



## Electrical measurements

With emphasis on simple methods and instruments, materials aspects, electrochemistry, and impedance spectroscopy

Truls Norby

Department of Chemistry, University of Oslo  
FASE/FERMIO  
Gaustadalléen 21  
NO-0349 Oslo, Norway

## ***Welcome to KJM-MENA4010, Module 2; Electrical measurements***

In this module we will learn the most important principles of making electrical measurements. This involves measurements of voltages and currents using the appropriate instruments and connections, and to understand and minimize sources of error. Furthermore, we will discuss selected electrical measurement methods used to obtain physical and chemical properties of solids, liquids, and interfaces. We will cover direct current (DC) methods as well as alternating current (AC) measurements, and impedance spectroscopy (IS).

We aim at the end of the course to be understand and have some practical experience in

- simple electrical measurements of voltage, current, and resistance using handheld multimeters
- more sophisticated, scientific electrical measurements using stationary multimeters,
- use of AC signals, AC generators, and an oscilloscope,
- use of impedance spectrometers and impedance spectroscopy
- use of a potentiostat/galvanostat

The course is considered passed when the student has fulfilled the following:

- attended a major part of the lectures,
- done instructed exercises,
- taken part in the setup of a laboratory measurement
- written and have accepted a short report (typically 5 pages) of the setup and results

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## Electrical charge, current, potential, voltage, power, and energy

**Electrical charge** is a physical property of matter that causes repulsive or attractive forces between objects of charge of the same or opposite sign. Charge is quantized in multiples of the elementary charge  $e = 1.602 \times 10^{-19}$  C (coulomb). As symbol of charge we use, for instance,  $q$ . A proton has charge  $e$  while an electron has charge  $-e$ . Neutrons have charge 0.

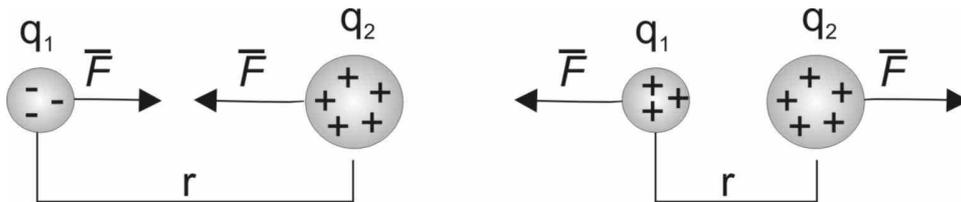


Figure 1. Electrical charges are multiples of positive or negative elementary charges, Objects of opposite or the same sign of net charge attract or reject each other, respectively.

**Current,  $I$** , results from the flux of charged particles and is thus expressed as the amount of charge per time:  $I = q/t$ . The unit for current is A (ampere).  $1 \text{ A} = 1 \text{ C/s}$  (coulomb per second). There are 96485 C/mol (Faraday's constant) of elemental charges (e.g. electrons). Consequently, a current of 1 A corresponds to approximately  $10^{-5}$  mol/s of charges. Current density  $i$  is current per area:  $i = I/a$ .

We often operate with direct current (DC) or alternating (e.g. sinusoidal) current (AC).

Current can be measured by the deflection of a magnetic pointer by the field around a coil. In modern instrumentation it is instead measured by the voltage generated over a standard resistor. The standard resistor for a current measurement should be as small as possible to pose a minimum series resistance in the circuit where the current is measured.



Figure 2. Three old amperemeters. The leftmost and middle have coil-driven analog pointers, while the rightmost is an electronic digital research multimeter (electrometer) from the 1980s which measures the current by the voltage over standard resistors.

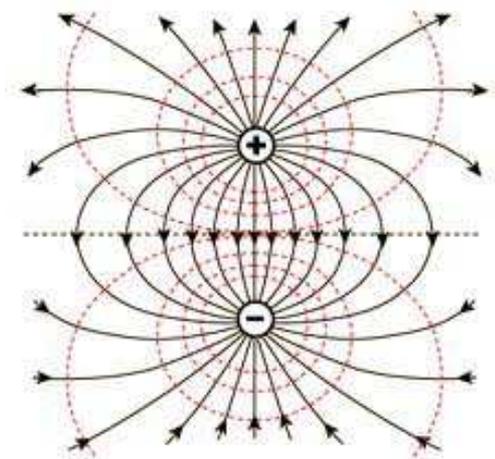
An amperemeter usually has a fuse that protects it from too high currents that will burn the coil or resistor or other circuitry if the instrument is connected directly to a voltage source (e.g. battery) without any other resistance in the circuit. Good advice for using amperemeters:

Don't connect it directly to a battery or other voltage source. Check that the fuse for the amperemeter circuit is intact (especially if the instrument indicates always zero current).

Some amperemeters (like the one in Figure 2 (right)) can measure charge by integrating the current over time.

The **electric potential** is defined and used in different ways. It is in one definition equal to the electric potential energy, namely the energy needed to add more charge. It thus has the unit joule per coulomb, J/C. The unit of electrical potential is volt  $V = J/C$ . As symbol for electric potential we use for instance  $\phi$  (phi).

An electric field is the region of space surrounding electrically charged objects. The electric field depicts the force exerted on other electrically charged objects. The electrical field strength  $E$  is depicted by the density of field lines.  $E$  is the derivative of potential in space:  $E = -\nabla\phi$ .  $E$  is the force exerted on a charged particle per unit charge:  $E = F/q$ . From the above definitions, electrical field strength  $E$  has units of V/m or N/C.



**Voltage,  $U$** , is the difference in **electrical potential,  $\phi$**  between two locations:  $U = \Delta\phi = \phi_2 - \phi_1$ . The unit for voltage  $U$  is V (volt).

**Electrical field strength,  $E$** , is the negative of the gradient in electrical potential, i.e. it is defined to be directed from positive to negative pole:  $E = -\nabla\phi$ . In one dimension it is  $E = -d\phi/dx$ . If the gradient is linear and homogeneous, the voltage over a length  $L$  is  $U = -EL$ .

Electrical **power  $P$**  is the product of voltage and current:  $P = UI$ . Power has the unit of W (watt). Electrical **energy  $Q$**  is the product of power and time:  $Q = Pt$  and has units J (joule). 1 W for 1 s gives 1 J (joule) of energy.

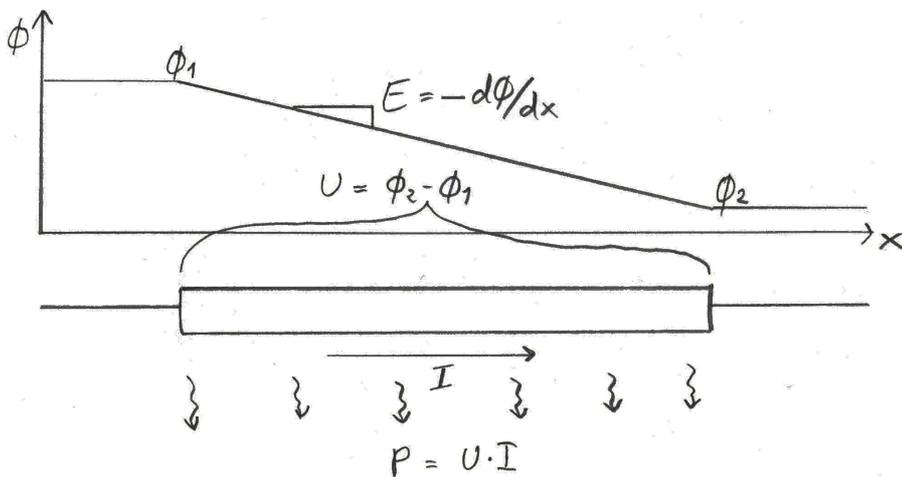


Figure 3. Schematic illustration of electrical potential, field, voltage, current, and power in relation to current passing through a resistor.

## Mobility, conductance, resistance, Ohm's law

In the following we derive some simple relationships between voltage and current valid for constant voltage and current in homogeneous media (conductors).

All types of charge carriers in a conductor are in constant random motion due to thermal energy, but there are many classes of charge carriers.

In many electronic conductors the electrons are *itinerant* – they travel freely as electrons in half-filled bands (metals) or in conduction bands or as holes in valence bands (semiconductors). The limitations to this travel are the scattering at impurities and other defects and by lattice vibrations (phonons).

In other electronically conducting materials the electrons are trapped in valence defects or by their own relaxation (deformation) of the surrounding lattice, and they must move by diffusion; activated jumps from site to site. Such deeply self-trapped electrons and holes are called *small polarons*. Weakly (shallowly) trapped electrons and holes are called *large polarons*, and they move by intermediate kinds of mechanisms.

Ionic charge carriers in the solid state move by diffusive jumps.

In the classifications above we have disregarded tunneling and superconduction as well as convective flow (liquids).

Electrical transport is normally simply a small shift of the random motion, so as to obtain a net drift velocity in one direction.

Assume that a particle has a charge of  $ze$ . It then feels a force  $F = zeE$  in the electrical field  $E$ . This gives rise to a drift velocity  $v = BF = BzeE$ , where  $B$  is the mechanical mobility of the particle. We now define a **charge mobility**  $u = Bze$ , so that  $v = uE$ . The flux density of particles then becomes  $j = cv = cuE$ , where  $c$  is the volume concentration of particles. The current density is obtained by multiplying the flux density by the particles' charge:  $i = zej = zecuE$ . Current is then obtained by multiplying by the cross-sectional area  $A$ :  $I = iA$ . By replacing  $E$  with  $U/L$  we finally get  $I = zecuUA/L$ .

The product of charge, concentration, and charge mobility is called **conductivity**  $\sigma$ :

$$\sigma = zecu \quad (1)$$

and when multiplied with area and divided by length we get **conductance**  $G$ :

$$G = \sigma A/L \quad (2)$$

Conductance,  $G$ , is a property that relates to a particular sample, and has unit S (siemens) while conductivity  $\sigma$  (often called specific conductivity) is a materials property with unit S/m. Because samples typically are of sizes in the cm-range, tradition has made it common to use S/cm rather than the SI unit S/m.

The inverse of conductance is **resistance**  $R = 1/G$  and the inverse of conductivity is **resistivity**  $\rho = 1/\sigma$ . Obviously,  $R = \rho L/A$ . The unit for resistance is ohm (=1/S).

We can now from the above equations and definitions express the current as

$$I = UG = U/R \quad (3)$$

known as **Ohm's law**.

We have not said anything about the physical basis for mobility of charge carriers. It can be derived from various formalisms, e.g. diffusion or collisions, depending on the type of transport and the traditions in different fields of application and science. Moreover, we have not said anything about the concentration of charge carriers, which depends on materials, temperature and composition. While these are the interesting parameters for us as chemists, physicists or materials scientists, this course is not so much about that. Instead it is about the methodology to measure electrical properties as *part* of what may be needed to get hold of those parameters.

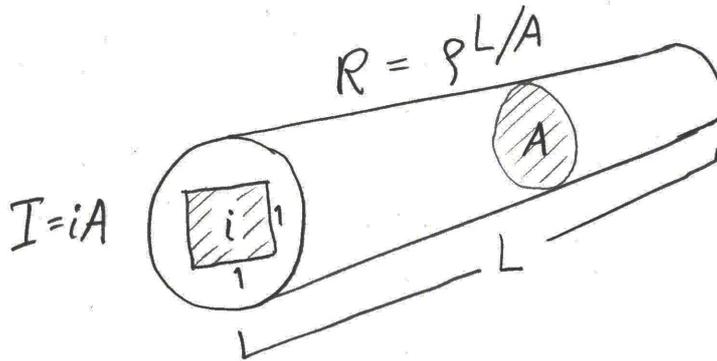


Figure 4. Schematic illustration of terms relating to current and resistance

## Direct and alternating current (DC and AC)

The voltage and resulting current can be constant with time and are then referred to as DC (from “direct current”).

The voltage can also be varied in numerous ways, e.g. referred to as sine, square or sawtooth waves, noise, etc. Most important, and the only we will treat here, is the sine voltage, resulting in sine current and thus referred to as AC (from “alternating current”). The sine voltage is characterized by its **frequency  $f$**  and **angular frequency  $\omega = 2\pi f$**  as well as its amplitude  $U_0$ :

$$U = U_0 \sin \omega t \quad (4.)$$

The amplitude can also be specified as the peak-to-peak voltage,  $U_{p-p} = 2U_0$  or the root mean square (rms) voltage  $U_{rms} = U_0/\sqrt{2} = U_{p-p}/(2\sqrt{2})$ .

The term  $\omega t$  is called the phase angle. A sinusoidal AC current resulting from the applied AC voltage will have the same frequency as the voltage, but may have a different amplitude and phase angle:

$$I = I_0 \sin(\omega t + \theta) \quad (5.)$$

The phase shift  $\theta$  results from non-ohmic (capacitive or inductive) elements in the circuit.

A sine AC voltage or current can be superimposed on a DC voltage  $U_b$  or current  $I_b$ . The DC part of the voltage or current is called bias, and shifts the AC curve off symmetry around zero voltage or current.

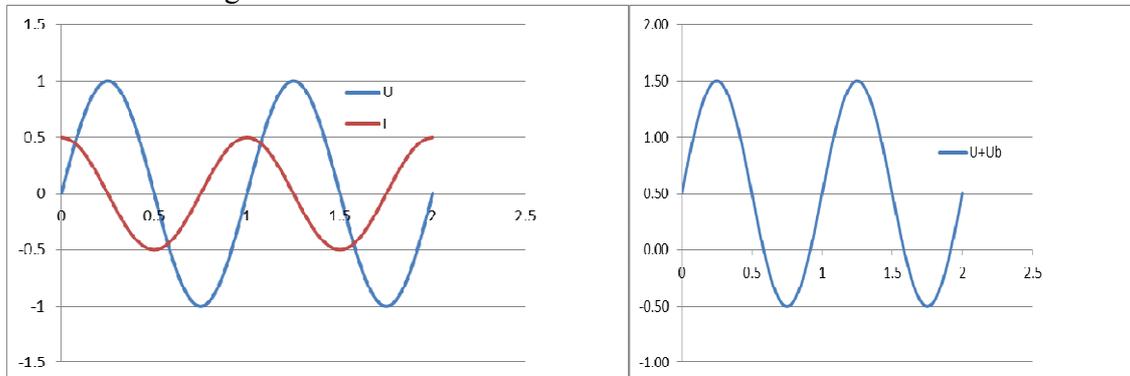


Figure 5. Left: AC voltage and current. Right: Biased AC voltage.

Sine waves can be troubled by harmonics (usually overharmonics; presence of voltage and current components that is a multiple of the fundamental frequency) or distortion (deviations from ideal sinusoidal curve form). These are usually generated by the AC source itself or by non-ideal electronic components in the electric pathway.

We will treat AC signals in more detail later, under impedance spectroscopy.

## Electrical circuit elements and circuits

### Passive electrical circuit elements

We now consider some passive electrical circuit elements, in the form of discrete components.

#### Resistors (conductors)

A **resistor** (or **conductor**) is an element with long-range transport of charge carriers. The number of charges, concentration, and mobility of the charge carriers give rise to conductance  $G$  and resistance  $R = 1/G$  as we have discussed earlier. In an ideal resistor, voltage gives rise instantly to current and vice versa. Thus, AC voltage and current in a resistor are in phase. Power (heat) is dissipated in the resistor, and via integration of  $P=UI$  over one period it turns out to be:

$$P = \frac{1}{T} \int_0^T UI dt = \frac{1}{T} \int_0^T I_0 U_0 \sin^2 \omega t dt = \frac{I_0 U_0}{2} \quad (6.)$$

The resistance is given as

$$R = \frac{U}{I} = \frac{U_0 \sin \omega t}{I_0 \sin \omega t} = \frac{U_0}{I_0} \quad (7.)$$

i.e. identical to the DC case. Note that the resistance of a resistor is independent of the frequency.

Resistors for electronic circuitry come in many fashions. Computers would nowadays have many of the resistors built into chips or integrated circuits. When using single (discrete) resistors, we need to deal with the nominal value and perhaps accuracy, power rating, and temperature coefficient. A colour coding scheme is in use for small discrete resistors with small power ratings (typically  $\frac{1}{4}$  W). For low-accuracy resistors this is given as 2 rings for value and one ring for the number of additional zeros. The colours are black=0, brown=1, red=2, orange=3, yellow=4, green=5, blue=6, violet=7, gray=8, white=9. For instance, brown-black-red means  $10 + 2$  zeros = 1000 ohm = 1 kohm and brown-green-blue means 15 000 000 = 15 Mohm. In addition, a fourth ring may signify the accuracy: Silver=10%, Gold=5%.

## Capacitors

A **capacitor** comprises an ideal insulator between two conductors. Most typically it is constructed as parallel plate conductors separated by vacuum, a gas, or dielectric material. The plates can be charged by applying a voltage over them; a current flows in the leads to the plates, and the charges end up in the plates where they are attracted to the opposite charges in the other plate. The larger the area and the shorter the distance between the plates, the smaller is the voltage needed to store a certain charge. The capacitance is defined as  $C = Q/U$  and has unit F (farad). The charge  $Q$  has unit C (coulomb). Thus, a capacitor has capacitance 1 F if 1 C of charge gives 1 V over the plates.

If a polarizable medium is placed between the plates, the dipoles of that medium become directed according to the electrical field set up by the voltage. The orienting of the dipoles depolarizes the field between the plates and reduces the voltage over them. Thus, the capacitance increases. The ratio between the new capacitance and the capacitance without a medium (vacuum) is called the relative permittivity  $\epsilon_r$  of the medium, and in general the capacitance of a capacitor is given as

$$C = \epsilon_0 \epsilon_r \frac{A}{d} \quad (8.)$$

, where  $\epsilon_0$  is the permittivity of vacuum,  $A$  is the area and  $d$  the distance between the plates.

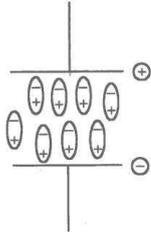


Figure 6. Depolarisation of a capacitor by dipoles in the dielectric.

Since the current to a capacitor is the change in its charge  $Q$  with time, we have  $I = dQ/dt = C dU/dt$ . With an applied AC voltage as above, we further get

$$I = C \frac{d(U_0 \sin \omega t)}{dt} = \omega C U_0 \cos \omega t = \omega C U_0 \sin(\omega t + \frac{\pi}{2}) \quad (9.)$$

The current over a capacitor is thus phase-shifted  $\pi/2$  (or  $90^\circ$ ) ahead of the AC voltage over it.

The power dissipated over the capacitor is zero:

$$P = \frac{1}{T} \int_0^T UI dt = \frac{\omega C U_0^2}{T} \int_0^T \sin \omega t \cos \omega t dt = 0 \quad (10.)$$

The ratio between the peak voltage and peak current when an AC voltage is applied over a capacitor is  $R_C = 1/(\omega C)$  and is called the capacitive resistance. We shall see later that it is not a real resistance. However, we may note that it is inversely proportional to the frequency.

Discrete capacitors come in various types. Small capacitances are obtained using e.g. ceramic dielectrics. Larger ones are so-called electrolytic capacitors having very thin electrochemical double-layers between an electrolyte and the electrode. An important parameter for capacitors is the maximum voltage rating before breakdown. Most capacitors tolerate high voltages. However, for electrolytic capacitors the maximum voltage is usually modest, and is specified on the component. Moreover, it is most often directional, i.e., the capacitor only tolerates voltage in one direction, not backwards, and hence it is marked with + signs for the terminal that must be connected to a positive potential.

## Inductors

The last linear (passive) circuit element we shall mention here is the **inductor**. This is ideally simply a length (straight or coiled) of an ideal conductor with no resistance. If a sinusoidal current passes in the conductor, a corresponding magnetic field is set up around it, and this in turn induces an AC voltage  $U_L$  over the conductor. The AC voltage  $U$  that was applied originally to pass the current must have been equal and oppositely directed as  $U_L$ :

$$U = -U_L = L \frac{dI}{dt} = L \frac{d(I_0 \sin \omega t)}{dt} = \omega L I_0 \cos \omega t = \omega L I_0 \sin(\omega t + \frac{\pi}{2}) \quad (11.)$$

where  $L$  is the inductance of the inductor. The unit for inductance is henry, H. Here the voltage is  $\pi/2$  (or  $90^\circ$ ) ahead of the current. Also here, the dissipated power is zero. The inductive resistance is  $R_L = \omega L$  (i.e. proportional to frequency).

There is in principle no difference between a coil and a normal conductor with respect to it acting as an inductor, the coil is just a more efficient way of packing a long length of conductor. The inductance is proportional to the susceptance of the medium that the magnetic field is set up in, and placing a material with high susceptance as the core in a coil gives the coil a high inductance.

## Parallel and series connections

Electrical circuits consist of connections of various elements, in series and/or in parallel. In order to deal properly with circuits we need to know the laws of summation of currents and voltages.

Kirchhoff's 1<sup>st</sup> law says that the sum of currents flowing into a branching point is equal to the sum of currents flowing out in the branches. In other words, the total current equals the sum of currents in all parallel pathways; current is summed in parallel. Since the voltage over each parallel branch is the same, the current flowing in each is proportional to the conductance (or inversely proportional to the resistance) of that branch.

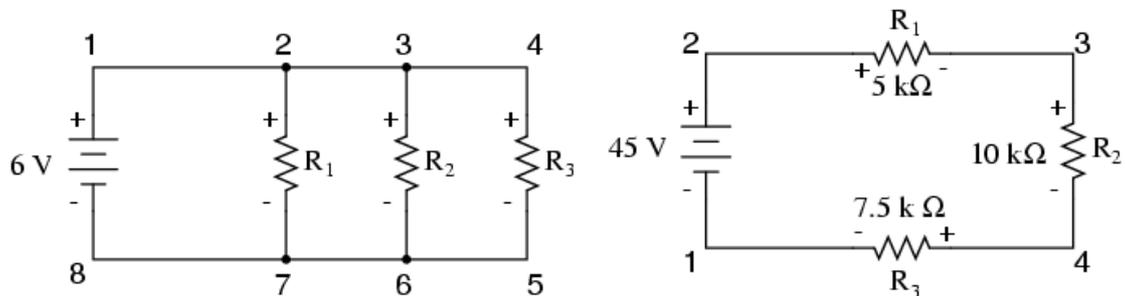


Figure 7. Illustrations of Kirchhoff's 1<sup>st</sup> (left) and 2<sup>nd</sup> (right) law.

Kirchhoff's 2<sup>nd</sup> law says that the sum of all potential changes (voltages) in a chosen direction around a closed circuit is zero. In other words, voltages are summed in series. Since the current is the same in all serial parts of the circuit, the voltage over each part is proportional to the resistance of that part.

## Active and non-linear electrical circuit elements

Among many other types of elements representing discrete components as well as physical or chemical processes in materials and interfaces, we shall only mention rectifying junctions,

such as in diodes and transistors made from semiconductors. This is because some knowledge of them enables understanding of how electrical instruments affect the measured signals. They are also representative of non-linear components.

## Diodes

A **diode** is a connection between a p-type and an n-type semiconductor; a p-n junction. On the interface between the two we have a depletion zone, where neither holes or electrons are present for conduction.

When current flows in a direction where electrons move away from the depletion zone (and holes similarly move away in the opposite direction), the junction becomes insulating; this is the blocking direction of a diode. If, on the other hand, the current is reversed, electrons and holes flow into the depletion zone, making the junction conducting. The diode now conducts. In effect, the diode is a rectifier.

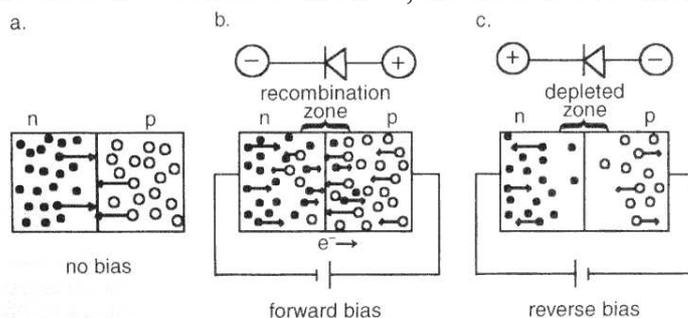


Figure 8. Illustration of a p-n junction and its conducting and blocking actions under forward and reverse bias.

## Transistors

A **transistor** contains an assembly of three layers of semiconductors: n-p-n or p-n-p. The first junction in each is put under forward bias, while the next is blocked (reverse bias), see Figure 9 (left). However, charge (voltage) is supplied to the central layer (base) to counteract the depletion of the second junction and causing current to flow. The current is proportional to the input voltage on the base, and a small DC or AC or otherwise modulated signal can thus be amplified to a large current.

In a real circuit, various resistors are used to balance the potentials, and capacitors are used to filter out or through AC components of the voltages and currents, see Figure 9 (right).

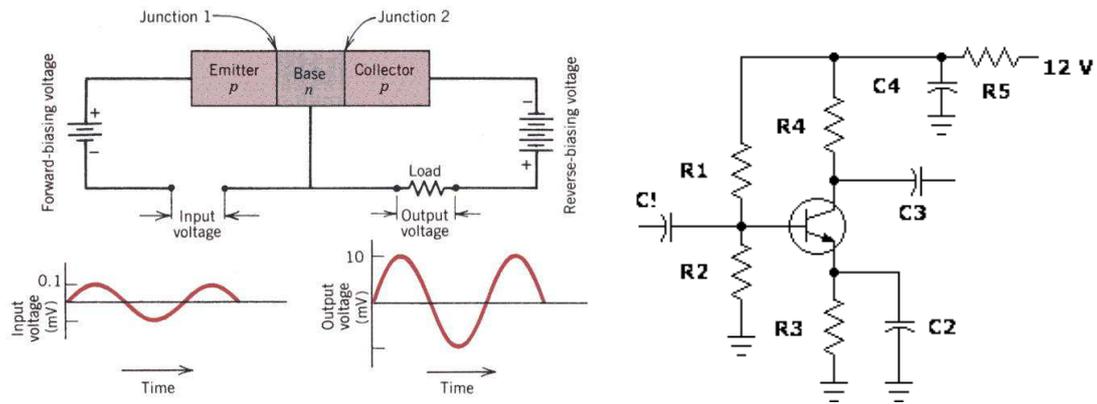


Figure 9. Left: Illustration of a pnp transistor and its use as an amplifier. Right: A transistor in a real amplifier circuit.

Transistor-based amplifiers are used both to generate electrical voltages and currents, and to measure voltages. In generators, the impedance of the transistor should be low, so that the circuit connected does not change significantly the output voltage. Correspondingly, the input stage of an amplifier used for voltage measurements should have a high resistance so that it does not draw significant currents from the circuit being probed. As a general rule in voltage measurements, an output stage should have much smaller resistance than the following input stage.

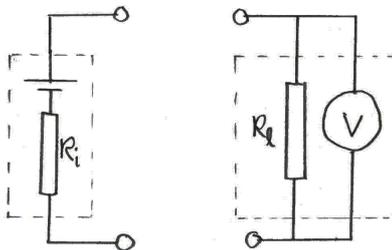


Figure 10. Schematic illustration of the internal resistance  $R_i$  of a DC voltage source (generally any generator, transistor, battery, fuel cell, etc.) and the input load resistance  $R_i$  of an input stage (e.g. voltmeter, amplifier).

The introduction of so-called Metal Oxide Field Effect Transistors (MOSFETs) enabled input stages that draw only minute amounts of charge, i.e. with very high input resistances. This has, in turn, enabled faster and less power-consuming digital computer circuits, but also voltmeters that can probe voltages generated over large internal resistances.

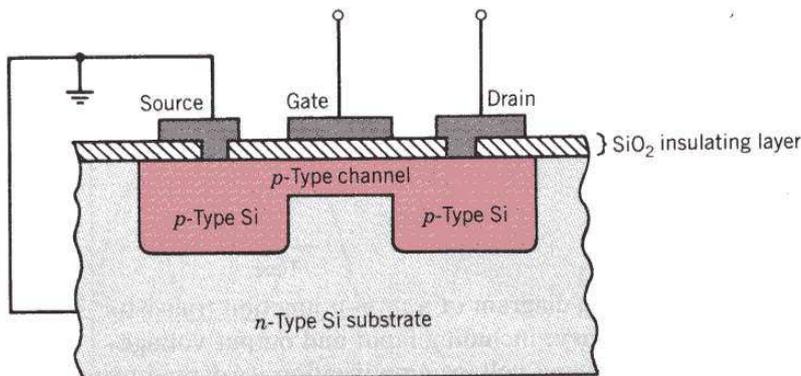


Figure 11. In this MOSFET transistor, the p.type channel is normally depleted and thus blocking because of its neighbouring n-type substrate. However, input signals to the gate charges the channel electrostatically through the thin insulating oxide layer. This opens the otherwise depleted channel and allows current to pass between source and drain.

## Symbols for circuit elements

The figure below shows some common elements and typical symbols used for them in circuit diagrams.

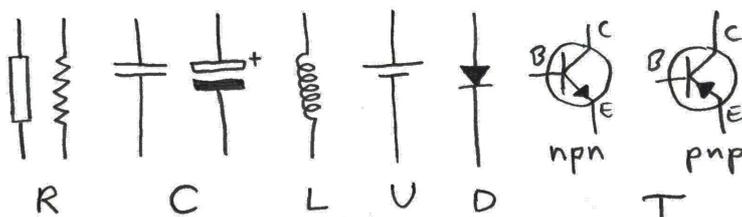


Figure 12. Symbols for resistor (R), capacitor (C), inductor (L), DC voltage source (U), diode (D), transistors (T).

## Measurements of voltage, current and impedance

We will now deal with the actual measurements of voltage and current, and, in turn, impedance. We will only partially touch the actual physics of the measuring equipment, as this is highly sophisticated and complex electronics in most cases. All three parameters may be direct or indirect measures of the thermodynamics of a chemical reaction, the difference in potential of electrons, the number and flux of charged chemical or physical species, the mobility of the same, etc. Here we will however generalize, and deal with the measurements as such.

## Voltage

Originally, voltage - DC voltage that is - was measured by **electrometers**; here the voltage to be measured was contacted to two objects in vacuum, e.g. a fixed one and a foil. The deflection of the foil indicated the charge and thus the voltage on the objects. Since no current could flow through the vacuum, the device had infinitely high resistance. Therefore, high input resistance voltmeters are today also sometimes referred to as electrometers.

In more modern times it became more practical to use voltmeters where the voltage created a tiny current through the coil of an electromagnet on an indicator and caused the indicator to move on a panel against a very soft spring force. This is used in many simple handheld analog multimeters and panel instruments. The input impedance of such instruments is usually modest, e.g. 10 kohm, and the accuracy also poor. They are thus only useful for simpler test and service applications. Multimeters and other simple analog instruments can measure AC voltages by rectifying them over one or more diodes before measuring the resulting DC voltage as above. This makes the AC measurement less sensitive, and correct only over a rather restricted frequency range. The various voltage ranges of analog instruments come about by attenuating the voltage over selectable voltage dividers (with selectable ratios of resistors).

Modern hand-held (battery-powered) multimeters use electronic circuitry to measure voltage, and display the result digitally. The input amplifiers may have reasonably high resistances, e.g. 1 Mohm. They thus measure various voltage sources with better reliability than analog ones, and with better accuracy and resolution, typically four digits or 0.01 %.

Instrumentation (stationary) multimeters are not necessarily much different than hand-held digital ones, but being associated with higher cost and power consumption they usually have more features, larger measurement ranges, and computer communication. More importantly for us, they have higher input resistances, typically  $10^9 - 10^{12}$  ohm (1-1000 Gohm) or even higher in the case of electronic electrometers. Moreover, they can typically reach a resolution of 6 digits or 1 ppm. They may have features like filtering or averaging that take some noise or variations out of DC measurements. Another useful feature is the auto-ranging that lets you automatically get the highest available resolution.

We finally mention the oscilloscope. This device measures a voltage and displays it graphically versus time or versus another voltage. The time base can be selected freely or one may use the AC component of the voltage to trigger the time base and thus display the voltage as a standing wave. The oscilloscope is useful for displaying combined DC and AC signals as well as the actual wave-forms, i.e. noise, over-harmonics, distortion, phase-relationships etc.

## Current

For all practical purposes we can assume that current is measured by passing the current over a standard resistor and measuring the voltage generated in the same manner and by the same instruments as listed under voltage measurements. Thus, current can be measured by simple analog instruments and multimeters, and by stationary multimeters and electrometers. Both AC and DC currents can be measured. The quality of the measurement follows that of the

voltage measurement and of the standard resistors. The current ranges are set by selecting resistor and/or voltage divider, but these processes are usually hidden to the user.

In the voltage measurements we have discussed above, the input resistance should be as high as possible. In current measurements the resistance (the standard resistor) should be as small as possible in order to affect the current as little as possible.

## Impedance – basic principles and methods

Impedance is a more general expression for what we have called resistance up to now. While resistance mainly is used for DC conditions, impedance covers both AC and DC. It is the ratio of voltage over current. It has units of ohm. Measuring it is thus a matter of measuring voltage and current – it's as simple as that.

That is, it is that simple today, since we benefit from automated and intelligent devices that measure both voltage and current with ease and accuracy, as described above. Earlier impedance measurements were done by Wheatstone's bridges; devices where current was run in two parallel paths, and components on one side changed manually until they accurately matched that of the sample, as monitored by measuring the voltage developed between the two paths. We will not deal any further with such devices here.

Nowadays we measure the impedance of a test object by

- 1) Generating a voltage (AC or DC) that is applied to the circuit of which the object is part, thereby getting a current through the circuit,
- 2) measuring the voltage  $U_D$  developed over the device under test,
- 3) measuring the current  $I$  in the device by measuring the voltage  $U_s$  generated over a standard resistor  $R_s$  placed in the circuit, and
- 4) dividing the numbers and obtain the impedance;  $Z_D = U_D/I = U_D/(U_s/R_s)$ . If we wish, we may multiply by the cross-sectional area  $A$  of the object or test cell in order to get area-specific impedance, and further divide with the length  $l$  (distance between electrodes) if we want to get the (volume-)specific impedance.

The accuracy of the overall measurement is best if the standard resistor has a value of the same order of magnitude as the sample. In the following, we will not discuss in any further detail the selection of standard resistors - we assume this is something you do manually, or the impedance measuring device does automatically.

Handheld instruments use battery power to supply a DC signal, while stationary instruments may supply higher quality DC or AC signals. It may be noted that the current or voltage output from the instrument to the sample need not be constant or at a particular value, as long as the actual current is measured. For instance, the sample may well have a lower resistance than the output stage of the instrument, so that the actual voltage output is lower than nominal – without causing a problem. Many instruments have feedback circuitry that ensures that the output voltage or the voltage developed over the sample stays at a predefined value (potentiostatic mode) or that the current stays at a predefined value (galvanostatic mode).

Impedance devices may have a number of terminals, varying between 2 and something like 6. However, the standard is to have 4 terminals: Two for the current loop (including generator and internal current measurement) and two for the measurement of

voltage over the object. If it has only two, then the voltage is measured over the object at the terminals of the current loop.

In addition to these terminals, instruments may also have a range of shield and ground terminals; we shall come back to their functions later.

The main concern in impedance measurements is to ensure that the voltage you measure is the one developing over the part of the object that you are interested in, and that the current you measure is the current running in the part of the object that you are interested in. The former is usually our biggest concern, and we shall deal with that in some detail in the following.

There are numerous impedances in series with the object under test. They all develop voltage by the current in the loop. Where we measure the voltage – i.e., where we attach the voltage probes in the current loop - will determine which contributions we get included in our impedance result.

2-wire 2-electrode measurements: If the instrument has only 2 terminals or if the current and voltage terminals are connected close to the instrument, the measurement effectively includes the impedances of the wires (and any bad contacts on the way), the electrodes and the sample. This mode is only acceptable in simple test routines or if the sample or object under test exhibits a large impedance compared with the other contributions. Simple hand-held multimeters operate in this mode, and cannot measure accurately resistances (impedances) below, say, 1 ohm.

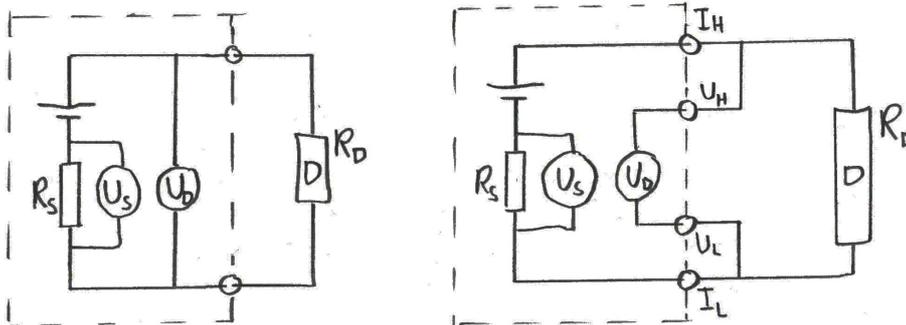


Figure 13. Schematic principle of resistance measurements using 2 electrodes and 2 wires. Left: 2-terminal instrument (typical handheld). Right: 4-terminal instrument. In both cases the wires to the device (D) contribute to the voltage drop and thus to the resistance. The terminology  $I_H$ ,  $U_H$ ,  $U_L$ ,  $I_L$  for the four terminals is typical, reflecting current and voltage terminals in order of going from high to low potential.

4-wire 2-electrode measurements: By letting the voltage probe wires run separately all the way to the object under test, we eliminate the resistance in the current wires, and need in principle not worry about poor contacts or too thin, resistive wires. The measurement then includes only the electrodes (contacts) and the sample.

4-electrode (often called 4-point) measurements: By letting the voltage wires probe the voltage using separate electrodes on the sample, also the impedance of the current electrodes are eliminated. The measurement then includes only the sample substance.

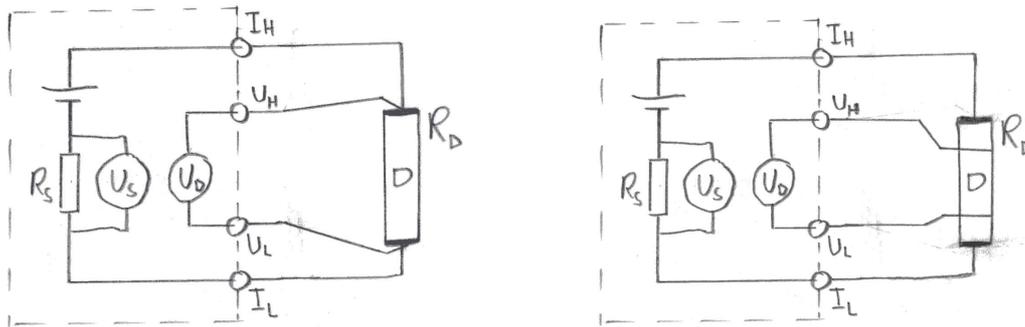


Figure 14. 4-terminal instruments used with 4 wires. Left: 2-electrode measurement (sample and electrodes). Right: 4-electrode measurement (sample material only).

3-electrode measurements: This mode is a combination of the 2- and 4-electrode modes, and is used to study electrode impedances. One electrode is used as both current and voltage probes, and the impedance of this electrode is thus included in the measurement. This electrode is called the Working electrode. The two other are the Counter electrode for current and the Reference electrode for voltage. Since the reference electrode is free of current, its impedance is excluded from the measurement. 3-electrode measurements may use 3 or 4 wires, i.e., the working electrode may be contacted by one or two wires.

## AC impedance

As we have seen previously, AC voltage and current may be out of phase with each other. Thus, the ratio between the two has a phase angle.

In AC impedance measurements, current and voltage are measured as sinusoidal voltages, one over the sample and one over a reference resistor. In addition to the magnitude of the two voltages, the device measures the phase angle between the two.

Alternatively, the current may be taken to have two components; one that is in phase with the voltage, and one that is  $90^\circ$  degrees out of phase, and the impedance-measuring device may work by splitting the current into those two components. The result is thus given as one impedance which is the voltage divided by in-phase component of current, and one which is the voltage divided by the  $90^\circ$  out of phase component of current.

The in-phase part of the impedance is called the **real** part. This reflects that it comprises real, impeded transport of charge carriers through the impedance element and that it gives rise to heat dissipation when AC current passes. The real part of an impedance is called **resistance**, **R**. A resistor is an example of a component with real impedance.

The  $90^\circ$  out of phase component of impedance is called the **imaginary** part. This may reflect that charge carriers are not really transported through the impedance (only stored there temporarily, as in an ideal capacitor) or are not really impeded (as in an ideal coil). Imaginary parts of impedance do not give rise to heat dissipation when AC current flows through it. The imaginary part of the impedance is denoted **reactance**, **X**.

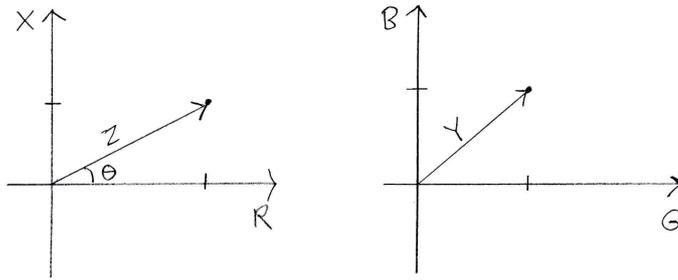


Figure 15. Representation of complex impedance (left) and complex admittance (right) in Cartesian coordinates.

The total impedance may now be taken as a vector in the two-dimensional real-imaginary space. The impedance  $Z$  is then represented as a complex number – the complex impedance  $Z^*$ :

$$Z^* = Z' + jZ'' = R + jX \quad (12.)$$

We recall from the introduction of resistors, capacitors and inductors (coils) that they have resistances given by  $R$ ,  $R_C = 1/(\omega C)$ , and  $R_L = \omega L$ . The first is real, while the two latter are imaginary. Moreover, the actual division of voltage by current in an ideal capacitor comes out as  $-R_C = -(1/\omega C)$  such that the impedance of a series connection of a resistor, a capacitor, and a coil is

$$Z^* = R + j\left(\frac{-1}{\omega C} + \omega L\right) = R - \frac{j}{\omega C} + j\omega L \quad (13.)$$

The inverse of impedance is **admittance**:  $Y^* = 1/Z^*$ . It is obtained as the ratio between current and voltage, and is similarly to admittance a complex number. The real part of admittance is called **conductance**,  $G$ , and the imaginary part is called **susceptance**,  $B$ :

$$Y^* = Y' + jY'' = G + jB \quad (14.)$$

An ideal resistor is also an ideal conductor and for this we have  $G = 1/R$ . For an ideal capacitor we have  $B_C = -1/X_C = \omega C$  and for an ideal inductor we have  $B_L = -1/X_L = -1/(\omega L)$ . A parallel connection of a resistor (conductor), a capacitor and a coil thus has three contributions to admittance – one real and two imaginary:

$$Y^* = G + j\left(\omega C + \frac{-1}{\omega L}\right) = G + j\omega C - \frac{j}{\omega L} \quad (15.)$$

Let us briefly look at the conversion from impedance to admittance:

$$Y^* = \frac{1}{Z^*} = \frac{1}{R + jX} = \frac{R - jX}{(R + jX)(R - jX)} = \frac{R - jX}{R^2 - (jX)^2} = \frac{R - jX}{R^2 + X^2} = \frac{R}{R^2 + X^2} - \frac{jX}{R^2 + X^2}$$

(16.)

Similarly,

$$Z^* = \frac{1}{Y^*} = \frac{G}{G^2 + B^2} - \frac{jB}{G^2 + B^2} \quad (17.)$$

We see that the transformation leads to a new complex number based on the components of the other representation. However, the transformation between  $R$  in the series representation to  $G$  in the parallel representation is not a straightforward inversion as one might perhaps have thought. *Only* when there are no significant contributions from the imaginary parts ( $B$  or  $X$  are zero) is  $G = 1/R$ .

It may be mentioned that the term **immitance**,  $I^*$ , is used to denote impedance and admittance together.

A device measuring AC impedance or admittance does not and cannot know how to interpret the result. It only knows the ratio of voltage and current and the phase angle. This it can calculate into  $Z^* = R + jX$  or  $Y^* = G + jB$ . In order to interpret it further, it must know whether the real part of the impedance or admittance is connected in series or parallel with the imaginary parts. Many instruments have the possibility to choose automatically one or the other. For this it uses the total impedance; if it is high it assumes a parallel connection (between something you probably are interested in and something else adding up in parallel). If it is low it assumes a series connection. The reasoning behind this will become clearer in later sections.

If a series connection is chosen (by the instrument automatically or by you manually) the instrument uses  $Z^*$  to obtain  $R$  and  $X$  and in turn calculate the capacitance  $C$  or inductance  $L$  of the element that is in *series* with the real part  $R$ . Again, there is in principle no possibility to separate  $C$  and  $L$ , so you have to tell which one you want. The sign of  $X$  does however change, depending on which one you have or which one dominates, so that you or the impedance measuring device can make a judgment based on this. Circuit elements interpreted from an AC impedance measurement based on a series connection model are denoted  $R_s$ ,  $C_s$ , and  $L_s$ .

Similarly, if you tell the device that you have a parallel connection, it uses  $Y^*$  to obtain  $G$  and  $B$  and interprets them in terms of  $G_p$ ,  $C_p$  and  $L_p$ . The real part  $G_p$  can also be expressed as parallel resistance  $R_p = 1/G_p$ .

We have here described how an AC impedance measurement can be interpreted as a simple series or parallel connection of one real and one imaginary impedance or admittance element. If this with sufficient accuracy describes the real situation, then we have a useful result. A good sign of a correct interpretation is that the element values  $R$ , or  $G$  and  $C$  or  $L$  remain constant independent of applied frequency.

If we don't know how the elements are connected, or if we may assume that the circuit is more complicated than a simple connection of two elements, we may measure

complex impedance or admittance over a range of frequencies, and in that way rule out some combinations. This is what we do in impedance spectroscopy, which we shall deal with in more detail later on.

## Correction for sample geometry in impedance measurements

In impedance measurements it is usually required to recalculate the results from measured values into materials specific values. For this we need to correct for the sample's geometry and sometimes also microstructure. In measurements on liquids the geometry of the measurement cell remains constant, and can be measured once and for all or calibrated against a known standard. The corrections are often collected in a cell constant that translates e.g. a measured conductance or capacitance into a specific conductivity or capacity, that can be used to calculate for instance concentrations of ions or the relative dielectric constant.

For solids, it is more tricky, since each sample in principle is different, and we shall consider a few factors of importance.

For disks (2-electrode measurements) the relevant length of the measurement is the thickness. For bars (4-electrode measurements) the relevant length is the distance between the voltage probes. Both are straightforward to identify, but usually not easy to measure with a great deal of accuracy.

For bar samples the relevant cross-sectional area is the one for the part of the sample that lies between the voltage probes, again straightforward to identify, and possible to measure with reasonable accuracy.

For disk samples the cross-sectional area may or may not be equal to the superficial area of the electrodes. This is certainly the case if the electrodes are well conducting (no spreading resistance) and cover all of two identical surfaces on both sides.

If the electrodes do not cover all of the surface, one may as a first approximation still use the superficial area if the electrodes are placed symmetrically and the disks are thin compared to the electrode dimensions. If the electrodes are of different areas one may then also take the average of the areas.

For symmetrically placed electrodes that are considerably smaller than the sample area, **one may take into account the spreading of the current** so as to get a larger effective area. This becomes increasingly important as the ratio between sample thickness and electrode dimensions increases.

If the electrodes are not well conducting, the outer parts (away from the contact of the wires) may contribute less, and a complicated situation will arise. Simply seen, the effective cross-sectional area becomes smaller than the superficial area. A particular warning may be issued against having the current and voltage wires contacting different areas of a poorly conducting electrode; if the current goes in part of the sample and the voltage is measured elsewhere, the impedance results surely becomes erratic. Thus the seeming similarity with the 4-point contact mode makes no sense in this case, and it is better to ensure that the two wires are in good contact with each other and with as much as possible of the electrode.

After such correction for external sample geometry, one may have to consider its microstructure, notably porosity. In the following we assume that the pores is an ideally

insulating phase distributed in the matrix of the material whose specific conductivity we want to obtain. Clearly, the pores affect the measured conductivity depending on how they are distributed. If they were all laying as planes or coloumns parallel to the current, the conductivity would be decreased simply according to the volume fraction of pores. If they were planes normal to the current, the measured conductivity would be zero. In real samples the effect of pores accordingly vary with their volume fraction (porosity) and distributions on size, shape, connectivity, and directions (texture), and ends up in between the two extremes mentioned. For a real sample we must thus rely on empirical relationships established for that particular type of material. Such relationships are in general not established at present, and we commonly use a very general one, that seems to give reasonable corrections for fairly low porosities:

$$\sigma_{measured} = \sigma (1-p)^2 = \sigma d^2 \quad (18.)$$

where p is the pore fraction and d is the relative density. Thus, a material with 10% porosity (90% density) is estimated to exhibit only 81% of the true conductivity of dense material. A measured conductivity is thus to be corrected by division of 0.81 to obtain the estimate of true material conductivity.

## ***Sources and minimization of offsets, noise, and parasitic elements***

### **Thermal and other offsets**

Voltages may be introduced in a circuit by contact potentials between different materials and by thermal asymmetries. These may affect measurements of DC voltage, but also of DC resistance measurements. For instance, if one attempts to check the state of an operating thermocouple by measuring its resistance with a multimeter, the thermoelectric voltage imposed by the thermocouple may well overshadow the voltage set up over the sample by the current from the instrument. Thus, the reading of resistance will be erratic and moreover change a lot (e.g. from plus to minus) depending on which direction one measures in.

Thermal variations and offsets can be attempted reduced by using cables and components with materials that create small thermoelectric forces. In particular, the two voltage probes of measurements should be kept symmetric in terms of materials and temperature gradients.

Stable remaining offsets can often be subtracted by adjusting zero-points of voltmeters, or in the post-measurement treatment of data.

Offsets can also be part of the instabilities in the measuring instrument itself.

### **Noise**

Noise – instabilities in the electrical signals and readings - may have several sources.

Electromagnetic fields may induce voltage and currents in the sample and measuring circuit. The source may be communication signals (radio, TV etc.), fields from displays, lamps, and neighbouring scientific equipment, and from the electric currents used to heat or cool the sample. Noise from external sources thus cover a wide frequency range, from radio-frequency to hum (50 or 60 Hz). Such noise can thus be reduced by appropriate filtering or screening.

Many measurements, instruments and circuitry have limited high frequency response, and are thus insensitive to radio frequency noise.

External noise has to pass an impedance to enter the sample or measuring circuit whereafter it experiences the impedance of the sample and circuitry; it is attenuated by the voltage divider consisting of the transfer impedance and sample+circuitry impedance. Therefore, the lower the impedance of the sample and the circuitry, the smaller the residual external noise that enter the measurement: A sample with low impedance short-circuits noise.

Noise may also come from the sample itself. This is thermally generated noise – fluctuations in the concentrations and energy of charge carriers. Such noise is generated with a statistical distribution in frequency and level and thus in principle covers all frequencies.

Finally, noise is also part of the measuring instruments, for the same reasons as above. Thus, as the measured value approaches zero, some level of noise will inevitably remain, depending on the quality of the instrument.

## Accuracy

Electrical instrumentation (voltmeters and amperemeters) are in general quite accurate, and often, this accuracy is not the limiting factor in electrical measurements, but rather factors such as stability, dimensions or composition of the system to be investigated, or other physical measurements that enter the overall investigation, e.g. for temperature or chemical potentials.

Resolution is a property of the measuring instrument, e.g. to be able to give the result with 4, 5, or 6 significant digits. This is eventually reduced by noise.

Precision is related to the zero-level (offsets), which we have treated above, and which is relatively easy to correct for, by applying zero volts, zero current, zero impedance or zero admittance – all situations that are fairly easy to realize as long as one does not ask for extremes.

Accuracy has to do with the slope in actual value vs displayed response, often called amplification in many electrical measurements. This is where it is more difficult to check the instrument and where we usually trust it. If we don't then here is where the most difficult part of calibration comes in. In order to check a voltmeter you need a calibration voltage source. In order to check an amperemeter you need basically a standard resistor above which you measure the voltage with your calibrated voltmeter. In order to check impedance measuring equipment you again need standard resistors as a minimum.

Other parameters may also affect the accuracy; linearity and, not least, temperature stability. Most measuring equipments specify the limits of error as a function of temperature

or deviations in temperature. Keep this in mind; note the ambient temperature in your log-book, check that the fan of the equipment works, and that the fan and instrument interior is not clogged by dust.

## Parasitic impedances and admittances

When measuring impedances we have to be aware of things that add to the impedance, i.e. things that act in series with our device or sample under test, but are not intended to be part of the result. These are called parasitic impedances. We also have to be aware of things that are adding to the admittance of the measurement – things that are in parallel and thus contribute parasitic admittances. The figure below illustrates the action of parasitic impedances and admittances. One may object that the connection points of the two with respect to each other is not obvious, but in practice only one makes a significant contribution at a time, and then the order of connection is not an important issue.

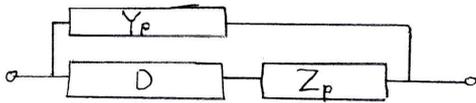


Figure 16. Parasitic impedance  $Z_p$  in series and admittance  $Y_p$  in parallel with a device  $D$ .

Parasitic impedances comprise the resistance and inductance in the wires that lead to the sample. The resistance is typically of the order of an ohm or less. They can be eliminated by 4-wire measurements. Next we have spreading resistance in the electrode, contact resistance to the material or electrochemical resistance in the case of an ionic conductor. If these are not part of the measurement of interest, they can be eliminated by using 3- or 4-electrode measurements. Finally, resistance and inductance remain as two elements that make up the impedance of the sample or component under test.

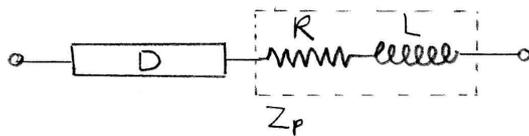


Figure 17. Parasitic impedance elements; resistance and inductance.

Parasitic admittances are parallel to the sample and thus comprise all possibilities that current has to flow between the two sides of the sample. In DC measurements this includes transport on and in insulators. In particular, adsorbed humidity on surfaces provides some conduction. In AC measurements, signals may furthermore be transmitted between wires across the capacitance in air or insulators. These sources of parasitic admittances are usually attempted eliminated by shielding the conductors from each other (see below). Parasitic admittance furthermore includes transport on the surface of the solid samples or components themselves. The latter may be eliminated in some cases by surface guards (see below). At high temperatures even the gas phase around the sample provides some conduction; this may

be eliminated by physical hinders. The interior of a solid may provide conduction on the surfaces of open pores, a problem that cannot be eliminated by other means than to use more dense samples.

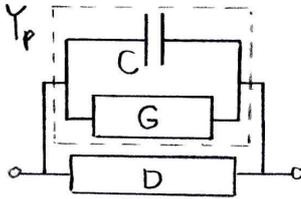


Figure 18. Parasitic admittance elements; conductance and capacitance.

Be aware that your hands provide a considerable parasitic admittance if you hold both terminals of a sample. In the exercises you can measure it with a multimeter or impedance spectrometer.

In summary, parasitic impedances trouble measurements of low impedances, they usually have resistive or inductive origins, and are combated using measurements with 4 wires and 3- or 4-electrodes. Using sample geometries that increase the sample's own impedance decreases the problem. Similarly, parasitic admittances trouble measurements of low admittances (high impedances), they usually have conductive or capacitive origins and are combated using physical or electrical shields and guards. Using sample geometries that increase the sample's own admittance decreases the problem.

In a normal measurement of a normal impedance at DC or a normal AC frequency and with normal demands for accuracy you may often disregard parasitics. When you move in the direction of low or high impedances you may have to start considering parasitic impedances or parasitic admittances, respectively, but usually not both.

When you have residual parasitics that you cannot remove but have to correct for, the parasitic has to be known, estimated, or measured. Often, parasitics can be delineated by impedance spectroscopy (see below) or by varying a dimension of the sample.

## Grounding, guarding, screening

### Floating and grounded measurements

A hand-held multimeter in a plastic housing clearly has no sense of ground or other reference potentials around it. When a voltage is output in a resistance measurement or a voltage is measured in a voltage measurement, neither of the voltages at the two terminals is defined with respect to any other voltage in the surroundings. We know the difference in potential between the two terminals, but we do not know the individual potentials, and we do not put any restrictions on it. The voltage and the instrument **float**.

Similarly, a sample may have terminals that are insulated from the surroundings and thus floating.

Advanced electrical instruments like stationary multimeters and impedance spectrometers have one or several ground levels. These may comprise the neutral terminal of the mains power supply (varies between countries), the earth terminal of the mains power

supply, the chassis of the instrument, the zero-voltage of the DC power supply and electronics of the instrument, and a reference level or zero-potential of the measurement signals. In general, those of these that are present are more or less connected to each other, passively or actively, so that they are mostly at the same potential. It is thus usually sufficient to think of all these as “ground”, but certain applications are sensitive to currents running between the different physical parts relating to these potentials. In particular one should be aware that if mains power earth contact is made through several power chords, external factors may cause currents to flow in our ground system – we have unwanted earth-loops. Similarly, physical contacts to the laboratory building etc. may provide loops to the electrical earth system. Thus, one may try to contact earth through only one physical connection (chord) in a collection of instruments.

In some instances it is useful to make contact between one of our sample’s terminals and ground. We refer to this as grounded measurements. In this case, the voltages measured refer to ground potential, and one is zero. Usually, the reason for using grounded measurements is that the instrument is designed for this or uses this as default. Grounding changes the potential of the sample and circuitry with respect to potentials of noise sources – sometimes to the better, sometimes to the worse. Grounding may be needed to reduce high voltages that otherwise bother amplifier inputs etc., arising from static electricity, induction from high currents in the surroundings, etc.

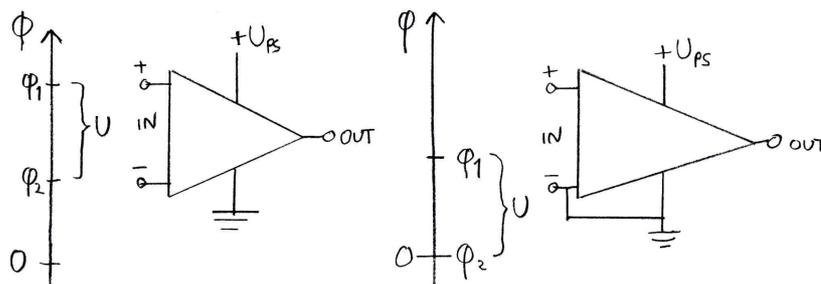


Figure 19. Floating and grounded measurements (schematic). The input of the measuring unit is represented by a so-called differential operation amplifier (the symbol of which is a triangle as here). The input adds the voltage on “+” and subtracts that at “-“ and amplifies the result ( $U$ ) before it is output.  $U_{PS}$  is the power supply voltage (e.g. 12 or 24 V DC). In the floating case both inputs are disconnected from Earth and both have a high impedance to Earth, so that the input potentials can float freely. In the grounded case the “-“ input is connected to Earth, pulling all potentials down to “zero” as reference.

Instrumentation usually comprises pairwise terminals where one is already closer to ground than the other (e.g. “high” vs “low” or vs “ref.”). It is then important to ensure that the terminal closest to ground – if any - is the one that is grounded.

Be aware that oscilloscopes often are grounded by default; the reference (“negative”) terminal of the input is internally connected to chassis and power supply chord ground.

We summarise simply by repeating that grounding consists of connection one of the sample terminals to ground, thereby moving all involved potentials close to and in reference to ground (earth) potential.

## Guarding

Often, current flows in considerable amounts in a path that we do not want to be included in our measurement of admittance. If we can insert a contact in that path, we can connect it to a guard terminal. The guard terminal is usually what we can consider a zero-potential of the instrument, and it is often simply a “ground” terminal (but not always). Being at zero potential, no net current flows to this point, the currents flowing to this point from the two current terminals are canceled and not measured by the current measuring circuitry. Thus, the admittance of the guarded path is excluded from the measurement.

We give two examples of the immediate use of guarding: You may want to measure the resistance of a resistor within an electronic circuit, but without removing it from the circuitry. By connecting points in parallel paths to the guard terminal they are eliminated and the remaining path measured as desired.

The second example is the surface conduction of a material that may dominate the measured conductivity of a high impedance sample. If the rim of a disk sample is equipped with a guard electrode, this can be contacted to the guard terminal and all conduction over the edge surface eliminated. In this case, also some volume conduction is lost to the guard, and the effective geometric factor of the measurement may be changed and should be determined by a separate measurement under other conditions (usually higher temperature) where volume conduction dominates.

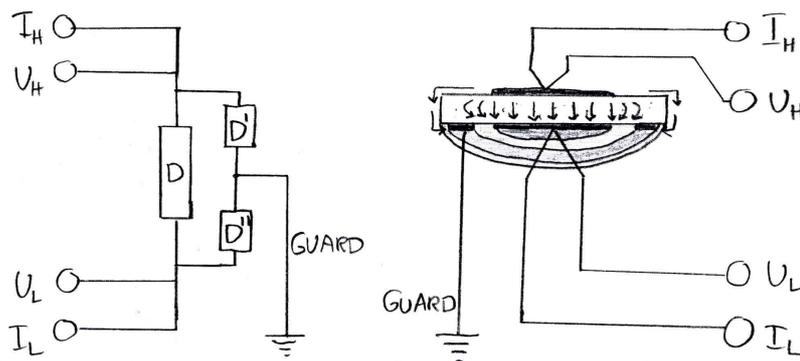


Figure 20. Guarded measurements to obtain the impedance of an element  $D$  in a circuit including other elements  $D'$  and  $D''$  (left) and to eliminate the surface conduction of a solid sample using a ring electrode on a disk (right). Arrows in the latter indicate currents.

## Shielding

As mentioned under our discussion of noise and parasitic admittances, these can be reduced by shielding. (Screening and shielding are terms used interchangeably for the same process.) This consists of metallic or other conducting shields around or close to the terminals of the measurements. The shields are connected to an earth or ground terminal. They thus function as to catch currents otherwise floating between the measurement wires. In this respect they work the same way as in guarding described above. They also reduce the intrusion of fields from external noise sources.

In simple instrumentation, using only two-wire connections to the sample, the “low” or reference terminal is often used to form a screen around the “high” terminal so as to prevent noise from reaching the “high” terminal.

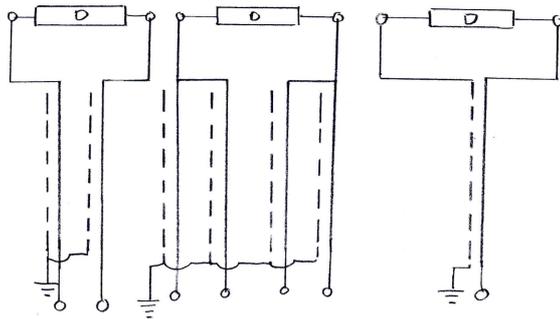


Figure 21. Simple representation of shielding principles. Left and right: Shields connected to ground in 2- and 4-wire setups, thereby acting as guards against crossover signals (capacitive and conductive). Right: A simpler setup in which the “low” (here grounded) is as a shield around the “high” conductor. This does not guard against crossover between the two (!) but merely shields against intrusion of external signals.

For very noise-sensitive measurements one may enclose the entire setup in a so-called Faraday cage – a box or entire room with grounded walls made of a metal suitable for catching all electromagnetic disturbance.

### Electrometers and potentiostats; use of driven shields

The above describes general ways of reducing noise by use of shields, and use of guards to remove unwanted current paths. But high impedance samples and cells are not necessarily helped: The shield and guard drains current from the sample, which lowers any voltage output and attempted measured from it.

Modern electrometers - name adapted from the early high-impedance instruments - handle this by not only having very high input impedances, but also offering one or more driven shields. Figure 22 shows two simple solutions.

In Figure 22 (a) a high-impedance preamplifier ("electrometer") is placed close to the sample or cell to be measured, minimizing the high-impedance wire length and thereby the noise and parasitic current between sample terminals and shields/ground. The following line to the potentiostat input is of low impedance and carries an amplified signal.

In Figure 22 (b) is shown the principle of driven shield. The voltage at each signal wire is fed through a high impedance amplifier to the shield of the same wire, so as to put the shield at exactly the same voltage as the signal wire. This prevents any current to run from the signal wire to the shield, and therefore there appears to be no parasitic load that draws current from the sample. Since each shield will be held at different voltages, the shields must be kept from contacting each other.

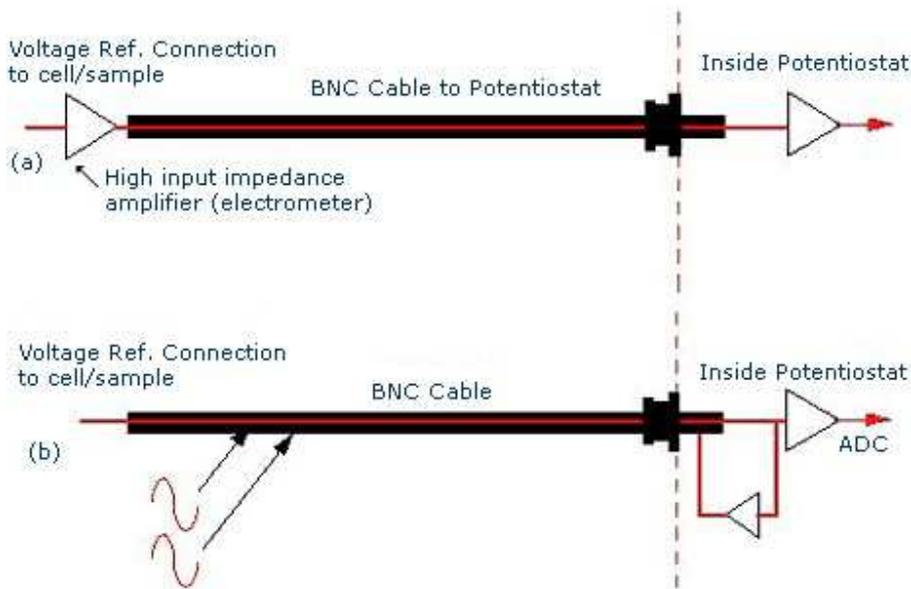


Figure 22. Two simple ways of reducing noise and losses in high impedance low level measurements. (a) A high-impedance (electrometer) preamplifier is placed close to the sample. (b) Driven shield. From Solartron.

### Impedance spectrometers; use of connected shields

While electrometers and many potentiostats use driven shields that must NOT be connected together, many dedicated stand-alone impedance spectrometers use shields in a different way, that actually require that they MUST BE connected together.

In this, the current returning from the sample at the low current terminal is not passed directly through the generator of the instrument, but is returned to the shield of the low current terminal and must run through this to the shield of the high current terminal. Via this it returns to the instrument generator, completing the current loop. In this way, any current running in the high and low current wires is accompanied by the same current running in the respective shield, in the opposite direction. This cancels the field induced by the two currents, minimizing induction of signals to the voltage probe wires.

This function is in use on models such as Hewlett Packard HP 4192A and Solartron SI 1260 FRA, and when using them alone (without potentiostats etc.) one must connect the shields together - otherwise the current loop is interrupted. On others, such as Novocontrol Alpha, one may choose whether to use connected shields or not - depending on sample interface.

One may note that if shields are to be connected together for the purpose of countercurrents in the shields, this should be implemented as close to the sample as possible, although a connection anywhere is better than no connection at all.

Older ProboStats have a shields bridge that can be inserted at the four shields feedthroughs at the bottom of the sample chamber. Newer versions have a switch that allows quick change from connected shields (for connection directly to impedance spectrometers) to disconnected shields (for connection to or via electrometers or potentiostats).

## DC voltammetry and related techniques

### Electrochemical processes at electrode-electrolyte interfaces

Here we will consider red-ox processes taking place on electrodes-electrolyte interfaces. Some types of such systems are shown in the figure below.

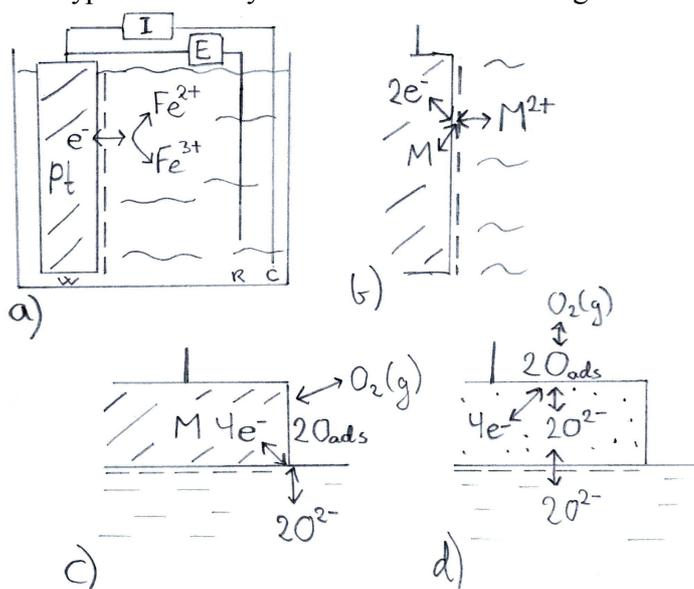


Figure 23. Some types of electrode-electrolyte interfaces. a) Example of electron transfer between electrolyte and inert electrode (W), including also reference (R) and counter (C) electrodes. b) example of ion transfer between electrode and electrolyte, c) oxygen reduction with electron conducting electrode on solid oxygen-ion conducting electrolyte, d) oxygen reduction with mixed conducting electrode on solid oxygen-ion conducting electrolyte. In all cases except the last, the electron transfer can be said to take place across the double layer between electrode and electrolyte (dashed lines). In d) electron transfer takes place at a surface while only ion diffusion takes place across the double layer to the electrolyte.

Some of the aspects of electrode systems can also be transferred to surface kinetics as such, but we will not discuss that here.

When a solid, a liquid, or an interface (solid-solid, liquid-solid, solid-liquid-gas triple phase boundary, or solid-solid-gas triple phase boundary) is in equilibrium, equal currents and mass flows pass in both directions. If we perturb this with small electrical or chemical potential gradients, we perturb slightly the flows so as to create a net flow in one direction. As long as the net flow is small compared to the overall flows, the system is considered linear; the net flux is proportional to the gradient. If the gradient is an electrical field, Ohm's law applies. This is fulfilled as long as we stay below a few millivolts across interfaces at room temperature. At higher temperatures we can apply several tens of millivolts. (In bulk we generally need not worry about this, as the distances are too big and the resulting fields too small.)

For those who may need it as a reference in their work, we put up relations between small overvoltages  $\eta$  and the current density  $i$  and the various parameters that express the kinetics of interfacial charge transfer:

$$\eta = R_e i = \frac{kT}{ne} \frac{i}{i_0} = \frac{kT}{(ne)^2} \frac{i}{k_i c} = \frac{kT}{(ne)^2} \frac{i}{r_0 s_i c} \quad (19.)$$

$$i = \frac{\eta}{R_e} = \frac{i_0 ne}{kT} \eta = \frac{k_i c (ne)^2}{kT} \eta = \frac{r_0 s_i c (ne)^2}{kT} \eta \quad (20.)$$

Here,  $R_e$  is the area specific charge transfer resistance,  $i_0$  is the exchange current density (resulting from thermal energy),  $k_i$  is the exchange rate constant,  $c$  is the concentration of charge carriers in the interface,  $r_0$  is the exchange rate, and  $s_i$  is the thickness of the interface.

If we apply higher overpotentials, the net flux becomes significant and eventually dominating, so that the reverse flux can be disregarded, we enter into the non-linear domain. Here, Ohm's law does not apply, and the net flux and current instead increase exponentially with the electrical field. For an interface between an electronically conducting electrode and an ionically conducting electrolyte, the electrical field is given by the overpotential, and the non-linear current may be given by the Butler-Volmer equation:

$$i = i_0 \left( e^{\frac{\alpha_a ne}{kT} \eta} - e^{-\frac{\alpha_c ne}{kT} \eta} \right) \quad (21.)$$

Here,  $\alpha_a$  and  $\alpha_c$  are the anodic and cathodic transfer coefficients, respectively. (We recall that anodic refers to oxidation – loss of electrons, while cathodic refers to reduction – gain of electrons.) We usually assume that  $\alpha_c = 1 - \alpha_a$  and often also that  $\alpha_c = \alpha_a = 0.5$ . When this is assumed, it may be shown that the Butler-Volmer equation approaches the linear case for small overpotentials.

In a linear plot of current versus overpotential, we may recognize a shift from the linear regime that we have around zero overpotential, to an exponential regime.

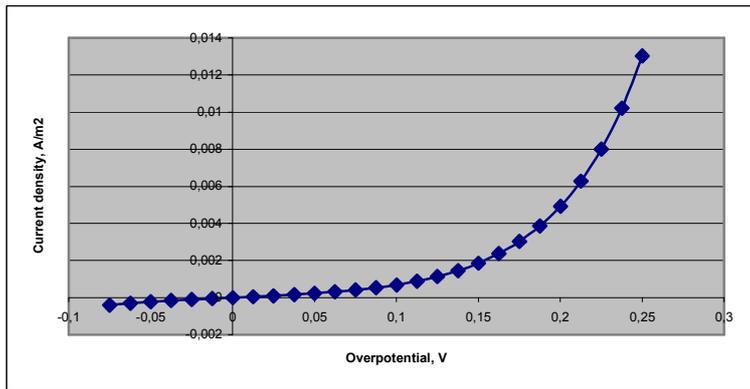


Figure 24. Current density vs overpotential for a system with  $i_0=0.0001 \text{ A/m}^2$ ,  $n=1$ ,  $\alpha_a = \alpha_c = 0.5$ ,  $T=298 \text{ K}$

In order to study the exponential regime we may plot  $\log |i|$  versus overpotential in a so-called Tafel plot. A Tafel plot will have a curved region at low current densities (linear regime) and straight lines at the anodic and cathodic sides at high current densities (Tafel regime). By assuming that the anodic or cathodic current dominate, we can rearrange the Butler-Volmer equation into

$$\log i_a = \log i_0 + \frac{\alpha_a n e}{2.3 k T} \eta_a \quad (22.)$$

$$\log(-i_c) = \log i_0 + \frac{\alpha_c n e}{2.3 k T} (-\eta_c) \quad (23.)$$

The slopes of the plots in the anodic and cathodic directions are thus a function of the transfer coefficient and the number of electrons in the rate-limiting charge transfer reaction, and may thus be used to obtain one or both of these.

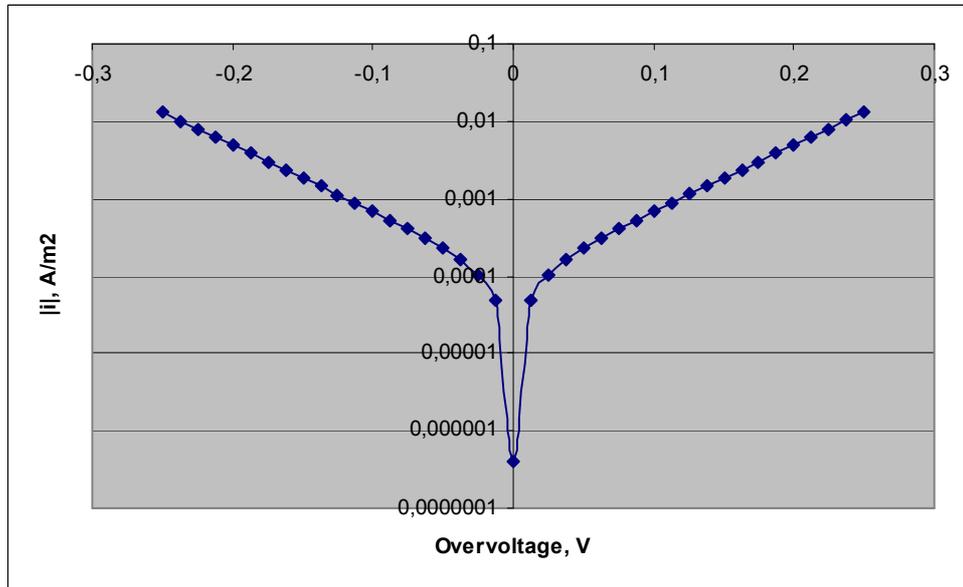


Figure 25. Tafel plot for the same parameters as in the previous plot ( $i_0 = 0.0001 \text{ A/m}^2$ )

The above considerations assume that the chemical potentials are constant at the electrode, such that the open circuit (Nernst) voltage remains constant. This may be fulfilled in buffered systems, where all reactants and products are present in excessive amounts. However, there are also many examples of the opposite. For instance, a fuel cell fed with dry fuel such as  $\text{H}_2$  will have a large open circuit potential. However, as soon as current is passed in the forward direction of the fuel cell, water is generated and the cell voltage drops considerably. This may therefore look like a polarization, but it is not related to kinetics. It is called concentration polarization.

At high currents, we usually run into a new region, where the current levels off toward a constant value regardless of overpotential. This is caused by mass transport

limitations, such as limited transport of reactants to the electrode or of products from the electrode. It is thus also a kind of concentration polarization.

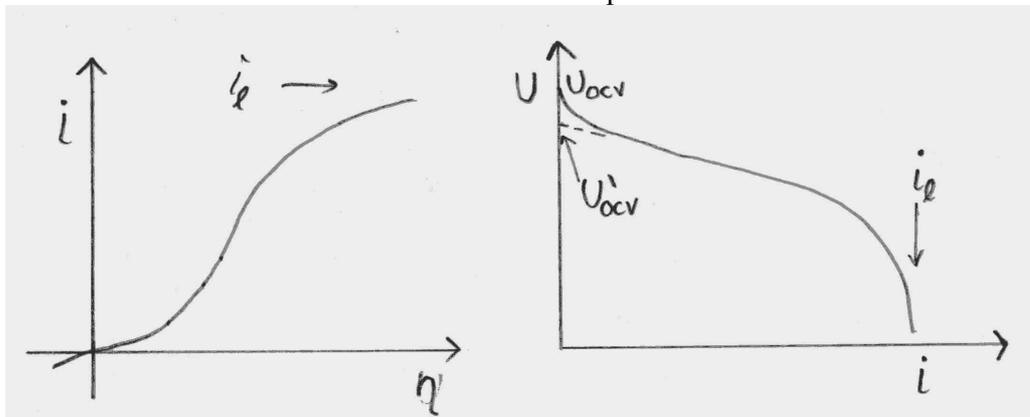


Figure 26. Plots illustrating effects of concentration polarization and mass transport limitations. Left: current density  $i$  vs overpotential. Right: Typical  $i$  vs  $U$  curve for a fuel cell: The open circuit voltage  $U_{OCV}$  falls by concentration polarization; as the electrodes get stable concentrations of products, the curve relates to a new open circuit voltage  $U'_{OCV}$ . Mass transport limiting current density is denoted  $i_l$ .

Studies of the different aspects of electrochemical reactions and electrodes is a field with rich traditions, and a number of methods have been established which are all basically different ways of exploring the current-voltage characteristics. In many of these measurements we may choose to set a voltage and measure the current or to set the current and measure the voltage. The former is called potentiostatic control, while the latter is called galvanostatic. We commonly use instruments capable of both types of control; potentiostat-galvanostats.

In order to measure a true DC voltage-current curve, we may measure individual points along the curve by stepping the voltage or current and reading the current or voltage. This simple way is called **chronovoltammetry or chronoamperometry**. We may instead program a continuous linear variation of voltage with time, and record the current using a recorder or computer. This should then be done slowly enough to represent steady state and thus DC characteristics. The method is called linear sweep voltammetry (LSV).

A number of other methods utilize time dependencies in the response after changes in the excitation of the electrode. The programming of the methods and interpretation of results are usually done by software developed for this kind of research, and accompanying the commercial potentiostats-galvanostats on the market.

Electrochemical measurements are usually done with a working electrode, a counter electrode and a reference electrode, representing what we earlier have referred to as a three-electrode setup. In aqueous systems, the reference electrode can be a standard hydrogen electrode (SHE) or a standard calomel electrode, such that the electrode potential of the working electrode is well defined (measured with respect to the standard electrode).

In solid state electrochemistry, a similar standard is not established. It would require a separate definition for each solid electrolyte.

In solid state electrochemistry one should also be aware that charge transfer and rate-limiting steps of the electrochemical reaction need not necessarily take place at the electrode-electrolyte interface. This is especially true for mixed conducting electrodes. In such a case,

the situation may be altered from the relatively simple relationships given by the Butler-Volmer equation.

In the present treatment we have up to now concentrated on the overpotential of an electrode. Needless to say, a two-electrode measurement will include overpotentials in both electrodes plus the voltage drop through the electrolyte. Such a setup is thus not very useful for characterization of electrodes. A three-electrode setup on the other hand eliminates the overvoltage of one electrode (the counter electrode) and includes only that of the working electrode plus the part of the electrolyte between the reference electrode and the working electrode. The voltage drop in the electrolyte, the so-called IR-drop, must be subtracted before the overvoltage can be analysed in a meaningful way for the electrode. The IR-drop can be found e.g. by its time constant being shorter than for the electrode. This can be done by impedance spectroscopy. Potentiostats/galvanostats have various ways of compensating it away already during measurements – refer to the manual of each model.

## **Battery electrodes**

To be considered for inclusion in later revisions.

## **Semiconductor junctions**

To be considered for inclusion in later revisions.

## **Photoelectrodes**

To be considered for inclusion in later revisions.

## ***Impedance spectroscopy***

### **General**

In impedance spectroscopy we measure complex impedance over a range of frequencies. This enables us to assign the results to a number of discrete circuit elements, or physical processes, if we know or have a model of their electrical response.

Most commonly, the impedance spectrum is taken with a small AC voltage or current imposed on the sample under zero DC current conditions. In this case, the AC signal probes the linear responses of the sample. How small the signal needs be depends on which process one is interested in. If we want primarily information about volume impedances, we can use a large signal in order to get a good signal-to-noise ratio. If we are interested in electrode responses, we better use a much smaller signal, so that the electrode processes remain linear.

The frequency is typically stepped logarithmically through the range. Early spectrometers were limited in frequency upwards or downwards or both, while modern ones typically cover all frequencies you and your system can take. For instance, a Solartron 1260 FRA delivers from  $10^{-5}$  to  $3.2 \cdot 10^6$  Hz (10  $\mu$ Hz to 32 MHz) The lowest of these require extreme patience by the user and stability of the sample and system, since each oscillation at 10  $\mu$ Hz takes 30 hours. Thus, 0.1 or 0.01 Hz is a practical lower limit in most cases.

In the other end, normal samples and sample holders/cells often limit the highest frequencies to 1-10 MHz due to parasitics and to the finite wavelength of the current at these frequencies. The electrons have the speed of light and a wavelength depending on the frequency. At 1 Hz and 100 kHz the wavelength is  $3 \cdot 10^8$  and 3000 m, respectively, both long enough that the AC current reaches the sample and the AC voltage reaches the instrument without any displacement of the phase of the two. But at 10 MHz the wavelength is only 30 m and the length of the leads starts to make a significant error in the phase angle measurement.

Below, we will first generate a few example spectra based on what we learned about certain discrete components and their frequency dependences. Then we will do the same for some physical systems and introduce some new circuit elements for this purpose. Finally, we will look at the process of using measured spectra to propose equivalent circuits and fitting them to obtain the parameters that we are interested in.

### **Generation and representation of example model spectra**

Assume a circuit consisting of one resistor and one capacitor in series. The complex impedance spectrum looks as in the figures below, so-called Nyquist plots. The impedance has two contributions; one real from the resistor and one imaginary from the capacitor. Thus, the Nyquits diagram will consist of a straight vertical line; the real part is constant, while the imaginary part becomes increasingly negative as frequency decreases. At infinitely high frequencies, the capacitor has zero impedance.

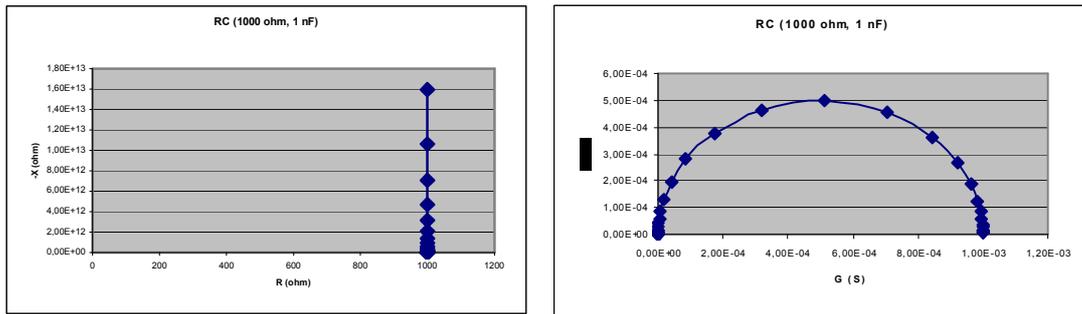


Figure 27. Nyquist-type impedance and admittance plots of a series circuit of one resistor and one capacitor, over a frequency range of  $10^{-5}$  to  $3 \cdot 10^7$  Hz (the range of a Solartron 1260). The impedance plot has  $-X$  as the  $y$ -axis according to common practice to get capacitive elements appear in the 1<sup>st</sup> quadrant.

We next plot the same circuit in an admittance diagram (of real and imaginary admittance). We may do this mathematically, but here we will take a simple intuitive and qualitative approach: At zero frequency, the admittance of the capacitor is zero; it dominates the total impedance of the series circuit, and the total admittance of the circuit is zero; the curve is at origo. At increasing frequency, the capacitor starts to conduct and at a resonance frequency they both contribute equally much to the total impedance. The admittance now has as much real as imaginary components and has come to the top of a semicircle starting from origo. As frequency continues to increase, the capacitor gets higher admittance, and eventually contributes none to the total impedance. The impedance is then given only by the resistor, and in the admittance plot, we are now back on the real axis, the value being the conductance of the resistor.

We note that the series connection gets a simple and intuitive representation in the impedance plot (straight line), and a more complex shape (semicircle) in the admittance plot.

Next, assume a parallel (lumped) connection of the same two circuit elements, a resistor and a capacitor. A similar exercise as above reveals that such a parallel circuit is represented by a simple vertical line in the admittance plot; where the real value is conductance of the resistor, and the imaginary part is zero at zero frequency and increases as the frequency increases. In this case, we get a semicircle in the impedance plot; the impedance is zero (origo) at infinitely high frequency where the capacitor is conducting. At zero frequency the capacitor does not contribute, and the impedance of the circuit is only given by the resistance of the resistor, and thus is at the real axis. In between there is a semicircle with a top where the two components contribute equally much.

We now note that a parallel connection thus gets a straight line in the admittance plot, and a semicircle in the impedance plot.

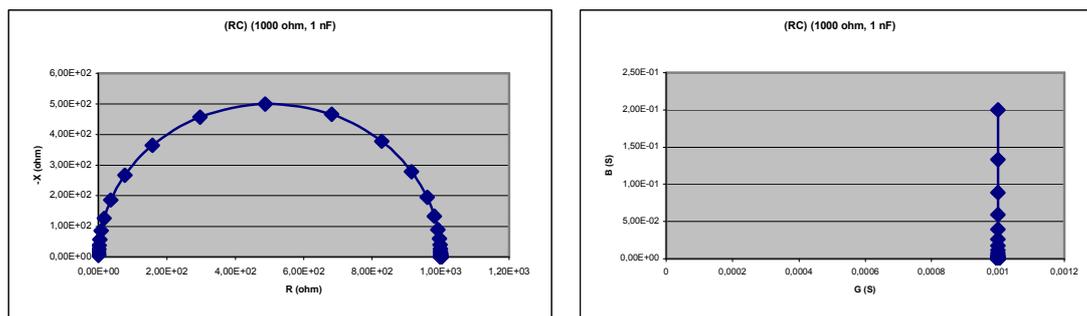


Figure 28. Nyquist-type impedance and admittance plots of a parallel circuit of one resistor and one capacitor, over a frequency range of  $10^{-5}$  to  $3 \cdot 10^7$  Hz.

## Physical systems and equivalent circuits

The parallel circuit of a resistor and capacitor is a typical representation of a solid or liquid conductor with a not too high conductivity, such as semiconductors, insulators, and ionic conductors.

The resistor represents the **long-range transport of charge carriers**. The conductivity contained in this element is the **total conductivity** – the sum of all conductivities of the various charge carriers. Each conductivity is the product of the charge, volume concentration, and mobility of the charge carrier.

The capacitor is what we call the **geometric, or bulk, capacitance** of the material, resulting from all dipoles present in it. These comprise electron-core dipoles, cation-anion-dipoles, and more complex dipoles relating to defects, reorientation of defect clusters, etc. These processes can for normal AC investigations be considered fast enough that the capacitor behaves ideally; the polarization and depolarization is instantaneous. However, the polarization of the electron-core dipoles is not infinitely fast, and may give dispersions at frequencies of light. Cation-anion dipoles are slower, and reorientation of defects even slower, sometimes appearing in the normal AC ranges.

The geometric capacitance of condensed phases is characterized by typical relative dielectric constants of between 1 and 10, giving typical samples (e.g.  $1 \text{ cm}^2$  area, 1 mm thickness) capacitances in the range of 10 pF. Some ionic liquids and solids with particular dipole mechanisms have much higher relative dielectric constants.

A conductor also contains an inherent **inductor**, since current through the sample may induce electromagnetic fields. This element is to be seen in series with the resistance. It will become dominating over the capacitance for highly conducting materials such as metals. Thus, impedance spectra of good conductors may look simply like a straight line, from a point at the real axis (the series resistance) and increasing into positive imaginary values as the impedance of the inductor increases. In  $-X$  vs  $R$  plots this is a line pointing straight down. For intermediate resistances, both the inductive and capacitive properties of a sample may come into play in the same impedance spectrum, such that the impedance spectrum looks like a semicircle, but at some point on the arc deviating into the line going straight down.

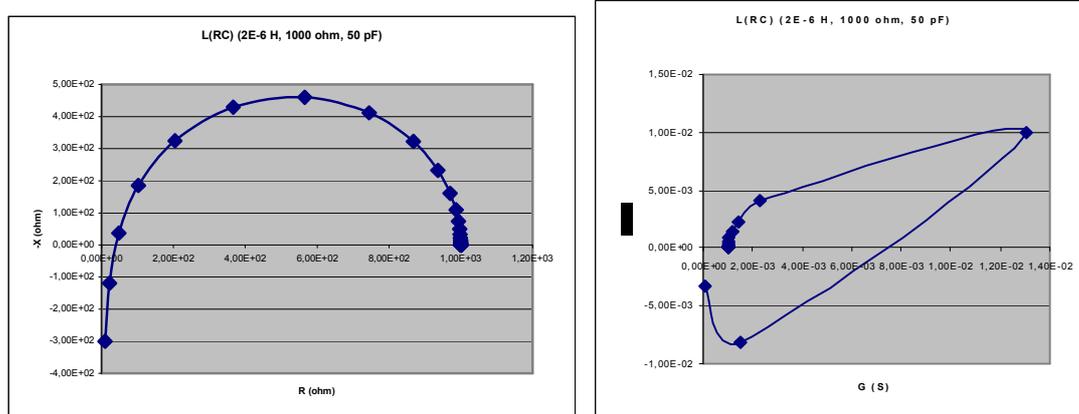


Figure 29. Nyquist impedance and admittance diagrams of the circuit  $L(RC)$  representing a bulk sample with conductance  $G=1/R$ , geometric capacitance  $C$ , and inductance  $L$  (real or parasitic). The points on the strange high frequency part of the curve in the admittance plot is in fact part of a circle.

**Grain boundaries** may be regions of higher or lower conductivity than the bulk. They may probably even have boundary cores that are highly conducting and space charge layers that are depleted of charge carriers, or *vice versa*. Highly conducting grain boundaries in polycrystalline materials cannot be identified by impedance spectroscopy; they come out as an extra lumped (RC) circuit element in parallel with that of bulk and in this way merges into the bulk element. However, highly resistive grain boundaries form an extra lumped (RC) element in series with bulk element. While the specific capacitance may be similar to that in bulk, the thickness is widely different. The grain boundary (RC) element thus gives rise to a new semicircle in the impedance diagram, occurring at lower frequencies. The zero frequency case contains the sum of the two resistances (bulk and grain boundaries). The two semicircles adding up illustrates why the impedance diagram is so popular in solid state ionics although an admittance diagram in principle gives a simpler curve for parallel circuits (one semicircle and one vertical line).

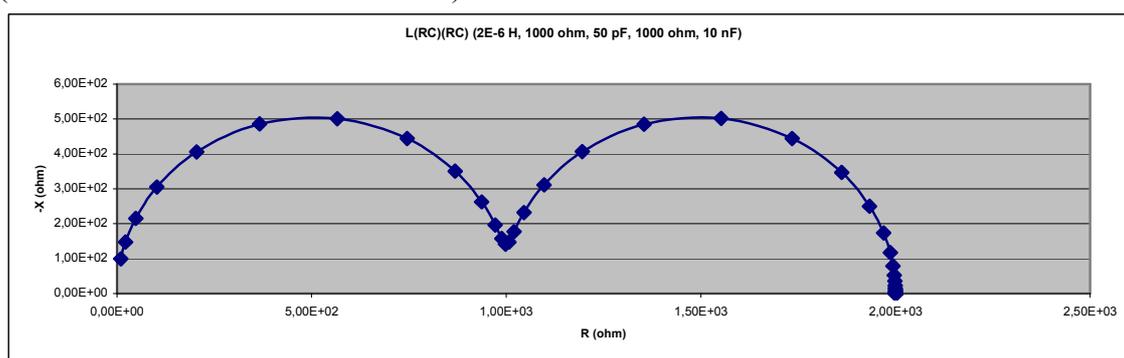


Figure 30. Nyquist impedance plot of an  $L(RC)(RC)$  circuit typical of a ceramic with bulk and ideal grain boundary contributions to the impedance.

Each grain boundary that the current passes adds to the observable grain boundary impedance. In this way, the resistance becomes the sum of the individual resistances, while

the capacitance becomes smaller the more grain boundaries. However, the time constant of the peak of the grain boundary semicircle remains constant – independent of the number of grain boundaries. If all boundaries are identical in characteristics, we should get a perfect semicircle, like we mostly do for the bulk impedance. However, the boundaries are not identical; they represent different angles of mismatch (giving different charging, space charges, and effective thicknesses) and they are differently oriented with respect to the current. Therefore, the resistance as well as capacitance of the individual boundaries vary, and the total grain boundary impedance becomes a result of a distribution of these parameters and of the time constants. This gives rise to a depression of the semicircle into an arc, as shown in the figure below.

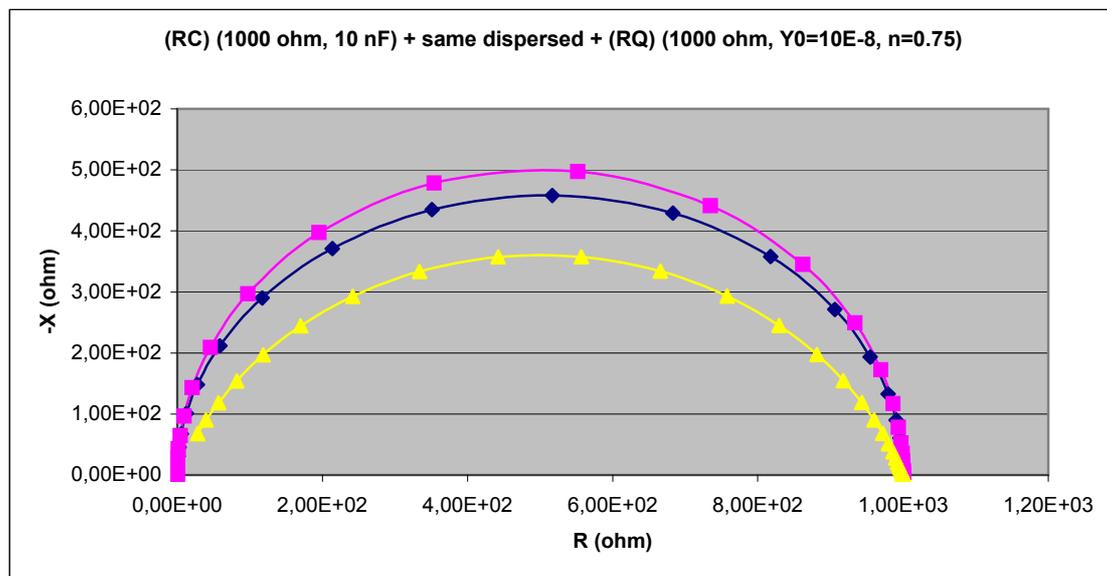


Figure 31. Impedance plot of various representations of a total resistance of 1000 ohms in parallel with a capacitance of 10 nF, typical of the grain boundaries in a polycrystalline ceramic sample. The uppermost curve is the ideal (RC) circuit representing one grain boundary or an ensemble of identical grain boundaries in series (RC)(RC)(RC).... The intermediate curve is drawn by calculating the response of four grain boundaries in series ( $R_1C_1$ ) ( $R_2C_2$ ) ( $R_3C_3$ ) ( $R_4C_4$ ) assuming a distribution in thickness and corresponding R and C values, but with the same total resistance. The lowermost curve is calculated for an (RQ) circuit with  $R = 1000$  ohms, and Q having  $Y^* = 10^{-8} (j\omega)^{0.75}$ .

One way of simulating a dispersion in time constants is to assign a **constant phase element, CPE or Q**, to the capacitance. A CPE has admittance

$$Y = Y^0 (j\omega)^n$$

where n is an exponent that in physical cases can vary between  $-1$  and  $+1$ . If  $n = 1$  it is clear that the expression is the same as for an ideal capacitor, with  $Y^0$  being the capacitance.

If  $n = 0$  it is furthermore clear that the CPE represents a pure conductor (resistor) with  $Y^0$  being the conductance.

If  $n = -1$  then the CPE represents a pure inductor,  $Y^0$  being the inverse of the inductance.

In intermediate cases, CPEs have both real and imaginary components, and in general their admittance  $Y^* = Y' + jY''$  can be expressed with

$$Y^* = Y_0(j\omega)^n = Y_0\omega^n \cos\left(\frac{n\pi}{2}\right) + jY_0\omega^n \sin\left(\frac{n\pi}{2}\right) \quad (24.)$$

CPEs can emulate a number of processes and having distributed time constants, by varying  $n$  between the integer values. A system of many grain boundaries is often well represented by a resistor (being the sum of all resistances) in parallel with a CPE having an  $n$  of ca. 0.75 (“capacitor-like”).

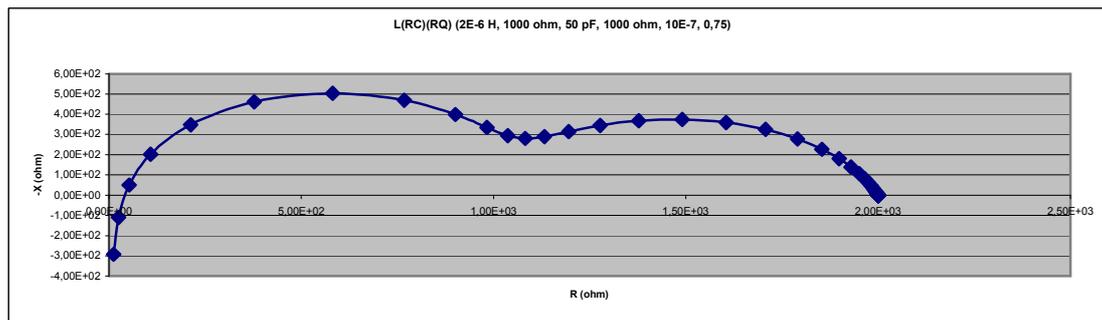


Figure 32. Nyquist impedance plot of an  $L(RC)(RQ)$  circuit typical of bulk+grain boundary impedances in a real ceramic.

An **electrode** is a contact between two different phases, of which one is typically a metal and the other an ionic conductor or a semiconductor (or mixed conductor). Firstly, the interface comprises an interface layer of a particular kind (whatever properties). In aqueous electrochemistry, this is the so-called double-layer. Regardless of system, such a layer may comprise adsorbed species. We assign a capacitance to this layer and denote it the **double-layer capacitance**. The layer is typically only a few atom layers thick, and its capacitance therefore very high. Unlike grain boundaries we only have one (or two) electrodes, so that the electrode double-layer capacitance becomes big, typically of the order of  $1 \mu\text{F}/\text{cm}^2$ .

Next, the electrode or contact has a **charge transfer conductance** (or **charge transfer resistance**) which represents the path electrons or ions use to jump the barrier, or, for electrode-electrolyte interfaces, the combined electrochemical process where both chemical species and electrons are involved. The charge transfer resistance is in parallel with the double-layer capacitance. Together they may thus form another semicircle in an impedance diagram, typically at much lower frequencies than the grain boundary and bulk semicircles.

Several transport processes may take place in series with a charge transfer at an electrode. This includes adsorption – desorption, diffusion in condensed phases and gases or on materials surfaces, and reactions. This gives rise to a wealth of behaviours and corresponding electrical “equivalents”. We cannot go through them all, but only mention a few characteristics. Firstly, these processes give rise to capacitances much larger than bulk, a grain boundary or a double-layer. This may be ascribed to chemical storage (actually **chemical polarization**); buildup of chemical species in condensed phases or on surfaces or interfaces, or in gas volumes. The capacitances typically reach and exceed the  $\text{mF}/\text{cm}^2$  range. In parallel with this storage diffusion and reaction processes take mass to the actual charge

transfer step. Along the way, charge carriers have the possibility to move on or to settle down. This gives a behaviour like RC-blocks connected like in a ladder of series resistances (diffusion) with parallel capacitors (storage). Such a ladder is well represented by a CPE with  $n = 0.5$ , and is called a **Warburg element W**. We may differentiate between two types of overall behaviour: A transport or reaction process forwards the electrode process past the storage processes and gives rise to steady (DC) reactions. This is represented by a resistor in parallel with the chemical polarization capacitance. The resistance may be large or small. For simplicity we may refer to this element as **diffusion resistance  $R_d$** . It may be the representation of the mass transport limitations that we discussed earlier under DC techniques. The diffusion resistance is to be seen in parallel with a chemical polarization CPE  $Q_d$  and its  $n$  will most typically be around 0.5, i.e. close to a Warburg element.

If the diffusion resistance is infinitely large, we have a **blocking electrode**. The impedance then ends up, at low frequencies, with the typical Warburg “look”; a straight line with a constant phase angle of  $45^\circ$ , sending the impedance to infinity at zero frequency (DC). The causes of the blocking can be many, e.g. a gas without reactants, infinitely slow surface reaction kinetics, infinitely slow solid state diffusivity.

All in all, electrodes of a conductor in contact with an electrolyte (solid-liquid or solid-solid) can often be represented by the so-called Randle’s circuit:  $(C_{dl}(R_{ct}(R_d Q_d)))$  while a blocking version of the same would be  $(C_{dl}(R_{ct} W_d))$ .

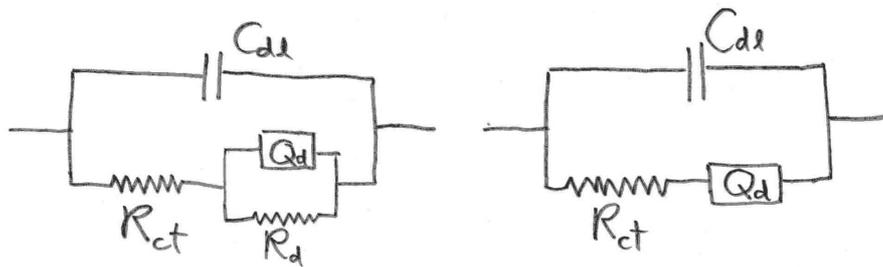


Figure 33. Typical equivalent circuits for non-blocking (left) and blocking (right) electrodes.

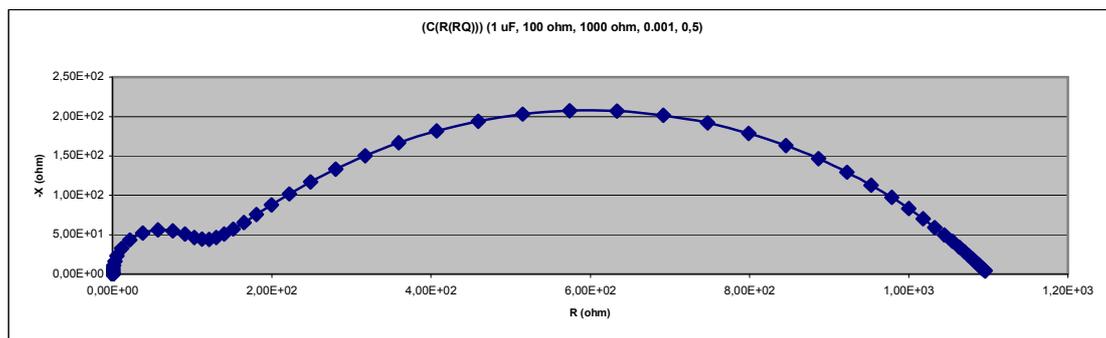


Figure 34. Nyquist plot of a Randle’s circuit for a typical poor, but not blocking electrode.

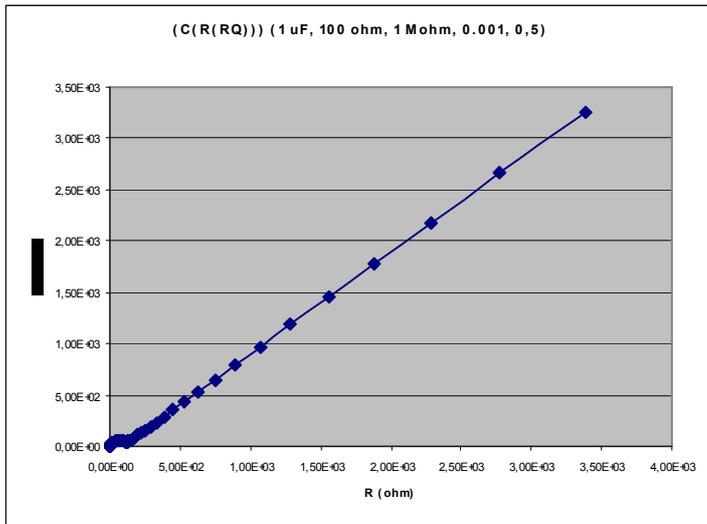


Figure 35. Nyquist plot of a Randle's circuit for a typical almost blocking electrode ( $C_{dl}(R_{ct}(R_dQ_d))$ ), with  $R_d = 1$  Mohm. Lowest frequencies omitted for clarity of illustration. Circuit effectively corresponds to  $(C_{dl}(R_{ct}W_d))$ .

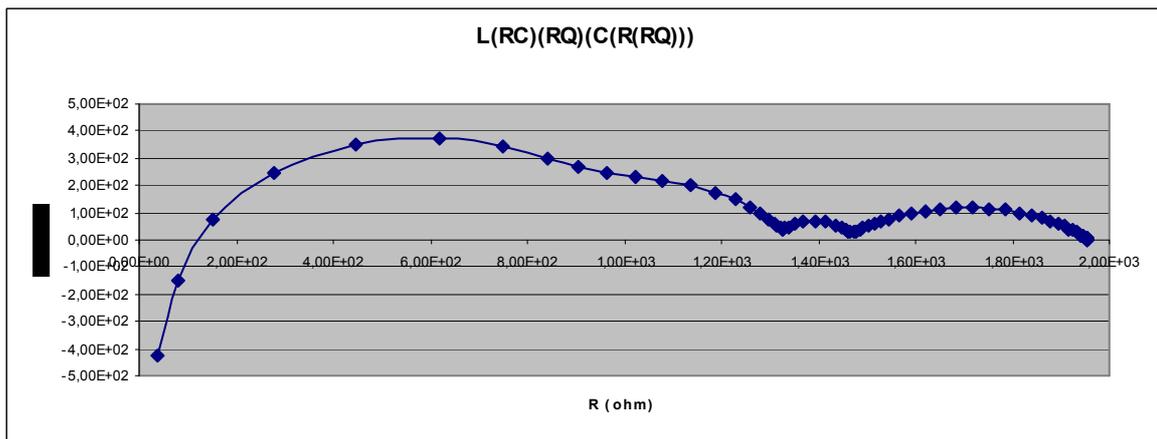


Figure 36. Nyquist impedance plot for a typical ceramic sample.

Contacts between two electronic conductors may have both contact layer capacitance and charge transfer resistance. However, most often they have much lower resistances than electrode-electrolyte combinations, and they do not have the large chemical capacitances. Therefore, the most typical representation of a sample with mixed ionic-electronic conduction and electrodes would be one with two pathways, one ionic and one electronic. The ionic is terminated at the electrodes with Randle's circuits, while the electronic to a first approximation could be assumed to make direct contact, or have much smaller charge transfer resistances.

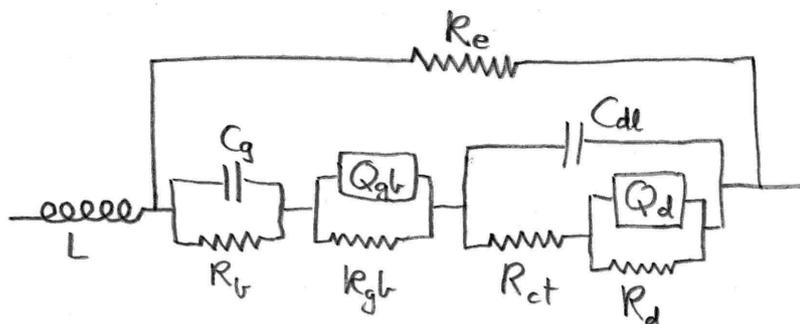


Figure 37. Equivalent circuit that may apply to a typical sample of a mixed ionic– electronic conductor. For simplicity, electronic conductivity assumed not to have grain boundary impedance.

Grain boundary resistance may also enter differently for different charge carriers.

In many cases, the placement of elements in the equivalent circuit is not obvious. For instance, the geometric capacitance was earlier placed in parallel with the bulk resistance. However, it might well have been placed in parallel with everything – it would hardly differ in the behaviour of the circuit. When we deal with mixed conductors it is natural to place the geometric capacitance in parallel with both the ionic and electronic paths, .i.e., in parallel with “everything”.

## Deconvolution and fitting of measured spectra

Now, we turn to the reverse process; the deconvolution of an impedance or admittance spectrum that we may not know *a priori* how to interpret. Our job is to identify possible equivalent circuits that reproduce the spectrum reasonably well, and to fit the values of the elements in that circuit.

First, it must be clear that several different circuits may create the same spectrum. The deconvolution can thus not unambiguously identify one circuit as the right one, it can only say how good one circuit is, and it can identify circuits that by no means fit.

In the deconvolution process we combine the possibility of differentiating between possible and impossible circuits with our intuition for which physical processes we may have and how their impedance behave, with reference to the preceding section.

The procedure we will adopt is that of the Equivalent Circuit (“EQUIVCRT” or “EQ”) software by Bernhard Boukamp of the University of Twente, The Netherlands. The procedure consists of several steps.

The first step is to inspect the spectrum in impedance and admittance modes and remove permanently data sets that are obviously spurious. Such data are usually a result of incidences in the lab during the impedance sweep, frequencies laying outside the range that the equipment otherwise can handle, noise, interference with other signals, etc. Often, one or two or three points around the hum frequency (50 or 60 Hz) are spurious and can be discarded. It may be a good idea to store the cleansed spectrum so that the process need not be reproduced.

The second step is the “crunching” of the data; the process of roughly determining how the equivalent circuit may look like. This consists of 3 subprocedures:

First, identify in the spectrum something reflecting a part of the equivalent circuit that is in series or in parallel with all the rest. This is the most difficult part of the whole thing, a handicraft that develops with training and experience, and with trial and error. In order to identify such parts of the circuit, pick out a feature of the spectrum such as a line or an arc or semicircle - usually at the high frequency end. If it is a line in the impedance spectrum, it is a series subcircuit. If it is a semicircle, it is a parallel subcircuit. The opposite is true for an admittance spectrum. Also note whether it is on the inductive or capacitive side.

When you have identified a subcircuit, fit it to the most relevant part of the spectrum (partial fit).

Finally, subtract the subcircuit (or part of it) from the spectrum. This means that the remaining spectrum will represent the rest of the circuit. If the subcircuit found was reasonable, the remaining spectrum should look physically sound, except for possible scatter of data in the frequency range where the subtraction was effectively done.

As you subtract elements, a subtracted circuit develops.

Now, go back and repeat the three steps until only random scatter remains – this signifies that a reasonable circuit has been built up by the elements you have subtracted.

When the circuit is established, move on to fit of the whole circuit to the whole spectrum – a full non-linear least squares (NLLS) fit.

If this converges, you next judge the result by comparing a simulated spectrum based on the circuit to the measured spectrum. The most effective plot is the error in real and imaginary components vs frequency. If this contains only random scatter, the fitted circuit is plausible. If it contains systematic (e.g. sine) errors, the final circuit is not optimal and possibly incorrect.

## **Further considerations of data from impedance spectroscopy**

Parameters found from fitting impedance spectra to models circuit are often used in finding temperature dependencies (activation energies) or dependencies on chemical activities, e.g. partial pressures of component gases. The latter may elucidate defect structures or electrode reaction mechanisms. If the fitting of the spectra gives uncorrelated parameters, they can be used as is. However, if they are strongly correlated, it should be a practice to redo all the fits, with parameters considered constant fixed at a value which may be for instance an average of the fitted values. For instance, the grain boundary impedance may come out with scatter in both the R and Q values as a function of temperature. It is reasonable to assume that R varies exponentially with temperature, while Q and its n should remain constant. Thus, a refit with fixed Q parameters may give less scattered R vs temperature.

The bulk data (bulk conductivity and geometric capacitance) may be corrected using sample dimensions into specific values. However, for the grain boundary and electrode impedances, the same correction makes little sense. The electrode parameters could be recalculated into area-specific parameters.

For grain boundaries we may do the following: If we assume that the grain boundaries have the same relative dielectric constant as the bulk, a brick-layer model for the

bulk and grain boundaries, and that we know the average grain size, then we can calculate the effective grain boundary thickness from the ratio between the bulk and the grain boundary capacitances. Once this is done, the measured grain boundary resistance can be recalculated into specific resistivity for the grain boundary phase.

### **Some specialties of advanced impedance spectrometers**

Impedance spectrometers such as the Solartron 1260 FRA and HP 4192A pass current not only through the current wires, but also through the shields of the current wires, in such a manner that the currents in the wire and its shield pass in opposite directions. This makes the induced fields of the two currents cancel, and the currents therefore, in turn, induce much less signal into other wires, e.g. the voltage wires. In order to accomplish this, current leaves the generator output, goes through the sample, enters the low current terminal and the current measuring circuit from this it exits through the shield of the wire it just came in through and goes back through this shield towards the sample. As close as possible to the sample, the shield must be connected to the shield of the generator output wire, so that it can follow this shield back to the generator, again canceling the fields of the current in the generator output. Connecting the shields of the current wires is thus the first thing to remember when using such impedance spectrometers. Also the voltage wires may be connected to the rest of the shields, but this is not essential.

Understanding the options in terms of averaging and integration of results is important. On the HP 4192A you can average 1, 2 or 10 measurements – an un-advanced and foolproof procedure. On the SI 1260FRA you can choose to measure until the standard deviation is less than 10 or 1 % for the current *or* voltage, within a maximum time. Or you can measure for a specified time and get the result irrespective of standard deviation. This gives great possibilities to get better measurements, but also to give so hard requirements (e.g. 1% deviation on a non-stable system) that you never get a result.

The spectrometers also have other options. For instance, the HP4192A applies a correction for the wave-length of electrons assuming that the wires to the sample are 0 or 1 m (selectable). The SI 1260FRA can apply a capacitor on the voltage inputs that filter out DC components of the voltage, thereby increasing the sensitivity of the voltmeter. This would affect low-frequency measurements, so you can select the frequency above which the capacitor is applied.

### **Combining impedance spectrometers with other units; electrochemical interfaces, boosters, dielectric interfaces**

An impedance spectrometer measures the slope of the voltage-to-current curve. If this is straight, as it usually is close to the open circuit voltage (zero current), the impedance is linear and follows ohm's law as we have pointed out earlier.

However, at larger currents and overpotentials, the curve may become curved, and it is of interest to use impedance spectroscopy to see what parts of the impedance spectrum and equivalent circuit that responds non-linearly. This can help identify rate limiting steps and

mass transport limitations and to assign characteristic parameters to these (e.g. activation energies).

Impedance spectrometers can usually apply bias – DC voltage or current – superimposed on the AC signal, and to some extent bring the measurements into regions of non-linear behaviour. However, their capability to keep DC voltage or current stable at the sample is limited, and there is also little possibility to monitor this. Therefore, it is common to apply and analyse the AC signal of the spectrometer through a galvanostat/potentiostat. All galvanostat/potentiostats thus have inputs for AC perturbation. Some are designed to work in pairs with spectrometers, such as the Solartron 1286 and 1287 – in this case therefore called Electrochemical Interfaces. In other systems such as Gamry potentiostats the impedance spectrometers and potentiostat are one unit and cannot be separated. We will not go into more detail here, but just list the pros and cons of electrochemical interfaces/ potentiostats/ galvanostats hooked onto impedance spectrometers: They give much better DC control and they provide usually much higher input impedance for the voltmeter function. However, they restrict the useful frequency range upwards to typically 300 kHz.

Impedance spectrometers typically manage up to 0.1 A of DC bias current. Potentiostats/galvanostats manage from one to a few amperes. For studies of fuel cells, electrolyzers and large battery systems more current is required (both for the DC and AC parts) to operate under realistic loads and to measure significant voltages. For this purpose one may use boosters – devices that amplify the applied voltages and currents, and handle tens or hundreds of amperes. For testing large fuel cell systems one also has something called electronic loads, which can drain high, constant currents from the system to be evaluated.

Dielectric interfaces specialize in providing super-high input resistances to impedance spectrometers, and are beneficial for measuring the conductivity and capacitance of insulators and other dielectrics.

## Some related techniques

In this section we will briefly mention some methods that are more or less related to impedance spectroscopy.

In impedance spectroscopy we have been mainly interested in resistance or conductance and we define these as real components since they produce or consume real energy when current passes. However, had we primarily been interested in the capacitance of a sample, and considered conductance as a side-effect, we could have chosen a different framework, and this is what is done in **dielectric spectroscopy**. The instrumentation and data measured are basically the same, but the parameters obtained are real and imaginary parts of the dielectric constant rather than of the impedance. Data from the two frameworks are mutually convertible.

In impedance spectroscopy we choose one frequency after another and record the current and voltage and the impedance. We could instead apply all frequencies at once, as noise (**noise spectroscopy**), record the voltage and current noise spectra over the sample, and obtain the real and imaginary impedances vs frequency by Fourier transformation.

We could also charge the sample by passing a certain current through it until the voltage was constant. Then the current is interrupted (e.g. using a fast switch in a

galvanostat) and the voltage recorded vs time. This drops according to the discharge of all the “capacitors” in the sample; the bulk geometric capacitance is small and drops fast, the grain boundaries come next, and finally the electrodes. Analysis of the decaying curve of such a **current interruption** gives in principle the same information as impedance spectroscopy.

In **cyclic voltammetry** we are basically back at a DC technique, but the voltage is cycled back and forth, and behaviours (peaks) of the current recorded reveals processes taking place at the electrodes. Variations with cycling speed give information of time constants for processes – much like the low-frequency information on electrodes obtained in impedance spectroscopy.