Ac-impedance - Electrochemical Impedance Spectroscopy (EIS)

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Electrochemical techniques

Time domain (*incomplete!*):

- Polarisation, (V – I)
- Potential Step, (ΔV – $I(t)$)
- Cyclic Voltammetry, ($V_{f(t)}$ – $I(V)$)
- Coulometric Titration, (ΔV - $\int I\, dt$)
- Galvanostatic Intermittent Titration (ΔQ – $V(t)$)

steady state
relaxation
dynamic
relaxation
transient

Frequency domain:

- Electrochemical Impedance Spectroscopy (EIS)

perturbation of equilibrium state

1. Introduction

Systems

Characterization of systems = Equivalent Circuits

Parameters of systems = Electric parameters (R, C, L..)

Mechanisms = Combination of Circuits

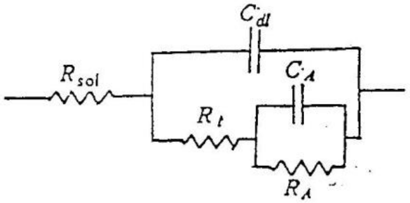
Ex. Electrochemical Systems

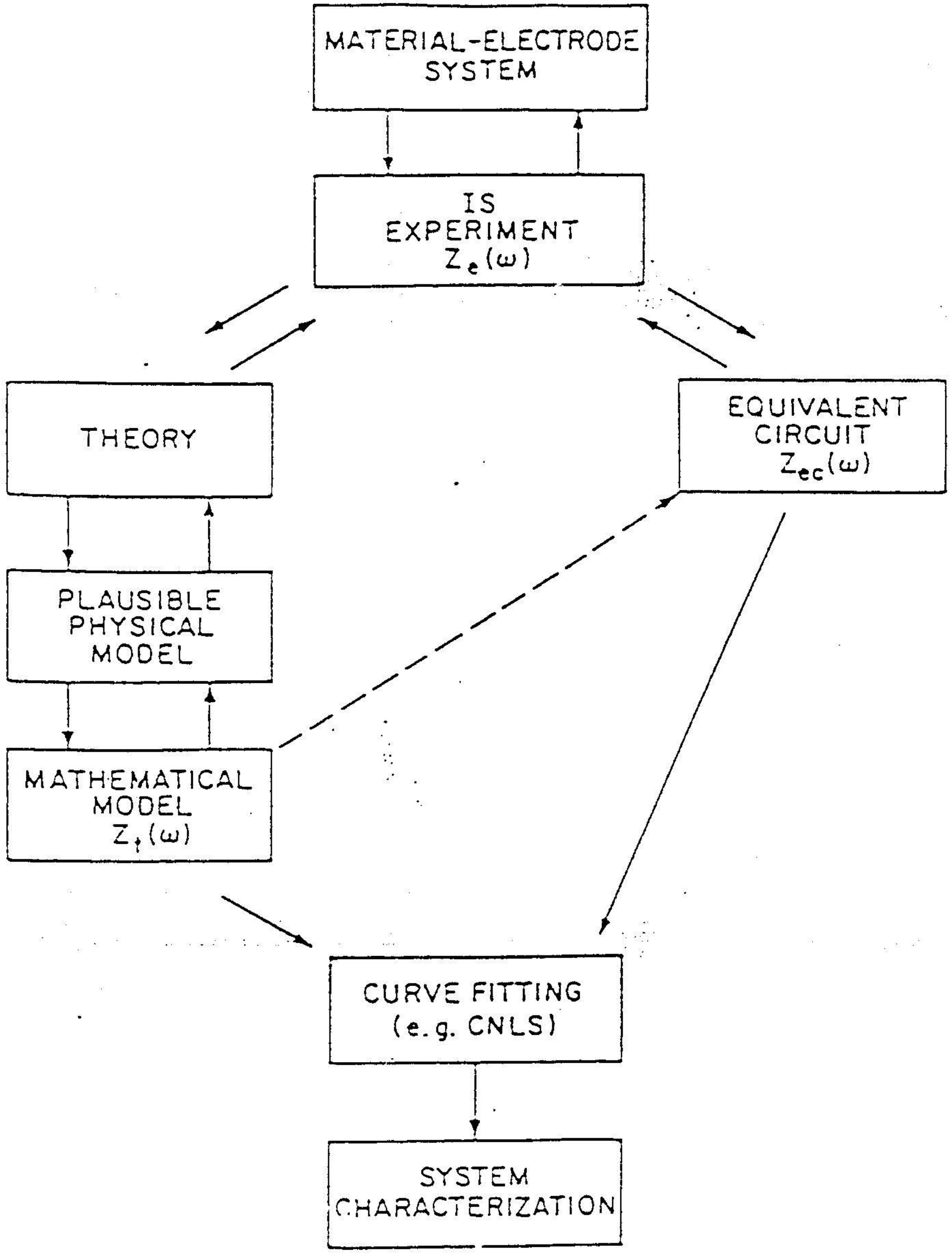
Kinetics of systems = Equivalent Circuits

Kinetic parameters of systems = Electric parameters

Kinetic mechanisms = Combination of Circuits

$$M + X^- \rightleftharpoons (MX)_{ad} + e$$
$$(MX)_{ad} \longrightarrow MX^+_{sol} + e$$
$$MX^+_{sol} \rightleftharpoons M^+ + X^-$$




MATERIAL-ELECTRODE SYSTEM
IS EXPERIMENT $Z_e(\omega)$
THEORY
EQUIVALENT CIRCUIT $Z_{ec}(\omega)$
PLAUSIBLE PHYSICAL MODEL
MATHEMATICAL MODEL $Z_t(\omega)$
CURVE FITTING (e.g. CNLS)
SYSTEM CHARACTERIZATION

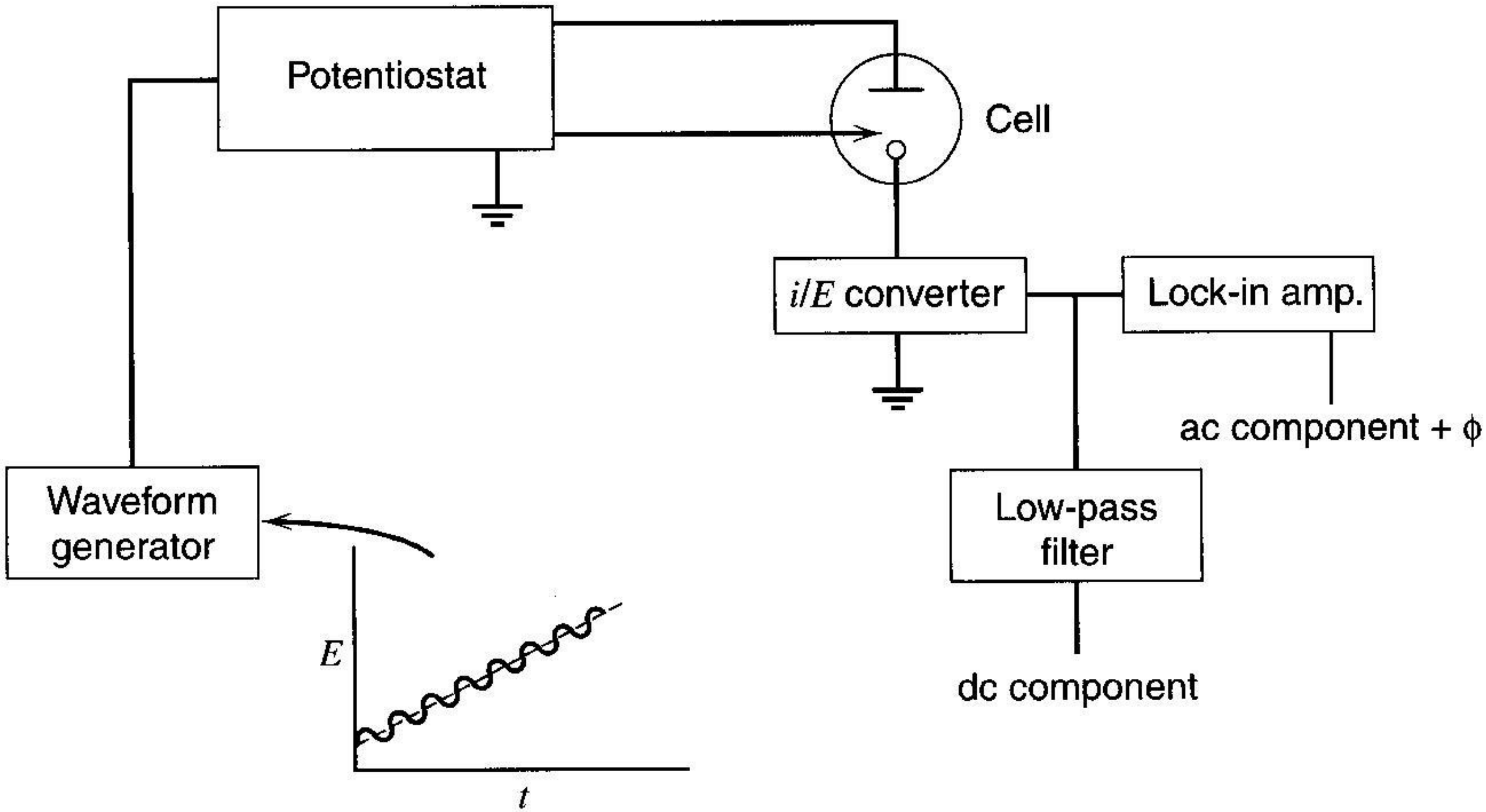
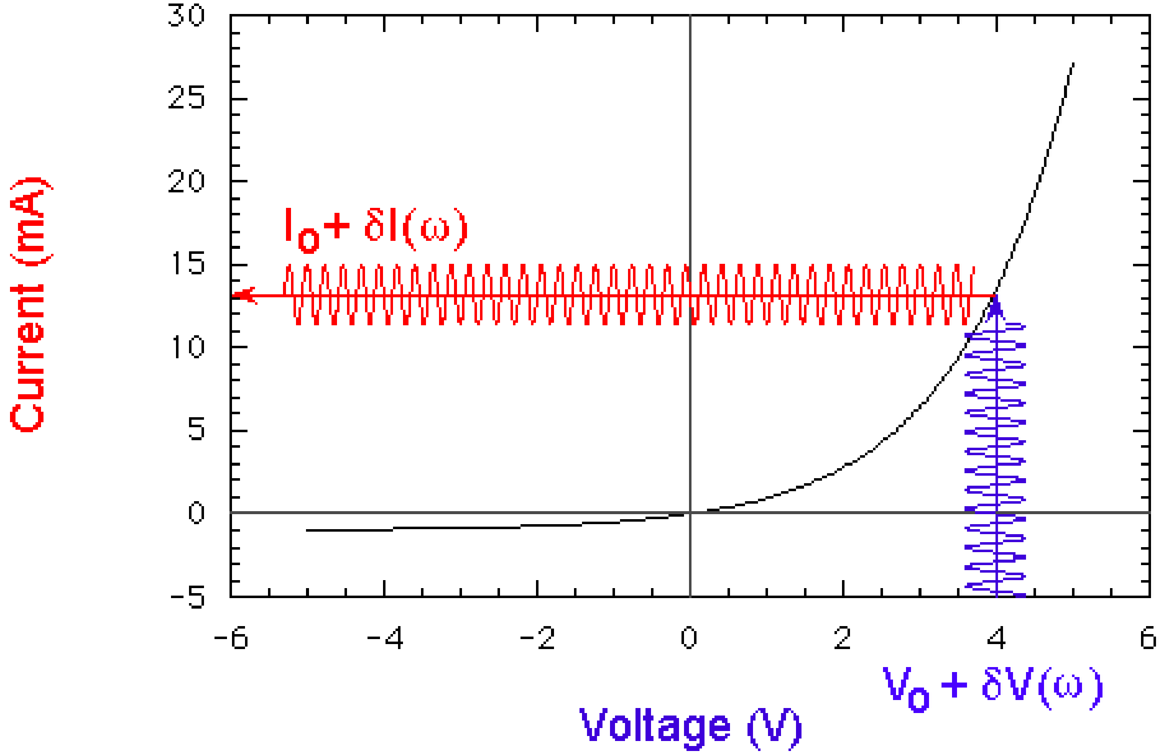


Figure 10.1.2 Schematic diagram of apparatus for an ac voltammetric experiment.

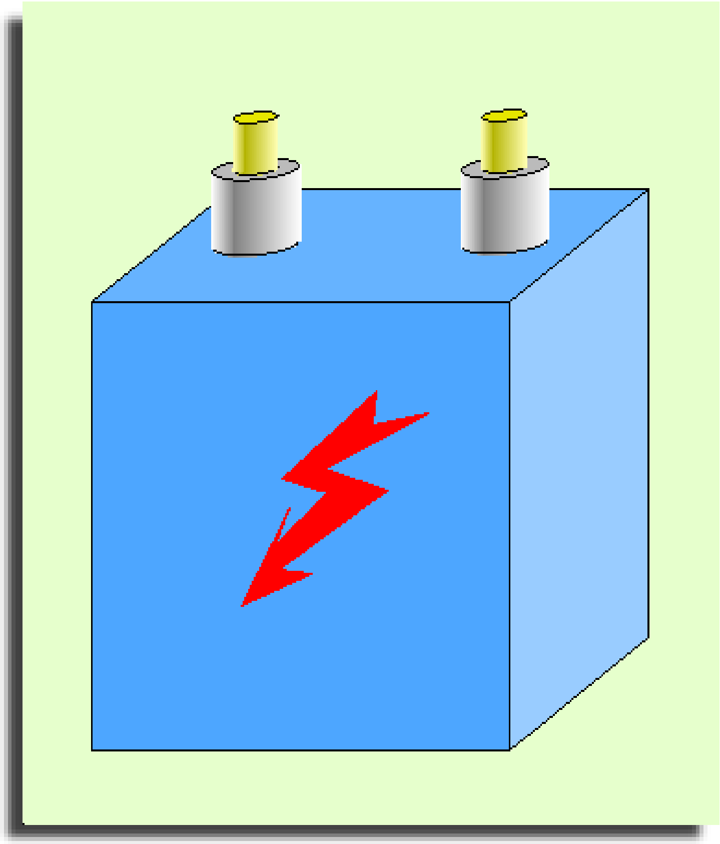
Measure $Z(\omega, V_{bias})$

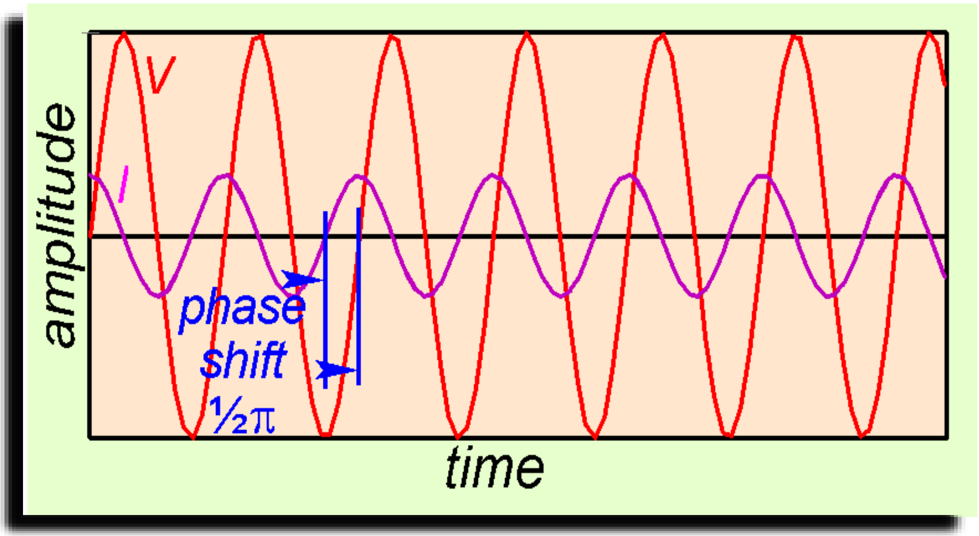


The result will be $Z(\omega, V_o) = \delta V(\omega$

Black box approach

Assume a black box with two terminals (electric connections). One applies a voltage and measures the current response (or visa versa). Signal can be dc or periodic with frequency *f*, or angular frequency $\omega = 2\pi f$, with: $0 \leq \omega < \infty$





Phase shift and amplitude changes with ω!

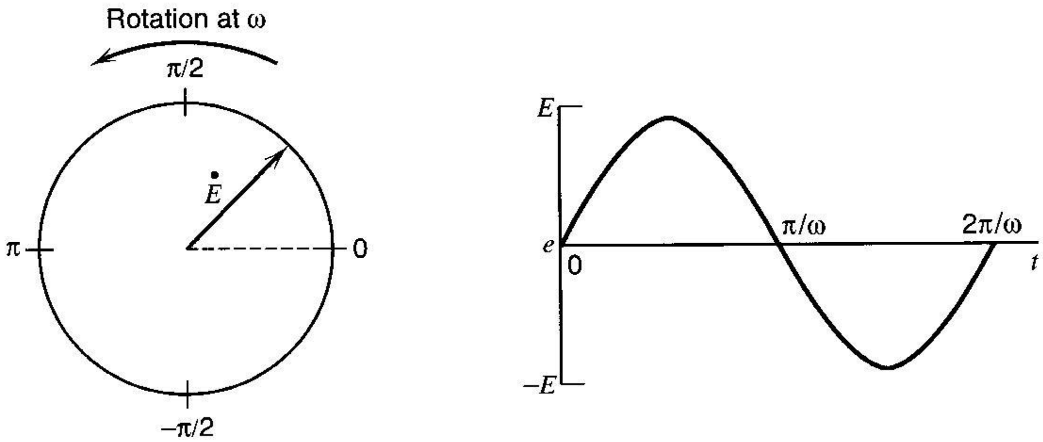


Figure 10.1.3 Phasor diagram for an alternating voltage, $e = E \sin \omega t$.

•The response is a current

$I = I_0 \sin(\omega t + \phi)$

where ϕ is the phase angle between perturbation and response

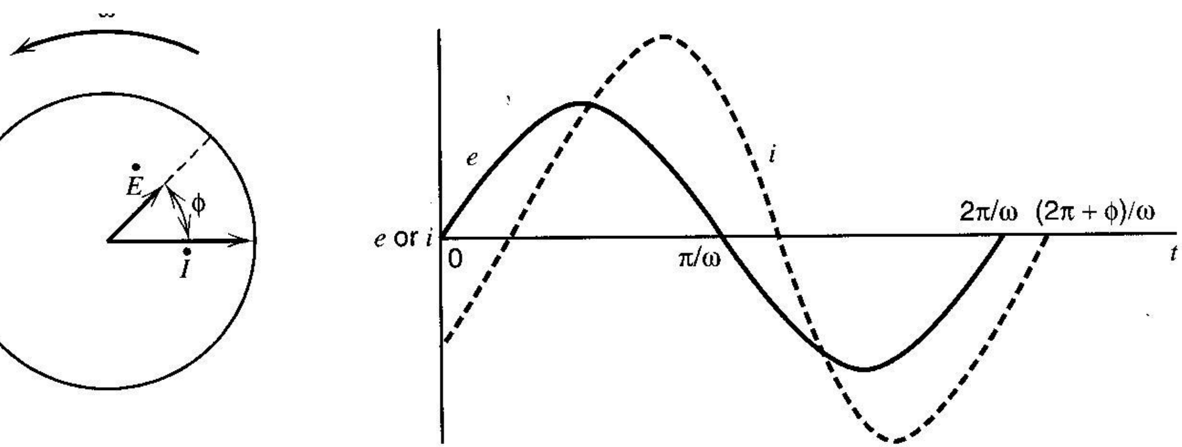


Figure 10.1.4 Phasor diagram showing the relationship between alternating current and voltage signals at frequency ω.

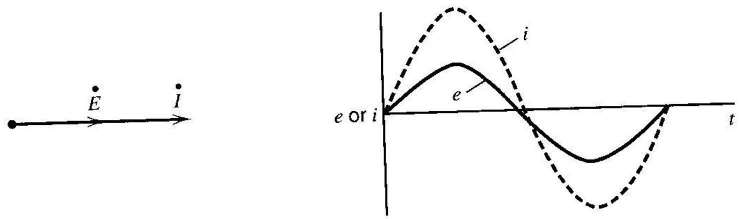


Figure 10.1.5
Relationship between the voltage across a resistor and current through the resistor.

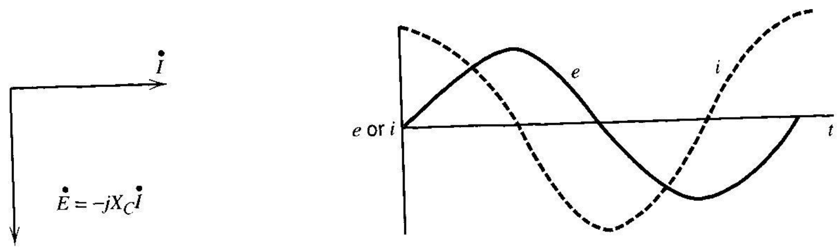


Figure 10.1.6
Relationship between an alternating voltage across a capacitor and the alternating current through the capacitor.

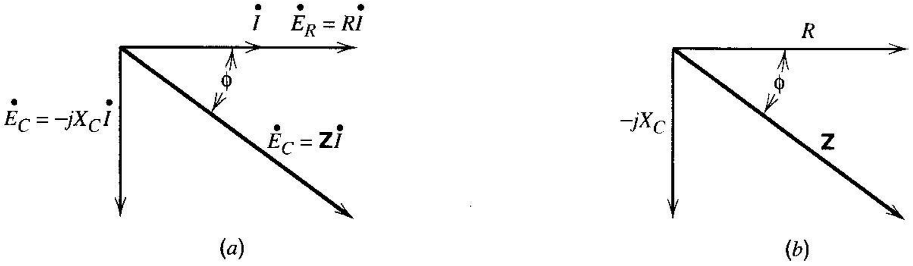


Figure 10.1.7 (*a*) Phasor diagram showing the relationship between the current and the voltages in a series *RC* network. The voltage across the whole network is $\dot{E}$, and $\dot{E}_R$ and $\dot{E}_C$ are its components across the resistance and the capacitance. (*b*) An impedance vector diagram derived from the phasor diagram in (*a*).

2. Theory

a. Response in the time domain

b. Response in the frequency domain

- A small-signal Stimulus

$$E = E_0 e^{j\omega t} = E_0(\cos\omega t + j\sin\omega t) \quad [1]$$

- Response

$$I = I_0\, e^{j(\omega t + \phi)} \quad [2]$$

- Impedance

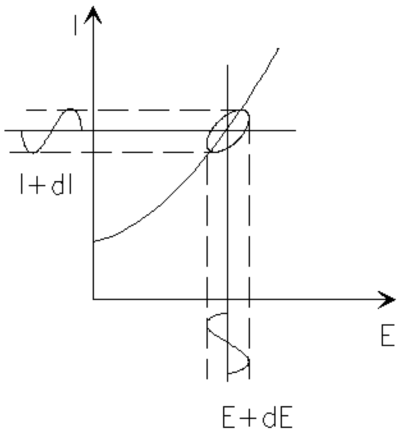
$$Z = E/I = E_0/I_0\, e^{-j\phi} = |Z|\, e^{-j\phi} \quad [3]$$

$$= |Z|(\cos\phi - j\sin\phi)$$

$$= Z_{Re} - j\, Z_{Im} \quad [4]$$

$$\tan\phi = Z_{Re}/Z_{Im} \quad [5]$$

Complex writing



$$Z(t) = \frac{E(t)}{I(t)} = \frac{E_0 \cos(\omega t)}{I_0 \cos(\omega t - \phi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \phi)}$$

Using Eulers relationship $\exp(i\phi) = \cos\phi + i \sin\phi$

it is possible to express the impedance as a complex function. The potential is described as,

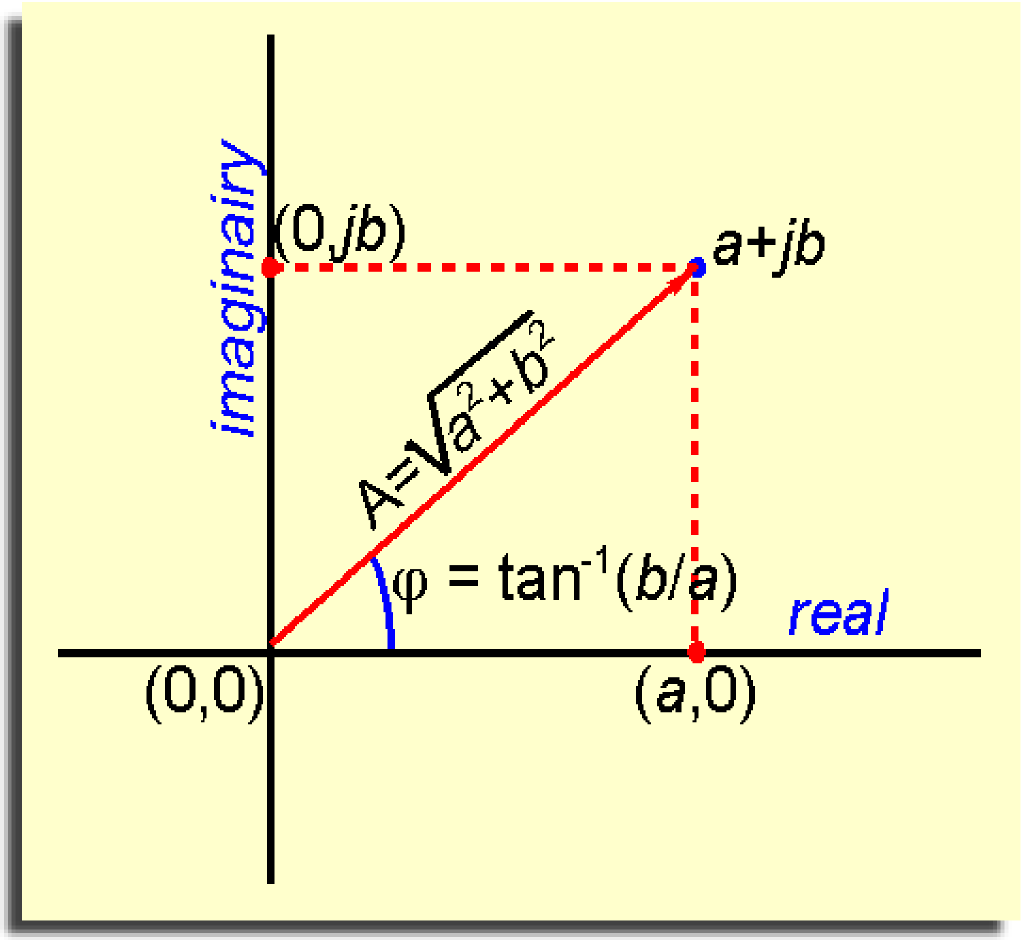
$$E(t) = E_0 \exp(j\omega t)$$

and the current response as, $I(t) = I_0 \exp(i\omega t - i\phi)$

The impedance is then represented as a complex number,

$$Z = \frac{E}{I} = Z_0 \exp(i\phi) = Z_0(\cos\phi + i \sin\phi)$$

Complex Plane



Impedance ≡ 'resistance'
Admittance ≡ 'conductance':

$$Y(\omega) = \frac{1}{Z(\omega)} = \frac{Z_{re} - jZ_{im}}{Z_{re}^2 + Z_{im}^2}$$

hence:

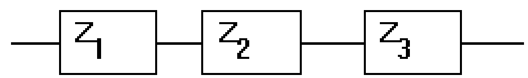
$$Z(\omega) = \frac{1}{Y(\omega)} = \frac{Y_{re} - jY_{im}}{Y_{re}^2 + Y_{im}^2}$$

Representation of impedance value, $Z = a + jb$, in the complex plane

Serial and Parallel Combinations of Circuit Elements

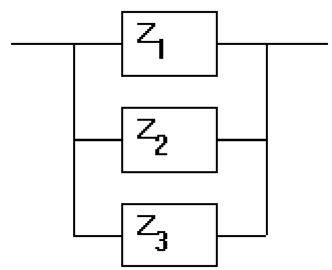
Very few electrochemical cells can be modeled using a single equivalent circuit element. Instead, EIS models usually consist of a number of elements in a network. Both serial and parallel combinations of elements occur.

Impedances in Series:



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

Impedances in Parallel



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

Capacitor

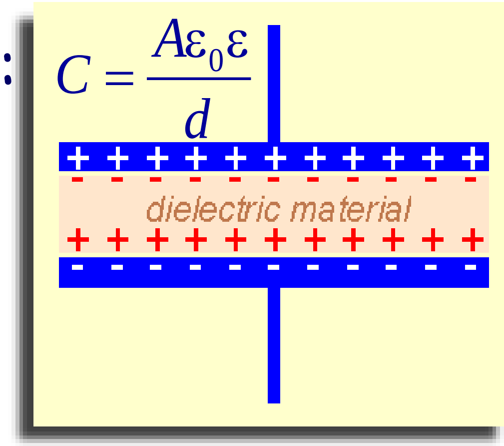
Take a look at the properties of a capacitor:

Charge stored (Coulombs):

$$Q = C \cdot V$$

Change of voltage results in current, I:

$$I = \frac{\mathrm{d}Q}{\mathrm{d}t} = C\frac{\mathrm{d}V}{\mathrm{d}t}$$



Alternating voltage (ac):

$$I(\omega t) = C\frac{\mathrm{d}V_0 \cdot e^{j\omega t}}{\mathrm{d}t} = j\omega C \cdot V_0 \cdot e^{j\omega t}$$

Impedance:

$$Z_C(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{1}{j\omega C}$$

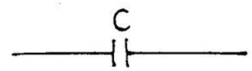
Admittance:

$$Y_C(\omega) = Z(\omega)^{-1} = j\omega C$$

Case 1 : Pure Resistance

$$Z_R = R \qquad [6]$$

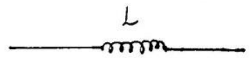
Case 2 : Ideal Capacitance



$$I_C = C\, dE/dt \qquad [7]$$

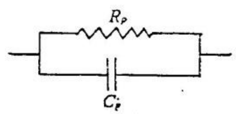
$$Z_C = -j/\omega C \qquad [8]$$

Case 3 : Pure Inductor



$$Z_L = j\omega L \qquad [9]$$

Case 4 : Parallel RC Circuit



$$1/Z = 1/R_p + j\omega C_p \qquad [10]$$

$$Z = R_p/[1+(\omega R_p C_p)^2]$$
$$- j\omega R_p^2 C_p/[1+(\omega R_p C_p)^2] \qquad [11]$$

$$Z_{Re} = R_p/[1+(\omega R_p C_p)^2] \qquad [12]$$

$$Z_{Im} = j\omega R_p^2 C_p/[1+(\omega R_p C_p)^2] \qquad [13]$$

$$|\mathbf{Z}| = R_p/[1+(\omega R_p C_p)^2]^{1/2} \qquad [14]$$

$$\tan\phi = \omega R_p C_p \qquad [15]$$

Bode diagram

At high frequency (ω) :

$$|Z| \fallingdotseq 1/\omega C_p \quad [16]$$

$$\log|Z| \fallingdotseq -\log C_p - \log\omega \quad [17]$$

$$|Z| \rightarrow 0 \quad [18]$$

$$\phi \rightarrow \pi/2 \quad [19]$$

At low frequency (ω) :

$$|Z| \fallingdotseq R_p \quad [20]$$

$$\log|Z| \fallingdotseq \log R_p \quad [21]$$

$$\phi \rightarrow 0 \quad [22]$$

As $\omega^* R_p C_p = 1$

$$\phi = \pi/4 \quad [23]$$

$$1/\omega^* = R_p C_p \quad [24]$$

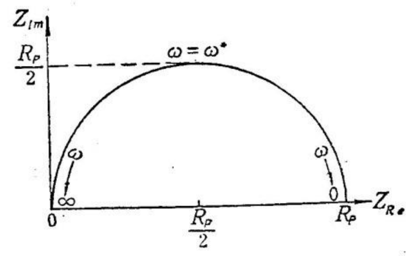
$$|Z| = R/2^{1/2} \quad [25]$$

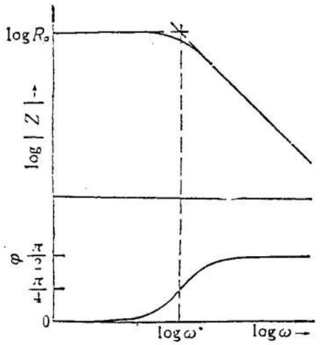
Nyquist diagram

$$Z_{Re}^2 - Z_{Re}R_p + Z_{Im}^2 = 0 \quad [26]$$

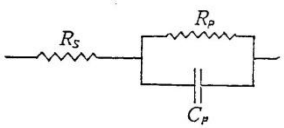
$$(Z_{Re} - R_p/2)^2 + Z_{Im}^2 = (R_p/2)^2 \quad [27]$$

$$C_p = 1/\omega^* R_p \quad [28]$$





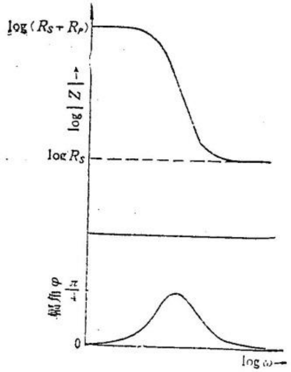
Case 5 : Parallel R_pC_p + Series R_s

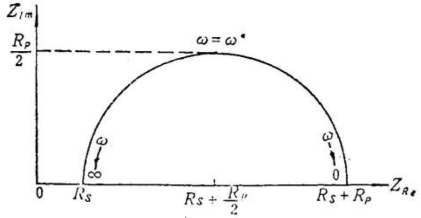


$$Z = R_s + R_p/(1+j\omega R_pC_p)$$

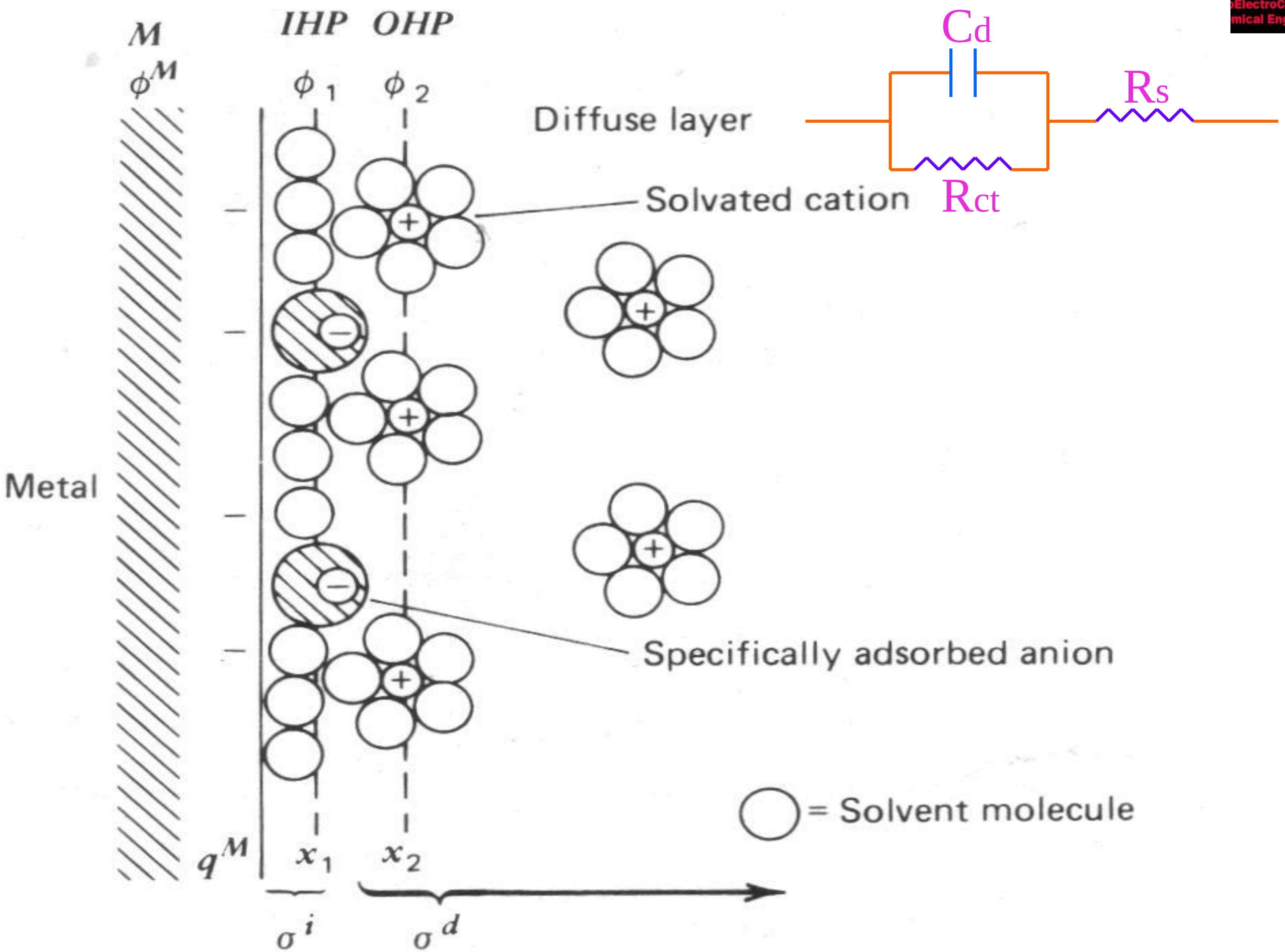
$$Z' = Z - R_s = R_p/(1+j\omega R_pC_p) \qquad [29]$$

$$[Z_{Re} - (R_s + R_p/2)]^2 + Z_{Im}^2 = (R_p/2)^2 \qquad [30]$$

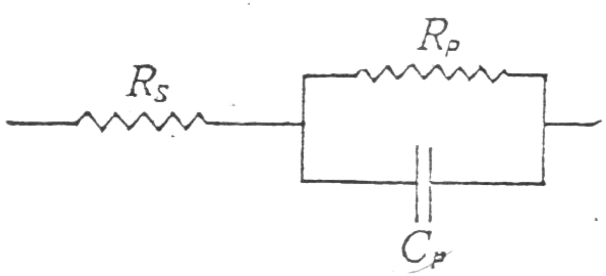


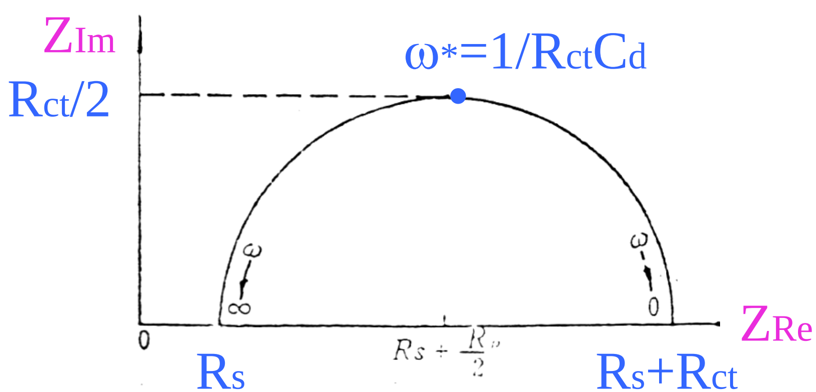


Model of Double Layer



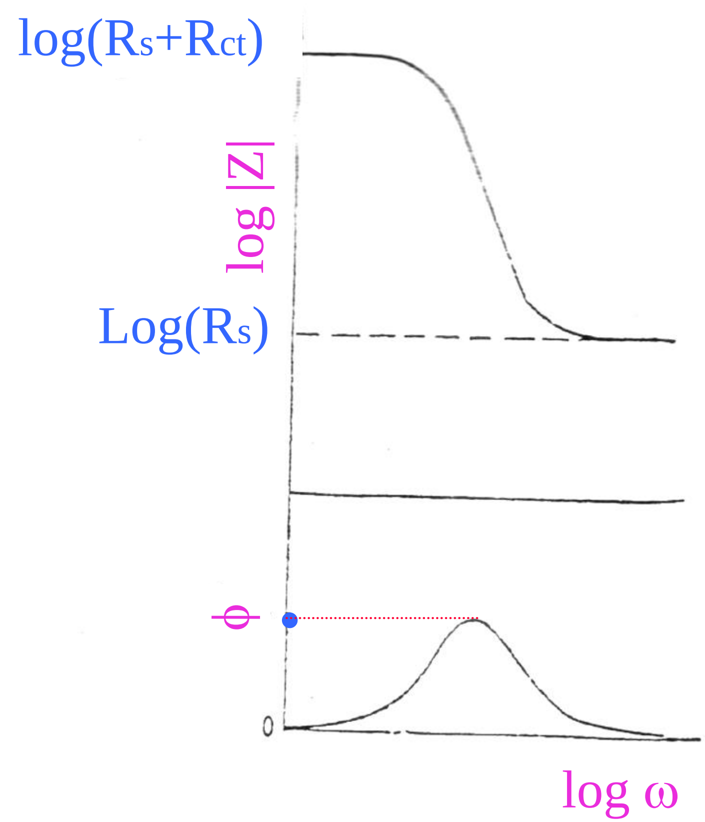
Typical AC Impedance Diagrams





Nyquist Diagram

$$(Z_{\mathrm{Re}} - R_s - \frac{R_{ct}}{2})^2 + Z_{\mathrm{Im}}{}^2 = (\frac{R_{ct}}{2})^2$$



Bode Diagram

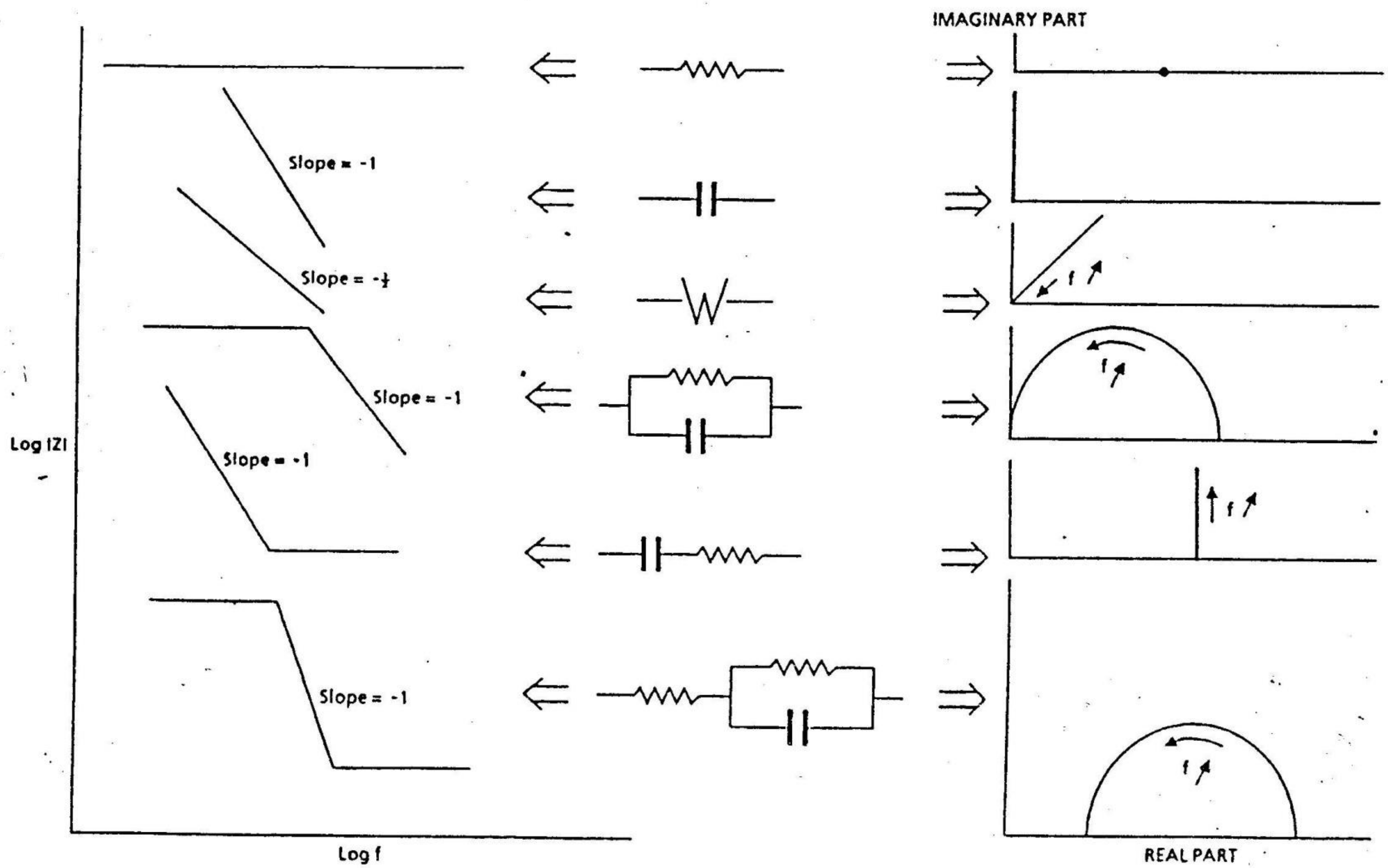


Fig. 20 Examples of Nyquist and Bode plane plottings.

Component	Symbol	Fundamental relation	Impedance, $Z(\omega)$
Resistor	R	$V = IR$	R
Capacitor	C	$I = C\frac{dV}{dt}$	$\frac{1}{j\omega C}$
Constant phase element	Q_n	$I = Q_n\frac{dV}{dt}$	$\frac{1}{(j\omega)^n Q_n}$
Inductor	L	$V = L\frac{dI}{dt}$	$j\omega L$

Overpotential

The overpotential measures the degree of polarization. It is the electrode potential minus the equilibrium potential for the reaction.
When the concentration in the bulk is the same as at the electrode surface, $C_o=C_o$* and $C_R=C_R$*. This simplifies the last equation into:

$$i = i_0\left[e^{\alpha \frac{nF}{RT}\eta} - e^{-(1-\alpha)\frac{nF}{RT}\eta} \right]$$

This equation is called the Butler-Volmer equation. It is applicable when the polarization depends only on the charge transfer kinetics.
Stirring will minimize diffusion effects and keep the assumptions of $C_o=C_o$* and $C_R=C_R$* valid.
When the overpotential, h, is very small and the electrochemical system is at equilibrium, the expression for the charge transfer resistance changes into:

$$R_{ct} = \frac{RT}{nFi_0}$$

From this equation the exchange current i_0 density can be calculated when R_{ct} is known.

Diffusion: Warburg impedance with infinite thickness

Diffusion can create an impedance known as the Warburg impedance. This impedance depends on the frequency of the potential perturbation. At high frequencies the Warburg impedance is small since diffusing reactants don't have to move very far. At low frequencies the reactants have to diffuse farther, thereby increasing the Warburg impedance.
The equation for the "infinite" Warburg impedance

$$Z = \sigma(\omega)^{-1/2}(1-j)$$

On a Nyquist plot the infinite Warburg impedance appears as a diagonal line with a slope of 0.5.
On a Bode plot, the Warburg impedance exhibits a phase shift of 45°.
In the above equation, σ is the Warburg coefficient defined as:

$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}}\left(\frac{1}{C_O^*\sqrt{D_O}} + \frac{1}{C_R^*\sqrt{D_R}}\right)$$

ω = radial frequency
D_O = diffusion coefficient of the oxidant
D_R = diffusion coefficient of the reductant
A = surface area of the electrode
n = number of electrons transferred
C* = bulk concentration of the diffusing species (moles/cm^3)

Diffusion: Warburg impedance with finite thickness

The former equation of the Warburg impedance is only valid if the diffusion layer has an infinite thickness. Quite often this is not the case. If the diffusion layer is bounded, the impedance at lower frequencies no longer obeys the equation above. Instead, we get the form:

$$Z_O = \sigma\omega^{-1/2}\,(1 - j)\,\tanh\left(\delta\left(\frac{j\omega}{D}\right)^{1/2}\right)$$

with,

δ = Nernst diffusion layer thickness

D = an average value of the diffusion coefficients of the diffusing species

This more general equation is called the "finite" Warburg. For high frequencies where $\omega \rightarrow \infty$, or for an infinite thickness of the diffusion layer where d $\rightarrow \infty$, this equation becomes the infinite Warburg impedance.

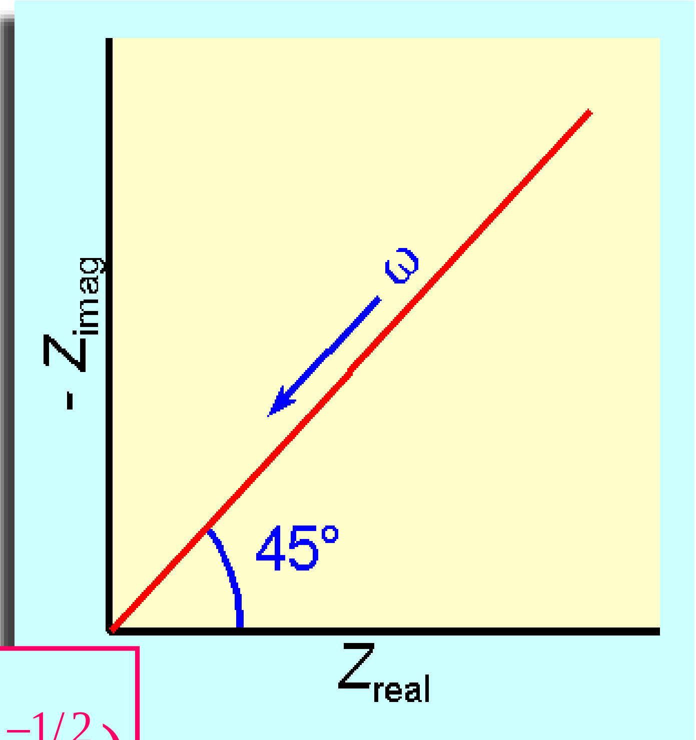
Warburg Impedance

$$Z(p) = \frac{E(p)}{I(p)} = \frac{RT}{(nF)^2 C^\circ \sqrt{D \cdot p}}$$

Take the Laplace variable, *p*, complex:

p = *s* + *j* ω. Steady state: *s* ⇒ 0,

which yields the impedance:



$$Z(\omega) = \frac{RT}{(nF)^2 C^\circ \sqrt{j\omega D}} = Z_0(\omega^{-1/2} - j\omega^{-1/2})$$

with:

$$Z_0 = \frac{RT}{(nF)^2 C^\circ \sqrt{2D}}$$

In solution:

$$Z_0 = (\sigma =) \frac{RT}{n^2 F^2 A\sqrt{2}} \left(\frac{1}{C_O^* \sqrt{D_O}} + \frac{1}{C_R^* \sqrt{D_R}} \right)$$

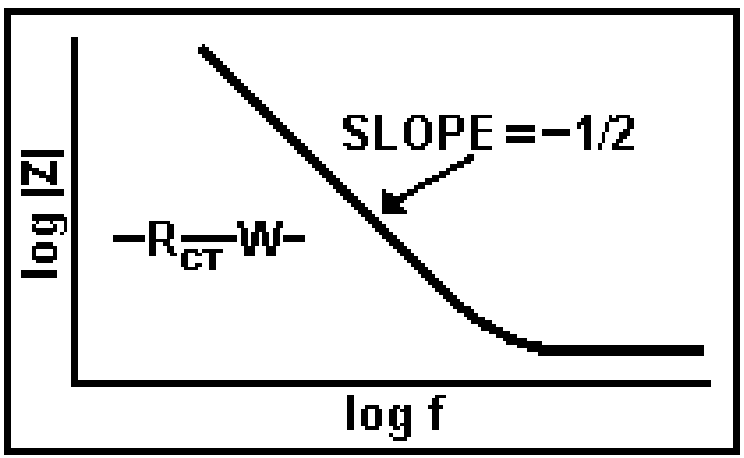
Diffusion (Warburg Impedance)

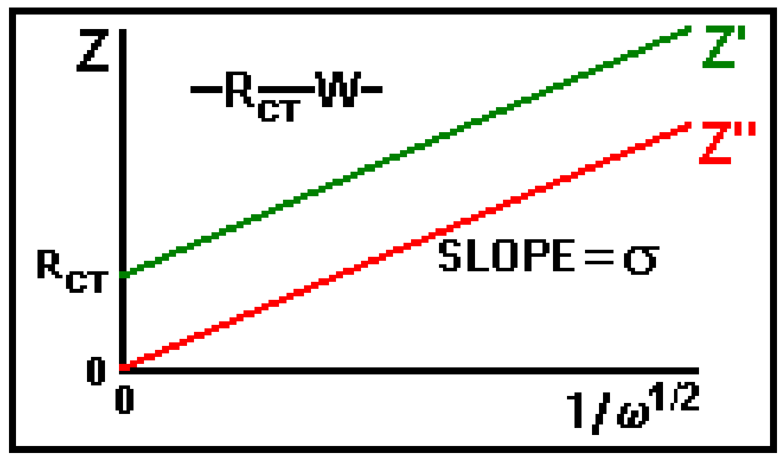
Warburg impedance = diffusion of chemical species to a large planar electrode

$$Z = \sigma(\omega)^{-1/2}(1 - j)$$

$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}}\left(\frac{1}{C_O^*\sqrt{D_O}} + \frac{1}{C_R^*\sqrt{D_R}}\right)$$

$$Z_O = \sigma\omega^{-1/2}(1 - j)\tanh\left(\delta\left(\frac{j\omega}{D}\right)^{1/2}\right)$$





Coating Capacitance

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

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

With,

ε_o = electrical permittivity

ε_r = relative electrical permittivity

A = surface of one plate

d = distances between two plates

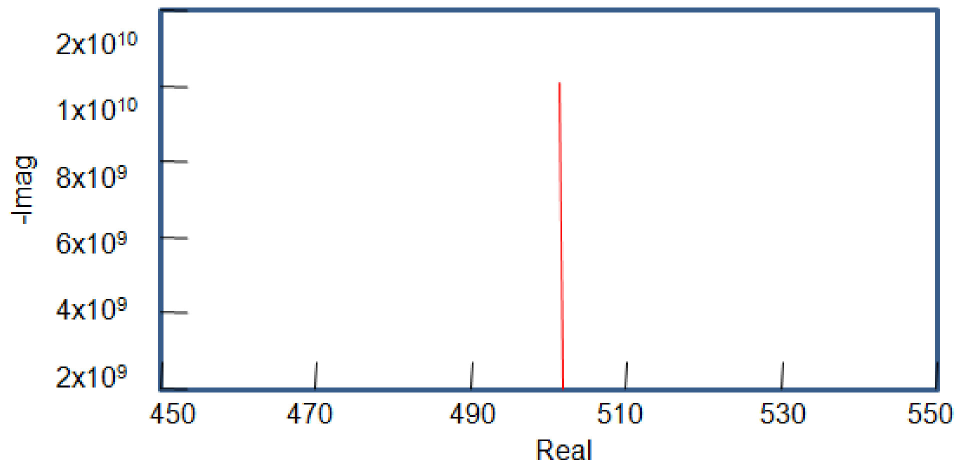
Whereas the electrical permittivity is a physical constant, the relative electrical permittivity depends on the material. Some useful ε_r values are given in the table:

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 $\varepsilon_r = 6$)

f_i = 0.1 Hz (lowest scan frequency -- a bit higher than typical)

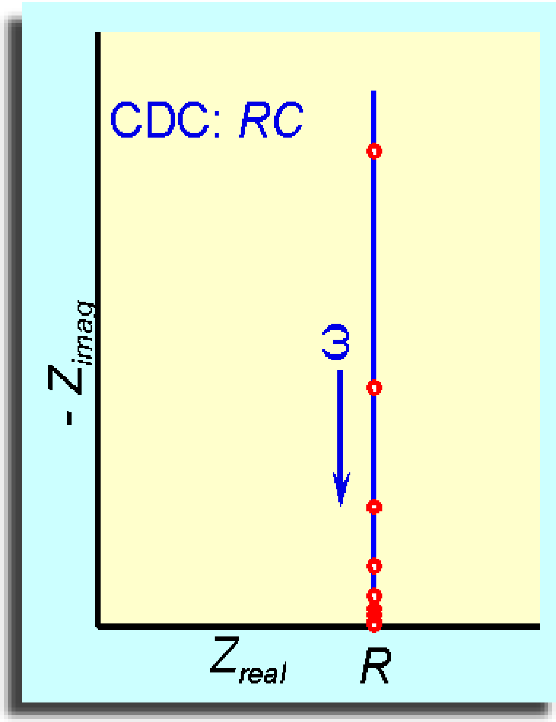
f_f = 100 kHz (highest scan frequency)

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

What is the impedance of an -R-C- circuit?

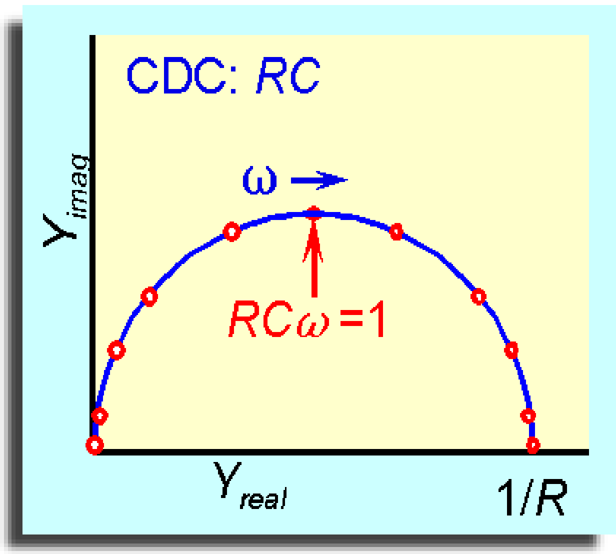
$$Z(\omega) = R + \frac{1}{j\omega C} = R - j/\omega C$$



Admittance?

$$Y(\omega) = \frac{1}{R - j/\omega C} =$$

$$\frac{\omega^2 C^2 R}{1+\omega^2 C^2 R^2} + j\frac{\omega C}{1+\omega^2 C^2 R^2}$$



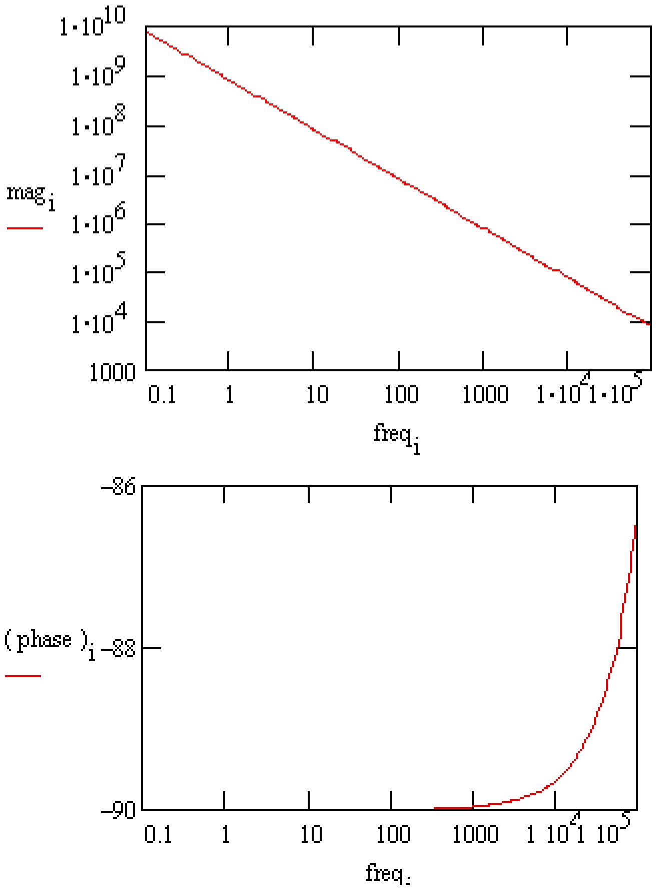
Semi-circle

'time constant':

τ = RC

A Purely Capacitive Coating in the Bode Plot

The same data are shown in a Bode plot in Figure. Notice that the capacitance can be estimated from the graph but the solution resistance value does not appear on the chart. Even at 100 kHz, the impedance of the coating is higher than the solution resistance



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.

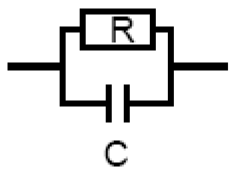
$$Z = A(i\omega)^{-\alpha}$$

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 a 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.

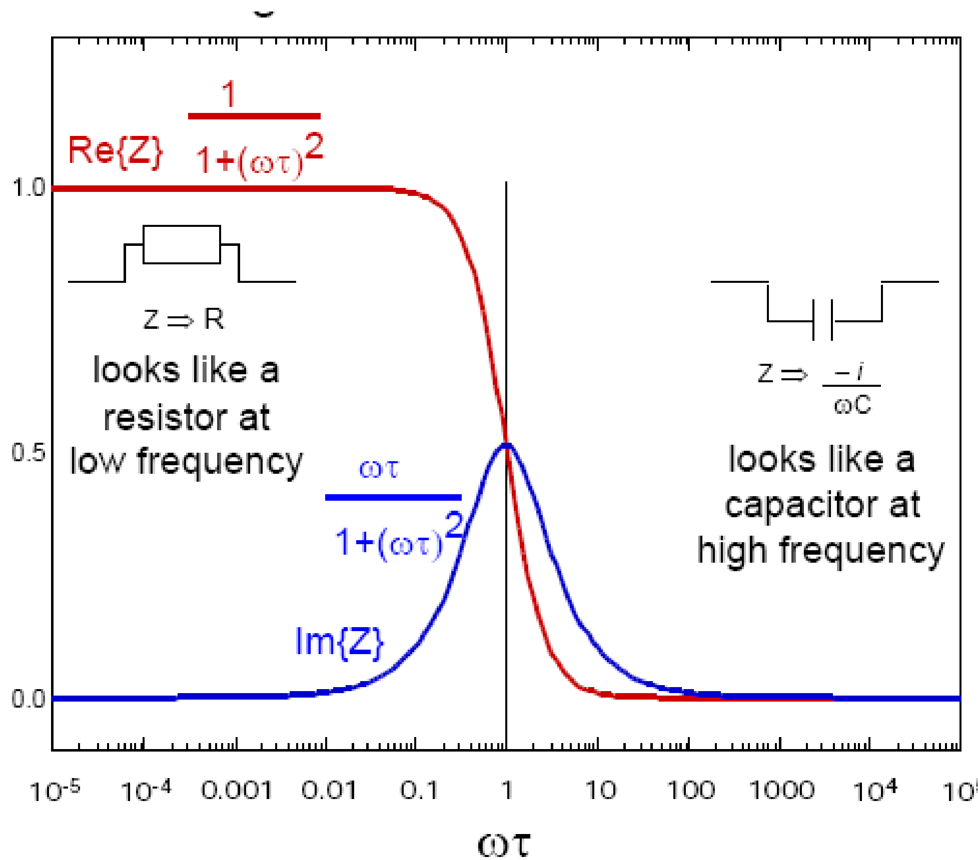
The Voigt network

An electrical layer of a device can often be described by a resistor and capacitor in parallel



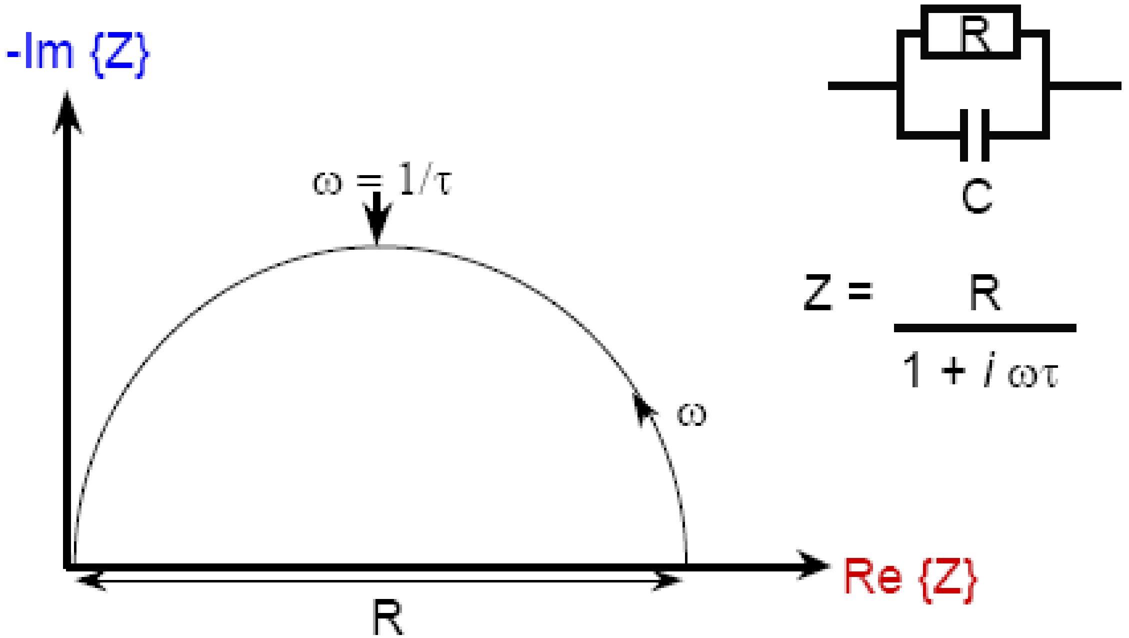
$$Z = \frac{R}{1 + i\,\omega\tau}$$

$$\tau = RC$$



Cole-Cole Plots: Impedance Plots in the Complex Plane

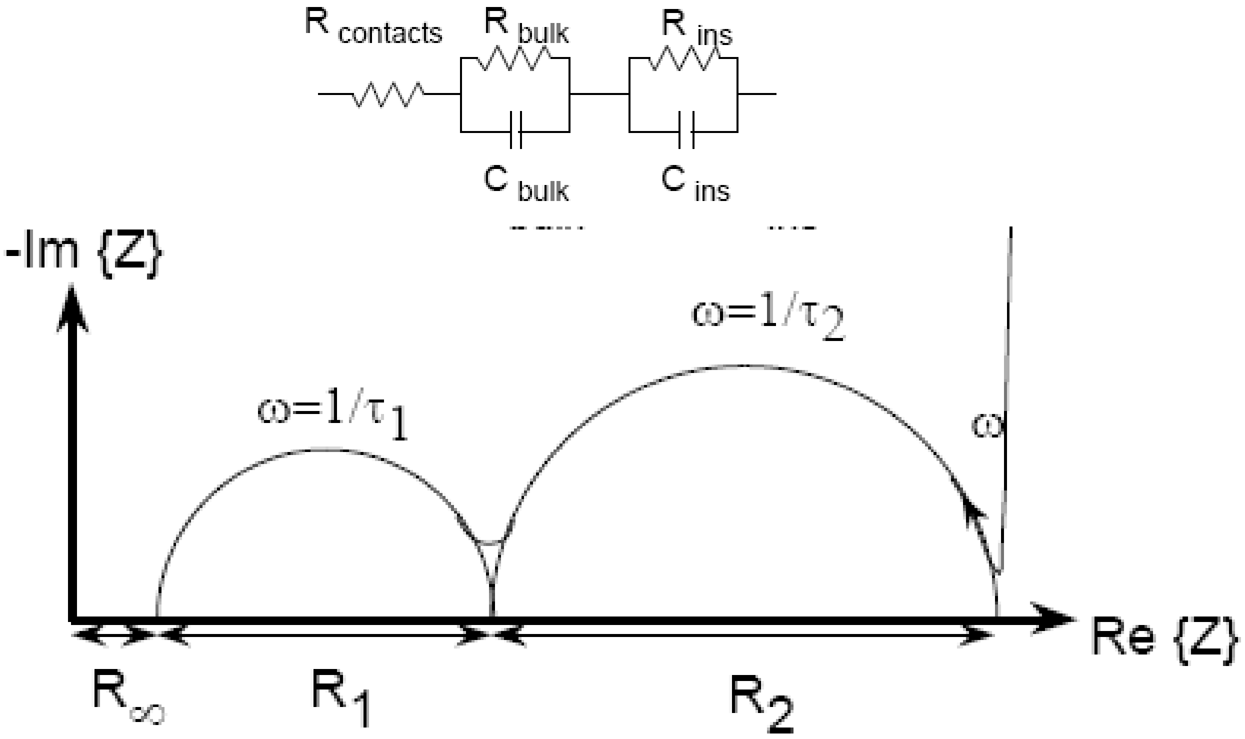
When we plot the real and imaginary components of impedance in the complex plane (Argand diagram), we obtain a semicircle or partial semicircle for each parallel RC Voigt network:



The diameter corresponds to the resistance R.
The frequency at the 90° position corresponds to 1/t = 1/RC

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

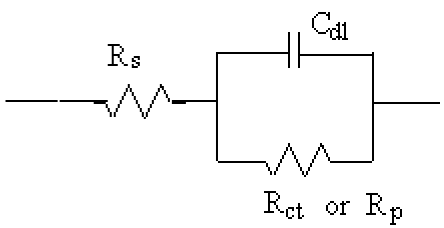


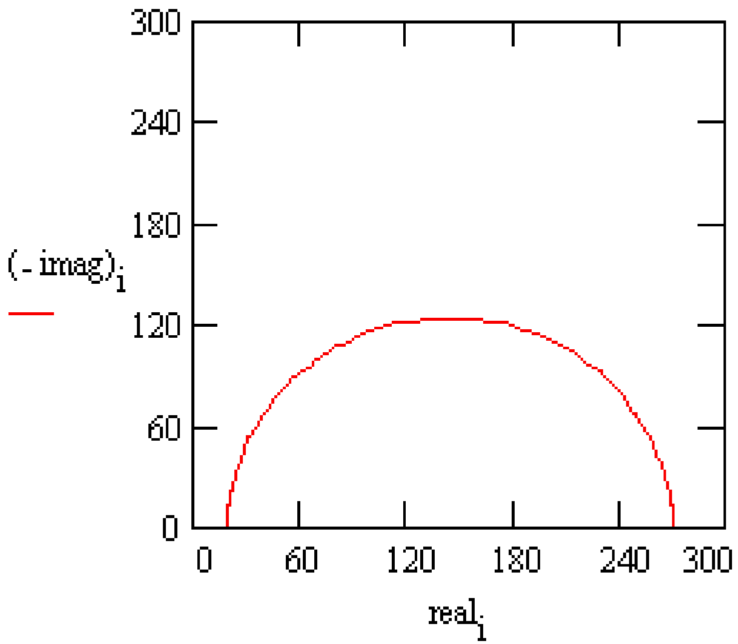
By doing this over a range of bias voltages, we can obtain:
the field distribution in the layers of the device (potential divider) and the relative widths of the layers, since C ~ 1/d

Randles Cell

The Randles cell is one of the simplest and most common cell models. It includes a solution resistance, a double layer capacitor and a charge transfer or polarization resistance. In addition to being a useful model in its own right, the Randles cell model is often the starting point for other more complex models.

The equivalent circuit for the Randles cell is shown in the Figure. The double layer capacity is in parallel with the impedance due to the charge transfer reaction





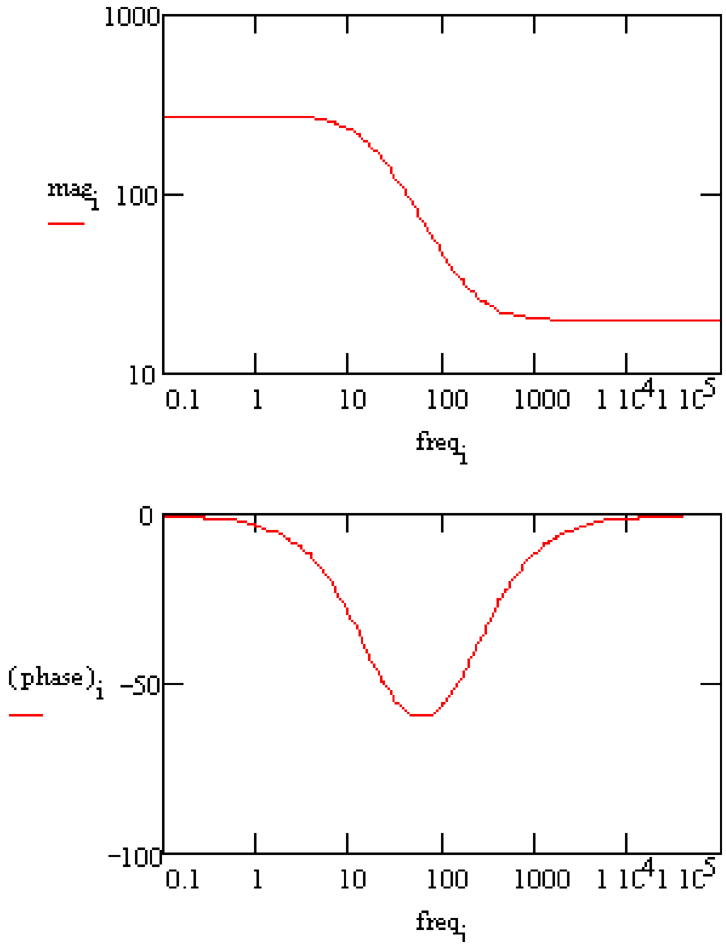
The Nyquist plot for a Randles cell is always a semicircle. The solution resistance can found by reading the real axis value at the high frequency intercept. This is the intercept near the origin of the plot. Remember this plot was generated assuming that R_s = 20 Ω and Rp= 250 Ω .

The real axis value at the other (low frequency) intercept is the sum of the polarization resistance and the solution resistance. The diameter of the semicircle is therefore equal to the polarization resistance (in this case 250Ω).

Bode Plot of Randalls cell

This Figure is the Bode plot for the same cell. The solution resistance and the sum of the solution resistance and the polarization resistance can be read from the magnitude plot. The phase angle does not reach 90° as it would for a pure capacitive impedance. If the values for R_s and R_p were more widely separated the phase would approach 90°.

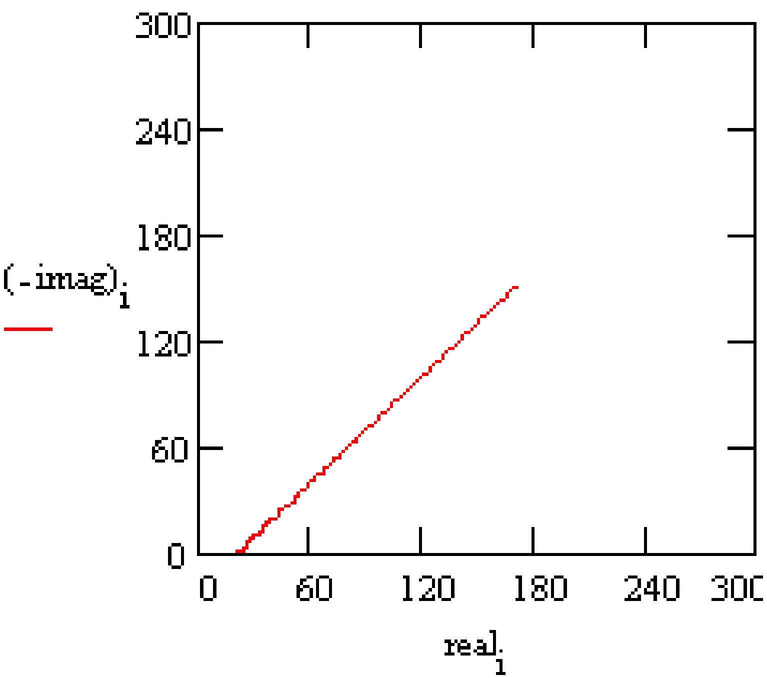
Bode Plot for 1 mm/year Corrosion Rate

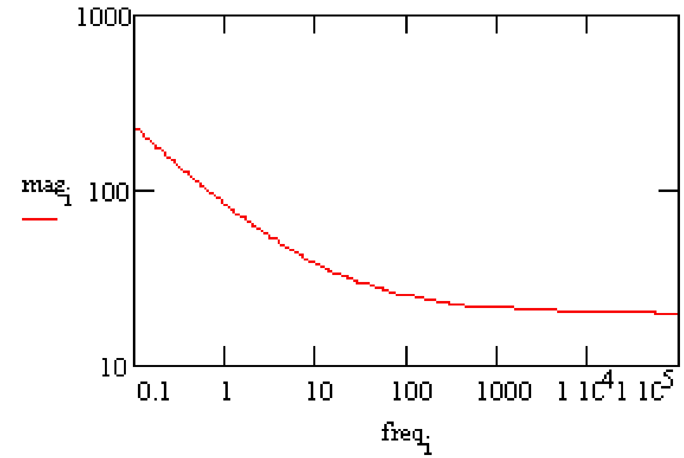


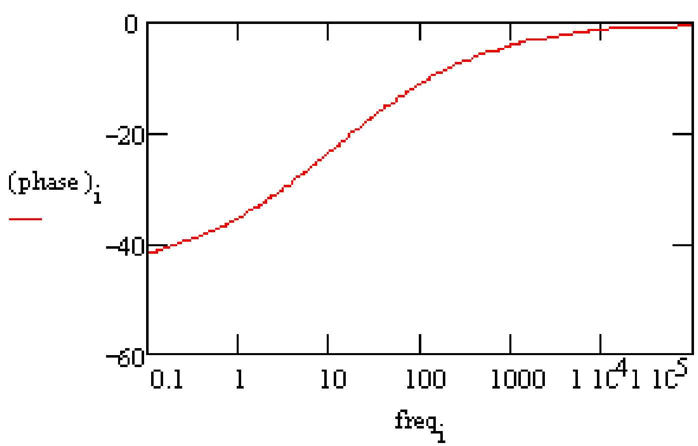
Mixed Kinetic and Diffusion Control

First consider a cell where semi-infinite diffusion is the rate determining step, with a series solution resistance as the only other cell impedance.

A Nyquist plot for this cell is shown in Figure 2-17. R_s was assumed to be 20 W. The Warburg coefficient calculated to be about 120 $\Omega sec^{-1/2}$ at room temperature for a two electron transfer, diffusion of a single species with a bulk concentration of 100 µM and a typical diffusion coefficient of 1.6 x10^{-5} cm^2/sec. Notice that the Warburg Impedance appears as a straight line with a slope of 45°.

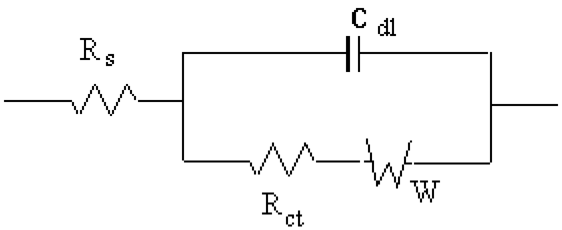




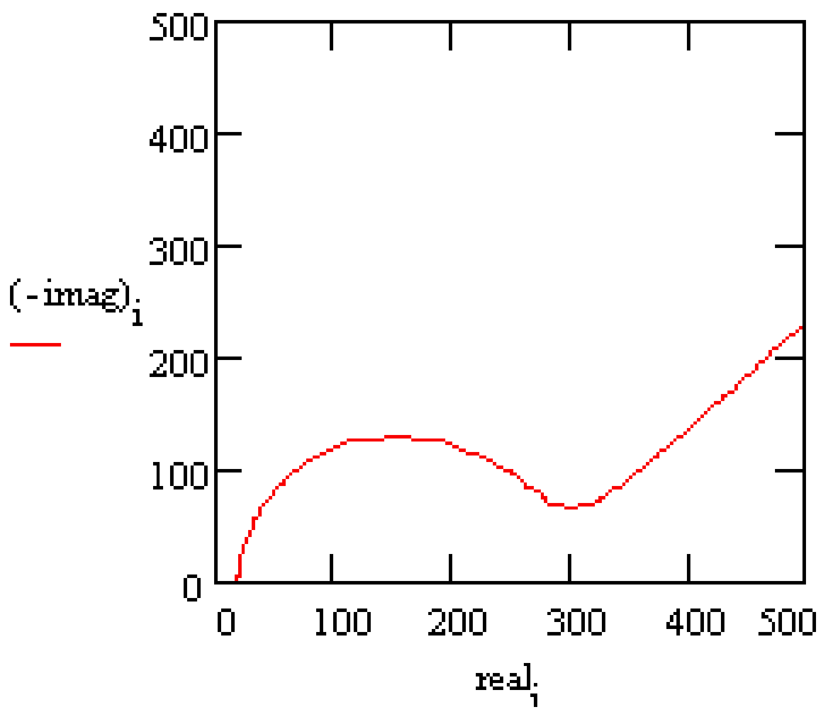


Example: Half a fuel cell

Adding to the previous example a double layer with capacitance and a charge transfer impedance, we get the equivalent circuit:

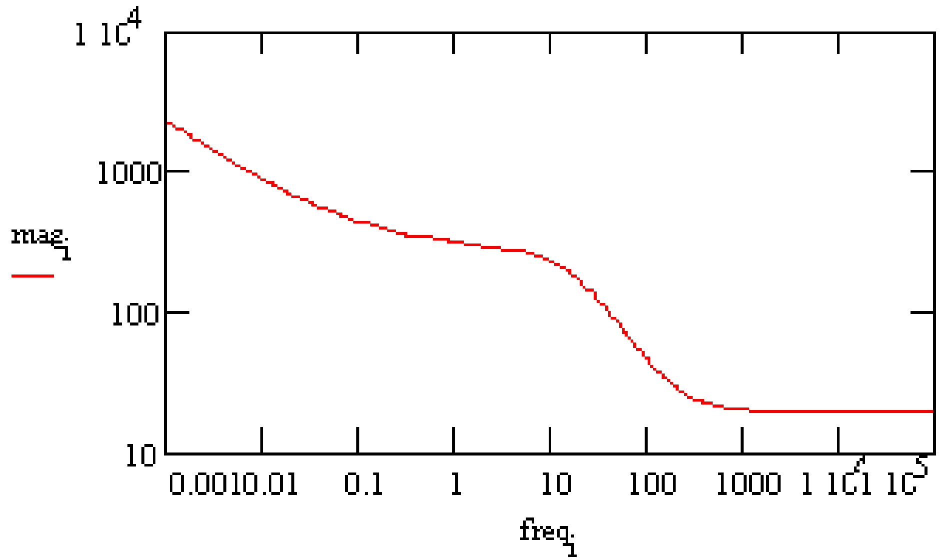


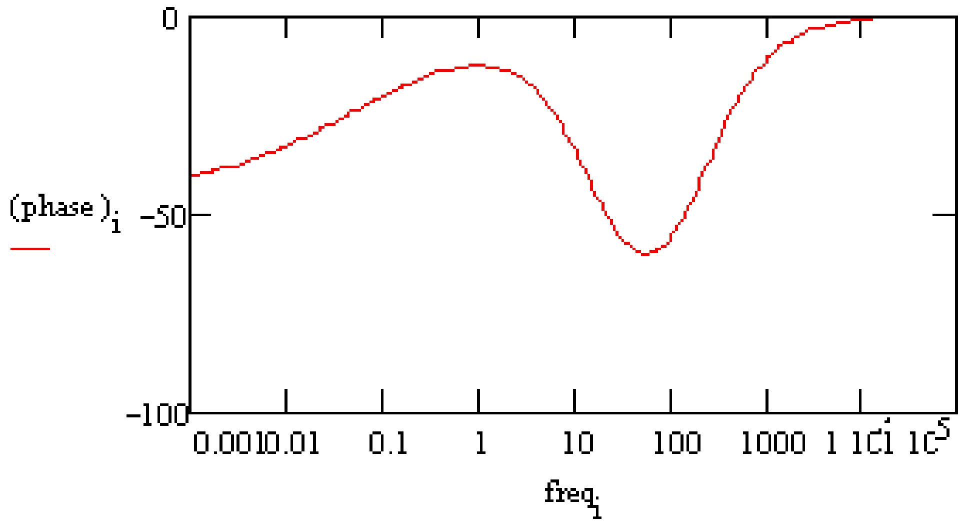
This circuit models a cell where polarization is due to a combination of kinetic and diffusion processes. The Nyquist plot for this circuit is shown in the Figure. As in the above example, the Warbug coefficient is assumed to be about 150 W sec$^{-1/2}$. Other assumptions: $R_s = 20\ \Omega$, $R_{ct} = 250\ \Omega$, and $C_{dl} = 40\ \mu F$.



Bode plot

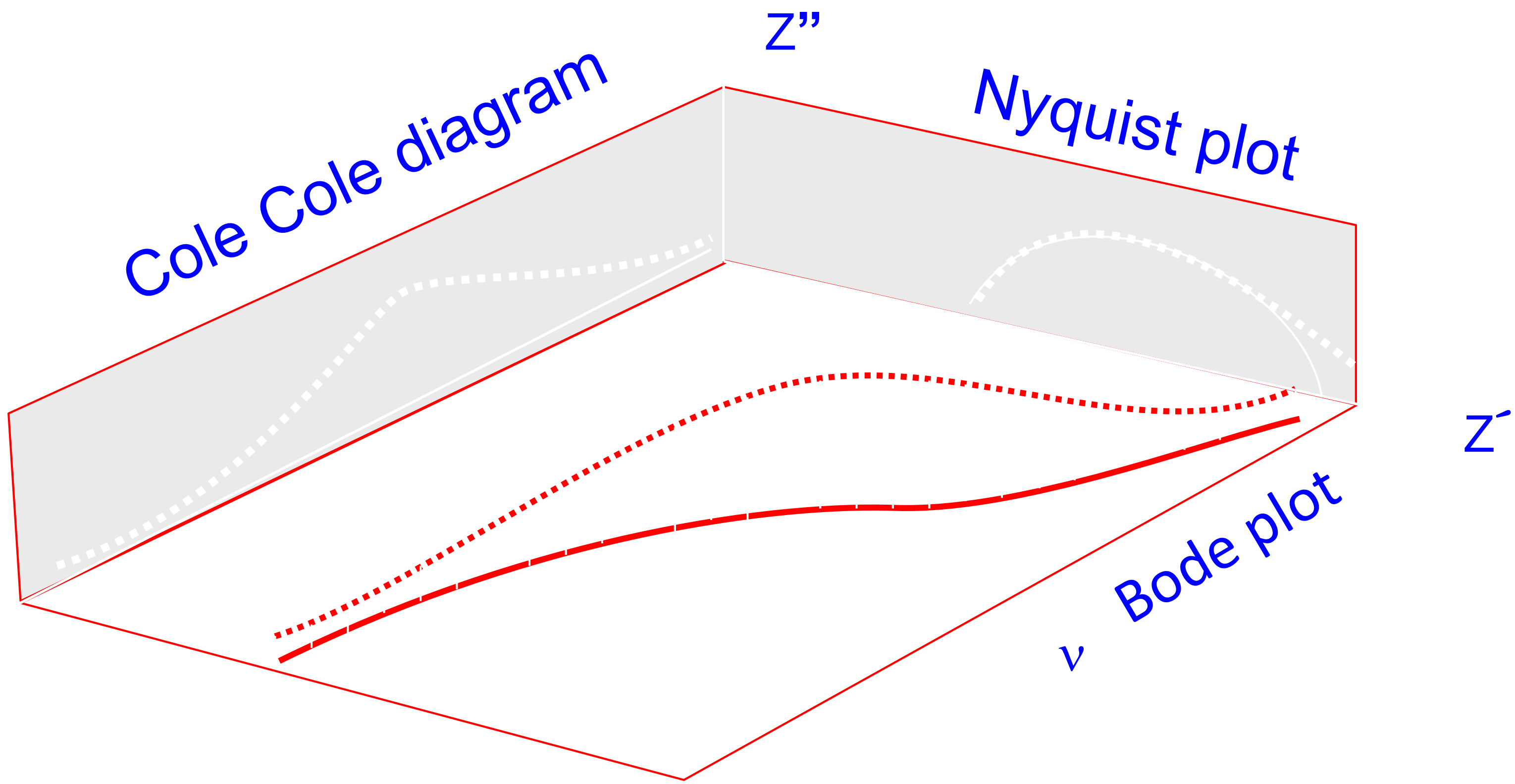
The Bode plot for the same data is shown here. The lower frequency limit was moved down to 1mHz to better illustrate the differences in the slope of the magnitude and in the phase between the capacitor and the Warburg impedance. Note that the phase approaches 45° at low frequency.

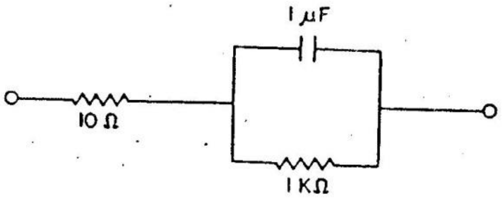


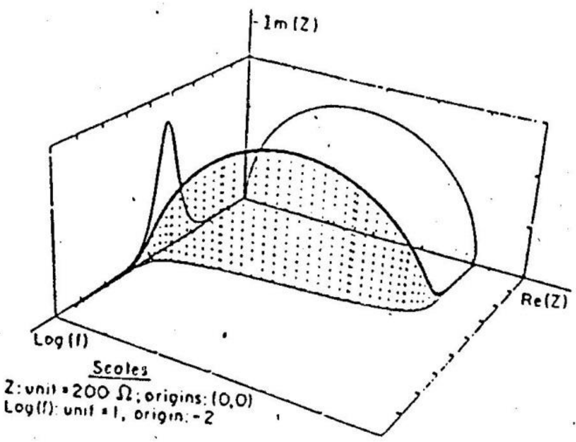


The different views on impedance data

The impedance data are the red points.
Their projection onto the Z"-Z' plane is called the Nyquist plot
The projection onto the Z"-ν plane is called the Cole Cole diagram







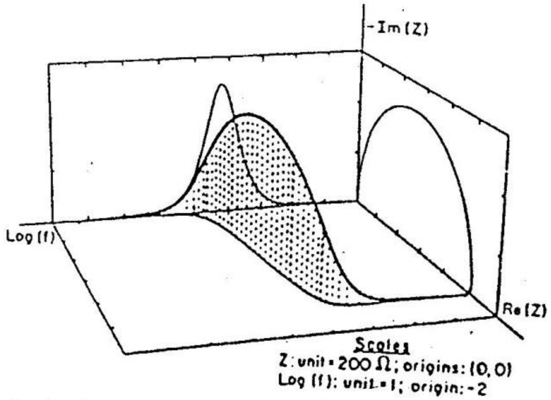


FIGURE 3.2.1. A simple circuit and 3-D plots of its impedance response. The 3-D plots are for different viewpoints. (Reprinted from J. R. Macdonald, J. Schoonman, and A. P. Lehnen, *Solid State Ionics* 5, 137–140, 1981.)

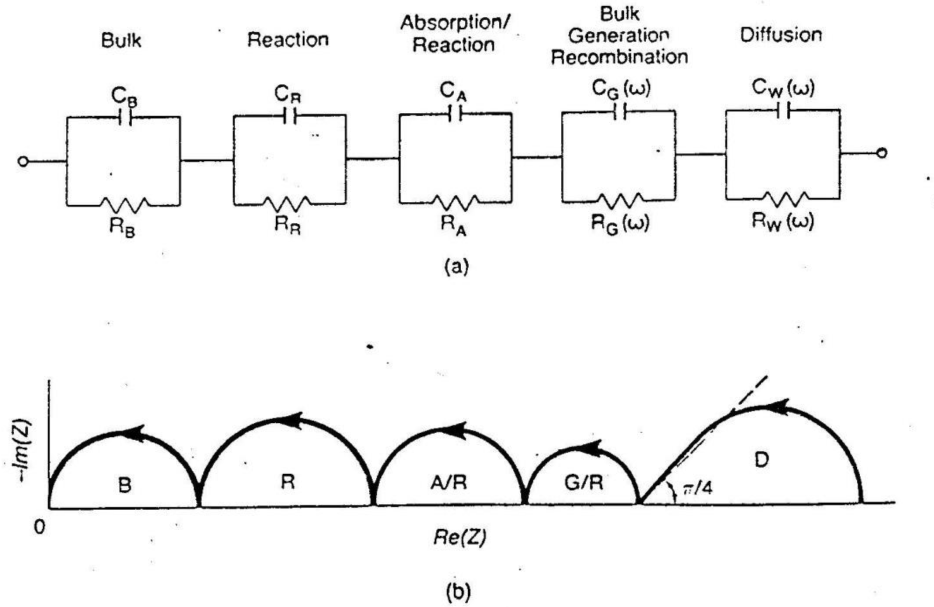


Fig 3.29 *Impedance schematic of an ideal solid electrolyte (from [118])*

a) equivalent circuit

b) impedance plot

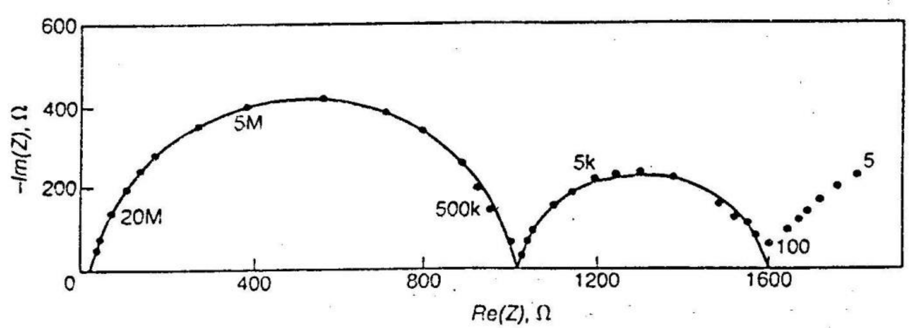


Fig 3.30 *Impedance measurement of a Pt/YSZ/Pt cell in O_2 at 457.4°C (from [124])*

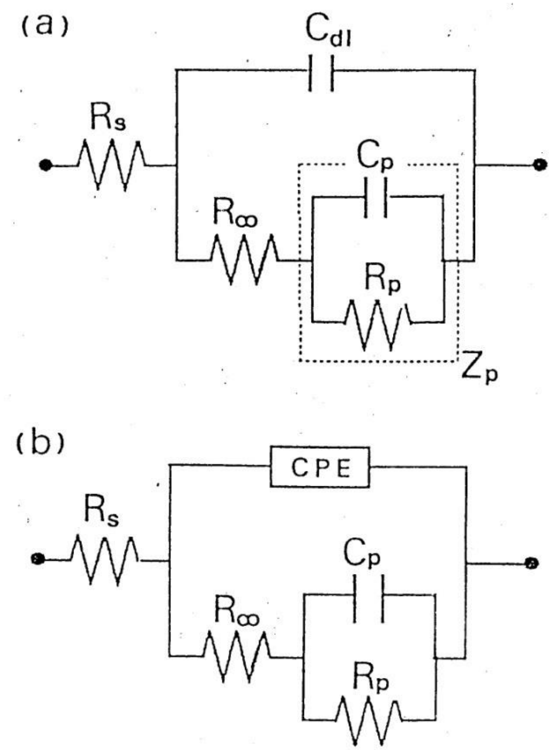


Fig. 1. Equivalent circuit for the HER on (a) nickel electrode, and on (b) Raney nickel-coated electrode.

$$M + H_2O + e^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MH_{ads} + OH^- \quad (\text{rate } v_1) \qquad [1]$$

$$MH_{ads} + H_2O + e^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} H_2 + M + OH^- \quad (\text{rate } v_2) \qquad [2]$$

$$MH_{ads} + MH_{ads} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2M + H_2 \quad (\text{rate } v_3) \qquad [3]$$

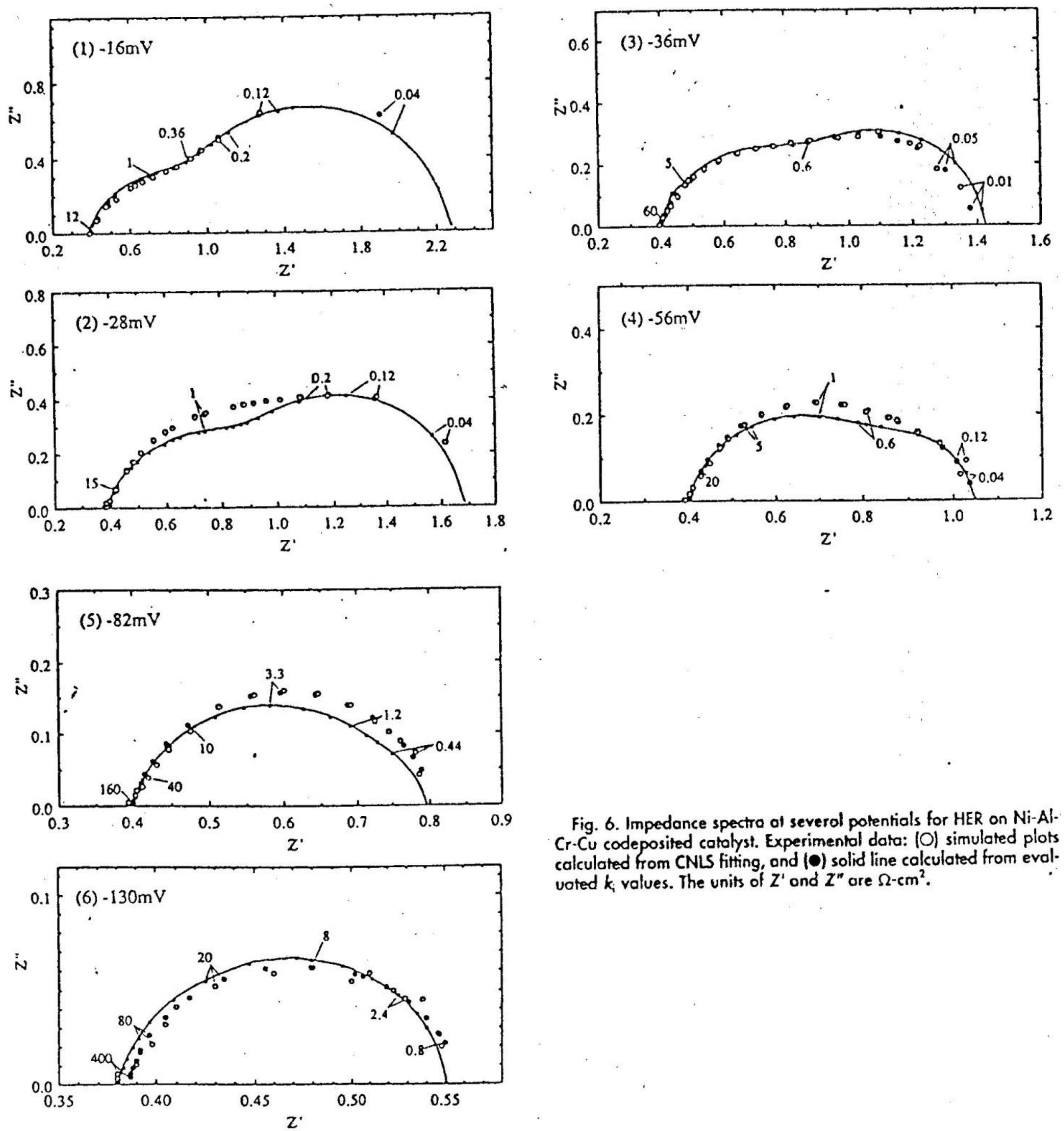
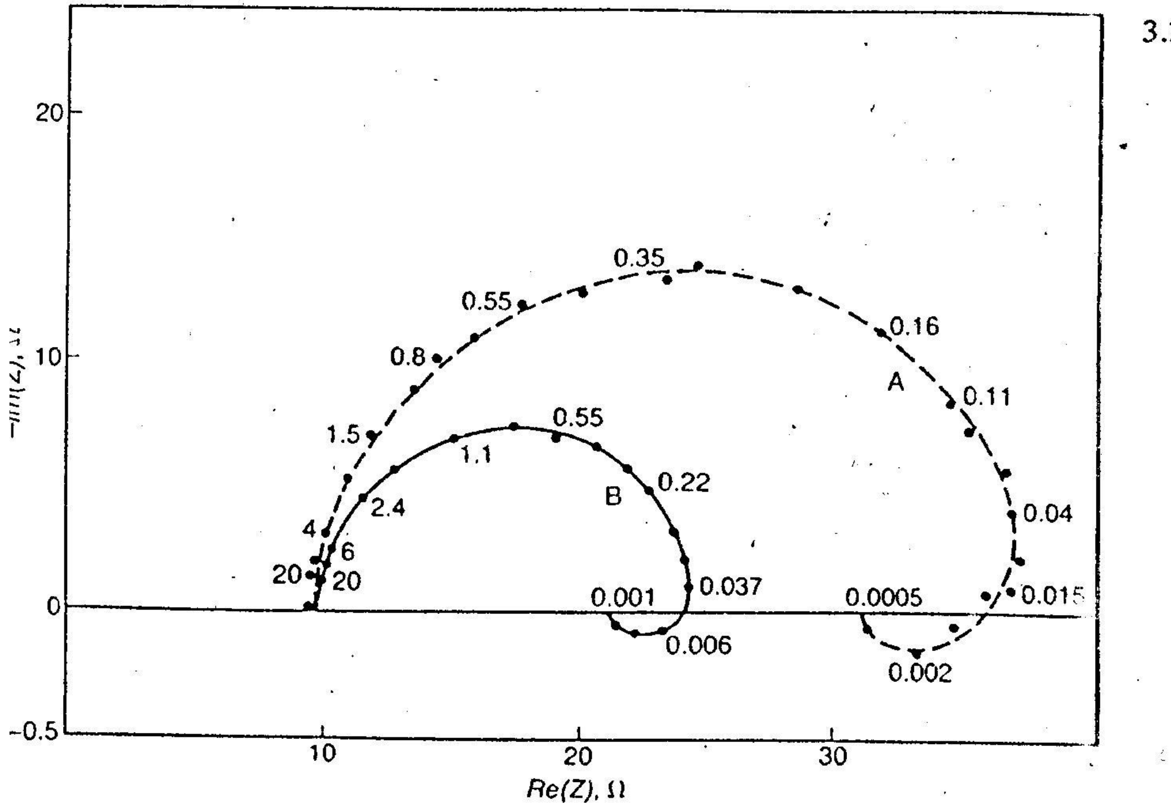


Fig. 6. Impedance spectra at several potentials for HER on Ni-Al-Cr-Cu codeposited catalyst. Experimental data: (O) simulated plots calculated from CNLS fitting, and (●) solid line calculated from evaluated k_i values. The units of Z' and Z'' are Ω-cm^2.



$$Ni^{2+} + H_2O \rightarrow (Ni\,OH)^+ + H^+$$

$$(NiOH)^+ + e \rightarrow (NiOH)_{ads}$$ Mechanism VI

$$(NiOH)_{ads} + (NiOH)^+ + 3e \rightarrow 2Ni + 2OH^-$$

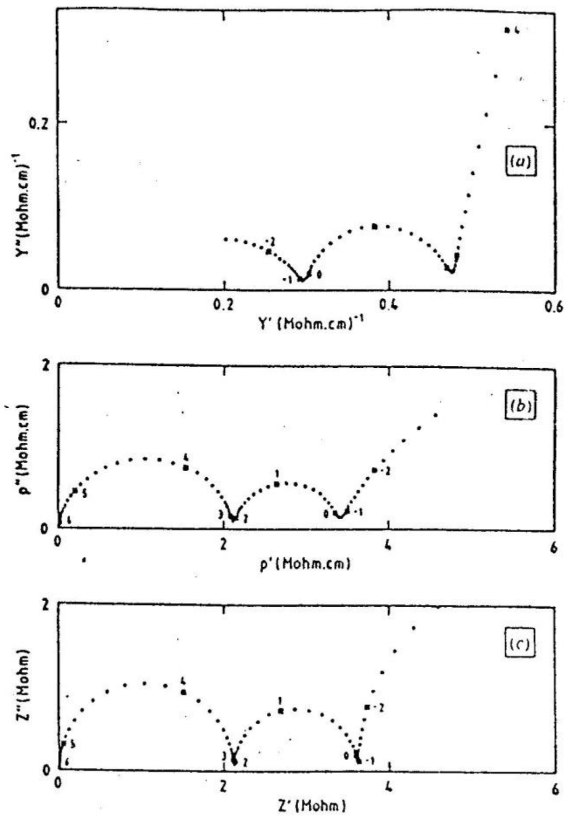
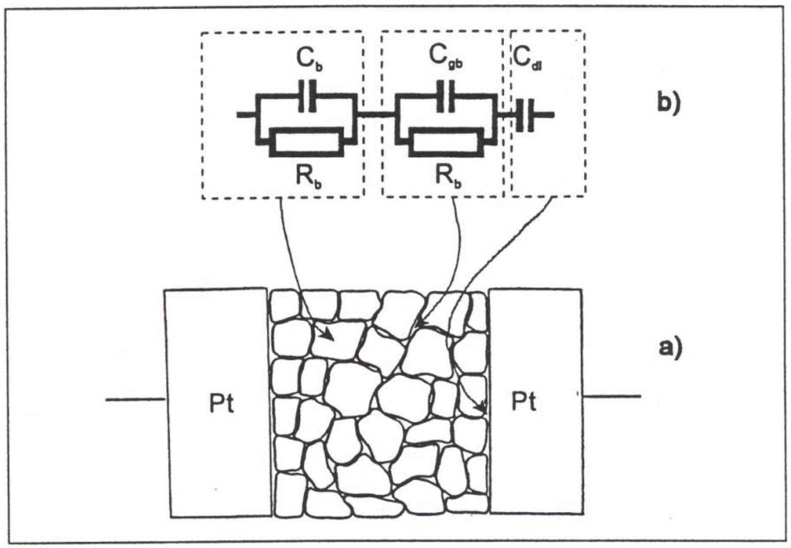


FIGURE 4.1.19. Comparison of admittance and impedance spectra for a zirconia solid electrolyte (ZrO_2: 6 mole % Y_2O_3) at 240°C: (*a*) Experimental admittance spectrum. (*b*) Experimental impedance spectrum. (*c*) Simulated impedance spectrum, using the circuit of Figure 4.1.18 and parameter values given in Table 4.1.4.



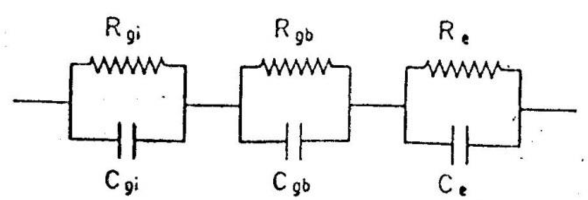
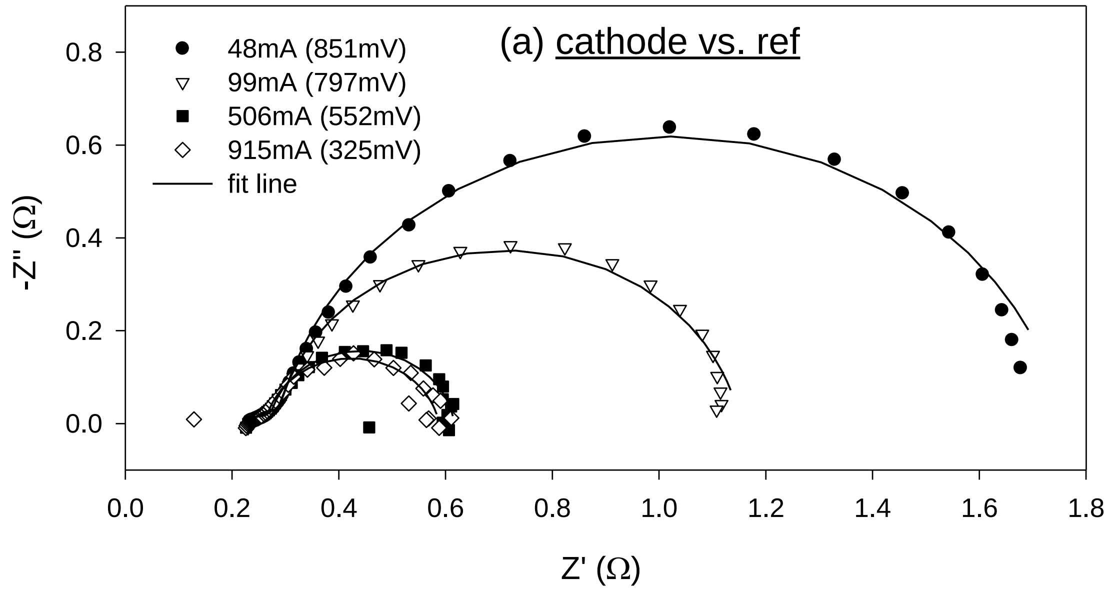
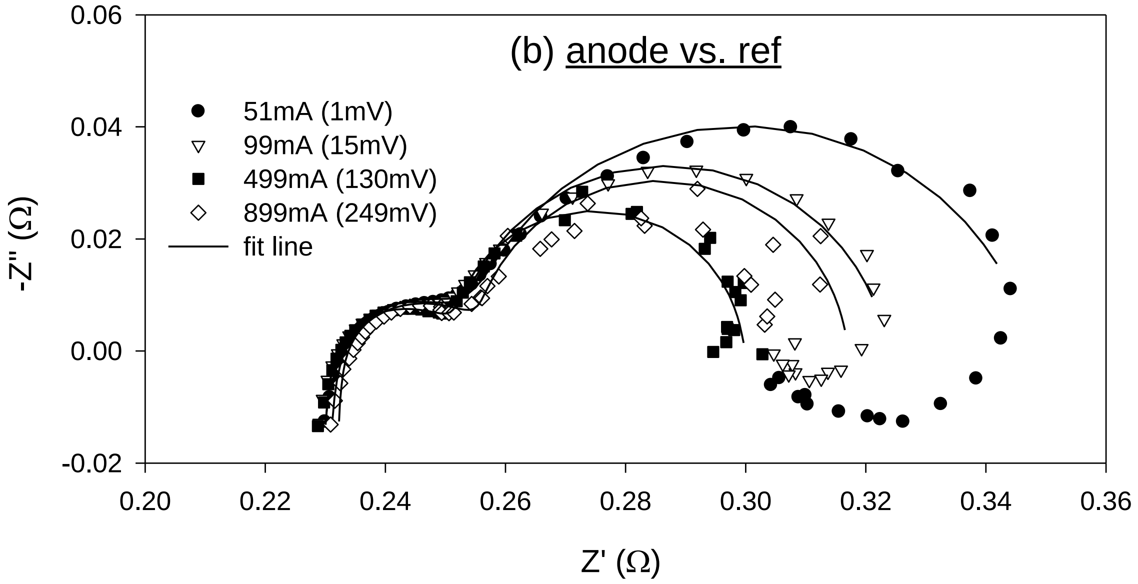


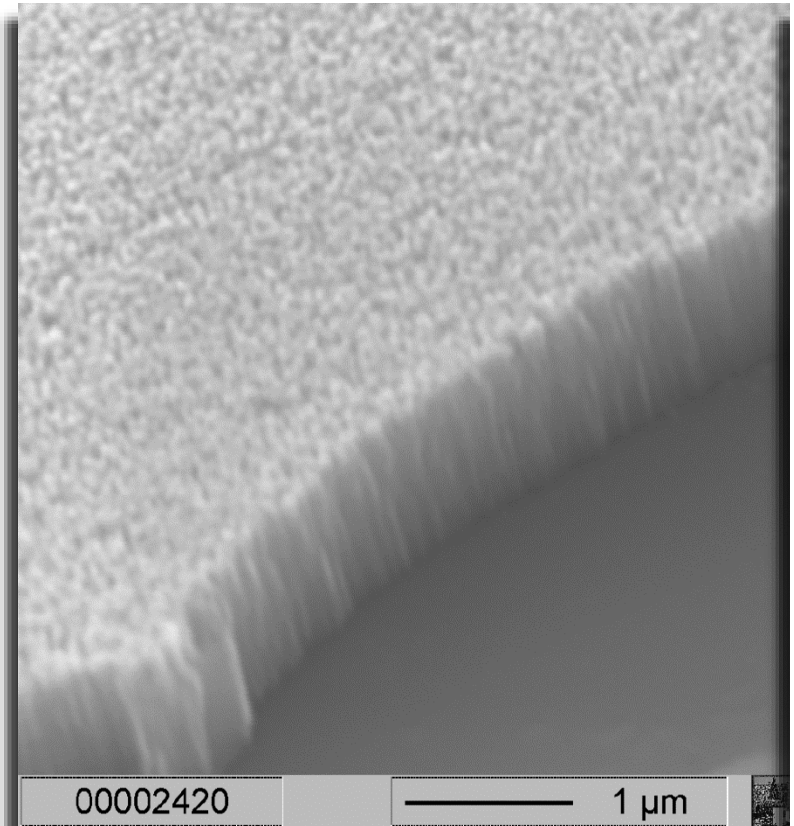
FIGURE 4.1.18. Circuit equivalent for a ceramic electrolyte according to Bauerle (1969) and modeling the impedance of the grain interiors (gi), grain boundaries (gb) and electrode (e).

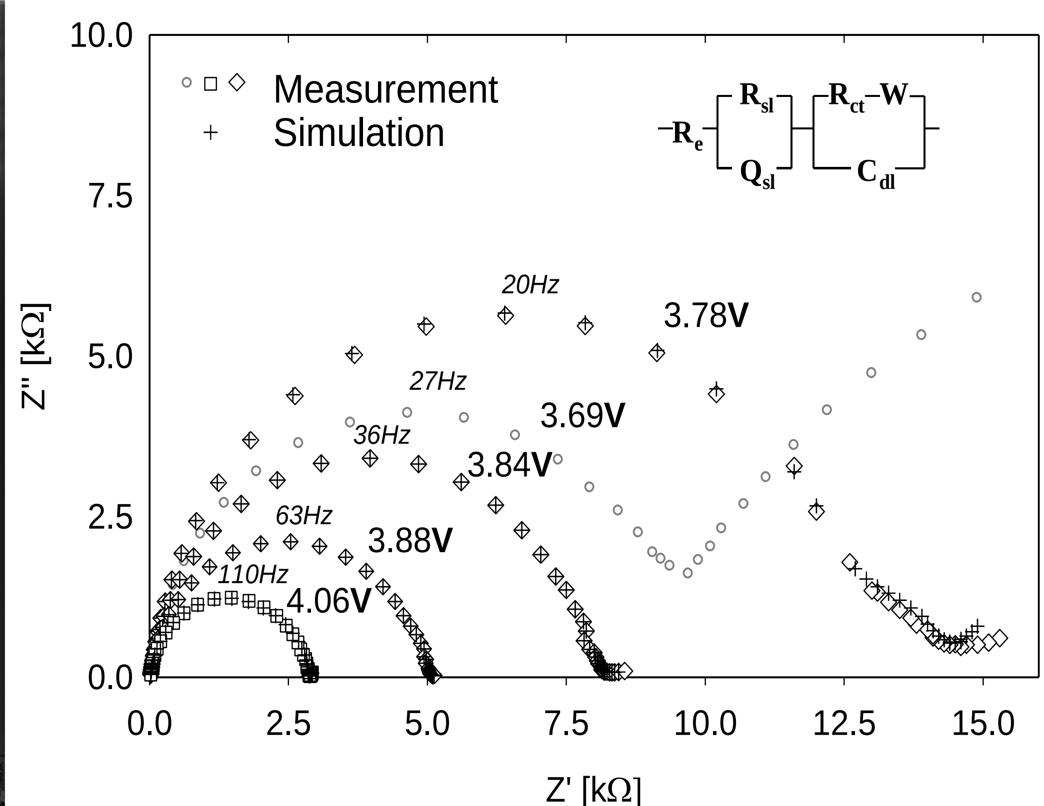
Impedance on individual electrode





Real cathode: Li_xCoO_2





$LiCoO_2$, RF film on silicon.

Peter J. Bouwman, *Thesis*, U.Twente 2002.

IS of a RF-film electrode: (○) 'fresh'; (□) charged; (◇) intermediate SoC's. (+) CNLS-fit. Range: 0.01 Hz – 100 kHz.