Transport Measurement:
DC conductivity

Why to bother about resistivity?

Resistivity contributes to:

- Device series resistance
- Transport of carrier upon harvesting light
- Affects performance of devices

Resistivity

$$\rho = \frac{1}{q\left(\mu_n n + \mu_p p\right)}$$

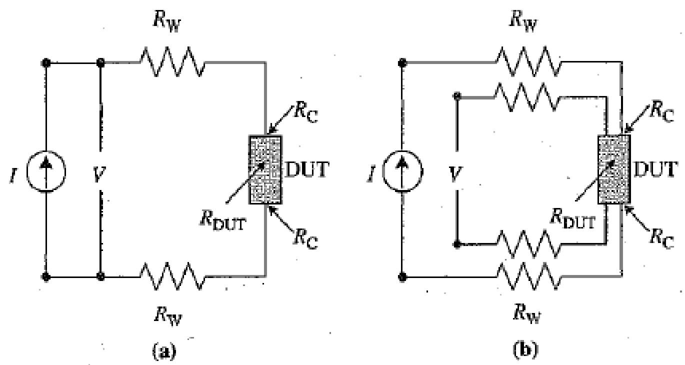
ρ can be calculated from the measured carrier densities and mobilities

Extrinsic materials:
Majority carrier density » minority carrier density, enough if we know majority carrier density

Carrier density and mobilities are not generally known.

Best is to look for alternate measurement techniques – direct resistivity measurement.

Two-point versus four-point probe

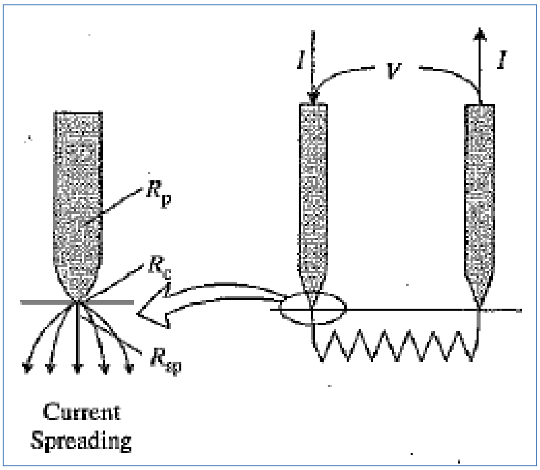


Two-terminal and four-terminal resistivity measurement arrangements

Two - probe methods appear to be easier to implement – but difficult to interpret

Four – probe method commonly used to measure resistivity of semiconductor– is an absolute measurement without need of calibrated standards.

Two-probe measurement



Probe, contact and spreading resistance of a two-probe arrangement on a semiconductor

Measured total resistance

$$R_T = V/I = 2R_W + 2R_C + R_{DUT}$$

Impossible to determine R_{DUT} accurately using 2-probe measurement.

Remedy: four-point probe or four-contact arrangement

Current path is identical to that for 2-probe method

In addition, 2 more leads for voltage measurements

How to avoid contact and wire resistance ?

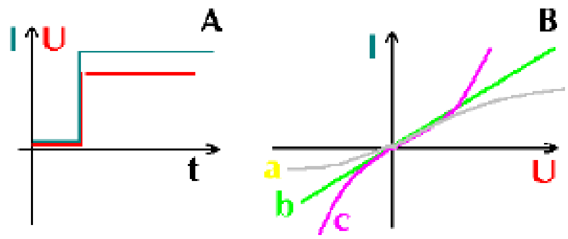
- Although voltage path contains R_W and R_C the current flowing through the voltage path is very low due to high input impedance of the measuring voltmeter (10^{12} ohms and higher)
- Voltage drop across R_W and R_C are negligibly small – neglected, measured voltage is essentially the voltage drop across the DUT
- Eliminated parasitic voltage drops using 4-lead measurements – Kelvin measurements (Lord Kelvin)

Impedance Spectroscopy

How to characterize an electrical system

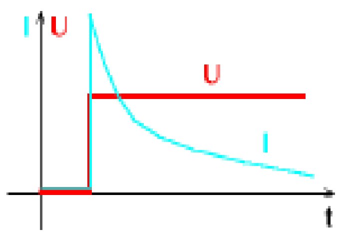
Case A: Steady state current-voltage curve

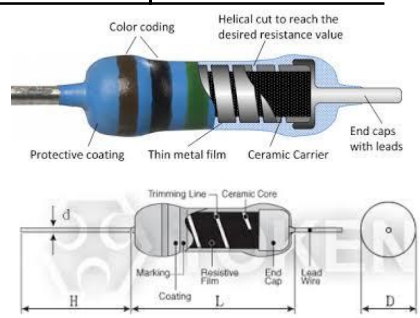
I(U) exist if the device under test (DUT) is a pure resistor



How to characterize an electrical system

Case B: the current-voltage curve also depends on time t





System under test can be characterized using time dependence of current I(t)

We analyze the I(t) – U(t) relation

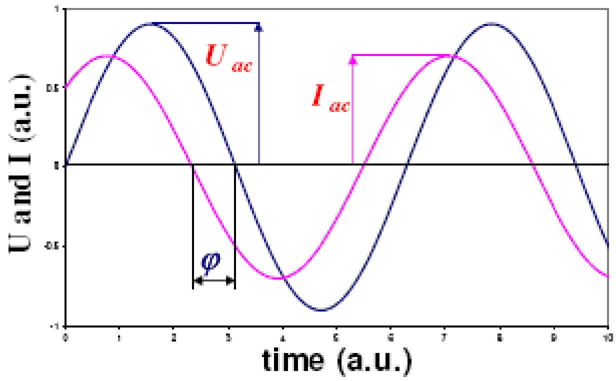
Possibilities:

a. Transient response following a jump or pulse
b. AC methods, by applying a sinusoidal curve at different frequencies

Definition of impedance

Stimulus: $U(t) = U_{ac} \cdot \sin(\omega t)$

Response: $I(t) = I_{ac} \cdot \sin(\omega t + \varphi)$



Impedance is defined as $Z \equiv (U_{ac}/I_{ac}$ and $\varphi)$

Introduction to impedance

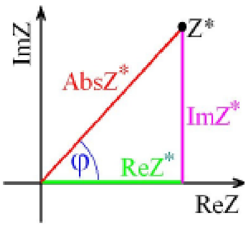
Impedance (at one frequency):

- is defined as $Z^* \equiv (U_{ac}/I_{ac}$ and $\varphi)$, complex number
- $Z^* \equiv U_{ac}/I_{ac} \cdot e^{i\varphi} = |Z|\cos(\varphi) + i \cdot |Z| \sin(\varphi)$ Euler's formula

with $|Z| = Z_{abs} \equiv U_{ac}/I_{ac}$ and $i \equiv \sqrt{-1}$

- admittance: $Y^* \equiv 1/Z^*$ ($Y_{abs} = 1/Z_{abs}$ and $\varphi_Y = -\varphi_Z$)

Impedance on the complex plane:



$Z^*(ReZ^*, ImZ^*)$

$Z^* = ReZ^* + i \cdot ImZ^*$

$Z^*(AbsZ^*, \varphi)$

$ReZ^* = AbsZ^* \cdot \cos(\varphi)$

$ImZ^* = AbsZ^* \cdot \sin(\varphi)$

RCL elements

Impedance of a network of RCL elements can be calculated just in the same way as the resistance of a network of resistors.

Impedance:

- of serially connected elements: $Z_s = Z_1 + Z_2$

  $1/Y_s = 1/Y_1 + 1/Y_2$
- of parallely connected elements: $Y_p = Y_1 + Y_2$

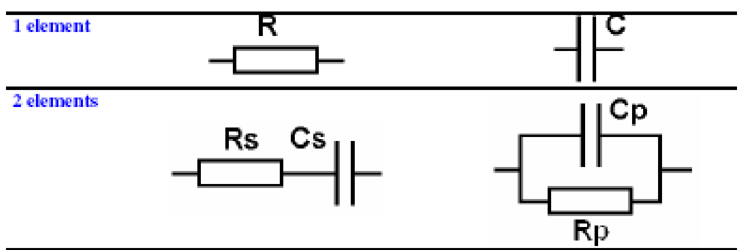
  $1/Z_p = 1/Z_1 + 1/Z_2$

Impedance:

- of a resistor: $Z_R \equiv R$
- of a capacitor: $Z_C \equiv 1/(i\omega C)$
- of an inductor: $Z_L \equiv i\omega L$

Equivalent circuits

How do the spectra look like? Examples of simple circuits:



Electrical Circuit Elements

EIS data are commonly analyzed by fitting it to an equivalent electrical circuit model. Most of the circuit elements in the model are common electrical elements such as resistors, capacitors, and inductors. To be useful, the elements in the model should have a basis in the physical electrochemistry of the system. As an example, most models contain a resistor that models the cell's solution resistance.

Some knowledge of the impedance of the standard circuit components is therefore quite useful. The Table lists the common circuit elements, the equation for their current versus voltage relationship, and their impedance:

Component	**Impedance**
resistor	**Z = R**
inductor	**Z = iωL**
capacitor	**Z = 1/iωC**

Notice that the impedance of a resistor is independent of frequency and has only a real component. Because there is no imaginary impedance, the current through a resistor is always in phase with the voltage.

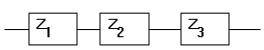
The impedance of an inductor increases as frequency increases. Inductors have only an imaginary impedance component. As a result, an inductor's current is phase shifted 90 degrees with respect to the voltage.

The impedance versus frequency behavior of a capacitor is opposite to that of an inductor. A capacitor's impedance decreases as the frequency is raised. Capacitors also have only an imaginary impedance component. The current through a capacitor is phase shifted -90 degrees with respect to the voltage.

Serial and Parallel Combinations of Circuit Elements

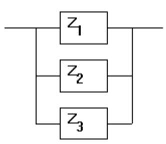
Very few electrochemical cells can be modeled using a single equivalent circuit element. Instead, EIS models usually consist of a number of elements in a network. Both serial and parallel combinations of elements occur.

Impedances in Series:



$$Z_{eq} = Z_1 + Z_2 + Z_3$$

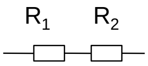
Impedances in Parallel



$$\frac{1}{Z_{eq}} = \frac{1}{Z_1} + \frac{1}{Z_2} + \frac{1}{Z_3}$$

Serial and Parallel Combinations of Circuit Elements

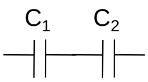
Suppose we have a 1Ω and a 4 Ω resistor is series. The impedance of a resistor is the same as its resistance. We thus calculate the total impedance Z_{eq}:



$$Z_{eq} = Z_1 + Z_2 = R_1 + R_2 = 1\Omega + 4\Omega = 5\Omega$$

Resistance and impedance both go up when resistors are combined in series.

Now suppose that we connect two 2 µF capacitors in series. The total capacitance of the combined capacitors is 1 µF



$$\frac{1}{Z_{eq}} = Z_1 + Z_2 = \frac{1}{i\omega C_1} + \frac{1}{i\omega C_2}$$
$$= \frac{1}{i\omega(2e^{-6})} + \frac{1}{i\omega(2e^{-6})} = \frac{1}{i\omega(1^{e-6})} = 1\ \mu\text{F}$$

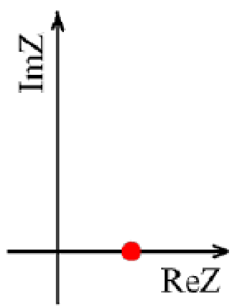
Impedance goes up, but capacitance goes down when capacitors are connected in series. This is a consequence of the inverse relationship between capacitance and impedance.

Pure resistance:

impedance do not vary with frequency

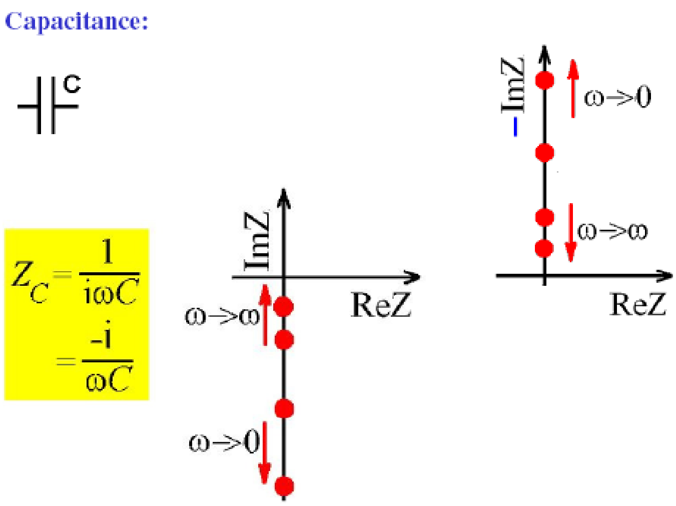
Resistance:

$Z_R = R$

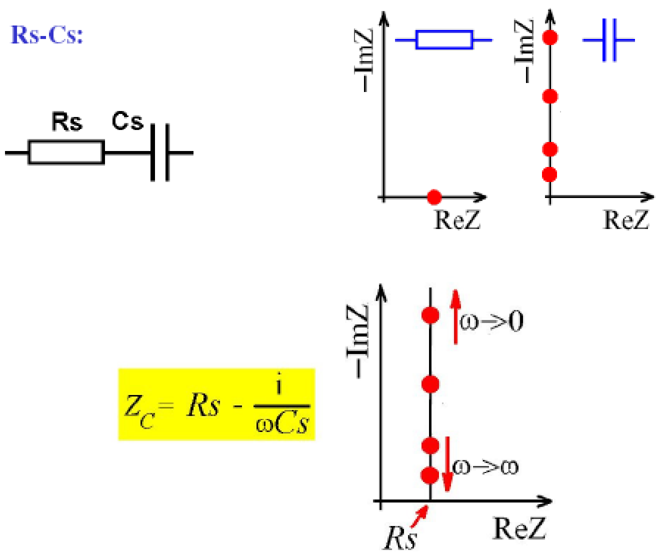


Pure capacitance:

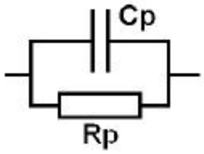
impedance varies linearly with frequency



Resistance and capacitor in series



Resistance and capacitor in series

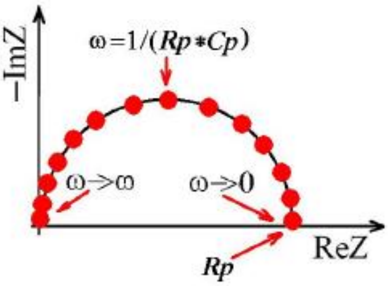


Semicircle

Characteristic frequency $\omega_0 = RpCp$

Time constant $\tau_0 = 1/\omega_0$

$$\frac{1}{Z} = \frac{1}{Rp} + \frac{1}{1/(i\omega Cp)}$$

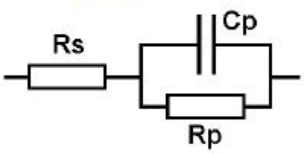


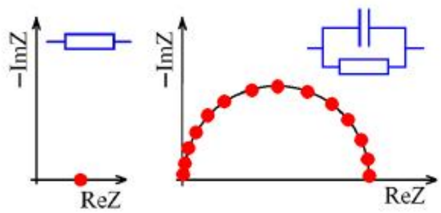
$$Z = \frac{Rp}{1 + i\omega Rp{*}Cp}$$

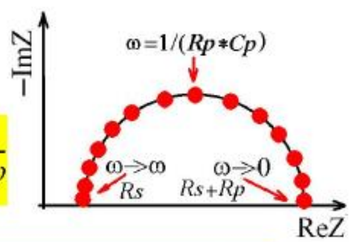
$$Z = \frac{Rp}{1+\omega^2 Rp^2 Cp^2} - i\frac{\omega Rp^2 Cp}{1+\omega^2 Rp^2 Cp^2}$$

Typical system observed in practice

Rs-Cp||Rp







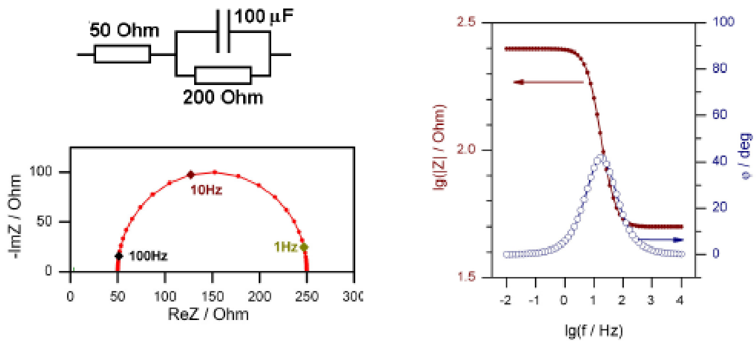
$$Z = Rs + \frac{Rp}{1 + i\omega Rp{*}Cp}$$

$$Z = Rs + \frac{Rp}{1+\omega^2 Rp^2 Cp^2} - i\frac{\omega Rp^2 Cp}{1+\omega^2 Rp^2 Cp^2}$$

Impedance: different representations

Nyquist vs Bode representations:

$\ln(r\cdot e^{i\varphi}) \equiv \ln(r)+i\cdot\varphi$

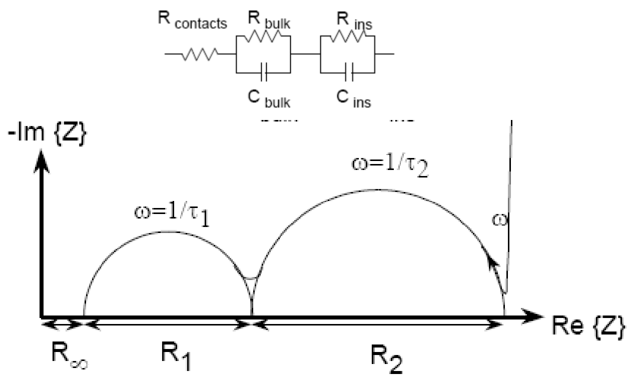


Advantages (both are good):

- **Nyquist: „structures" are better seen**
- **Bode: complete documentation of the data**

Analyzing Circuits

By using the various Cole-Cole plots we can calculate values of the elements of the equivalent circuit for any applied bias voltage



By doing this over a range of bias voltages, we can obtain:
the field distribution in the layers of the device (potential divider) and the relative widths of the layers, since C ~ 1/d

ANNEXURE - I

Additional Information

Electrochemistry and Equivalent Circuit Elements

Electrolyte Resistance:

Electrolyte resistance is often a significant factor in the impedance of an electrochemical cell. A modern 3 electrode potentiostat compensates for the solution resistance between the counter and reference electrodes. However, any solution resistance between the reference electrode and the working electrode must be considered when you model your cell.
The resistance of an ionic solution depends on the ionic concentration, type of ions, temperature and the geometry of the area in which current is carried. In a bounded area with area A and length l carrying a uniform current the resistance is defined as:

$$R = \rho \frac{l}{A}$$

where r is the solution resistivity.

The conductivity of the solution, σ , is more commonly used in solution resistance calculations.

Its relationship with solution resistance is:

$$R = \frac{1}{\sigma}\frac{l}{A} \Rightarrow \sigma \frac{l}{RA}$$

Electrolyte Resistance

Standard chemical handbooks list σ values for specific solutions. For other solutions and solid materials, you can calculate σ from specific ion conductance. The units for σ are Siemens per meter (S/m). The Siemens is the reciprocal of the ohm, so 1 S = 1/Ohm

Unfortunately, most electrochemical cells do not have uniform current distribution through a definite electrolyte area. The major problem in calculating solution resistance therefore concerns determination of the current flow path and the geometry of the electrolyte that carries the current. A comprehensive discussion of the approaches used to calculate practical resistances from ionic conductances is well beyond the scope of this manual.

Fortunately, you don't usually calculate solution resistance from ionic conductance. Instead, it is found when you fit a model to experimental EIS data.

Coating Capacitance

A capacitor is formed when two conducting plates are separated by a non-conducting media, called the dielectric. The value of the capacitance depends on the size of the plates, the distance between the plates and the properties of the dielectric. The relationship is:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}$$

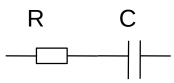
With,
ε_o = electrical permittivity
ε_r = relative electrical permittivity
A = surface of one plate
d = distances between two plates
Whereas the electrical permittivity is a physical constant, the relative electrical permittivity depends on the material. Some useful ε_r values are given in the table:

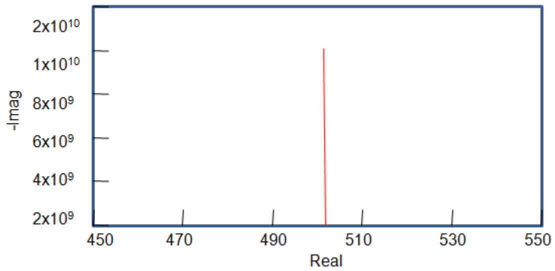
Material	ε_r
vacuum	1
water	80.1 (20° C)
organic coating	4 - 8

Notice the large difference between the electrical permittivity of water and that of an organic coating. The capacitance of a coated substrate changes as it absorbs water. EIS can be used to measure that change

A Purely Capacitive Coating

A metal covered with an undamaged coating generally has a very high impedance. The equivalent circuit for such a situation is in the Figure:





The model includes a resistor (due primarily to the electrolyte) and the coating capacitance in series.
A Nyquist plot for this model is shown in the Figure. In making this plot, the following values were assigned:
R = 500 Ω (a bit high but realistic for a poorly conductive solution)
C = 200 pF (realistic for a 1 cm^2 sample, a 25 µm coating, and ε_r = 6)
f_i = 0.1 Hz (lowest scan frequency -- a bit higher than typical)
f_f = 100 kHz (highest scan frequency)

The value of the capacitance cannot be determined from the Nyquist plot. It can be determined by a curve fit or from an examination of the data points. Notice that the intercept of the curve with the real axis gives an estimate of the solution resistance. The highest impedance on this graph is close to 10^{10} Ω. This is close to the limit of measurement of most EIS systems

Constant Phase Element (for double layer capacity in real electrochemical cells)

Capacitors in EIS experiments often do not behave ideally. Instead, they act like a constant phase element (CPE) as defined below.

$$Z = A(i\omega)^{-\alpha}$$

When this equation describes a capacitor, the constant A = 1/C (the inverse of the capacitance) and the exponent α = 1. For a constant phase element, the exponent α is less than one.

The "double layer capacitor" on real cells often behaves like a CPE instead of like a capacitor. Several theories have been proposed to account for the non-ideal behavior of the double layer but none has been universally accepted. In most cases, you can safely treat α as an empirical constant and not worry about its physical basis.