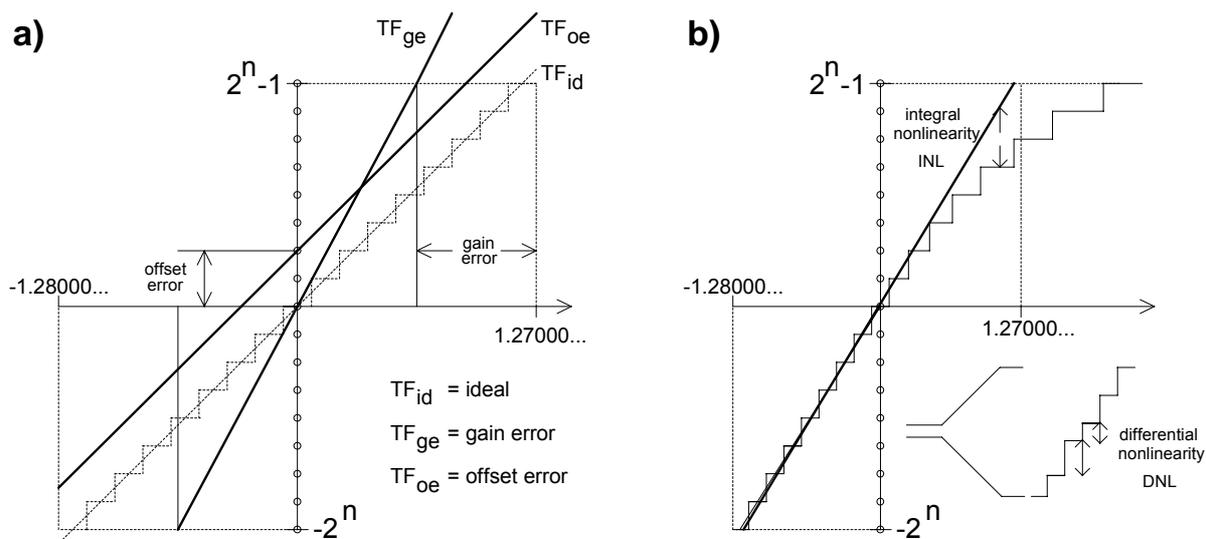
Fig. 39 Converter transfer functions. Precise transfer function TF and affected ones by gain and offset error (a). Transfer function affected by linearity error (b).

If the DNL does not exceed the average step height (the bit step for the least significant bit, LSB), then the contribution to the total static error can usually be neglected. If, however, the DNL is larger than one bit step, the transfer function is, at that location, not monotonic. Conversely, if a converter can be

classified as monotonic, this means the same as DNL < 1 LSB. In systems involving feedback, such as digital controllers, non-monotonic ADCs can cause greater problems than might be expected from their contribution to the static error. This point aside, ADCs with moderate DNL are a lot less problematic than corresponding DACs. This is because if DACs are used for a dynamic drive, the DNL contributes a strong noise to the signal output magnitude. There are a large number of electrochemical methods, such as cyclic voltammetry, where this leads to a drastic deterioration in the measuring precision. Fig. 40 shows the cyclic voltammetry curve (CV) of a capacitor when the controlling DAC has significant INL and DNL errors.

Fig. 40 Oscilloscope diagram of a CV measurement from a capacitor, controlled by a DA-converter which exhibits different types of linearity error.

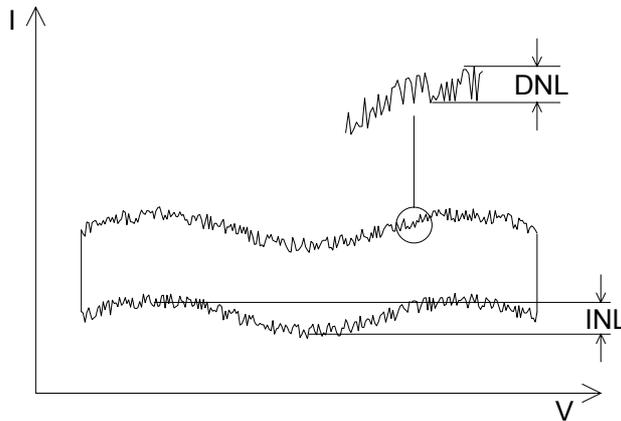The result of replacing analog ramps by digitally controlled staircase functions during voltammetry measurements will be discussed in more detail in the tips for the associated measuring methods. We can also see in the example illustrated in Fig. 40 that the dynamic behaviour of the converter is also significant, on top of the static error specification. Because their dynamic behaviour is primarily determined by the way in which they function, the properties of the most popular A/D and D/A converter architectures are discussed below.

Tab. 3 provides a summary of the name, typical word lengths, conversion rates (in measurements/s), popular applications and fundamental properties of ADCs.

Functional principle/name	Word length	Conversion rate	Application	Comment
Successive approximation	8 - 16	100 kHz – 300 MHz	Universal, multi-channel measurement acquisition	Sampling principle S/H circuitry required
Sigma/delta	16 – 24	10 Hz – 100 kHz 192 kHz	Low-frequency, audio	Partially integrating
Ramp	Decimal 4 – 8 digits	0.1 Hz - 10 Hz	Precision DC measurement, multimeters	Continuously integrating
Parallel	6 – 10	MHz – GHz	High-frequency, video, radar	Continuous

A/D converters that use the principle of successive approximation (SAR-ADC) find a digital value representing the value of the input voltage for a short period as it changes over time. The input voltage must not change during the "conversion time" – that is the time between taking the sample and determination of the digital value. This is usually ensured by using an integrated sample-and-hold circuit (S/H) that acquires the available signal within a very short time span and then supplies it, as a constant value, for the converter to measure during the conversion time.

SAR-ADCs can be used very broadly, and their behaviour is easy to understand. They are less suitable for the highly accurate measurement of slow processes or for DC. They are, however, most suitable as "workhorses" in electrochemistry for applications such as fast voltammetry, pulsed processes and EIS.

SAR-ADCs can be non-monotonic, but the INL is nevertheless sufficient for many applications. Economical 16-bit SAR-ADCs have a typical INL of ± 4 LSB and a DNL of ± 1 LSB at conversion rates of 100 kHz. In microprocessor-controlled applications the gain and offset errors can be calibrated out, so that a typical static precision of 14 bits is achieved. The precision of individual measurements does not drop dramatically even when acquiring signals that are changing rapidly.

The short signal acquisition time also means that measurements can be taken at signal frequencies

that are much higher than the maximum conversion rate. It is therefore necessary to remain aware of the Nyquist criterion, which states that:
The highest frequency, f_g, present in a mixed signal may not be higher than half the conversion rate, f_s (Eq. 49).

$$f_s \geq 2 \cdot f_g \quad \text{The Nyquist criterion} \tag{49}$$

The Nyquist criterion quantifies a straightforward statement: if a signal changes so fast that a sequence of A/D conversions cannot keep up, then the digital values that are found do not represent the signal.
In practice, preceeding low-pass filters are used in an attempt to prevent this problem of "aliasing". Such filters suppress frequencies in the signal mixture that are above a specified "limit frequency", and in this way reduce the speed with which the signal changes. If the limit frequency is set to a value significantly below half the conversion rate, as required by the Nyquist criterion, aliasing errors are avoided.
The unpleasant consequences of aliasing are discussed in the subsection describing EIS measurements.

Sigma-delta ADCs operate more slowly than SAR-ADCs, and the measurement represents the signal level over almost the full conversion time, or even a multiple of that (integrating measurement by approximation). If the measuring rate approaches the maximum conversion rate of the converter, the Nyquist criterion is satisfied approximately, even if higher frequencies are present.
Sigma-delta ADCs are generally also more precise. A monotone transfer characteristic and a low DNL are automatically ensured by the principle of operation. Integrated microcontrollers often compensate offset and gain errors by an automatic calibration. The INL, however, is usually significantly worse than the resolution might suggest. Systematic noise at certain frequency ranges also impairs the achievable precision. Because it is usually essential in electrochemical measuring systems for the electronic circuits described above for signal acquisition and preparation (buffers, amplifiers, INAs, filters) to precede the ADCs, and because these are not included in the auto-calibration process, the attractive specifications of such converters are, in practice, of low use.
Sigma-delta ADCs are not very suitable for sampling a large number of channels, because they either require long conversion times or a number of conversions in order to settle to a stable final value. Sigma-delta ADCs for audio applications are not suitable for instrumentation purposes.
Still more time consuming are ramp ADCs. They are the best option when high static precision, stability and low noise are important, and when time plays a subsidiary role. The conversion processes are self-calibrating and integrating. Most ramp ADCs are used in digital multimeters, for which reason they often supply their output in decimal rather than binary form, so that a display can be driven directly. This is not very suitable for the acquisition of measurements by microprocessor. The electrochemical engineer should nevertheless surround himself with a few ramp ADCs in the form of accurate multimeters. This allows him to keep close tabs on his instruments.
Parallel ADCs are specialists in acquiring rapidly changing signals. Rather than using a sequential procedure to determine the individual bits, as in the other processes, they are determined in parallel at the same time. Parallel ADCs allow to achieve high sampling rates at the expense of low static precision, high price and high power consumption.

As the cyclic voltammetry graph of Fig. 40 demonstrates, the flow of data from the computer to the object being measured also calls for our attention.
Only the first two types of DAC listed in Tab. 4 are suitable for instrumentation purposes. Whereas the principle of construction of DACs based on switched voltage dividers ensures that they are monotonic, the INL nevertheless leaves a lot to be desired. This is due to the fact that it is constructed internally of a number of segments, which is why it is alternatively known as a segmented DAC.

In this respect, the performance of the single bit converters, primarily familiar from audio technology, is much better. Their function is similar to an inverse of the sigma-delta A/D converters.

Like these, however, they also suffer from systematic noise at certain frequency ranges. This is not a problem in audio applications. The noise and the poor static precision of single bit converters means, however, that they are of little use for electrochemical purposes in spite of their outstanding linearity.

Tab. 4 Summary of the name, typical word lengths, conversion rates, popular applications and fundamental properties of common D/A converter types.

Functional principle/name	Word length	Conversion rate	Application	Comment
CMOS - R2R	8 – 16	DC – 1 MHz	Universal voltage divider	Multiplying
Switched current sources	6 – 16	DC – 100 MHz	Signal synthesis Video	Low noise High power consumption
Switched voltage divider	12 – 16	DC – 100 kHz	Digitally operated control loops	Construction-dependent monotonic
Single-bit converter	16 – 24	DC – 100 Hz, 192 kHz	Voltage sources, audio	Construction-dependent linear and monotonic

CMOS-R2R DACs are also used as digitally programmable voltage dividers. They have the disadvantage for these applications that higher frequency interference does not become proportionally reduced when very low output voltages are set.

High resolution converters of this type are nevertheless the first choice for control sources in electrochemistry. Because perfect linearity is difficult to achieve with these devices, only the high price component batches with the best specifications should be used.

It must be recognised that the specification of DACs must be seen as more problematic than is the case with ADCs. It is therefore better, when attempting to choose devices, to first look at the specification for the output voltage and the output current of potentiostats and galvanostats. An impressive low uncertainty of a few µV when measuring the potential may look good in the brochure, but what use is this to the electrochemical engineer if the set voltage can be wrong by a full millivolt?

In the end, the method applied also determines whether a statement of resolution or of precision has any real relevance. This can be seen in an example from EIS: the stability, resolution and precision of the stationary component of the set voltage in the potentiostat in use is just as important here as it is in most other electrochemical procedures. The principle of EIS, moreover, is based on the superimposition of a small excitation on top of the stationary magnitudes. The question, however, of whether the excitation amplitude here is 1 mV or 2 mV does not have any systematic effect on the result, provided only that it is sufficiently small. Under these circumstances, it is irrelevant whether the setting range of the excitation amplitude is set with a high resolution of 0.01% with the aid of D/A converters, or just in large steps of 1-2-5 using a long chain of electromagnetic relays. There is one property that usually does not appear in specifications, but is more important than the resolution: the setting procedure should ensure that the noise and interference voltage components also shrink proportionally at small excitation amplitudes. Otherwise it is almost impossible to take precise impedance measurements in markedly non-linear systems.

It is also important in a computer-controlled electrochemical workstation for the A/D and D/A conversions to be perfectly synchronised. This implies that the appropriate option of integrating or sampling A/D conversion is used for the particular method.

IV. THE STANDARD ELECTROCHEMICAL METHODS FROM THE POINT OF VIEW OF INSTRUMENTATION TECHNOLOGY

The electrochemical engineer would be likely to classify the various working techniques as observational, chemical-analytic and preparative methods. The first group is the largest, with prominent representatives such as Tafel methods, EIS, cyclic voltammetry and electrochemical noise analysis, or ENA. The second group includes polarography and related methods [8]. Preparative methods generally exploit electrolysis.

Such a division in accordance with the purpose of the application is unfortunately not very helpful in terms of the instrumentation techniques employed. A more suitable approach would be to make the classification according to the way time is handled, and whether the electrochemical system under test is actively controlled:

1. **Passive**: These methods are restricted to observation of the electrochemical system under investigation in an open electrical circuit. Examples of this would include measurements of equilibrium potential over time, or measurements of the electrochemical potential noise.
2. **Static**: Here the circuit including the electrochemical cell being investigated is closed under specific external electrical conditions. Polarisation measurements, such as current against time in potentiostatic operation, the galvanostatic complement of this, or measurements of electrochemical current noise are typical examples of this group.
3. **Variable steady state**: As in the static case, the system being investigated is set into a specified state in a closed circuit, and the observable parameters are measured. The measurements are repeated a number of times as the conditions are systematically varied. It is expected that the system's response to the modified conditions has settled by then to a new, steady state condition. Examples of this include the recording of current-voltage curves for Tafel evaluation, or measurements of the effect of loading on fuel cells.

4. **Dynamic**: As in the steady state case, dynamic measurements are taken while the system is being actively controlled, while systematic changes are made over time. The difference is that it is, however, not expected that a steady state has been achieved with respect to the control magnitude. Instead, we are also, or even mainly, interested in the time response of the system. EIS, CV, linear and pulse voltammetry, polarography and current interruption methods are the most familiar representatives of dynamic procedures.

PASSIVE MEASUREMENTS OF EQUILIBRIUM POTENTIALS

The passive methods present the fewest headaches. The general requirements for an instrument to measure potential, such as high input resistance, good static precision and CMRR have already been extensively discussed. They are particularly significant for potentiometry in analysis and sensor technology.

When investigating electrochemical potential noise, however, the static precision is of less importance than a high dynamic range. In ENA we are mostly interested in small fluctuations in the potential over a period of seconds. The electrodes being investigated often, in addition, have a much greater drift in the mean potential over long time periods (Fig. 41). In order for the relevant small component of the signal to be recorded with sufficient precision, and for it to be separated
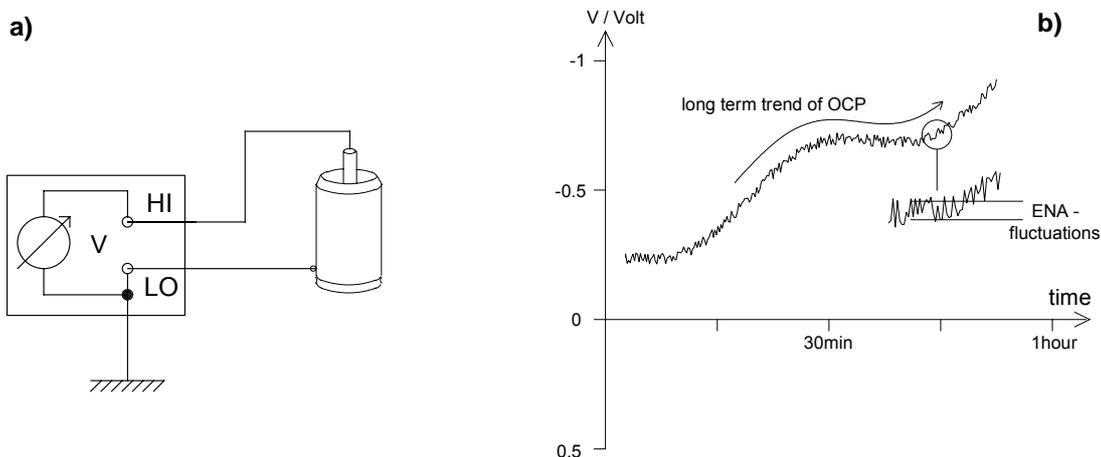
Fig. 41 The electric arrangement for the ENA of the OCP is common with the usual passive potential measurement methods (a). In contrast to that methods, ENA is more interested in small fluctuations in short time scales which are superimposed to the long term trend of the potential (b).

through computation from the larger long-term trend, analog signal conditioning with the lowest possible intrinsic noise is first necessary. Further, the subsequent A/D converter requires a high resolution, and must be monotonic, although the INL is, in this exceptional case, of lower significance. This means that sigma-delta A/D converters with medium resolution (around 20 bits) and with a sufficiently high conversion rate (100 Hz or more) can usefully be employed.

STATIC SYSTEM CONTROL

The static methods generally require, in addition to the measuring instrument, a potentiostat or galvanostat to control the state of the system when the electrical circuit is closed. In order to measure electrochemical current noise it is sometimes sufficient to set the potential to zero. Using a ZRA to provide a virtual short-circuit for the current measurement is an adequate approach. The same considerations that apply to ENA of the potential apply, in this form of ENA, to the ZRA and the A/D converter.

If potentiostats like those of Fig. 30 are used to generate a fixed potential for the measurement of current over time (Chronoamperometry) it is of crucial importance that the generation of the set potential and the power stage are stable and that they produce little noise. Because the dynamic behaviour of electrochemical cells over a wide range of times is dominated by the capacitive components of the double layer and transport processes, small fluctuations in the controlled voltage are powerfully amplified in the current response – the faster the fluctuations are, the higher is the amplification.

It is therefore important to pay attention to the specification of the frequency spectrum of the potentiostatic noise. If the application does not require high output voltages and currents then, as so often, it may be a case of "less is more": providing the facility for high power levels makes it more difficult to construct a low-interference potentiostat – less powerful devices usually create less noise and are more stable.

How much interference in the flow of the data itself finally makes its unwanted way through to the evaluation depends on the filtering and on the type of A/D conversion. As has already been mentioned when discussing the Nyquist criterion (Eq. 49), low-pass filtering or integrating A/D conversion processes can minimise the effects of high frequency interference.

There is, furthermore, a question to be answered regarding the most favourable position for the current measuring set-up within the circuit. If the manufacturer inserts the ammeter in the current feed to the working electrode (Fig. 42a), the requirements on the CMRR of the current sensing path are light, and do not depend on the voltage of the counter electrodes. It is therefore easy to achieve a large range of output voltages for the counter electrode in this arrangement.
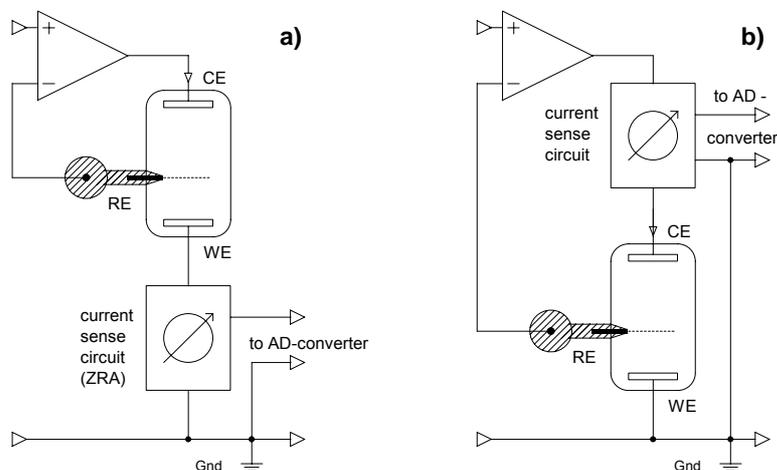

Fig. 42 Two alternatives for the placement of the current sensing path within a potentiostatic arrangement: The solution a) easily allows the application of high output voltage and current to the cell, due to low CMRR requirements.
The more expensive version b) has the advantage that the working electrode is insensitive to interference, due to their direct connection to the LO reference.

Alternatively, Fig. 42b, shows an ammeter inserted in the circuit for the counter electrode. Because the instrument in this case "floats" at the potential of the counter electrode, a good CMRR is very important. Specially constructed INAs with wide frequency ranges are therefore used in fast potentiostats, although their range of DC potentials is restricted to less than ± 15 V. Potentiostats with the structure of Fig. 42, right, therefore have a restricted range of output voltages. The advantage of this arrangement is that the working electrode is connected directly to the arrangement's reference potential. Whereas the arrangement of Fig. 42a, means that all the electrodes in the cell are sensitive to electrostatic interference, it is even possible in the arrangement in Fig. 42b, like that of Fig. 36, right, to touch the working electrode without fear of interference.

Galvanostatically controlled Chronopotentiometry and ENA are less critical than their potentiostatic equivalents – as we shall see below, however, this does not apply to their dynamic cousins.

MEASUREMENTS WITH VARYING BUT STEADY STATE POTENTIAL AND CURRENT

First, it is of course true that in the physical world strictly steady state parameters cannot be achieved – in fact, the term "quasi-steady state" would be more appropriate. The intention is to change the electrical conditions of the electrochemical system being investigated so slowly that the contributions of its "electrical memory" to the system response are negligible. In the case of the acquisition of a current-voltage curve this has the effect that noticeably slower or faster recording does not have any effect on the resulting measurements.

It should also be obvious that a steady state, according to the definition above, cannot be achieved in systems that are dominated by capacitance or inductance.

Having made these basic points, we can now turn to the instrumentation technology involved in steady state methods. This does not differ greatly from that used for static system control.

The requirements for the dynamic current measuring range, however, do become sharper when the potential is being varied. Let us imagine a typical "state-of-the-art" A/D converter intended to measure the current. It has a resolution of 24 bits, and a precision of a full 18 to 19 bits – limited by the INL and by noise. If we begin recording our current-voltage curve with around 1 mA to exploit the converter's full range, we achieve a fantastic precision, better than $\pm 10^{-5}$. Nevertheless, measurements close to the equilibrium potential, displaying a few nA, can be incorrect by a full 100 %! In other words it is not possible to rely on the dynamics of the A/D conversion process when measuring current, any more than it is for the magnitudes that depend on it, such as impedance. A good electrochemical workstation has a dynamic range for current measurement of about 10^{12}, which is about a million times better than the best A/D converter. If currents over a range from 1 pA up to 1 A are to be measured accurately, the range of measurements must be adapted to the current flowing at any one time by switching the circuitry.

The requirements for rapid response in quasi-steady state methods are relatively relaxed. For this reason, range switching during the measurements can be automatic.

When assessing the capacities of an electrochemical workstation it is therefore important to consider how many current measuring ranges are available and how great are the steps between them. It should be possible, when using slow methods, for the equipment to search for the optimum current measuring range itself.

A little scepticism is particularly appropriate when thinking about small currents. If the most sensitive current measuring range is quoted as having a full-scale value of ± 1 nA, and if a high resolution A/D converter, as described above, is available, then it is not possible to estimate the sensitivity simply by combining the full-scale deflection with the resolution of the A/D converter. The result would be unrealistic. A universal electrochemical workstation can not, of course, count individual electrons like peas. Measurements in the fA range and below can only be successfully carried out using special probes in the immediate neighbourhood of the object being measured, and in the presence of perfect screening. Painstakingly accurate control of temperature, air humidity, air ionisation levels and all sources of piezo-electric effects are essential here. A simple experiment can make this clear. Obtain a small 1 GΩ test resistor. Applying 10 mV should result to current of 10 pA. In order to get a feel for the problem, do a small breath on the resistor. This will change the current dramatically.

Steady state methods usually operate according to a fixed time scheme: this starts with setting up the new system conditions – this is followed by waiting until a quasi-steady state is achieved (settling phase) – the steady state measurements are then taken. The loop is then closed by starting the next cycle. Under these circumstances, continuously integrating measurements have no value – they would mean that the measurement was affected by information from the settling phase in addition to the wanted information relating to the measurement. Instead of this, a sample must be
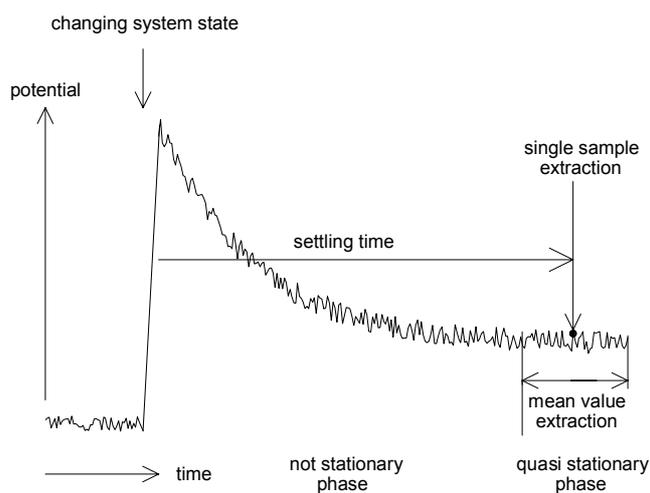

Fig. 43 Applying steady state methods means that one has to wait for a certain settling time after changing the system state. Instead of extracting just one sample which is representative for a very short time, one should take the mean value of a certain interval.

taken for measurement at the end of the settling phase (Fig. 43). This does not allow aliasing effects to be completely avoided.

But instead of using a fast A/D converter to take precisely one measurement in each cycle, it is a better idea to form the mean over a rather large measuring interval. As has been explained above, the mains frequency is a principal component in the mixture of interfering signals. If the measuring system uses a multiple of the mains period as the measuring interval, the worst interference can be suppressed.

DYNAMIC METHODS

It is a particularly demanding task for a universal electrochemical measuring system to master the broad field of dynamic measuring methods.

DYNAMIC PULSE METHODS

We begin with dynamically sampled pulse methods, because the requirements here are at least similar to those of the quasi-steady state methods. In contrast, however, the requirements for time response are not at all simple – on the contrary.

The quality of the measurements depends crucially on the precision of the timing, which often must be synchronised with external events. As a representative for a range of methods, most of which are applied to electro-analytic purposes, Differential Pulsed Polarography, DPP, will be used.

It is well known that the attraction of mercury as an electrode material for polarography is due to two particular properties: one is that mercury has the highest hydrogen over-voltage of all metals. The other is that by periodically generating drops of liquid metal it is convenient to continuously provide a fresh electrode surface.

If the DPP is to yield reproducible relationships from drop to drop in relation to the electro-active surface while measurements are being taken, it is necessary for the acquisition of samples for the measurement accurately to be synchronised with the growth of the drops.

In DPP it is assumed that the component of the current that cannot be assigned to the electrode reactions is approximately independent of the potential.

For this reason the stable, yet still unsaturated, electrode surface is used, so that by applying a potential step it is possible to separate this component of the current from the component of the Faraday current that is independent of potential, through computing the differences. Fig. 44 illustrates the principle of DPP.
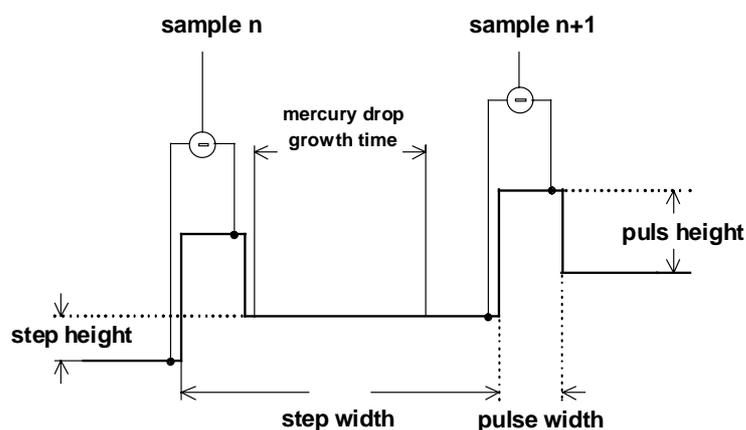
The time intervals for the individual phases of DPP lie in the range from seconds down to milliseconds, the droplet growth phase being the longest.

Even small time uncertainties have noise effects with an immediate influence on the measurement. A PC running a multi-tasking operating system cannot provide the necessary precision for time control. An effective instrument for polarography should therefore be controlled by a powerful microprocessor system of its own.

The high level of information yielded by sensitive electro-analytic methods depends on the

Fig. 44 The principle of DPP. Potential steps are applied, clocked with the controlled growth of the mercury drops. The current is sampled at times just before and after a certain delay behind the steps. The current difference will be processed.

accurate measurement of extremely small electrode currents. In addition into the need for accurate time control and current sensitivity in the instrument, the process is also challenging to the user. It is essential that he takes the guidance for avoiding electrostatic interference seriously.

LINEAR VOLTAMMETRY

The methods of linear voltammetry, or LSV, are typical examples of dynamic techniques. A potential changing at a constant rate – a ramp – is applied to the electrode under test. Cyclic voltammetry, CV, is the most widely applied example of these techniques. In this approach, ramps with rising and falling potential alternate periodically.

The ramp's rate of potential rise, $\Delta V/\Delta t$, has a characteristic effect on the dynamic component of the various current mechanisms in the electrode. Current due to capacitive effects rises in proportion to $\Delta V/\Delta t$. If diffusion processes are also responsible for limiting the charge transfer current, the current rises approximately in proportion to the square root of the rate of rise of potential. If the curve along the $\sqrt{t}$ axis is integrated, the effect of diffusion can be largely suppressed, and a quasi-stationary curve is obtained. Under ideal circumstances it is also possible to determine kinetic information such as the order of reactions, rate, valency and degree of reversibility of the transfer reactions involved by carefully analysing the potential level and the magnitude of anodic and cathodic peak currents and their dependency on $\Delta V/\Delta t$.

CV does sometimes demonstrate a certain weakness. The theories applied to interpret the measurements are based on the assumption that there is a constant rate of rise of the immediate electrode potential – a potentiostat, however, is only able to set the sum of the electrode potential and the voltage drop in the column of electrolyte above the electrode, U_Ω (Ohmic component). A significant Ohmic component impairs the analysis of the data. The traditional approach to this problem has been through modifications to the apparatus, by applying a variety of techniques to compensate for U_Ω. This will be considered again in the section covering current interruption methods. The "queen" of the dynamic methods, EIS, is not heavily disturbed by the Ohmic component – in the past, this has caused CV to rather trail behind EIS. However, the use of micro-electrodes allows the Ohmic component to be largely avoided in the simplest way imaginable: A comparable value of electrolyte conductivity as is found with a traditional large-area electrode is here associated with only a small fraction of electro-active surface. This is equivalent to a strong reduction of the electrolyte resistance share on the total potential drop. With the increasing popularity of micro-electrodes and ultra-micro-electrodes, and with the increase in the sensitivity of instruments that has occurred at the same time, CV has also regained some lost territory.

In the past, the linear voltage rise needed as the set value for the potentiostat has been generated with special analog OPA circuits[6]. Even if the circuitry is constructed carefully, the precision that can be achieved in this way is limited, especially when the rate of rise of potential is low.

As digital techniques have advanced, it has become natural to apply them to generate the linear rise using a digital controller and a D/A converter instead of using analog methods. In this way it is easy to generate any desired voltage waveform or slew-rate with a stable behaviour, even down to zero voltage rise.

This method of controlling electrochemical experiments with a microprocessor has now become popular, but has presented CV with a new problem. The output voltage of a D/A converter fed with successively increasing numerical values is, when examined closely, not quite like a ramp but rather a staircase (Fig. 39). Increasing the resolution makes little difference: instead of the smooth ramp, the steps of the staircase are still there, even though they are smaller.

Considering capacitive objects will help us to focus on the important difference between a ramp and a staircase. If one applies a voltage signal V(t) to a capacitor, the current $I(t) = C \cdot dV/dt$ will flow. A constant slew rate results in a constant current. In contrast, discrete steps will cause current pulses with δ-pulse shape - that means in theory infinite height for an infinite short time interval, but with a well defined integral charge of $Q = C \cdot \Delta V$. In practice the δ-pulse will be distorted to a short pulse of high amplitude accompanied by some ringing. Its shape is determined by the combined pulse response of the potentiostat and the electrochemical cell. If the measurement technique samples the response signal after a certain time delay relative to the step, the result must be wrong! The only way to get a correct current result is to measure the charge by integrating the total step interval and to calculate the mean current. This calculated current value is identical to the one measured under continuous analogue sweep conditions. The most exact way to perform integrating measurement technique under this conditions is to use fast AD-conversion combined with low pass filtering – with a bandwidth still high enough to avoid significant distortion of the potential waveform – but with a high

---

[6] If an IA is constructed with a capacitor feedback, C_{fb}, instead of a feedback resistor, R_{fb}, an integrator is obtained: the output voltage, V_{out}, is proportional here to the negative time integral of the input voltage. A constant input voltage therefore generates a linear voltage ramp at the output. If the input voltage is reversed when a particular maximum or minimum potential is reached, then the triangular voltage required for CV can easily be generated.

over-sampling AD-conversion rate.

Test your CV set-up. If your CV software offers you a facility for setting delay times, you should be warned. You will soon discover the wrong measurement strategy if you attempt to take a cyclic voltammetric graph on a capacitor: a 10 μF capacitor subject to a rate of rise of ± 100 mV/s should yield a rectangular cyclic voltammetry graph, with a current amplitude of ± 1 μA within the limits of component tolerance.
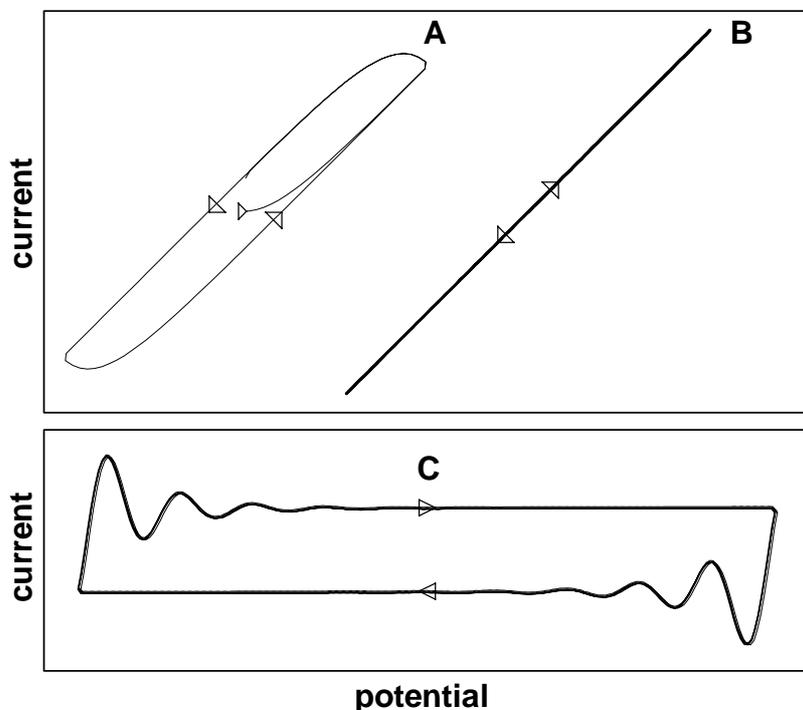

Fig. 45 Fast CV test runs can help to detect high frequency distortions. The first two curves exhibit, what one has to expect testing a high Ohmic resistor. Distortions compared to the proper response curve B are due to an excess signal delay in the low current sense circuit (curve A).
In curve C the effect of a reference electrode with high source resistance is displayed when testing a capacitor (refer also to Fig. 55).

Switching current ranges over many decades can only be managed using electro-mechanical relays if the requirements for accuracy relevant to electrochemistry are to be satisfied. The switching time of relays results in gaps, typically a few ms long, in the continuous current being measured. For this reason, the rates of rise encountered in CV, which can be high, mean that switching the measuring range for the rapidly changing currents cannot be done automatically without itself disturbing the experiment. It is therefore better to carry out continuous CV measurement within a fixed current measuring range. Before the final measurement, therefore, manual or automatic tests should be carried out in order to estimate the most favourable measuring range.

High scan rates associated with the measurement of small currents present a serious technical challenge. Under such conditions, CV must be looked on as a fast method. The consequences in terms of parasitic effects are similar to those occurring with EIS (Fig. 45). Constructional tricks described later for arrangements of cells that will function effectively at high frequency also help fast CV.

CURRENT INTERRUPTION METHODS

The electrical behaviour of any electrode is described by a network that always contains two elementary components (Fig. 6). These are the capacitance of the electrochemical double layer and the Ohmic resistance of the electrolyte. They form a series circuit. If the current flowing through the electrode is switched off suddenly the partial potentials on the capacitance and the resistance behave quite differently:
whereas the partial potential across the double layer changes relatively slowly, the voltage drop across the electrolytic resistance, R_{el} collapses with (almost) no delay. A potential jump can therefore be seen at the moment when the current is interrupted in the graph displaying the potential against time (Fig. 46a). This corresponds to the product of the series resistance, R_{el} and the current, I, before the interruption, which is the Ohmic share, U_Ω, of the total potential. It results, as was explained above in relation to CV, in an uncertainty in the determination of the immediate electrode potential. While it is possible to eliminate U_Ω after the measurement when using slow methods, it is worth striving in linear voltammetry to compensate for it within the measurement process. The traditional method for

compensating U_Ω combines the voltammetry with phases of interrupted current. The value of U_Ω that has just been found is automatically added to the set voltage value. This method may be popular, but it has problems. One reason for this is that switching circuits on or off, particularly in systems with feedback such as the potentiostatic loop, are always associated with the injection of charge. In other words, the electrical system being investigated is continuously disturbed to an unknown extent by the injection of charge.
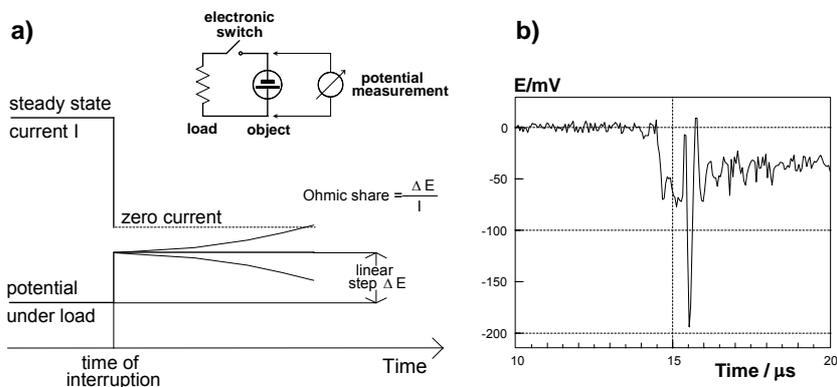

Fig. 46 The principle of the current interruption method for determining the Ohmic component from the potential step response is shown in an idealised form in the graph of Fig. 46a. The graph of Fig. 46b shows a real step response of a 300 cm^2 PEM fuel-cell when a current of 80 A is switched off.

Anybody who has done much work with EIS knows another reason: determining the voltage jump, U_Ω, in the time domain corresponds to observing the high-frequency behaviour of the electrode in the frequency domain. It can easily happen that the relevant frequency range is subject to heavy parasitic interference effects, so that equating the step response to U_Ω can lead to results with little significance (Fig. 46b).

The strategy of determining the resistance of the electrolyte as precisely as possible beforehand, such as by measuring the impedance, is subject to fewer problems. The measuring system calculates the correction component from the current flowing at the time, and adds it to the set voltage while the voltammetry is being carried out (digital feedback). It is alternatively possible to feed back a signal directly via an adder to the potentiostat (analog feedback), which is proportional to R_{el} and the current being measured.

Both forms of coupling, however, do impair the electrical stability of the arrangement of cells. If we attempt to eliminate U_Ω perfectly, the potentiostat tends to oscillate. As a rule of thumb we should content ourselves with compensating for no more than 90% of the Ohmic component.

The Ohmic components of electrodes, or of complete cells, not only interfere with electrochemical measurements, but are also important characteristic parameters when assessing the efficiency of batteries, accumulators, fuel cells and in electrolysis. As is also explained below, precise determination of the Ohmic component using EIS can fail, particularly in highly conductive systems, as a result of mutual inductance. It is, nevertheless, possible to obtain useful results under such circumstances from the high-current interruption method. It is, however, necessary to carry out an extensive mathematical analysis of the step response, as can be guessed from Fig. 46.

ELECTROCHEMICAL IMPEDANCE MEASUREMENT, EIS

Getting involved with EIS [9, 10] for the first time one may find it intuitively difficult to grasp the processes around. Not having an innate sense of alternating current is one reason for the problem. Another lies in the enormous dynamic range encountered in these methods: the conductivity of electrochemical cells in common use extends over range of about 12 orders of magnitude – it extends from the behaviour of an almost perfect conductor to almost total insulator. The highly conductive end of the range is marked by large batteries and fuel cells, while barrier coating systems are items that are close to being insulators. A 12 orders of magnitude are also necessary to cover the range of currents involved in stationary electrochemistry – but in EIS, frequency is added as a further dimension: with the electrochemically relevant range of frequencies starting at less than 10^{-5} Hz and extending to around 10^7 Hz, EIS covers a quite enormous range. This is doubled again, if the complex nature of impedance is taken into account.

With so much room, it is easy to overlook the fact that physics places drastic restrictions on this freedom to use high frequencies:

Theory might like to consider impedance two-poles as objects with no dimensions and two connections – in practice, EIS provides impedances only as electrochemical cells, more or less extended in space. In addition to this, the connecting leads from a cell to the measuring instrument

significantly add to the effective dimensions of the cell.

As a result, as cells are investigated at higher and higher frequencies, we cannot help but reach frequency ranges where the electrical behaviour is no longer determined by the contributions of the two-pole impedance, but by undesired parasitic effects. In other words, every cell has a characteristic limiting frequency, above which EIS makes no sense, as illustrated in Fig. 47. At lower frequencies almost the whole dynamic range is available to the experimenter with sufficient measurement precision. At high frequencies, two fundamental effects lead to increasingly tight restrictions on the relevant dynamic range: the curve for high impedances is affected by the unavoidable stray capacitances that appear to be connected in parallel with the impedance under investigation. Their origins are primarily to be found in cable capacitances and in the input capacitances of measuring instruments. Contrary to what we might guess, the series inducta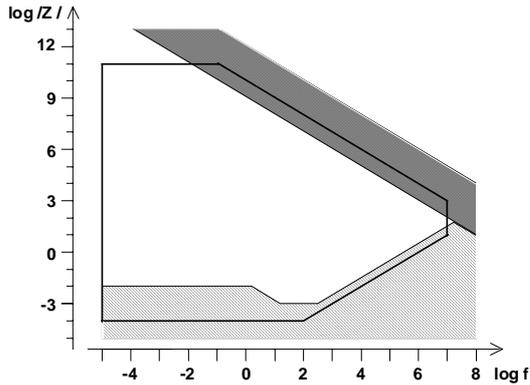nce of the cables (complementary to the stray capacitance) bears less responsibility for the curves for small impedances with well designed connection technology. This is because the effect of this inductance can be very effectively minimised, as described below. In contrast, the effects of electromagnetic coupling between the current-carrying leads on one hand and the leads for measuring the potential on the other hand are quite dramatic. This mutual inductance is usually given very little consideration, but it is the main reason why impedance spectroscopy on fuel cells, batteries and other low-resistance objects at high frequencies can be very difficult.

A general limitation for extremely high impedances results from the thermal noise in accordance with Eq. 44: a resistance of $1T\Omega$ at room temperature, with a signal bandwidth of 1 kHz generates an effective noise voltage of about 4mV – quite comparable to the small signal amplitudes that are preferred for EIS for the sake of maintaining linearity. About 12 orders of magnitude is, however, also the approximate limit of what can be covered by the best instruments in a fixed configuration of apparatus, because greater current sensitivity for even higher impedances prevents an instrument from being used to measure very small impedances – and vice versa.

Fig. 47 Estimated dynamic range for successful EIS measurements by means of a state of the art instrument. The limitations at high frequencies are mainly caused by stray capacitance (high impedance limit) and mutual induction (low impedance limit).

The shaded areas at the top of the diagram mark the typical impedance range of films and barrier coatings. The ones at the bottom sketch the impedance range of fuel cells. EIS measurements in both ranges are not easy to carry out.

We need to consider briefly the way in which EIS equipment functions if we are to design the experimental setup to be used for successfully EIS measurements.

It is well known that EIS is based on the principle of impressing a small excitation – one that allows to treat the investigated system as linear – onto a possibly non-linear object in a stationary condition (Fig. 8). In modern EIS measuring equipment, an integrated potentiostat holds the electrochemical cell in a stationary state as well as superimposing the test excitation. It is driven by a DC power source for stationary control, and by a frequency generator that is responsible for the dynamic component. The impedance cannot be measured directly, but is calculated from the measurable magnitudes of voltage and current. Fig. 48 illustrates the principles according to which such equipment is constructed.
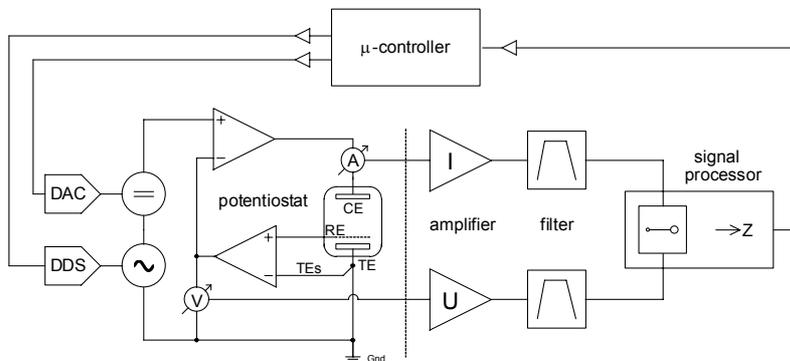
Although it might at first appear otherwise, the frequency response of the potentiostat is not, in this arrangement, critical for the achievable precision at high frequencies. The incomplete

Fig. 48 Functional scheme of a modern EIS equipment. The cell is controlled stationary as well as dynamically by a potentiostat. It is supplied by a DA-converter for the stationary set magnitude and a DDS[1] signal generator for the dynamic excitation. The dynamic shares of the measured voltage and current are separated from the steady state signals and processed in parallel. The impedance is calculated from the complex quotient of both signals.

reproduction of the set signal by the potentiostat at the location of the cell has an equal effect both on the voltage measured and on the current. If the amplitude of the exciting signal is still sufficient in comparison with interfering magnitudes, the potentiostat's errors are fully cancelled when measuring impedance. The symmetry of the parallel signal processing routes for voltage and current is nevertheless crucial if a precise result is to be obtained.

If a ZRA is used to obtain information about the current, then the symmetry is violated before we start. A perfectly symmetrical arrangement results, on the other hand, if we use the shunt principle shown in the Fig. 48 to measure the current. If, as the frequency curve is being registered, the shunt reference resistor used for measuring the current is adjusted to the measured impedance automatically by switching ranges, the amplitudes in the two signal routes remain of comparable size, and the error resulting from crosstalk is minimum. This is an effective way of coping with the possibly extreme dynamic range of EIS object. This route is, however, only open to impedance measurement carried out under potentiostatic control. If, instead of a small AC voltage, AC current is supplied as excitation, the current measuring range is determined. Instead of the many orders of magnitude that can be covered by switching ranges when using a potentiostat, only the internal dynamic range of the voltage measuring channel is available in galvanostatic mode. A fixed current amplitude also means that the resulting voltage amplitude when passing through the spectrum can not only become unwanted small, but also can reach unacceptably high values in relation to the non-linear properties of the electrodes being investigated. It is therefore generally a good idea to prefer potentiostatic operation, and to use galvanostatically controlled EIS only after careful thought, and to restrict it to objects with small impedance variation over frequency such as batteries.

Good measurement software can do one last thing to alleviate the situation. The desire for current control does not really spring from the need to actually specify the excitation amplitude in the form of a current. Voltage and current are, after all, of equal status in the realm of impedance. The point is rather that the flow of DC current is more often representative of the stationary state of a cell than a fixed cell voltage. We might consider in this respect the task of recording the impedance spectrum of a battery as it discharges. Small variations in process values like temperature or fuel gas pressure, which are changing the cell voltage, mean that similar considerations apply to fuel cells. Their operating conditions are also better characterised by a specific load current than by a stable potential.

In this situation, the measuring software in a potentiostatic set-up can exploit the short pauses between the impedance measuring samples to modify the potential, in order to regulate the DC current back to a constant value, while the impedance measurement then follows without difficulty under potentiostatic control ("pseudo galvanostatic" EIS).

A similar strategy is followed by the "pseudo equilibrium potential" measuring mode when EIS is used for corrosion research: pauses in the measurement are used here to give the system being investigated an opportunity, with the potentiostat switched off, of settling to the actual, free corrosion potential. Following this, the next impedance value is found at this potential, under potentiostatic control.

As explained in the section discussing the role of the measuring environment, the competition between wanted (signal) and unwanted (interference) components in the measurement plays a crucial role in determining the achievable precision. Let us "transform" this consideration to the consideration of impedance. It can be seen that the proportion of signals at interfering frequencies, $f_s \neq f$, that make unwanted contributions to the measurement is crucial for the precision of the impedance, $Z(f)$, at the desired signal frequency, f. There are clear advantages to using sine waves as the excitation signal.

Unfortunately, high spectral purity (low spectral bandwidth Δf) of a sine signal is directly associated with its oscillation duration Δt (Eq. 50) and in turn for the measurement time.

$$\Delta f \geq \Delta t \tag{50}$$

If sine waves are used, the interfering frequency components other than the signal frequency can be suppressed by means of electronic band pass filters.

In order to determine the impedance spectrum with sufficient frequency resolution in this way, the signal frequency is changed step-by-step. In the low-frequency part of the spectrum, this becomes a game of patience: after all, a single period at 10^{-5} Hz takes more than a whole day.

In terms of measuring time, it is not just the patience of the electrochemical engineer that is a problem, but the stability of the system under test, as will be described later.

Excitation functions and filtering can be designed in such a way that, instead of a mono-spectral sine wave, other harmonic frequency components[7] are exploited at the same time. The intriguing

---

[7] If we restrict ourselves, as is indeed essential if digital filter algorithms are to be used, to periodic signal forms, then all the other frequency components are integral multiples (harmonics) of the fundamental frequency, which is itself the inverse of the period.

consequence is that rather than merely measuring one point, a number of points in the spectrum can be determined at the same time in a single measuring cycle. At low frequencies, however, the time that can be saved by using multi-spectral methods in comparison with sine wave methods is not very large [1]. The time advantage also comes at a high price:
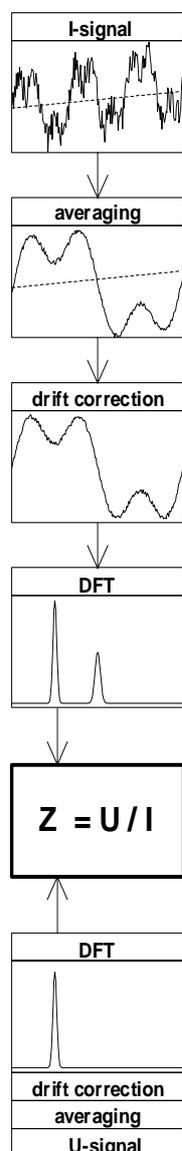
In an electrochemical cell can, like in any non-linear system, mono-spectral excitation result in interfering harmonics in addition to the regular system response. If we work with multi-spectral signals, the interfering components enter into the evaluation along with the desired higher frequency system response. In contrast to sine wave measurements, where the formation of harmonics as a result of non linearity is easily detected as interference, when using multi-spectral methods they inevitably lead to measurement errors. If comparable information density and precision are required, the time required using multi-spectral methods can even be longer than what is needed for sine wave methods.

As a result, sine waves have become generally accepted for use in EIS. Multi-spectral methods can, however, claim to have a certain importance in applications where the time advantage is of significantly greater importance than the loss in precision.

Because the discrete Fourier transform, DFT[8], is a precondition for the application of multi-spectral methods, it is often associated with the disadvantages of multi-spectral methods. Using the DFT here in combination with sine wave EIS can be very helpful: if fast A/D converters are used to sample the sine wave of the measuring signal synchronously with the measuring frequency at a large number of points, over-sampling can create a digital image of the signal with a high time resolution in the memory of a signal processor (Fig. 49). If, additionally, the mean course of a large number of sequential periods is calculated in the memory (averaging), then interference that is not correlated with the measuring frequency is effectively eliminated. DFT can then be applied to decompose the stored and averaged image from a large number of periods into its frequency components. The DFT has the effect here of a powerful digital filter. The fundamental wave corresponds to the measuring frequency. The fundamental components of the voltage and current signals can be used to calculate the desired impedance without error, even if the potentiostat can only partially follow the provided sine wave. If, in addition to the fundamental wave, close harmonics are found in the system response, this is also an indication of non-linearity. The ratio of the power of the fundamental wave and the weighted[9], summed power of the harmonics (a kind of signal/noise ratio) can be used to estimate the uncertainty of measurement.

Fig. 49 The principle of the high over-sampling impedance measurement technique. After the analog pre-processing the primarily acquired excitation and response signals are sampled synchronously with high rate. Several periods are averaged to one mean period course by adding up the samples of equal phase in consecutive cycles. Contributions of steady state signal drift may be compensated optionally. The impedance is calculated as the quotient of the DFT fundamental share of both signals. An uncertainty estimation can be obtained from the weighted integral of the lower harmonics share.

In summary, it can be stated that DFT sine wave methods involving a large number of samples (over-sampling methods) are, due to their insensitivity to interference and harmonics[10], superior to those of their simpler cousins that must content themselves with satisfying just the Nyquist criterion (Nyquist methods). Modern devices therefore no longer usually work with Nyquist methods, as represented by the traditional digital correlation or analog lock-in techniques.

Let us return again to the problem of measuring time. Strictly speaking, electrical impedance is only defined for stationary systems. Nevertheless, EIS has also to be applied to systems that are not perfectly stable. It is therefore not impossible for the drift to be large enough for a noticeable change in the stationary component of the system response to be caused while one point on the spectrum is being measured. It is possible - assuming that periodic methods are being used - for this drift to be measured while the spectral measurement is proceeding, and to be compensated for through

---

[8] The DFT is the discrete image in the digital domain for the familiar continuous Fourier transform. The DFT is most often applied in the form of the fast Fourier transform, FFT. If the digital image of a signal curve is available as a sequence of 2^n values with equal intervals between them, the FFT can very rapidly determine the frequency components of which it is composed.

[9] As well as being caused by non-linearity, lower order harmonics can also indicate components of interfering frequencies close to the measuring frequency that can partially pass through the digital filter.
In contrast to higher order harmonics, they should be taken seriously as an indication of measurement errors.

[10] Harmonics are also often generated when a potentiostat is required to operate simultaneously at high frequencies and high currents ("non-linear distortion factor").

calculation. There are, however, strict limits to this kind of "online drift compensation" (Fig. 49).
Even with a relatively weak drift it can still happen that the state of the object being investigated differs noticeably at the end of one complete measurement from its state at the beginning.

Impedance spectra from this kind of changing system are difficult to interpret. Time effects can, however, very easily be detected in EIS data. A normal electrochemical impedance spectrum corresponds, as a rule, to the spectrum of an ideal two-pole, and does not have any discontinuities, strong resonances or jumps. For the Bode diagram (Fig. 9 & 10b, Eq. 37) of such spectra, the logarithmic Hilbert transformation for impedance two-poles, Z-HIT, predicts that the impedance modulus course, H, can be determined to a good approximation from the course of the phase angle, φ (Eq. 51), [11, 12].

$$\ln|H(\omega_0)| \approx const. + \frac{2}{\pi}\int_{\omega_s}^{\omega_0}\varphi(\omega)\,d\ln\omega + \gamma\cdot\frac{d\varphi(\omega_0)}{d\ln\omega} \qquad \text{“ Z-HIT”} \qquad (51)$$

The integral of φ over the logarithm of the frequency, ω, is formed for this purpose. The additional correction provided by a fraction, γ, of the derivative of φ provides a high precision in the approximation.
If the impedance modulus course calculated in this way does not agree well with the impedance curve determined experimentally, differences in the low frequency region of the spectrum suggest temporal drift, whereas those in the high-frequency regions indicate interference resulting from mutual inductance.
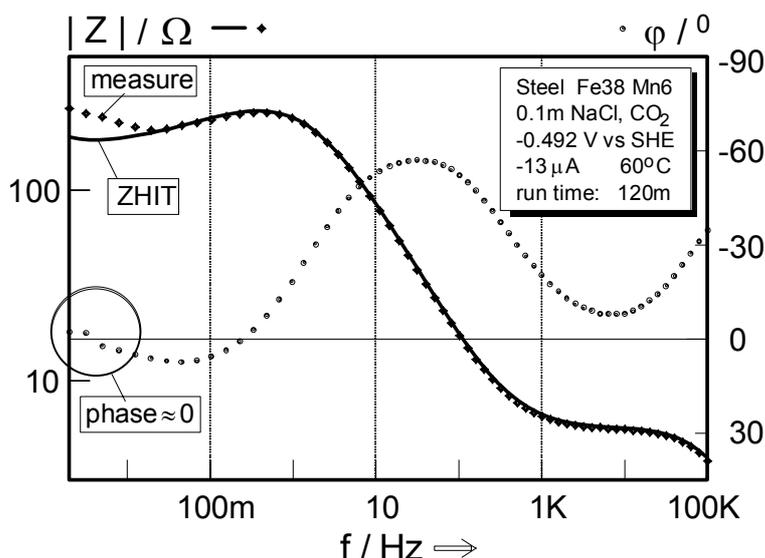

Fig. 50 Impedance spectrum of a non-stationary, corroding electrode in the Bode representation. The visual inspection unveils a violation of the ZHIT-rule moving to low frequencies: Impedance- and phase-course should depend approximately like a mathematical function and its first derivative, but the measured impedance modulus rises significantly, while the phase angle tends to zero.
The result of a precise calculation of the expected impedance course from the phase course after Eq. 51 is displayed as a solid curve.

There is a whole family of methods based on the so called Kramers-Kronig relations [13] with the intention to detect distortions in EIS data. Z-HIT is distinguished by simplicity: even without any mathematical treatment – simply by taking a close look at the Bode diagram – one is able to detect distortions of the proper shape of an impedance spectrum by comparing sign and magnitude of the phase angle with the gradient of the impedance modulus course.
Looking at the correctly measured Bode-diagram in Fig. 10b one observes, that a phase-angle, tending to zero for frequencies around 1 Hz and 10 KHz, corresponds to a gradient, tending to zero at this frequencies. The negative maximum of the phase angle in turn corresponds to the negative maximum gradient of the impedance at the 100 Hz inflection point – very close to the relationship between a mathematical function and its first derivative.
Differing from that, the impedance modulus course of a non-stationary (corroding) electrode in Fig. 50 exhibits a divergence at low frequencies: while the average phase angle is near zero, the gradient of the measured impedance (rhomb symbols) is clearly negative. The solid line in the diagram, calculated from the phase angle after Eq. 51, indicates the (correct) impedance course to be expected in the absence of any interference.

We can now summarize on what has been said about the EIS measuring technique:

• Time must be invested if meaningful results are to be generated with EIS. Anyone who ignores the fundamental laws of nature will immediately be punished by loss of information.

- Time should also be taken when studying the specifications of EIS measuring equipment. With such complex structures, it is easy to get lost in the jungle of impenetrable technical data. The frequency and amplitude resolution of the excitation, isolated data regarding converter resolution and the frequency range of the potentiostats are, like so much else, more camouflage than information.

- Of particular importance, in contrast, is the specification of the achievable accuracy of measurement in dependency on frequency, impedance value and excitation amplitude. A clear table or graph, such as Fig. 47, should not be missing. It is necessary to ensure here that this specification includes the entire measuring loop, including the potentiostat.

- Devices that work with oversampling are to be preferred. The weaknesses of devices that operate on Nyquist limit cannot be discovered either through the data sheet nor through measurements on a dummy cell. One will only get a clear picture through realistic electrochemical measurements under the most difficult conditions possible.

- Reliable data on electrochemical reaction mechanisms, kinetics, the electrical properties and topology of covering layers and electrodes are some of the strengths of EIS. One of its differences from other dynamic methods such as CV is that it does not supply any direct thermodynamic information. If we want to deal with the problem that there are always a few more unknowns in a system than can be determined by EIS, it must be combined with other methods. A factor to include in the assessment of measuring equipment is the extent to which other electrochemical methods are also supported. The facility of combining EIS with the measurement of the other internal and external physical magnitudes such as potential, time and temperature, and control of and by external events, are further important criteria.

- EIS measurements should be examined for signs of time effects – most easily by visually inspection based on Z-HIT. These effects, along with parasitic effects associated with the cell being measured and the cables, are the main causes of incorrect measurements. Intelligent software can minimise the coarsest effects of drift as the measurements are taking place, and it should support subsequent correction by means of the interpolation of spectral series vs. time.

THE CONSTRUCTION AND ELECTRICAL CONNECTION OF ELECTROCHEMICAL CELLS.

The construction of the electrochemical cell and its connection to the measurement instrument plays a key role in ensuring good quality measurements. This has already been seen in the section describing the effect of the electrical environment. This role is not, however, limited to the antenna effect of cables and cells.

The researcher does not generally have the freedom to optimise cells unilaterally from the point of view of electrical instrumentation. Electrochemistry must be carried out also in autoclaves, cryostats or furnaces, or it may be necessary to be able to move, observe or irradiate the electrodes during the experiment. The intended application can also dictate the form of the cell from the beginning – impedance measurements on batteries, or corrosion tests on beverage cans, fall into this category.

However the quality of the measurements – particularly those obtained from dynamic techniques – depends very sensitively on apparently insignificant details. For this reason it is vital to exploit the remaining possibilities for optimisation.

If current flows, the geometry of the cell is of critical importance, which is easy to understand. Any cell is, necessarily, a three-dimensional structure, and the current density distributes itself through this body in accordance with the electrical field and the conductors distributed across space. But as far as the homogeneity of the electrode material permits it, we attempt to simplify the model in such a way that only one dimension, z, parallel to the direction of the electrical field, has to be observed. Lateral movements in the xy-plane (the plane of the electrode being examined) should not find any differing relationships (Fig. 51).
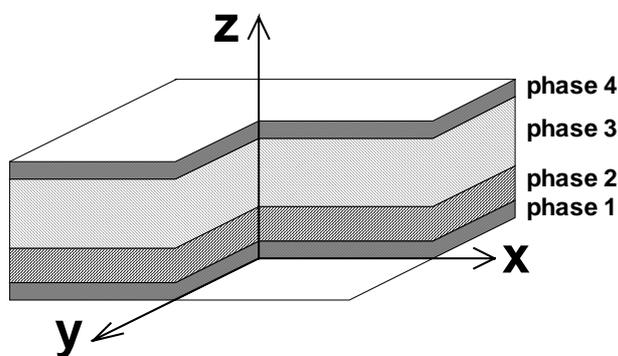

Fig. 51 One-dimensional effective electrode model. In direction z, which is also the direction of the electric field vector, different phases of matter may be stacked. Along the x or y direction one will find no differences at different sites.

Fig. 52 shows in two dimensions what must be observed with a planar arrangement of electrodes. Any possible effect of a reference electrode on the homogeneity of the field is ignored in the diagram.
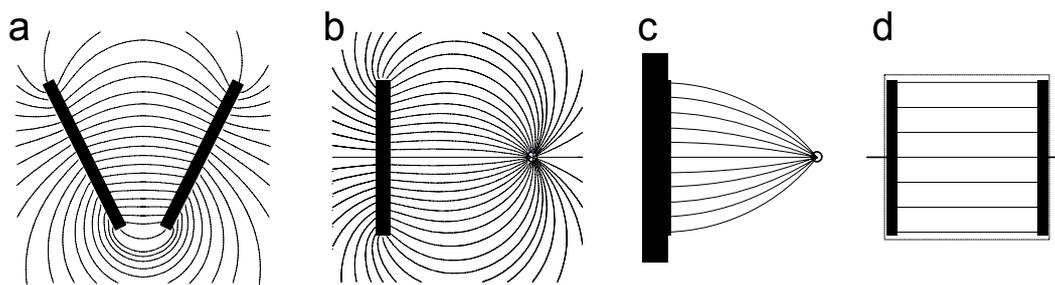

Fig. 52 There is a lot what can be done wrong regarding a simple arrangement of one or two planar electrodes within an electrolyte vessel. Only the arrangement *c* will produce an electric field in front of the working electrode of sufficient homogeneity. The ideal arrangement *d* has identical shape of both electrodes what is also the shape of all intersections along the electrolyte column.

A quasi one-dimensional geometry is, of course, not restricted to the planar arrangement of electrodes. Fig. 53 illustrates the important features of cylindrical electrodes. Similarly, when measuring with mercury droplets the counter electrode is best treated as an approximately spherical mesh electrode. It soon becomes clear that it is usually necessary to make compromises. An annular counter electrode with the droplet location in the centre is certainly a better solution here than an electrode plate located on one side.
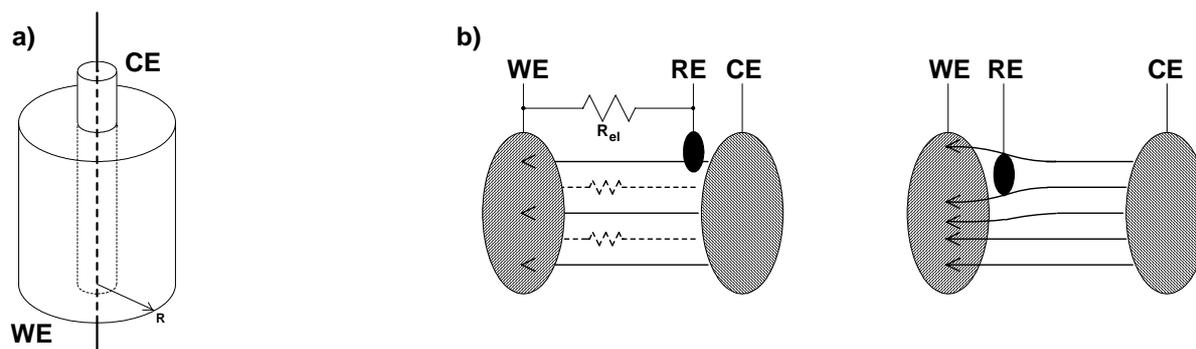

Fig. 53 a:: a cylindrical working electrode should have a cylindrical counter electrode accordingly in a symmetric arrangement. b: the position of the reference electrode obeys two contradicting rules: A site near to the counter electrode will increase the electrolyte resistance in an unnecessary manner. A position very close to the working electrode surface will distort the electric field nearby.

Unfavourable electrode geometry results in uneven current density over an electrode surface of uniform material. Moving away from one-dimensional geometry also makes it more difficult to separate the individual components of the total impedance into individual concentrated elements, such as the double layer capacitance and the electrolyte resistance. This is not such a severe problem for EIS. Methods based on the best possible compensation of the electrolyte resistance suffer more heavily. Because electrolyte columns of different heights are effectively in operation over different parts of the electrode surface, the compensation will fail.

Fig. 53 also suggests how the position of the reference electrode must be taken into account. Because no current flows in it, we might first think that it does not have any effect on the distribution of the field lines. In fact, both the position and the precise implementation of the reference electrode call for close attention. This has already been explained in the section about the role of the reference electrode position in the discussion of the potentiostatic arrangement (following Fig. 28 and Eq. 48).

The reference electrode disturbs the shape of the field lines in front of the working electrode as soon as their size in the region of its opening (capillary tube) is comparable with the distance to the electrode. The potential determined by the capillary is then no longer representative of the undisturbed region of the working electrode. If we approach the working electrode even more closely, the region in which the potential is being measured is strongly shielded from the field of the counter electrode. Fig. 54 illustrates this situation. The electrical model makes it clear that, instead of the undisturbed electrode potential, only a fraction of it is measured, which is delayed in time and phase-shifted by the distributed network R_2-Z_2.

The impedance spectrum from this kind of arrangement shows an unrealistically large negative phase angle, $\varphi < -90°$, in the frequency range that would normally be dominated by the double layer capacitance. This can be wrongly interpreted as a sign of a negative real component in the total impedance. The effects of this error on the impedance spectrum are still relatively easy to comprehend – in contrast to the situation with other dynamic methods.
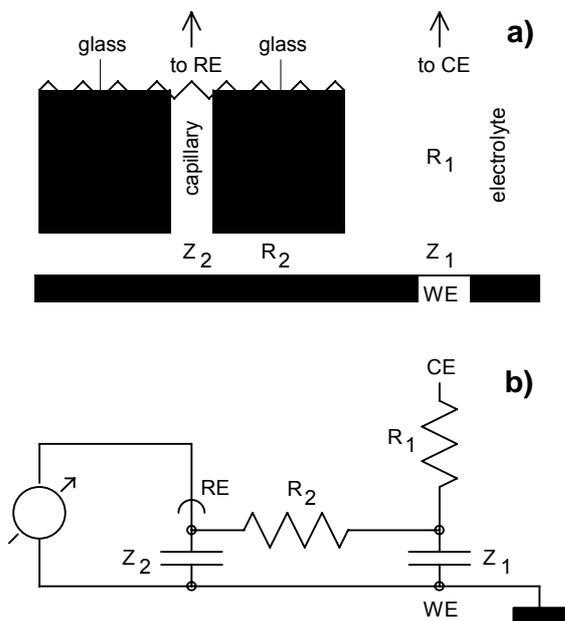
Fig. 54 a: A highly enlarged section around the RE capillary opening in front of the working electrode illustrates the role of the relevant impedance elements when determining the WE potential.
b: The corresponding (simplified) equivalent circuit shows, that the measured potential at RE is no longer representative for the undisturbed WE potential at the site of Z_1, if the capillary is brought close to the WE. R_2 increases if the distance capillary-WE is decreased.

If the electrode distance is made a little smaller again, the situation even becomes dangerous – at least for the cell, if a powerful potentiostat is connected. The function of the potentiostat turns into its opposite. Instead of stabilising the potential at a fixed value, the potentiostat falls into powerful electrical oscillation. Voltages and currents reaching the limits of the power capacity have been known to destroy a carefully prepared electrode. It can, for that matter, also become dangerous if a broken electrical circuit or a gas bubble separates the potentiostat from the actual potential information of the reference electrode.

When discussing the potentiostatic arrangement, it was also mentioned that the part played by the reference electrode in the quality of measurements goes beyond the effect of its geometry [14, 15]. The main reason for this is the source resistance of the potential probe (R_{ref} in Fig. 28). The combined effect of the unavoidable stray capacitances in the electrical structure distortes the potential i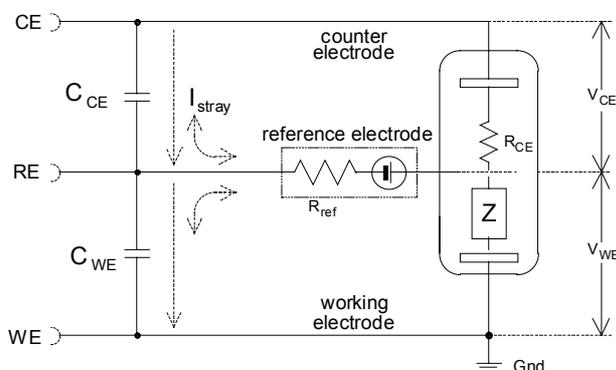nformation in a characteristic manner. These effects are most easily understood if we think in terms of EIS. Fig. 55 illustrates an electrical model of the measuring loop in which the parasitic components of the reference electrode circuit are included. The working electrode impedance being investigated, Z, together with the dominating electrolyte resistance of the counter electrode, R_{CE}, the source resistance of the reference electrode, R_{ref}, and its stray capacitances, C_{WE} and C_{CE}, form a voltage divider bridge for the measured voltage V_{RE} at the reference electrode terminal, across the test and counter electrodes.

It can be seen that, at high frequencies, V_{RE} depends almost exclusively on the

Fig. 55 The bridge coupling effect describes the parasitic behaviour of the reference electrode circuit at high frequencies. To calculate the impedance one is interested in the potential V_{WE} in front of the working electrode. But the only accessible voltage V_{RE} is affected by the current through the stray capacities C_{WE} and C_{CE}. High source resistance R_{ref} and high counter electrode resistance R_{CE} will favour strong high frequency distortions.

voltage divider formed by C_{WE} and C_{CE}, and hardly at all on the working electrode potential, V_{WE}.
The voltage drop, V_{CE}, across R_{CE} is usually many times greater than V_{WE}. Therefore as soon as the applied frequency is raised, leaving the interference-free low-frequency region, the flow of AC current from the counter electrode to the reference electrode through the stray capacitance C_{CE} is dominant. In this transition region, the error caused in the impedance spectrum can be approximately described as an inductance in series to Z.

We often see in the impedance spectrum of a classical 3-electrode arrangement that, instead of the constant impedance that corresponds to the electrolyte resistance, inductive behaviour is seen at high frequencies. This is not terribly surprising, because significant inductance in the feeds to the working electrode cause this to be expected. Sometimes, however, it is seen that the observed inductance is many times greater than the estimated lead inductance. It is a good idea not to ascribe this to some mysterious electrochemical process. It is more valuable to consider optimisation of the reference electrode construction, because the cause usually lies in the bridge coupling effect described above.
Once the effect has been understood, it is easy to think of effective improvements: both lowering of the stray capacitance and a low resistance construction, in particular of the reference electrode, allow the disturbance to be moved to less interesting, higher frequency, ranges.
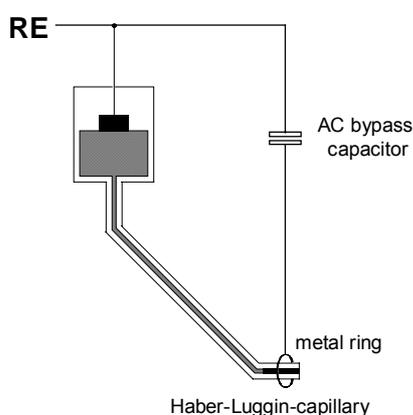

Fig. 56 An AC bypass enhances the high frequency performance of an usual reference electrode.

Reducing the size of the reference electrode and the length of capillary are very effective, as both of these have a favourable effect on lowering the stray capacitance and the internal resistance.
In addition to the reference electrode itself, its connecting leads make a significant contribution to the stray capacitance, and therefore a buffer amplifier close to the cell can often bring improvements, as has already been suggested in the section describing the voltage follower (Figs. 19 and 20).
The conductance of the reference electrode, $1/R_{ref}$, competes with the stray capacitances C_{WE} and C_{CE}. Lowering R_{ref} therefore improves the situation, even if only for AC. A little trick can be used to create a kind of AC bypass, in parallel with the DC path to the reference electrode, that does this job. Fig. 56 illustrates how a low resistance metallic auxiliary electrode (e.g. a Pt ring) is installed in the immediate neighbourhood of the capillary opening. The potential measured there is taken to the outside via an insulated wire. It can be connected via a capacitance, C, which should be significantly larger than the stray capacitances, to the standard output of the reference electrode.

There are a few lessons that we should draw from what has been said about the role of cell geometry and reference electrode construction:

- Provided the electrochemical system being investigated permits it, it is better not to turn a one-dimensional problem into a multi-dimensional one. In planar systems one should strive for geometrical similarity of the working and counter electrodes and of the electrolyte column. If the electrolyte column is not constrained to the electrode surface, at least seal off the rear of the working electrode from the electrolyte. It is not difficult to approximate a quasi one-dimensional arrangement in cylindrical, or sometimes even in spherical form.
- Do not attempt to minimise electrolyte resistance at any price – the cost can be too high. Estimates of favourable reference electrode positions have already been recommended in Eq. 48 and the section following this equation. The unfortunate reinforcement of the bridge-coupling effect resulting from raising the ratio of V_{CE} / V_{WE} provides a further argument in this direction. The reference electrode should never be brought so close to the working electrode that it hinders the passage of the field lines from the counter electrode in the region of the capillary opening.
- If one wants to carry out EIS successfully using three- or four-electrode techniques in the medium and high frequency ranges too, or if one is interested in clean dynamic measurements even at high rates of rise and with short pulse durations, the construction of the reference electrode should be at the centre of your attention. Avoid large dimensions, long electrolyte paths, bridges of low cross-sectional area and thick frits. The most reliable way to a good result can often be to construct a reference electrode or to fit the electrode with an AC bypass for the potential.

- Sometimes it is not possible to achieve the goal of a sufficiently low resistance reference electrode, perhaps because it is necessary to work in electrolyte of low conductivity. The best thing to do then is to decouple the reference electrode signal from the capacitance of the connecting leads and the input to the measuring instrument by means of a buffer amplifier. As shown in Fig. 20, the buffer can be used at the same time to provide screening against electrostatic interference.

A large part of the previous discussion of ways of ensuring good measurement quality has been concerned with the situation that applies to high resistance systems. This is no surprise. If the measured currents are systematically small, the competition with parasitic currents is of great relevance to interference. However, there are specific problems that occur when taking measurements on particularly low-resistance systems. Once again it is valuable to understand the causes, if opportunities for good measurement quality are not to be wasted. It has already been mentioned when discussing the limits of measurement using EIS equipment (Fig. 48) that mutual inductance is the main source of error there. This statement can be generalised to cover all the fast dynamic methods, with the exception of the current interruption technique. In order to take accurate electrical measurements on low-resistance objects, it is always necessary to employ four-conductor measurement techniques, in which there is a strict separation of the leads that carry currents from those that measure potential.
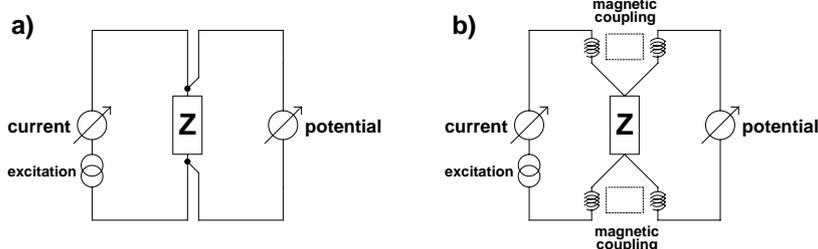

Fig. 57 The principle of the four electrode Kelvin connection scheme (a) and its high frequency equivalent circuit (b) explaining the mutual induction problem. High frequency mutual induction errors occur from the transformer like magnetic coupling between the current feeding and the potential sensing lines.

This has already been mentioned when discussing the principle of the four-electrode potentiostat (Fig. 30). This method of connection is also known as the Kelvin technique (Fig. 57a), [16]. The Kelvin technique alone, however, only avoids static measurement errors on low resistance objects. Mutual inductance must also be considered when taking dynamic measurements (Fig. 57b). Mutual inductance occurs when the magnetic fields from the current-carrying conductors in a Kelvin arrangement induce interfering voltages in the potential-measuring conductors.

Because mutual inductance is based on magnetic coupling, the usual defense mechanisms, instinctive to the electrochemical engineer, fail: screened wires, Faraday cages, earthing and similar techniques bring no improvement.

It is necessary to prevent as many magnetic field lines as possible from emerging out of a surface enclosing the current-carrying cables. One proven technique is to twist the pair of conductors together. The magnetic fields created by the current flowing to and from the object cancel each other almost perfectly because of their opposing directions. However, the finite distance between the pair of conductors means that a small residual field still emerges. If the pair of conductors used for the potential measurement is also twisted, the residual field causes almost identical interference in the two cables. Because the electronics that measures the potential only detects the potential difference between the two leads, the interference from the residual field has almost no effect.
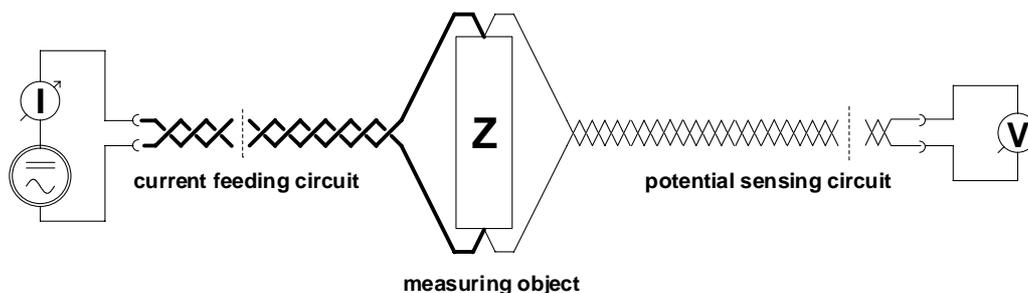

Fig. 58 Using two pairs of twisted cables for the current feeding as well as the current sensing circuit suppresses the mutual induction interference best. However, mutual induction in the immediate neighbourhood of the measuring object is nearly unavoidable.

Fig. 58 illustrates the principle of cancellation. It should, however, also be emphasised that perfect cancellation can never be achieved in practice. A structure that is absolutely free from mutual inductance is only possible in a few special cases having unusual symmetry. The object being measured also has a finite size, so that there is always an opportunity for mutual inductance to arise, at least in the immediate neighbourhood of the connections.

As explained, this represents the boundary for all dynamic measurement methods based on the simultaneous acquisition of voltage and current. For EIS, these effects can be summarised into a rule of thumb giving the upper frequency limit, f_{max}, for meaningful impedance measurements on typical objects, according to the expected impedance value, Z.

$$f_{max} \approx 10^6 \, Hz \cdot \, Z \, / \, \Omega \tag{52}$$

REFERENCES

1. R. P. Feynman, R. B. Leighton, M. Sands, in *The Feynman Lectures on Physics, Commemorative Issue*, Pearson Addison Wesley, 1989, p. 18-1

2. R. P. Feynman, R. B. Leighton, M. Sands, *The Feynman Lectures on Physics, Commemorative Issue*, Pearson Addison Wesley, 1989, p. 22-7

3. C. Kittel, in *Introduction in Solid State Physics*, 7th edition, John Wiley & Sons, 1996.

4. R. Woods, in *Electroanalytical Chemistry,* ed. A.J. Bard, M. Dekker, N.Y., 1976, vol. 9.

5. M. Abramowitz, I. A. Stegun in *Handbook of Mathematical Functions with Formulas Graphs and Mathematical Table,* Dover Pubns., 1974.

6. James K. Roberge, in *Operational Amplifiers: Theory and Practice*, John Wiley & Sons, 1975.

7. 'The Engineering Staff of Analog Devices', in *Analogue-Digital Conversion Handbook, 3rd* edition, ed. D. Sheingold, Prentice-Hall, Englewood Cliffs, NJ, 1986.

8. A. J.Bard, L. R.Faulkner, in *Electrochemical Methods*, John Wiley & Sons, NY, 1980.

9. J.R. Macdonald, in *Impedance Spectroscopy*, John Wiley & Sons, NY, 1987.

10. M. Sluyters-Rehbach, J.H. Sluyters in *Electroanalytical Chemistry,* vol. 4, ed. A.J. Bard, M. Dekker INC., N.Y., 1970.

11. W. Ehm, H. Göhr, R. Kaus, B. Röseler, C.-A. Schiller, *Acta Chimica Hungarica* **137**, vol. 2-3, 2000, p. 145

12. W. Ehm, R. Kaus, C.-A. Schiller, W. Strunz, in *Z-HIT – A simple relation between impedance modulus and phase angle, providing a new way to the validation of electrochemical impedance spectra*, ed. F. Mansfeld, F. Huet, O. R. Mattos, Electrochemical Society, Pennington, NJ, 2001, vol. 2000-24, p. 1

13. P. Agarwal and M. E. Orazem, *J. Electrochem. Soc.*, **142** , 1995, p. 4159.

14. H. Göhr, M. Mirnik, C.-A. Schiller, *J. Electroanal. Chem.,* **180**, 1984, p. 273.

15. G. Hsieh, S.J. Ford, T.O. Mason, L.R. Pedersen, *Solid State Ionics*, **91**, 1996, p. 191.

16. E. W. Golding, F. G. Widdis in *Electrical measurements and measuring instruments*, 5th edition, Wheeler and Co.