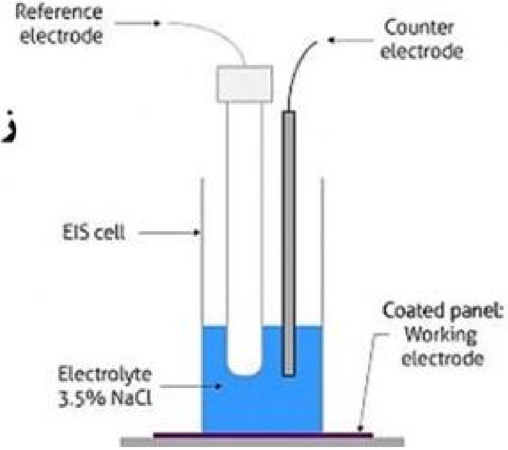
دانشگاه سمنان

دانشکده مهندسی مواد و متالورژی

کارگاه آموزشی مجازی

آشنایی مقدماتی با روش طیف سنجی امپدانس الکتروشیمیایی



زمان: شنبه ۲۴ آبانماه ساعت ۱۸–۱۹:۳۰
مدرس: دکتر محبوبه آزادی

آدرس مجازی کارگاه:

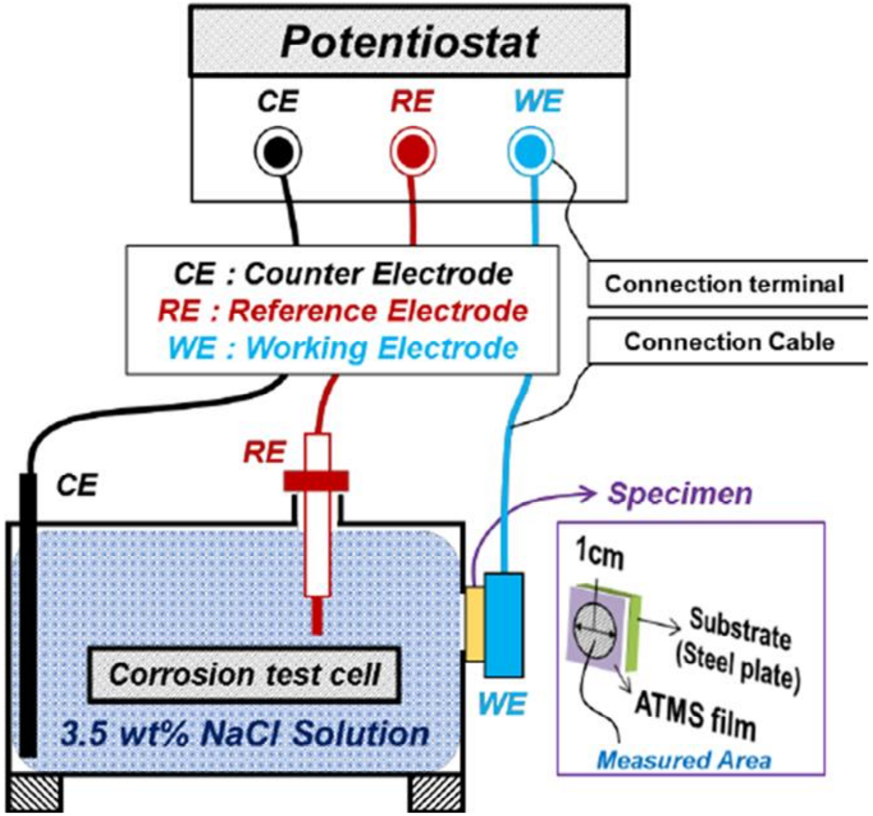
https://vc2.semnan.ac.ir/metal
Passcode : Metal2021

آزمون پولاریزاسیون

- روشی که برای اندازه گیری سرعت خوردگی (دانسیته جریان) مورد استفاده قرار می گیرد استفاده از منحنی پلاریزاسیون می باشد. روشهای پلاریزاسیون در مقایسه با روش کاهش وزن نیاز به زمان کمتری داشته وسریعتر انجام می شوند.

- آزمون پولاریزاسیون تافلی (برون یابی تافل)
- آزمون مقاومت پولاریزاسیون خطی

آزمون پولاریزاسیون



- Polarization
  - Cathodic
    - Activation
    - Concentration
  - Anodic
    - Activation
    - Passivation

Activation Polarization

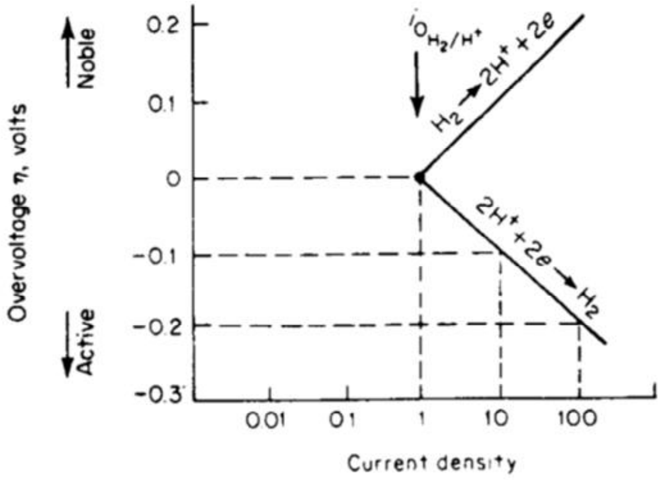


Figure 9-13 Activation-polarization curve of a hydrogen electrode.

$$\eta_a = \pm \beta \log \frac{i}{i_0}$$

Concentration Polarization

$$\eta_c = 2.3 \frac{RT}{nF} \log\left(1 - \frac{i}{i_L}\right)$$

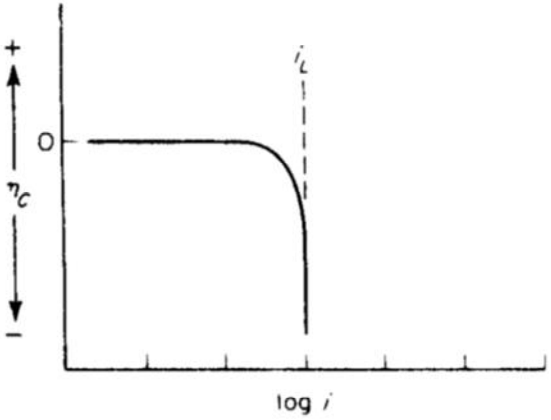


Figure 9-15 Concentration polarization curve (reduction process).

Combined Polarization

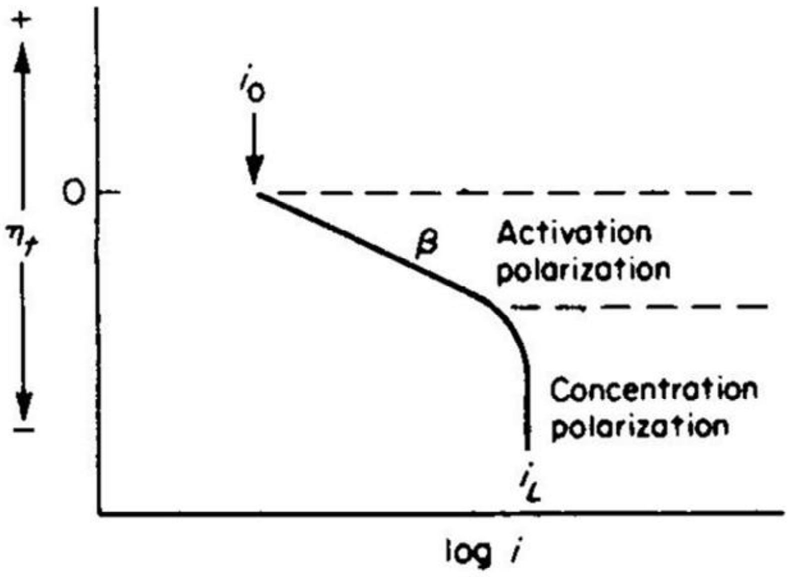
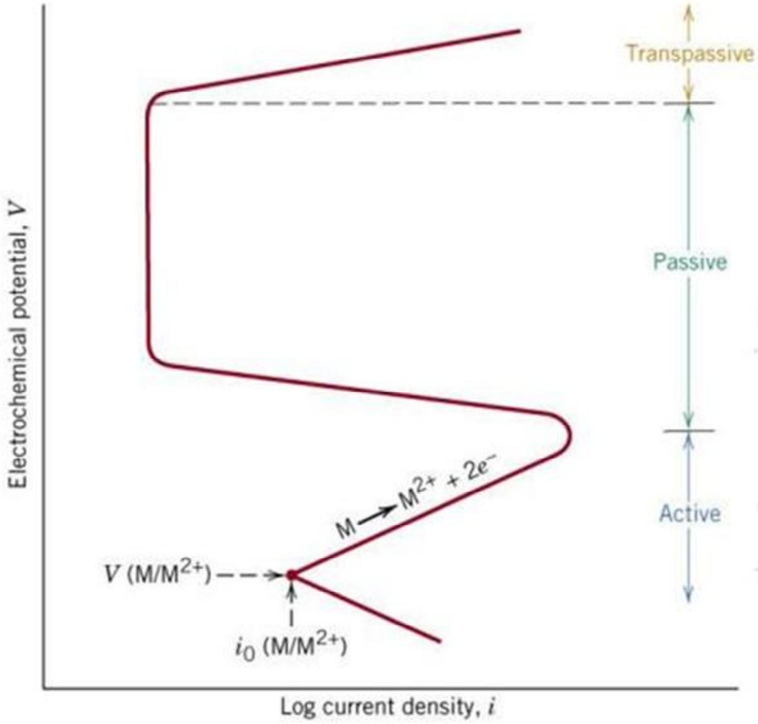


Figure 9-17 Combined polarization curve—activation and concentration polarization.

Anodic Polarization Curve -1



- This curve is usually scanned from 20 mV below the E_{oc} (open circuit potential) upward.
- The curve can be used to identify the following corrosion regions:

i_p - passive current density

E_{pp} - primary passivation potential

i_{crit} - critical current density

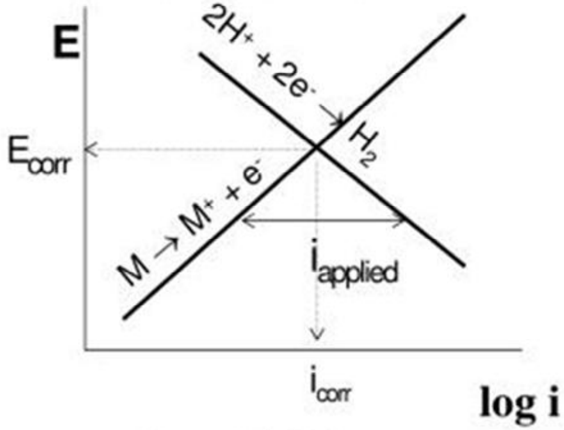
E_{trans} - transpassive potential

آزمون پولاریزاسیون تافلی

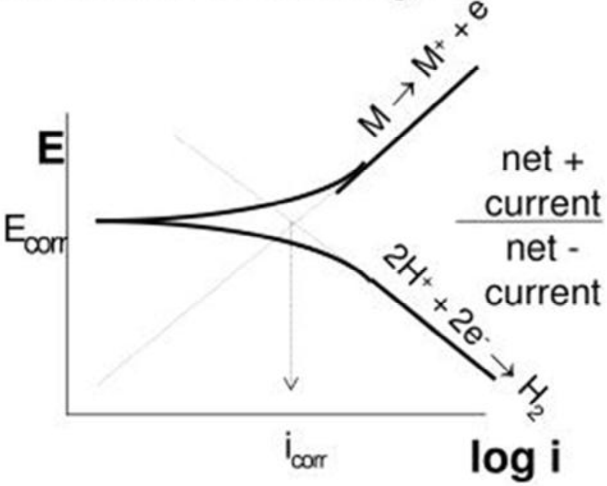
- رابطه تافل با کنترل اکتیواسیون فرآیندهای آندی و کاتدی مرتبط می باشد. برای یک واکنش الکتروشیمیایی تحت کنترل اکتیواسیون، منحنی های پلاریزاسیون در صفحه مختصات E بر حسب log(i) بصورت خطی بوده که رفتار تافل نامیده مي شود. برون یابی شیب منحنی های کاتدی و آندی تافل می توان پتانسیل خوردگی را بدست آورد. نقطه تقاطع نشان دهنده دانسیته جریان خوردگی یا سرعت خوردگی می باشد.

Potentiodynamic Curves

- An electrochemical test that measures the current response to an applied potential over a large potential range
- this test is used to analyze the overall behavior of the coating's corrosion protection



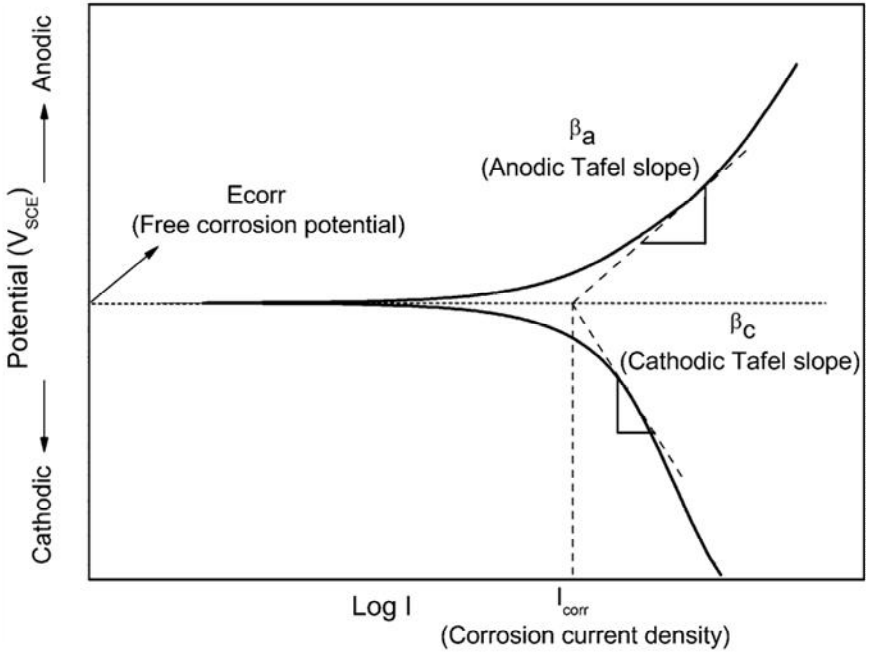
Evan's Diagram

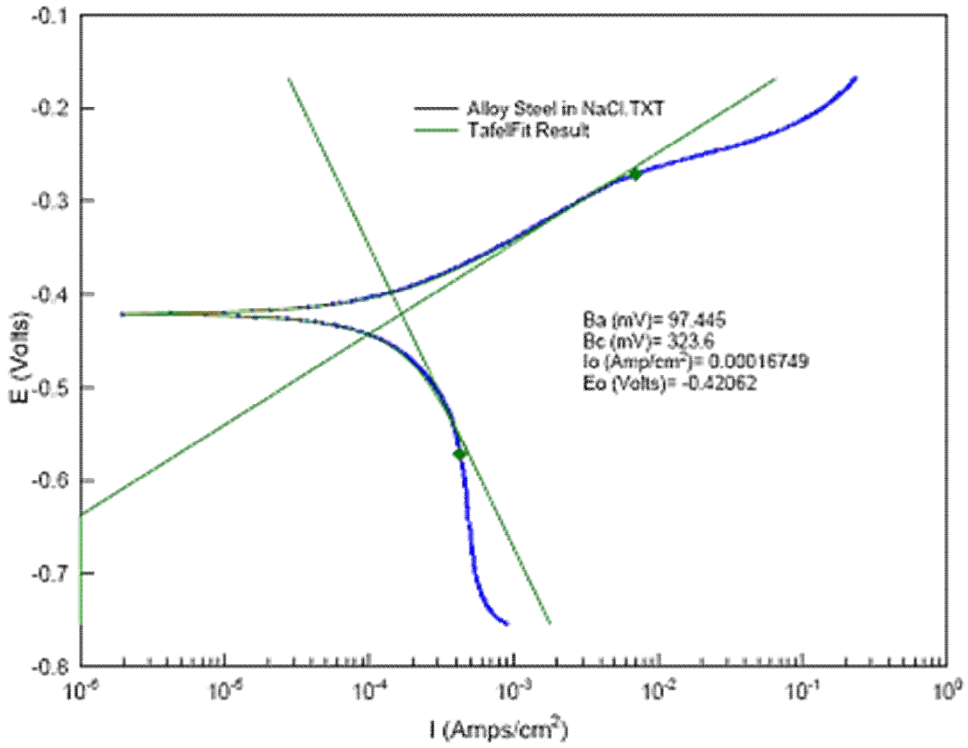


Polarization Curve

اطلاعات مستخرج از منحنی های پولاریزاسیون تافلی

E_{corr} (Vvs,SCE)	I_{corr} ($\mu A.cm^{-2}$)	β_a ($v.dec^{-1}$)	β_c ($v.dec^{-1}$)	R_p ($\Omega.cm^2$)




Alloy Steel in NaCl.TXT
TafelFit Result
Ba (mV)= 97.445
Bc (mV)= 323.6
Io (Amp/cm²)= 0.00016749
Eo (Volts)= -0.42062
E (Volts)
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
10⁻⁶
10⁻⁵
10⁻⁴
10⁻³
10⁻²
10⁻¹
10⁰
I (Amps/cm²)

روش پولاریزاسیون تافلی اگرچه بسیار سریع است (۱۰ دقیقه یا کمتر) اما محدودیت هایی نیز دارد.

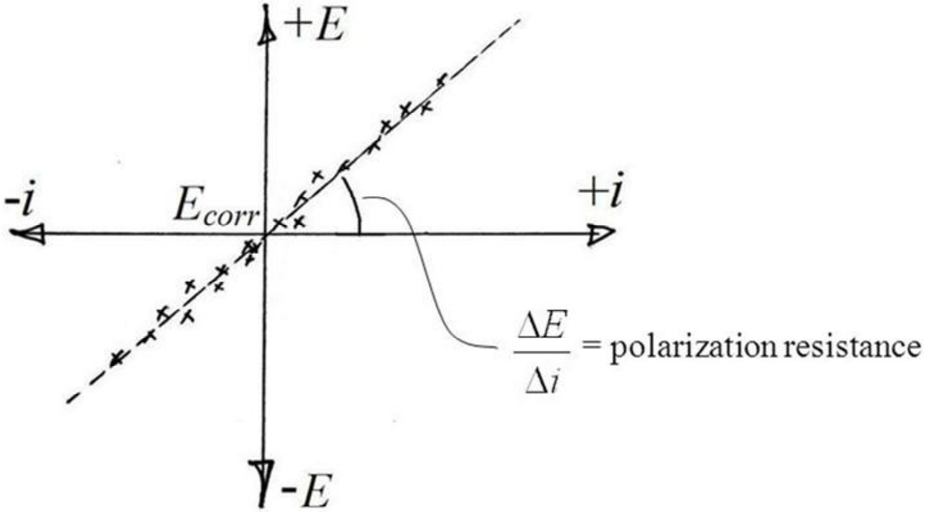
۱ - تنها برای سیستمهایی که حاوی یک واکنش احیا می باشند قابل استفاده است.

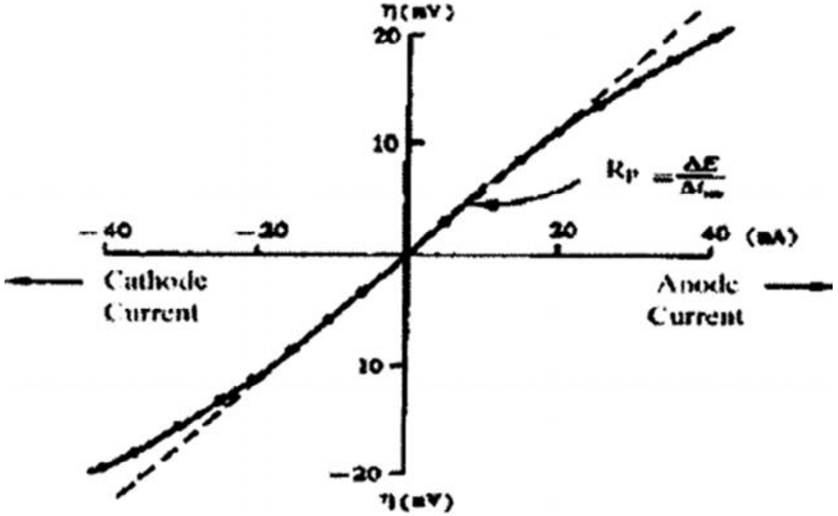
۲- برای اطمینان از دقت این روش، منطقه تافل را بایستی تا جریانهای بیشتری ادامه داد که در برخی از سیستمها

امکان پذیر نیست به دلیل تداخل با پولاریزاسیون غلظتی و دیگر اثرات

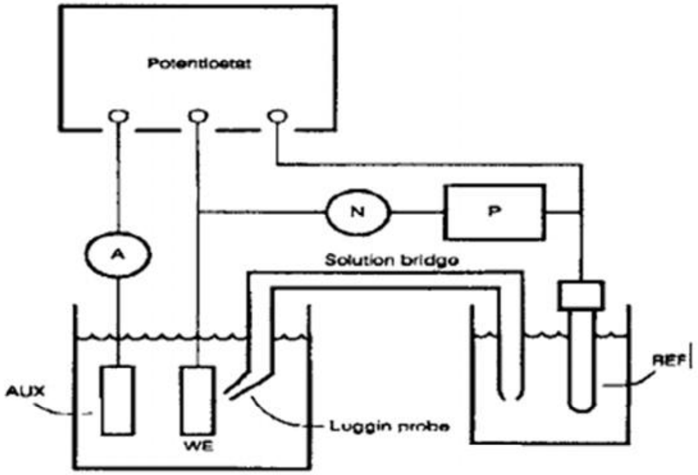
linear polarization resistance corrosion test

Remember: during linear polarization measurements we plot *E* vs *i* (not log *i*) around the corrosion potential:




η (mV)
20
10
−40
−20
20
40 (mA)
Cathode Current
Anode Current
$R_p = \frac{\Delta E}{\Delta I_{app}}$
10
−20
η (mV)

(a)


Potentiostat
N
P
A
Solution bridge
AUX
WE
Luggin probe
REF

(b)

Stern-Geary equation

$$R_p = = \frac{\Delta E}{\Delta I} = \frac{\beta_a \beta_c}{2.303\, I_{corr}\, (\beta_a + \beta_{c)}}$$

Rearranging of above equation, we get

$$I_{corr} = \frac{1}{2.303 R_p} \left(\frac{\beta_a \beta_c}{\beta_a + \beta_{c)}}\right)$$

Polarization Resistance, Rp

- This electrochemical technique enables the measurement of the instantaneous corrosion rate. It quantifies the amount of metal per unit of area being corroding in a particular instant.
- The method is based on the observation of the linearity of the polarization curves near the potential (E_{corr}). The slope expresses the value of the polarization resistance (Rp) if the increment is close to zero.
- This Rp value is related to the corrosion current (Icorr) by means of the expression:

$$R_P = \left(\frac{\Delta E}{\Delta I}\right)_{\Delta E \to 0}$$

$$icorr = \frac{1}{Rp}\frac{BaBc}{2.303(Ba + Bc)}$$

- Ba and Bc are the Tafel Slopes and are approximated to both be .1 V

These are three different electrochemical techniques to measure the corrosion rate and investigate the corrosion behavior of a desired working electrode.

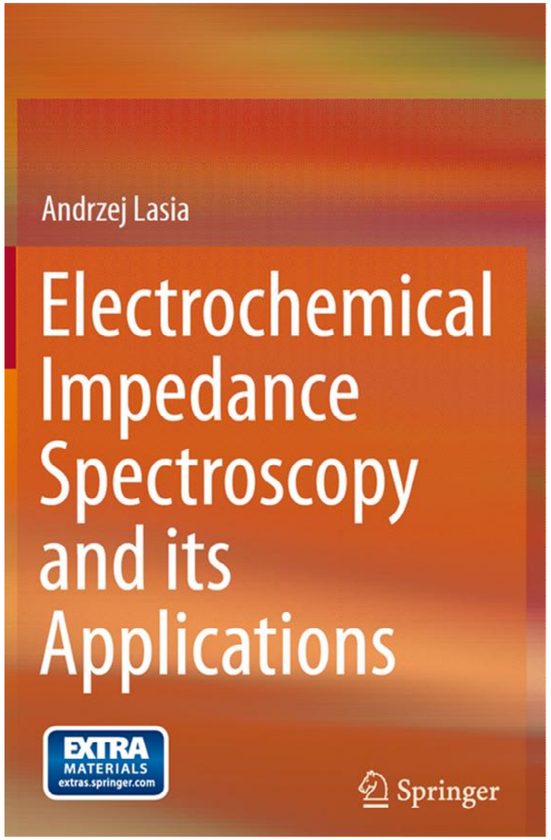
1-In LPR (Linear polarization resistance) you need to polarize the working electrode from -20 mV to +20 mV with respect to the OCP (open circuit potential or equilibrium potential) but in Potentiodynamic Polarization resistance (PPR) method you need to polarize the working electrode from about -250 mV up to +250 mV with respect to the OCP.

2- In LPR you need to measure the slope of the E-I curve in order to get polarization resistance and then by using the Stern-Geary equation you can get the corrosion current density but in potentioodynamic polarization method you can find the corrosion current on the curve of E-Log i

3-The LPR has minimal sample damage while the PPR has higher damage to sample.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

منابع مورد استفاده

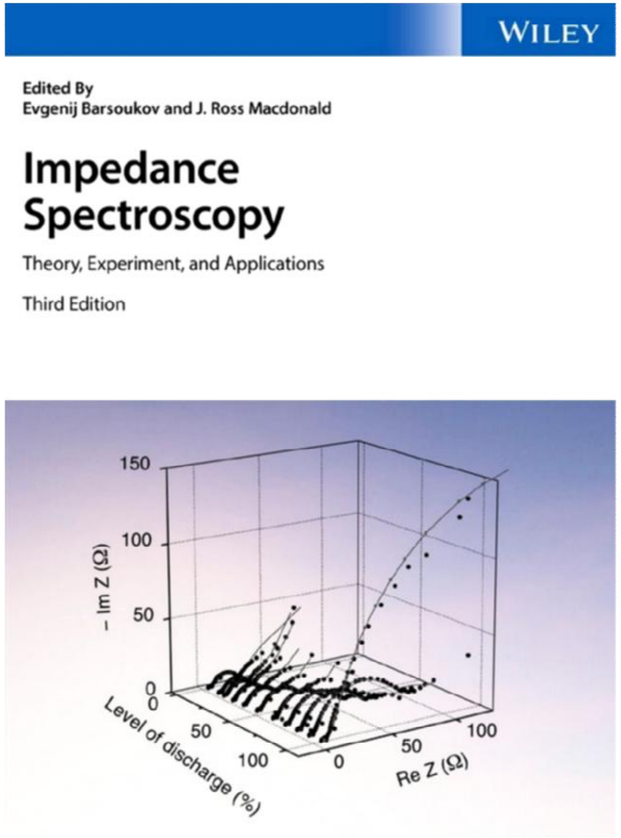


Andrzej Lasia

Electrochemical Impedance Spectroscopy and its Applications

EXTRA MATERIALS extras.springer.com

Springer



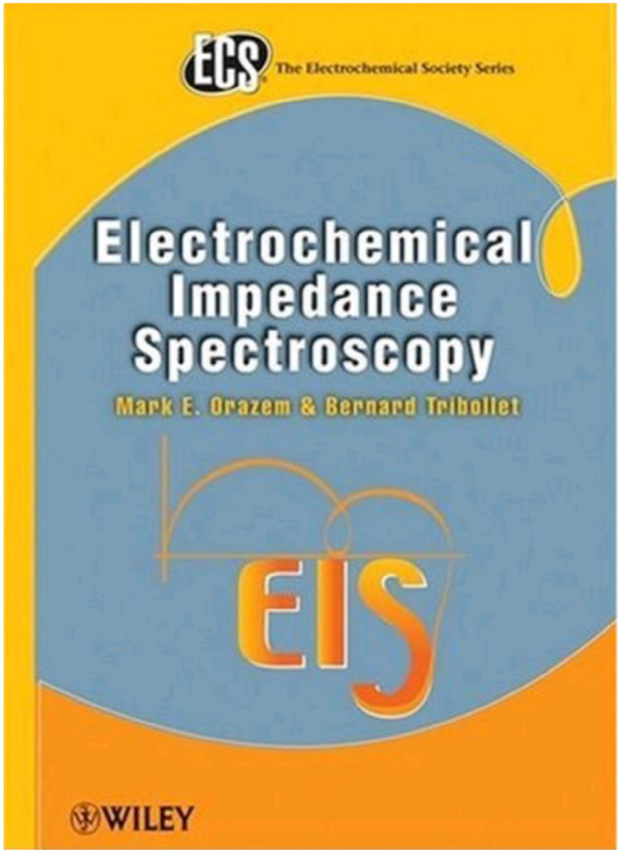
WILEY

Edited By
Evgenij Barsoukov and J. Ross Macdonald

Impedance Spectroscopy

Theory, Experiment, and Applications

Third Edition



ECS The Electrochemical Society Series

Electrochemical Impedance Spectroscopy

Mark E. Orazem & Bernard Tribollet

EIS

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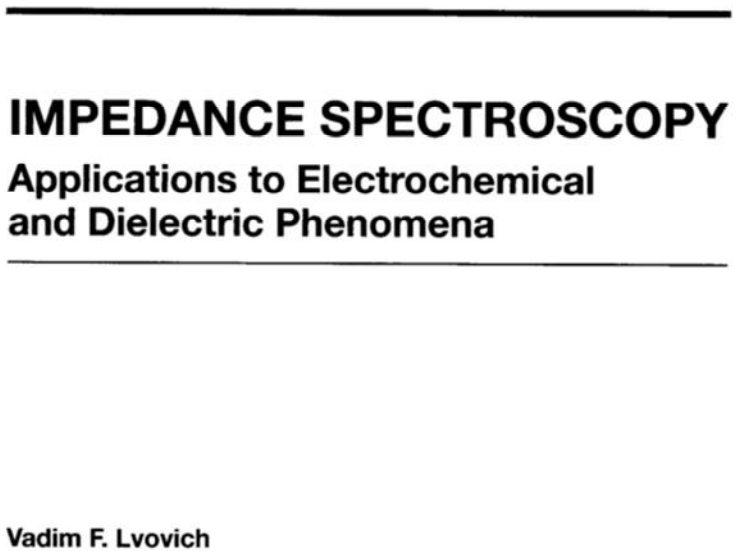
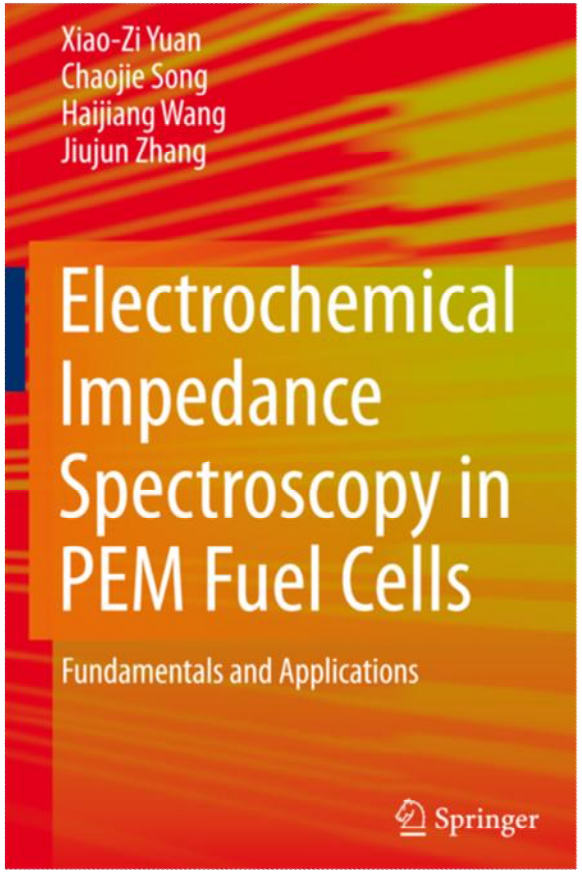
منابع مورد استفاده



IMPEDANCE SPECTROSCOPY

Applications to Electrochemical
and Dielectric Phenomena

Vadim F. Lvovich



Xiao-Zi Yuan
Chaojie Song
Haijiang Wang
Jiujun Zhang

Electrochemical Impedance Spectroscopy in PEM Fuel Cells

Fundamentals and Applications

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ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Introduction

Impedance Spectroscopy **is also called** *AC Impedance* *or just* *Impedance Spectroscopy*.

Electrochemical impedance spectroscopy is a recent tool in corrosion laboratories that is slowly making its way into the service environment as units are decreased in size and become portable.

The usefulness of impedance spectroscopy lies in the ability to distinguish the dielectric and electric properties of individual contributions of components under investigation.

آزمون امپدانس الکتروشیمیایی

طیف‌سنجی امپدانس الکتروشیمیایی

یکی از روش‌های بررسی سرعت خوردگی (مقاومت در برابر خوردگی) است. اساس کار این روش اندازه‌گیری امپدانس جریان متناوب در دامنه‌ای از فرکانس است.

در این روش پتانسیل کوچکی (در حدود مقدار ۱۰-۱ میلی ولت اطراف E_{corr}) به صورت متغیر با زمان به نمونه اعمال شده و جریان اندازه‌گیری شده و امپدانس سیستم و زاویه فاز امپدانس تعیین می‌شود.

واربورگ اولین کسی بود که مفهوم امپدانس را به سیستم‌های الکتروشیمیایی توسعه داد.

آزمون امپدانس الکتروشیمیایی

در این روش، پتانسیل اعمال شده به سیستم با مدولاسیون یک موج سینوسی کوچک، دچار اختلال شده و پاسخ به صورت جریان سینوسی بر حسب تابعی از فرکانس مدولاسیون اندازه گیری می شود. امپدانس به صورت نسبت ولتاژ به جریان سیگنال تعریف می شود.

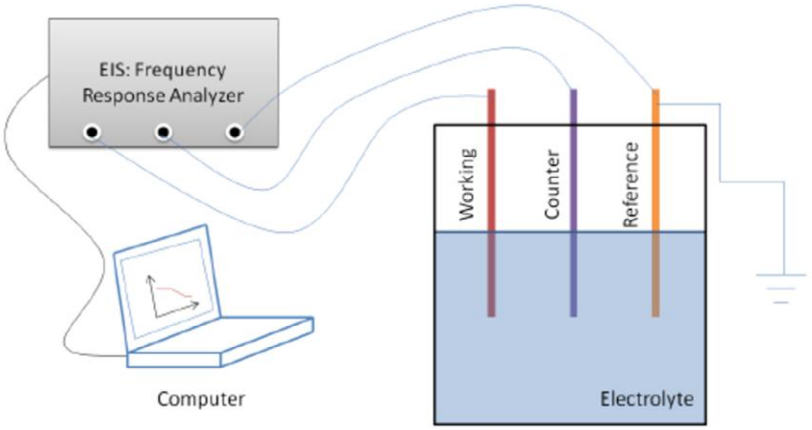
تفسیر طیف امپدانس با استفاده از مدارهای معادل انجام می شوند. اجزای سلول و سطوح تماس به صورت مولفه های الکتریکی مانند مقاومت ها و خازن ها نمایش داده می شوند. با تطابق طیف امپدانس اندازه گیری شده، با مدار معادل می توان مقادیر عددی پارامترهایی مانند مقاومت اجزای سلول، خازن های تشکیل شده روی مرزها و امپدانس در الکترولیت را به دست آورد.

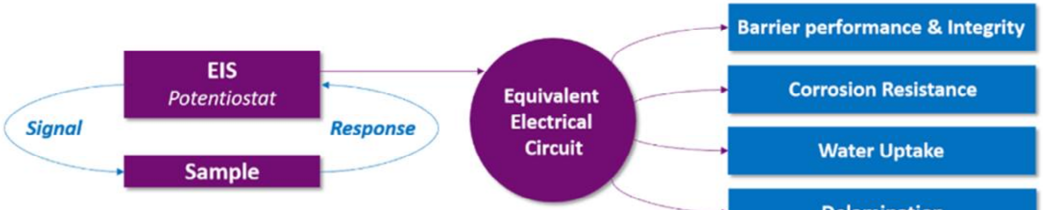
آزمون امپدانس الکتروشیمیایی

برنامه های مورد استفاده

1- ZView software (Scribner Associates)
2- ZSimpWin software
3- Gamry software
4-Zfit software

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY





EIS
Potentiostat

Signal

Response

Sample

Equivalent Electrical Circuit

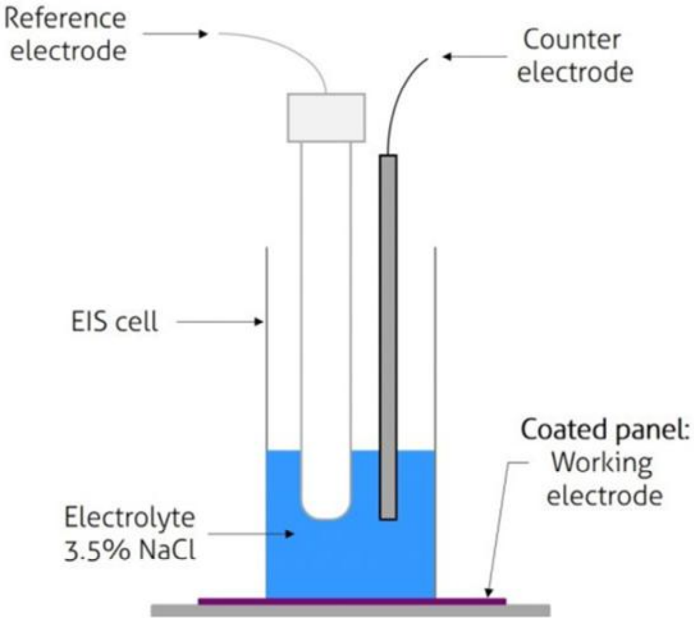
Barrier performance & Integrity

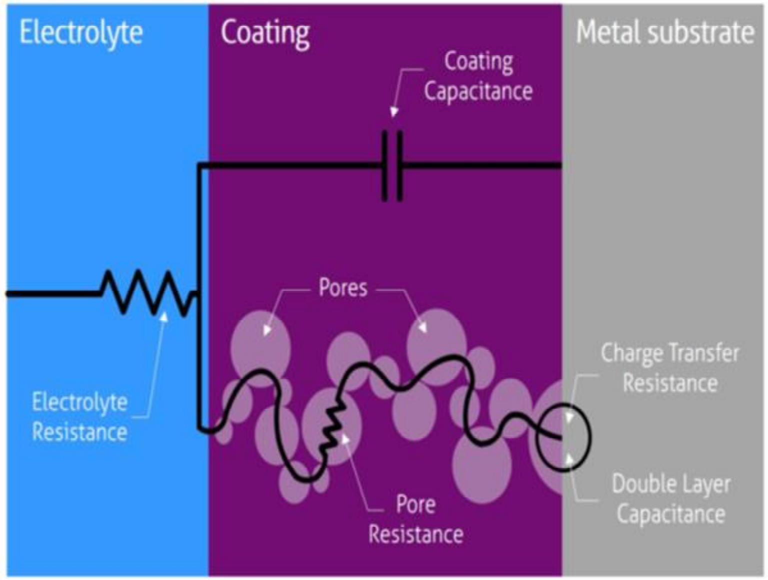
Corrosion Resistance

Water Uptake

Delamination

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY





Different types of EIS measurements

•Standard EIS (ISO 16773) measures barrier performance and water uptake during immersion, and gives relevant results within three weeks. It can be extended for even longer-term testing.
ISO 16773: Electrochemical impedance spectroscopy (EIS) on coated and uncoated metallic specimens

•Accelerated EIS (ISO 17463) applies electrical stress to promote delamination and speed up corrosion processes. This approach is very useful for barrier performance comparison in only 24 hours.
ISO 17463: Paints and varnishes-Guidelines for the determination of anticorrosive properties of organic coatings by accelerated cyclic electrochemical technique.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY.

Advantages.

1. *Useful on high resistance materials such as paints and coatings.*
2. *Time dependent data is available.*
3. *Non- destructive.*
4. *Quantitative data available.*
5. *Use service environments.*

Disadvantages.

1. *Expensive.*
2. *Complex data analysis for quantification.*

Impedance

- Like **resistance**, **impedance** is a measure of the ability of a circuit to resist the flow of electrical current. Unlike resistance, impedance is not limited by the simplifying properties.

- Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and measuring the current through the cell.

- Suppose that we apply a sinusoidal potential excitation. The response to this potential is an AC current signal, containing the excitation frequency and it's harmonics. This current signal can be analyzed as a sum of sinusoidal functions (a Fourier series).

- Electrochemical Impedance is normally measured using a small excitation signal. This is done so that the cell's response is pseudo-linear.

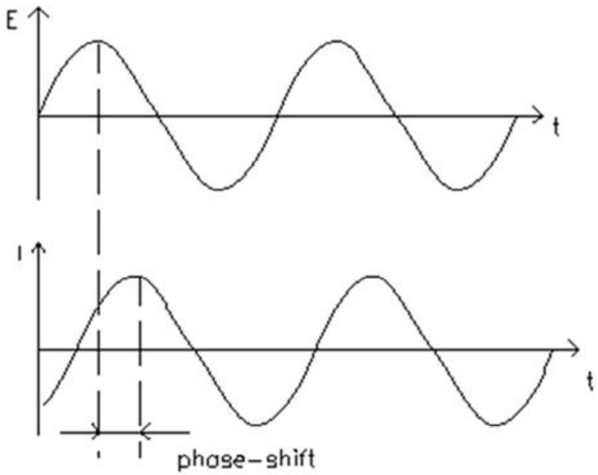
- In a linear system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase.

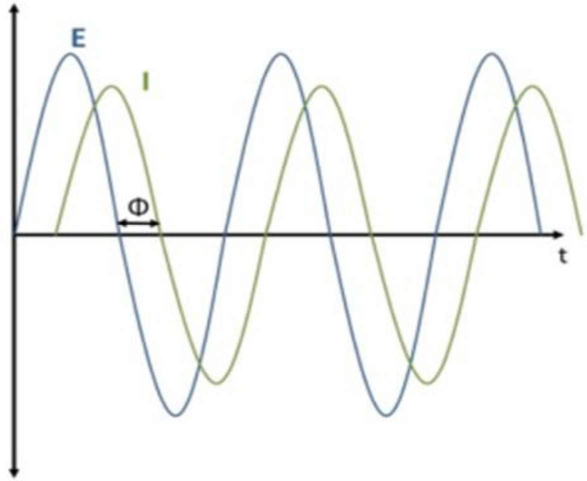
Impedance and resistance

- ✓ While **resistance** is the ratio of voltage or potential and current for a DC (direct current) system, the **impedance** is the ratio of voltage or potential and current for AC (alternating current) systems.

- ✓ The wave nature makes it necessary to define the impedance with two parameters. One is the total impedance Z and the other one is the phase shift Φ.

Sinusoidal Current Response in a Linear System





The excitation signal, expressed as a function of time, has the form of:

$$E(t) = E_0 \cos(\omega t)$$

E(t) is the potential at time t_r, E_o is the amplitude of the signal, and ω is the radial frequency. The relationship between radial frequency ω (expressed in radians/second) and frequency f (expressed in Hertz (1/sec).

$$\omega = 2\pi f$$

AC Circuit Theory and Representation of Complex Impedance Values

Ohm's law defines resistance in terms of the ratio between voltage E and current I.

$$R = \frac{E(t)}{I(t)}$$

The relationship is limited to only one circuit element -- the ideal resistor.
An ideal resistor has several simplifying properties:

Complex writing

$$\omega = 2\pi f \qquad E_t = E_0 \sin(\omega t) \qquad I_t = I_0 \sin(\omega t + \phi) \qquad Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}$$

Using Eulers relationship

$$\exp(j\phi) = \cos\phi + j\sin\phi$$

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,

$$I_t = I_0 \exp(j\omega t - \phi)$$

The impedance is then represented as a complex number,

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

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,

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

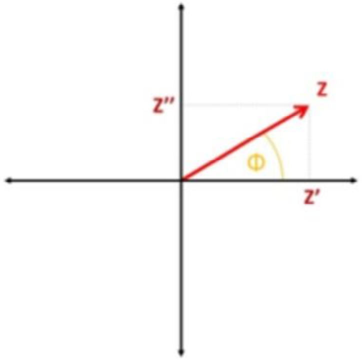
and the current response as,

$$I(t) = I_0 \exp(i\omega t - i\phi)$$

The impedance is then represented as a complex number,

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

Impedance Modulus

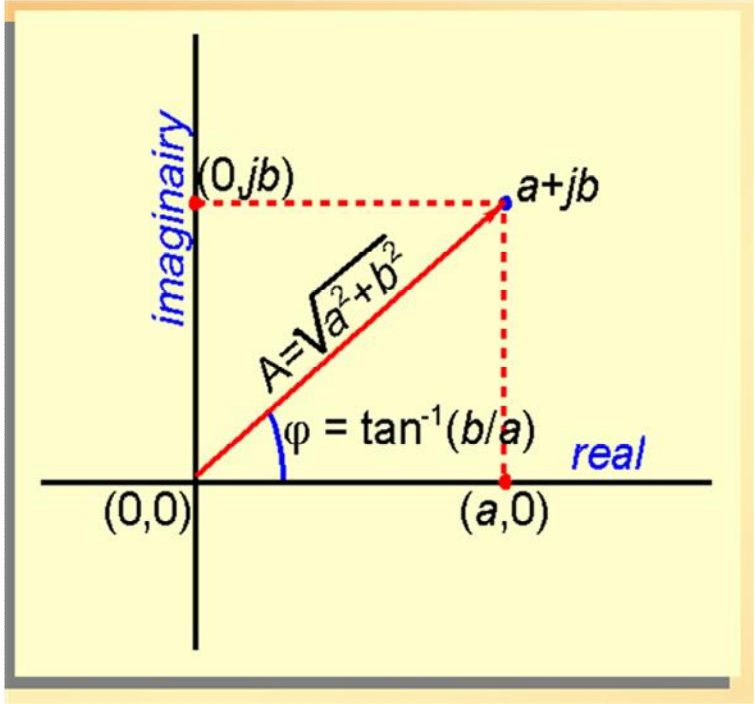


$$\hat{Z} = Z' + iZ''$$

$$|\hat{Z}| = \sqrt{Z'^2 + Z''^2}$$

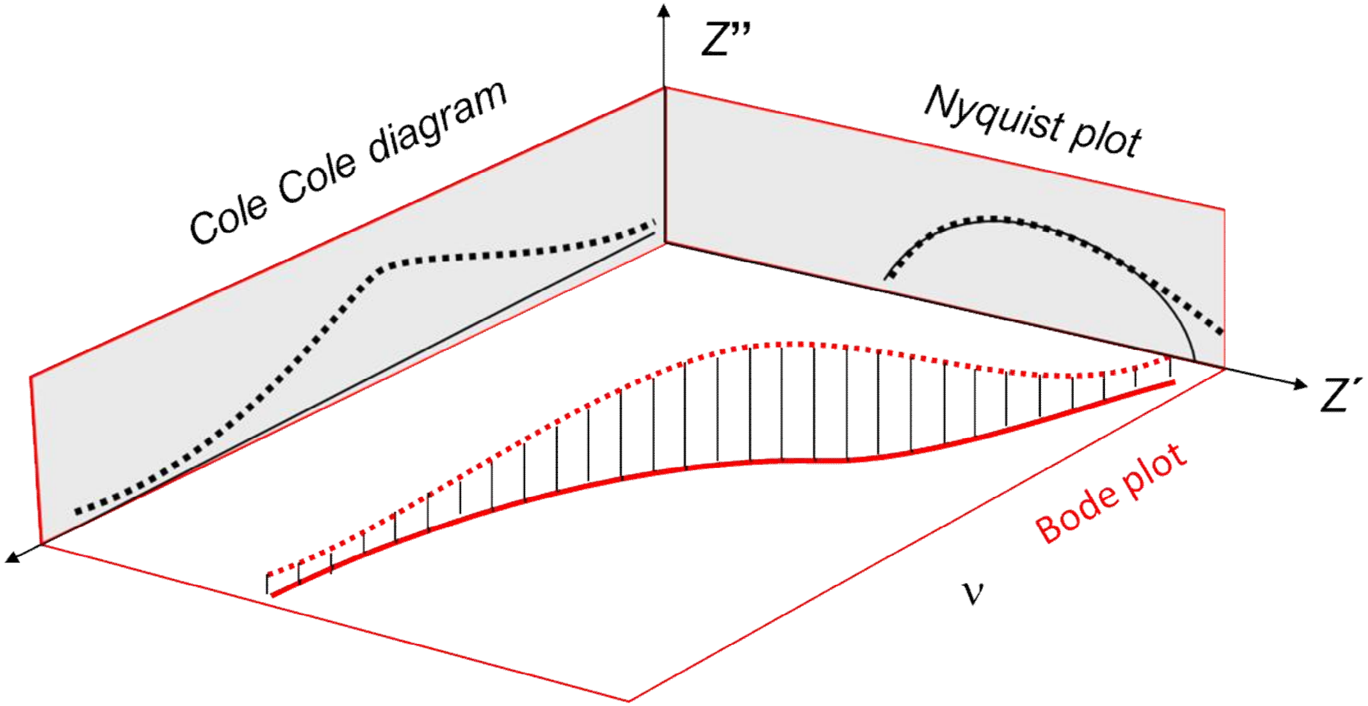
$$\tan\phi = \frac{Z''}{Z'}$$

Impedance Modulus



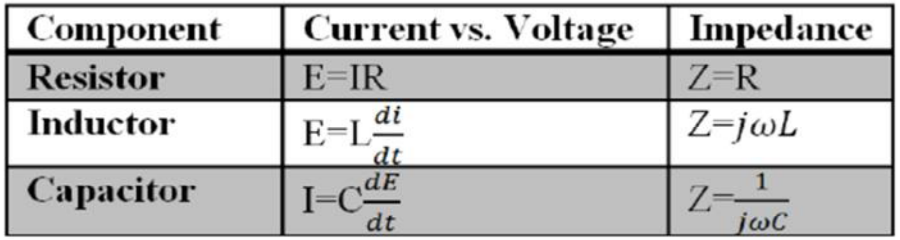
The different views on impedance data

The projection onto the Z“-Z‘ plane is called the Nyquist plot
The projection onto the Z ‘ -ν plane is called the Bode diagram
The projection onto the Z“-ν plane is called the Cole-Cole diagram



Electrical Circuit Elements

EIS data is commonly analyzed by fitting it to an equivalent electrical circuit model.



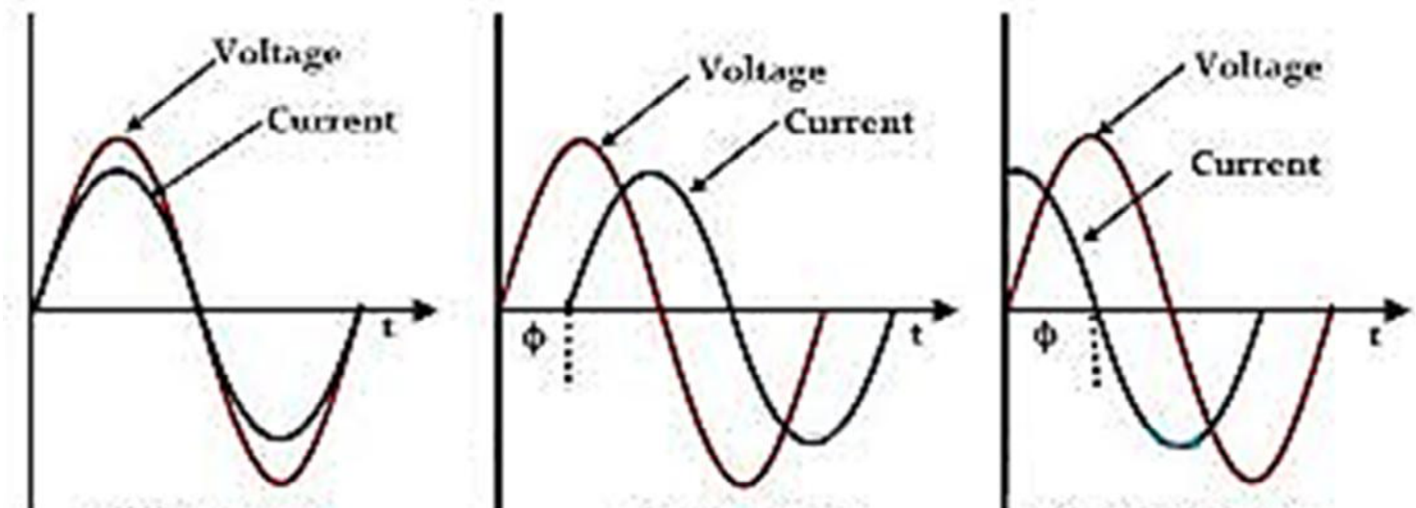
Component	Current vs. Voltage	Impedance
Resistor	E=IR	Z=R
Inductor	$E=L\frac{di}{dt}$	$Z=j\omega L$
Capacitor	$I=C\frac{dE}{dt}$	$Z=\frac{1}{j\omega C}$

- ✓ 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.

Electrical Circuit Elements



Resistive circuit
$\phi = 0$, Unity Power factor

Inductive circuit
Lagging Power factor

Capacitive circuit
Leading Power factor

Most utilized elements

1. The electrolyte resisatnce
2. Double layer capacitance
3. Polarization resistance
4. Charge transfer resistance
5. Diffusion: Warburg impedance
6. Coating capacitance

The electrolyte resisatnce

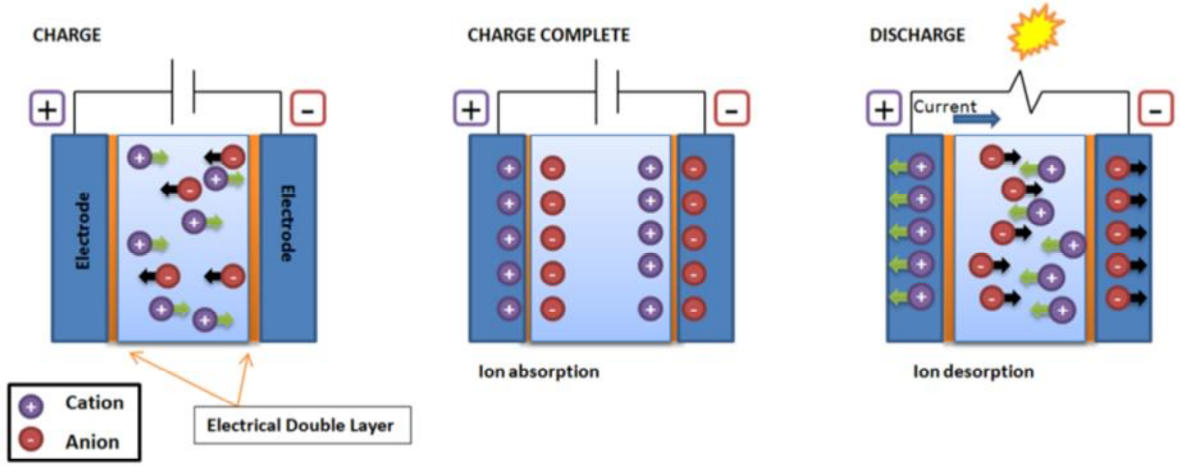
Standard chemical handbooks list σ values for specific solutions. For other solutions and solid materials, you can calculate σ from specific ion conductance. The units for σ are Siemens per meter (S/m). The Siemens is the reciprocal of the ohm, so 1 S = 1/ohm

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

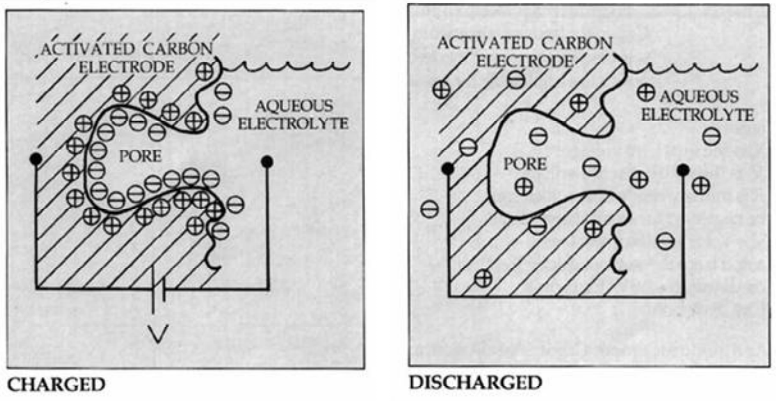
Double layer capacitance

- A electrical double layer exists at the interface between an electrode and its surrounding electrolyte.
- This double layer is formed as ions from the solution "stick on" the electrode surface. Charges in the electrode are separated from the charges of these ions. The separation is very small, on the order of angstroms.
- On a bare metal immersed in an electrolyte, you can estimate that there will be approximately 30 µF of capacitance for every cm^2 of electrode area.
- The value of the double layer capacitance depends on many variables including electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc.

Double layer capacitance



Principle of the Electric Double-Layer: Here C electrodes



Double layer

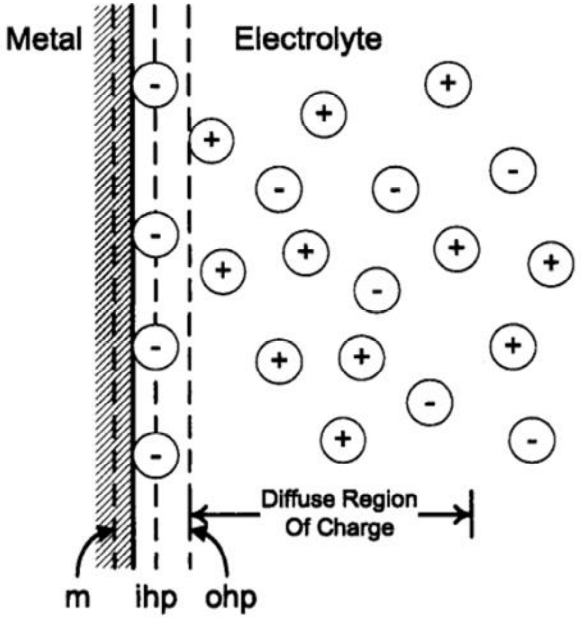


Figure 5.13: The structure of the electrical double layer.

Polarization resistance

Whenever the potential of an electrode is forced away from it's value at open circuit, that is referred to as polarizing the electrode.

When an electrode is polarized, it can cause current to flow via electrochemical reactions that occur at the electrode surface. The amount of current is controlled by the kinetics of the reactions and the diffusion of reactants both towards and away from the electrode.

Polarization Resistance

When there are two simple, kinetically controlled reactions occurring, the potential of the cell is related to the current by the following (known as the Butler-Volmer equation).

$$I = I_{corr}\left(10^{\frac{(E-Eoc)}{\beta a}} - 10^{\frac{-(E-Eoc)}{\beta c}}\right)$$

I is the measured cell current in amps,
I_{corr} is the corrosion current in amps,
E_{oc} is the open circuit potential in volts,
β_a is the anodic Beta coefficient in volts/decade,
β_c is the cathodic Beta coefficient in volts/decade

If E-E_{oc} is small

$$I_{corr} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} . \left(\frac{1}{R_p}\right)$$

Charge transfer resistance

Consider a metal substrate in contact with an electrolyte. The metal molecules can electrolytically dissolve into the electrolyte, according to:

$$Me \Leftrightarrow Me^{n+} + ne^{-}$$

In the forward reaction in the first equation, electrons enter the metal and metal ions diffuse into the electrolyte. Charge is being transferred.
This charge transfer reaction has a certain speed. The speed depends on the kind of reaction, the temperature, the concentration of the reaction products and the potential.
The general relation between the potential and the current holds:

$$i = i_0 \left[\frac{C_o}{C_o^*} e^{\left(\frac{\alpha n F \eta}{RT}\right)} - \frac{C_R}{C_R^*} e^{\frac{-(1-\alpha) n F \eta}{RT}} \right]$$

i_o = *exchange current density*
C_o = *concentration of oxidant at the electrode surface*
C_o^* = *concentration of oxidant in the bulk*
C_R = *concentration of reductant at the electrode surface*

F = *Faradays constant*
T = *temperature*
R = *gas constant*
α = *reaction order*
n = *number of electrons involved*
η = *over potential* $(E - E_0)$

Diffusion: Warburg impedance with **in**finite 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

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

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:

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

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 before. Instead, we get the form:

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

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.

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	2.5-10

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

Constant Phase Element (for double layer capacity)

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 $\alpha = 1$. 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.

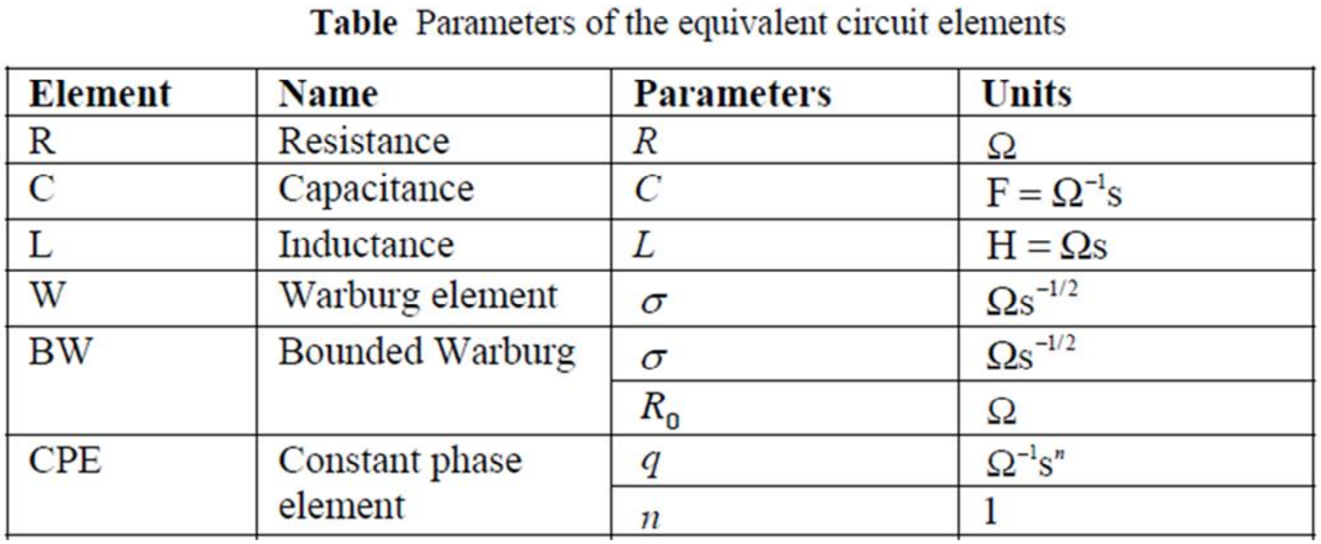


Table Parameters of the equivalent circuit elements

Element	**Name**	**Parameters**	**Units**
R	Resistance	R	Ω
C	Capacitance	C	$\mathrm{F} = \Omega^{-1}\mathrm{s}$
L	Inductance	L	$\mathrm{H} = \Omega\mathrm{s}$
W	Warburg element	σ	$\Omega\mathrm{s}^{-1/2}$
BW	Bounded Warburg	σ	$\Omega\mathrm{s}^{-1/2}$
		R_0	Ω
CPE	Constant phase element	q	$\Omega^{-1}\mathrm{s}^{n}$
		n	1

Inductance

The inductance is usually represented as a coil in which current induces an electromotive force that opposes a change in current. The potential difference developed at the inductance is

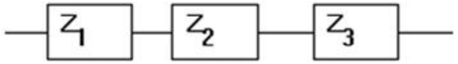
$$V(t) = L\frac{\mathrm{d}i(t)}{\mathrm{d}t}$$

where L is the inductance in henrys, H.

Serial and parallel combinations of circuit elements

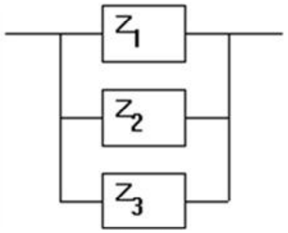
Very few electrochemical cells can be modeled using a single equivalent circuit element. Instead, EIS models usually consist of a number of elements in a network. Both serial and parallel combinations of elements occur.

Impedances in Series:



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

Impedances in Parallel



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

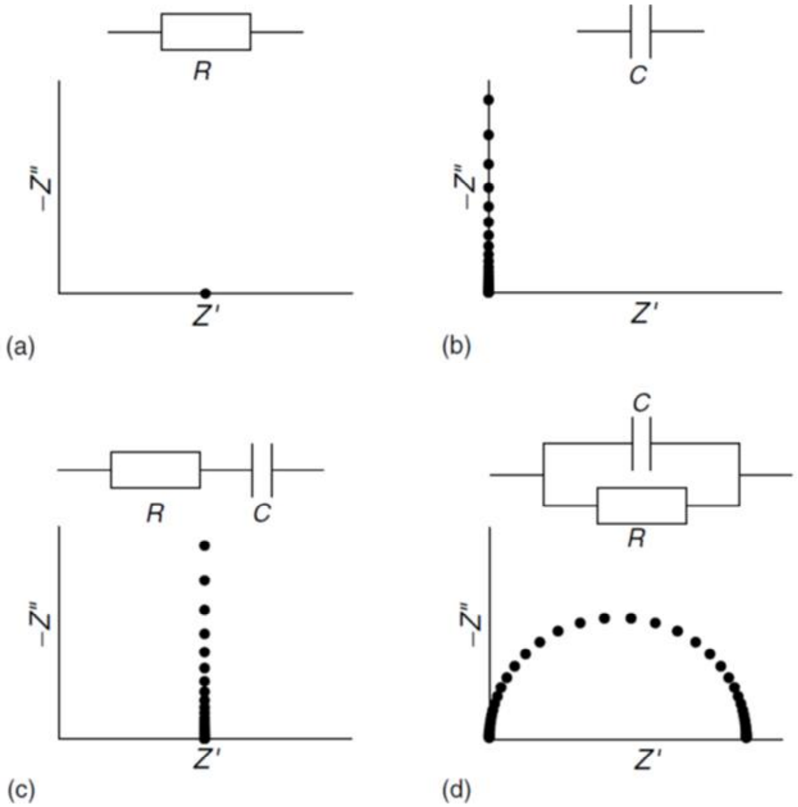


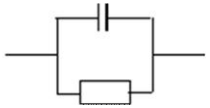
Fig. 3 Nyquist plots for different equivalent circuits.

Data Presentation

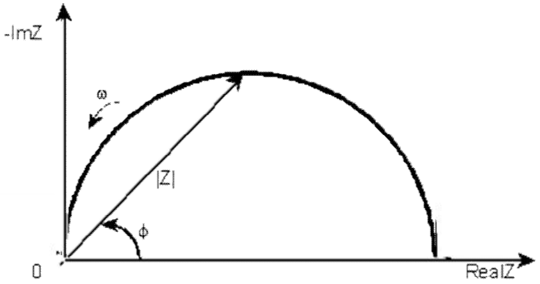
Nyquist Plot with Impedance Vector

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

- On the Nyquist plot the impedance can be represented as a vector of length */Z/.* The angle between this vector and the x-axis is *f.*
- Nyquist plots have one major shortcoming. When you look at any data point on the plot, you cannot tell what frequency was used to record that point.
- Low frequency data are on the right side of the plot and higher frequencies are on the left. This is true for *EIS* data where impedance usually falls as frequency rises (this is not true of all circuits).



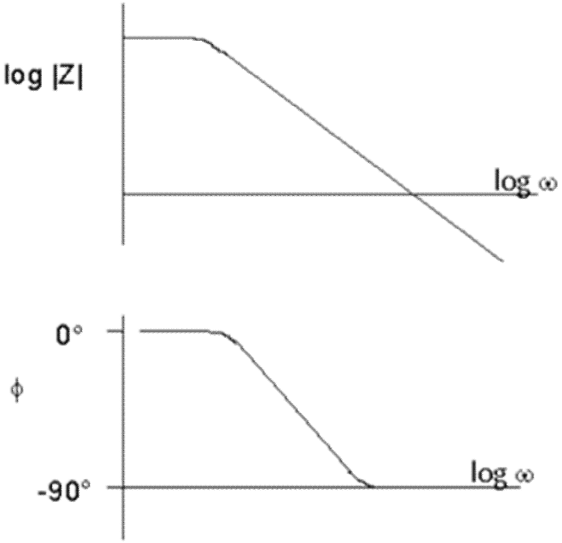
$$\frac{1}{Z} = \frac{1}{R} + \frac{1}{i\omega C}$$



The Bode plot

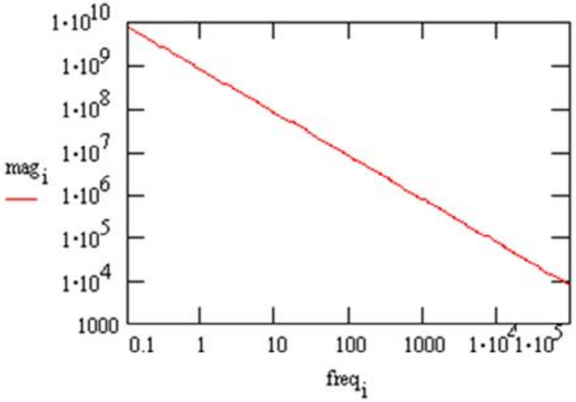
The impedance is plotted with log frequency on the x-axis and both the absolute value of the impedance ($|Z| = Z_0$) and phase-shift on the y-axis.

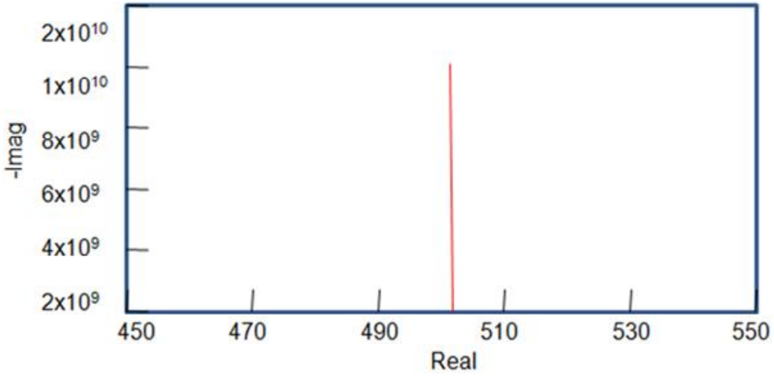
Unlike the Nyquist plot, the Bode plot explicitly shows frequency information.

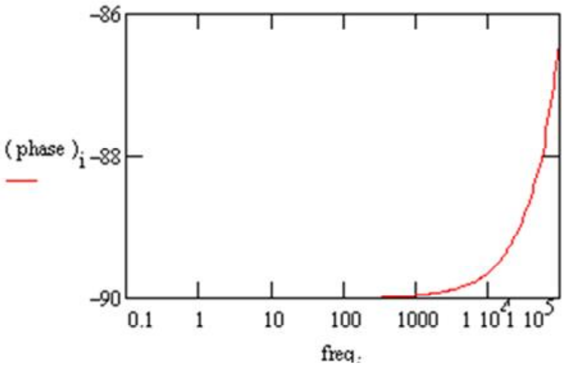


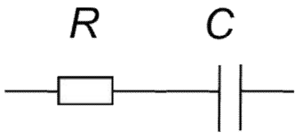
A purely capacitive coating

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

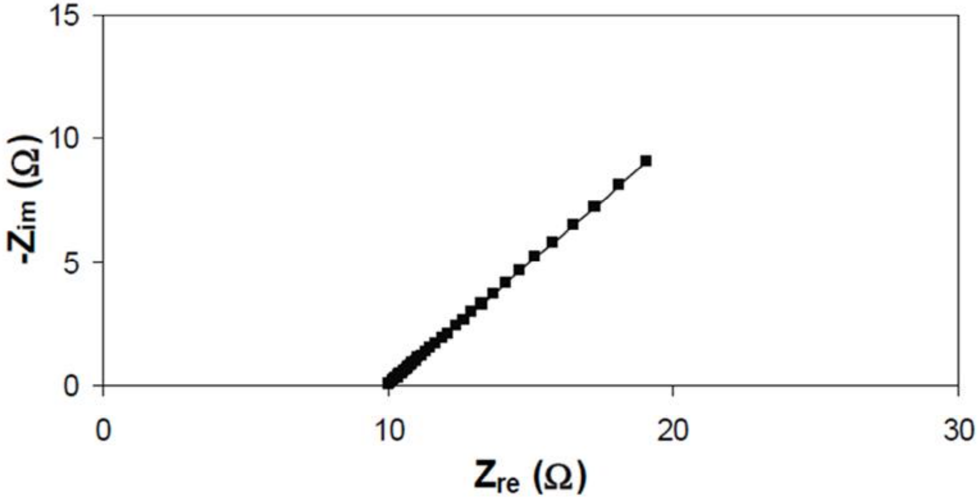




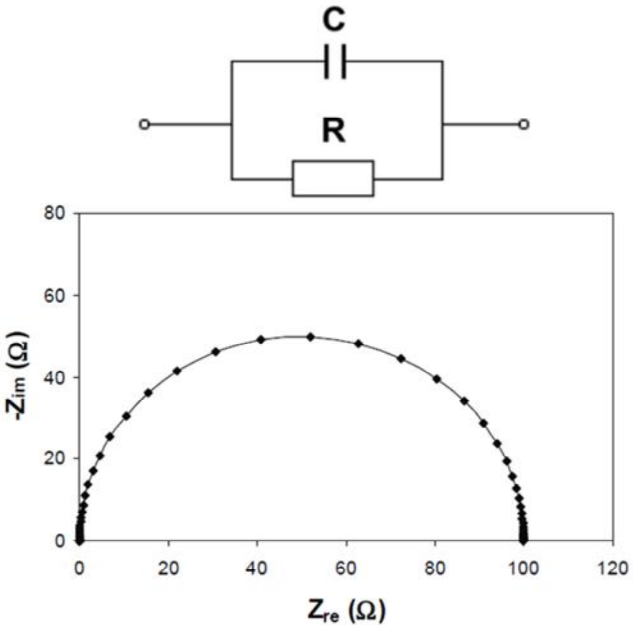


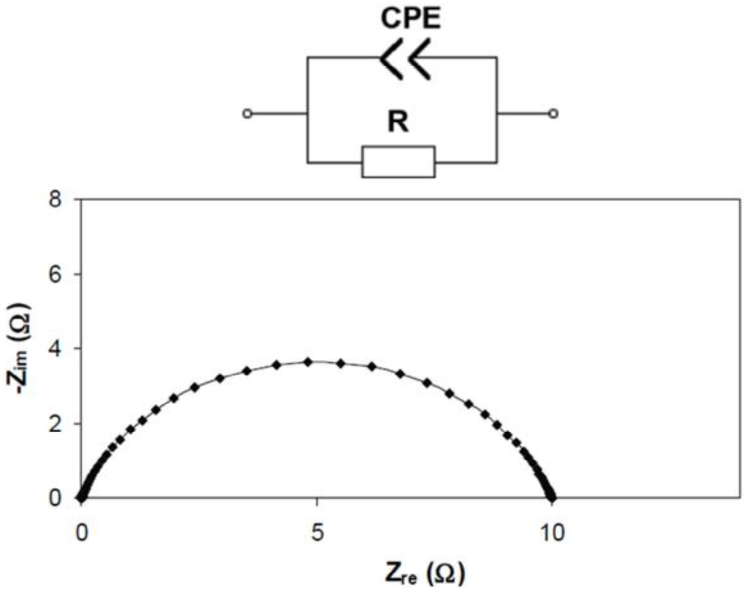


Resistance and CPE

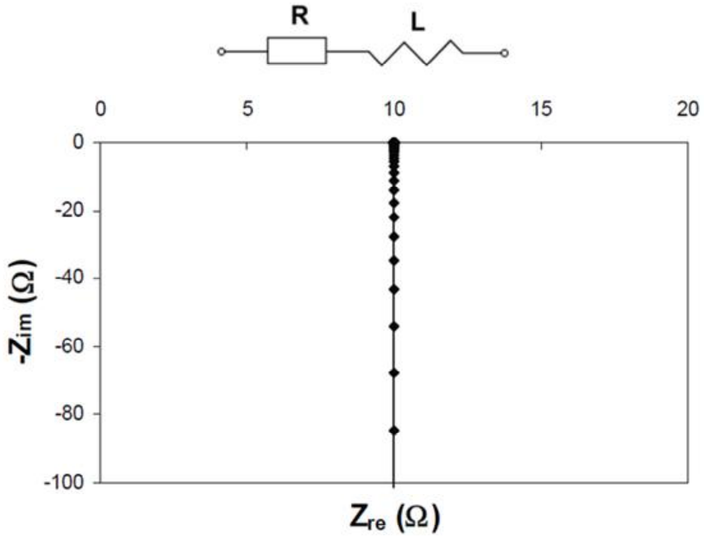


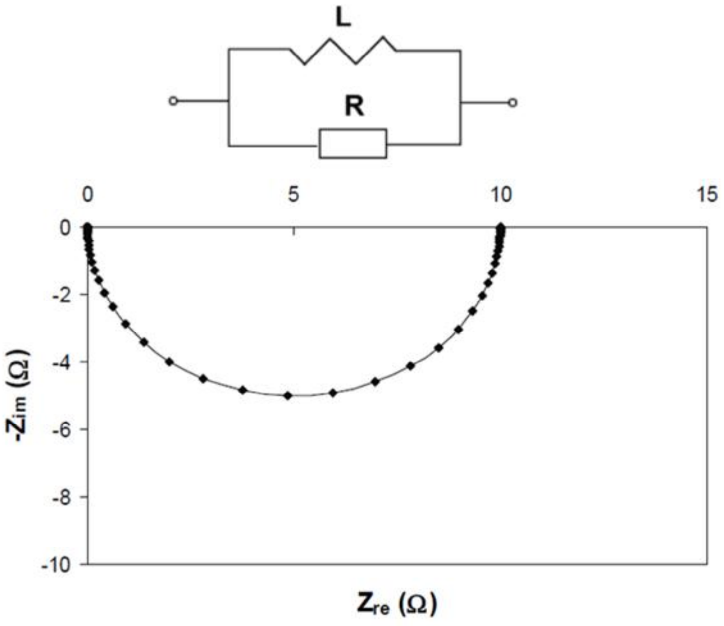
Resistor and CPE (capacitor) in parallel



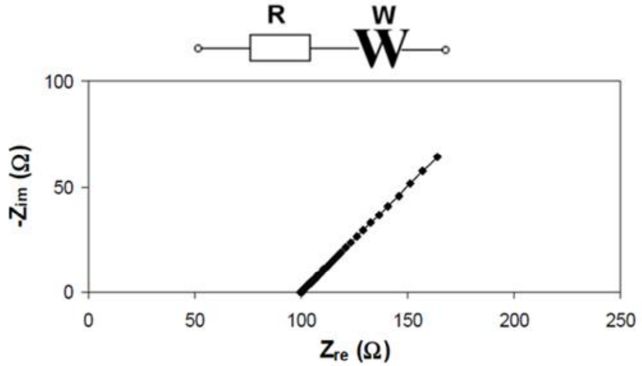


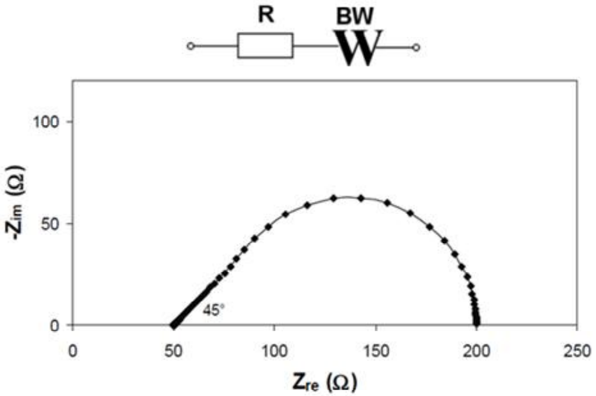
RL in Series and RL in Parallel

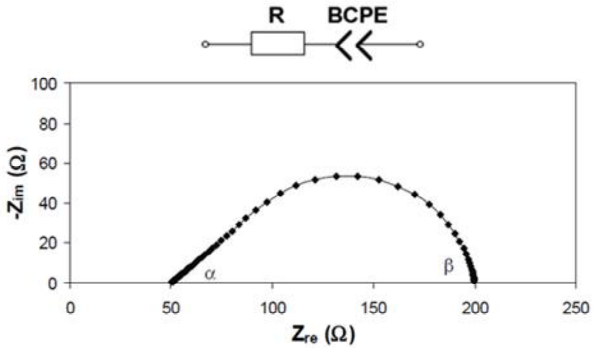




Resistor and Warburg element in series
Resistor and bounded Warburg in series



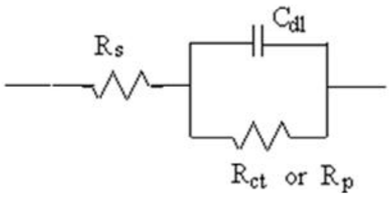


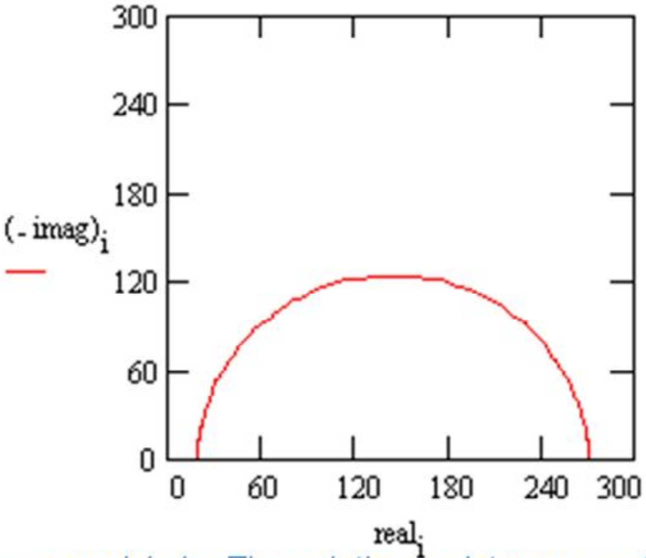


Resistor and bounded CPE in series

Randles cell

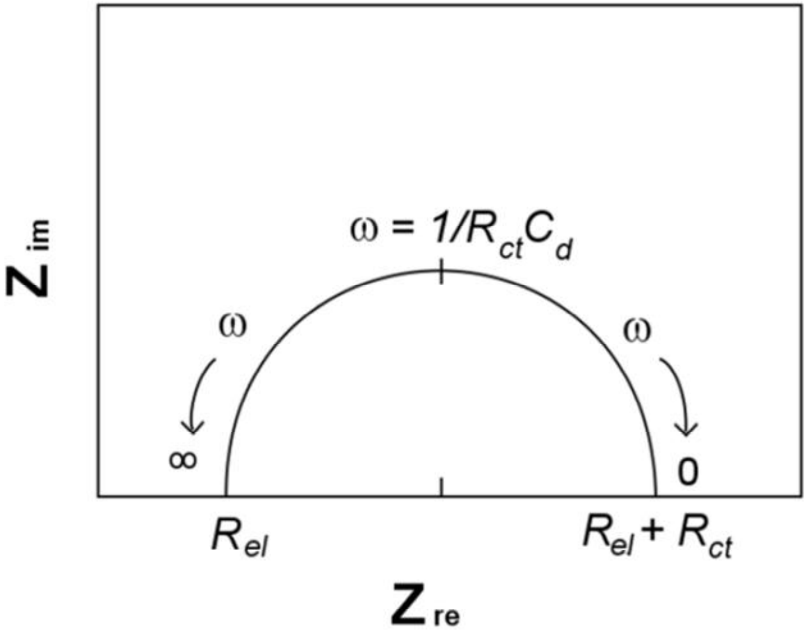
The Randles cell is one of the simplest and most common cell models. It includes a solution resistance, a double layer capacitor and a charge transfer or polarization resistance.
The double layer capacity is in parallel with the impedance due to the charge transfer reaction





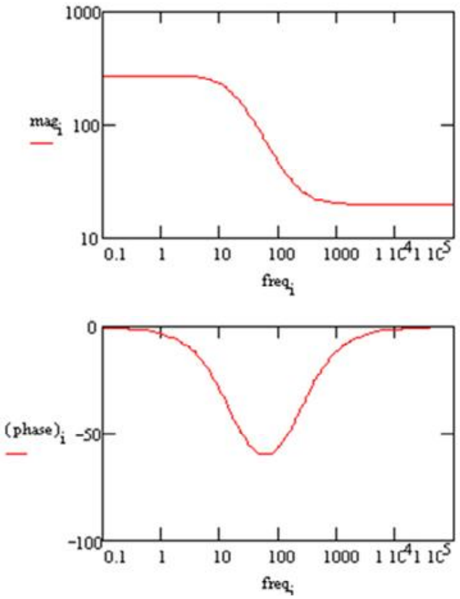
The Nyquist plot for a Randles cell is always a semicircle. The solution resistance can found by reading the real axis value at the high frequency intercept. This is the intercept near the origin of the plot. Remember this plot was generated assuming that R_s = 20 Ω and Rp= 250 Ω. The diameter of the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

Randles cell

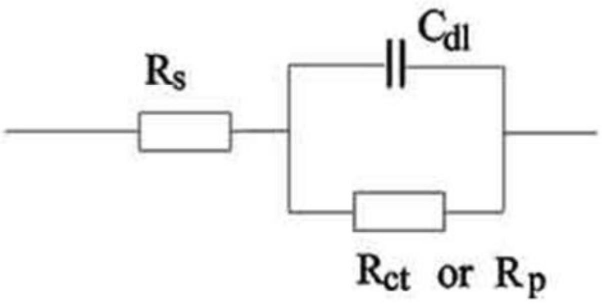


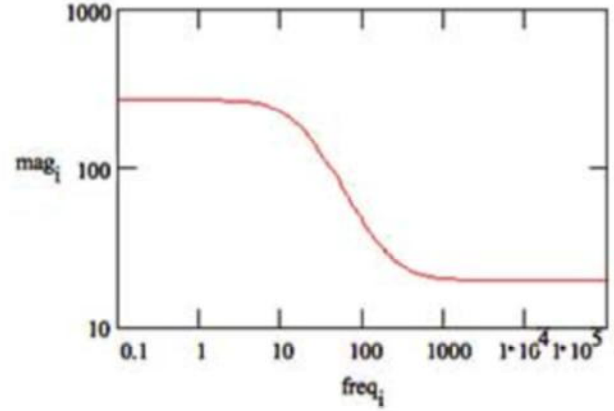
Bode plot of Randalls cell

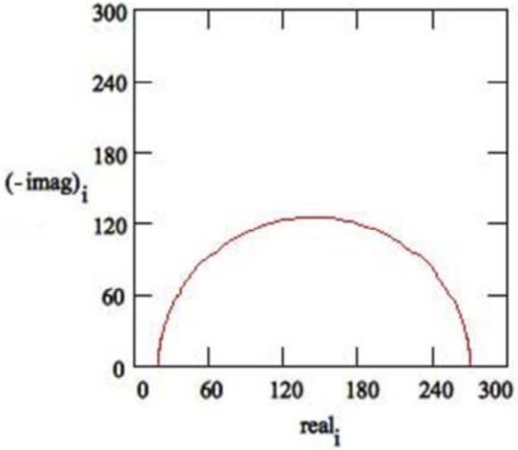
This Figure is the Bode plot for the same cell. The solution resistance and the sum of the solution resistance and the polarization resistance can be read from the magnitude plot. The phase angle does not reach 90° as it would for a pure capacitive impedance. If the values for R_s and R_p were more widely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

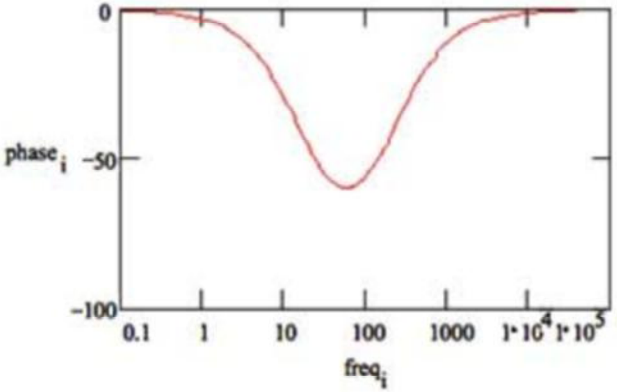


Randles cell

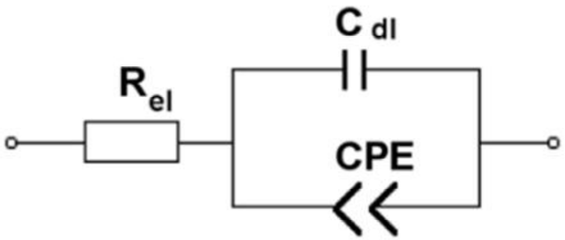


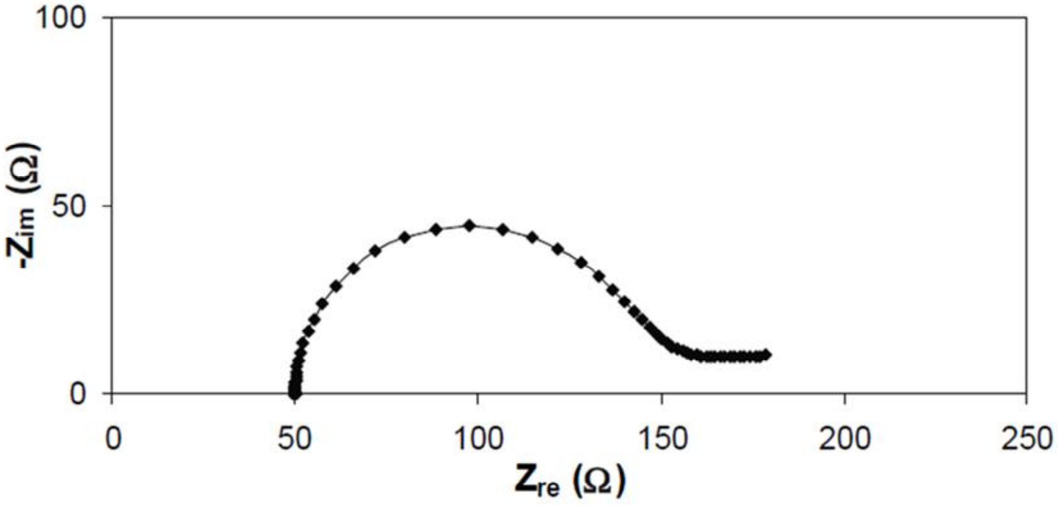




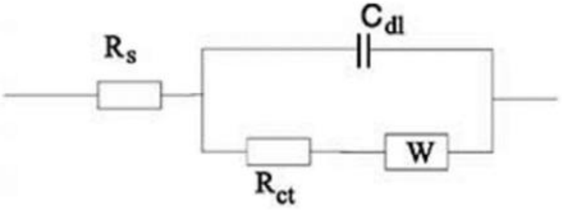


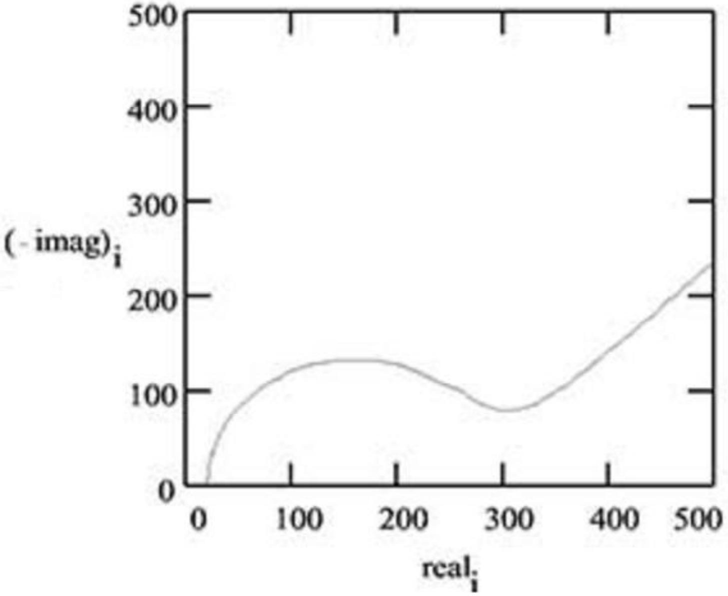
Randles cell with R_{ct} replaced by CPE

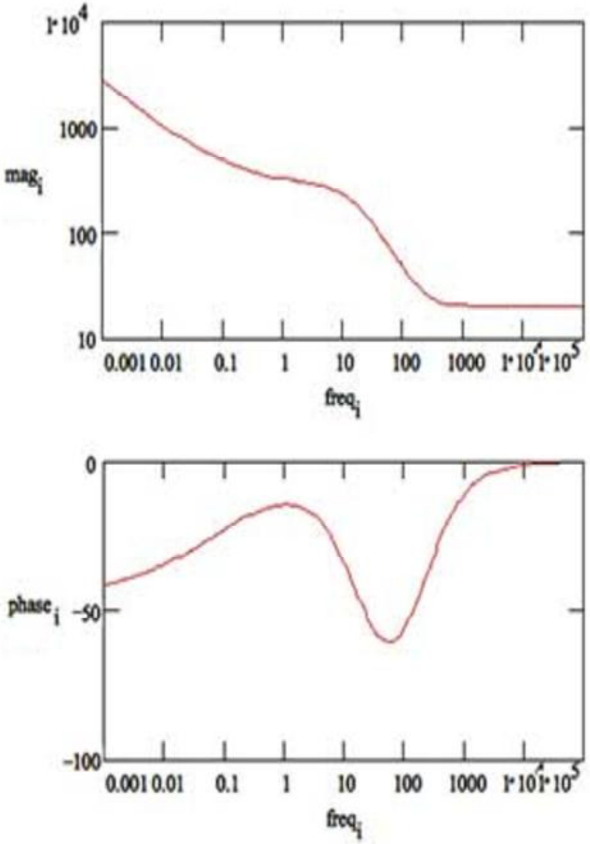




Mixed kinetic and diffusion control







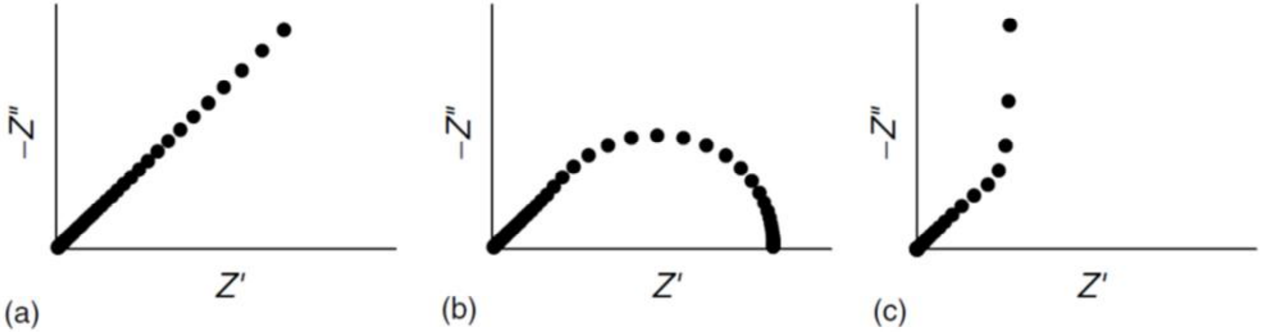
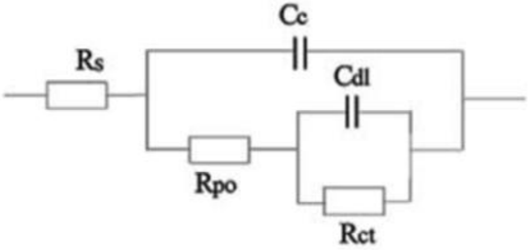
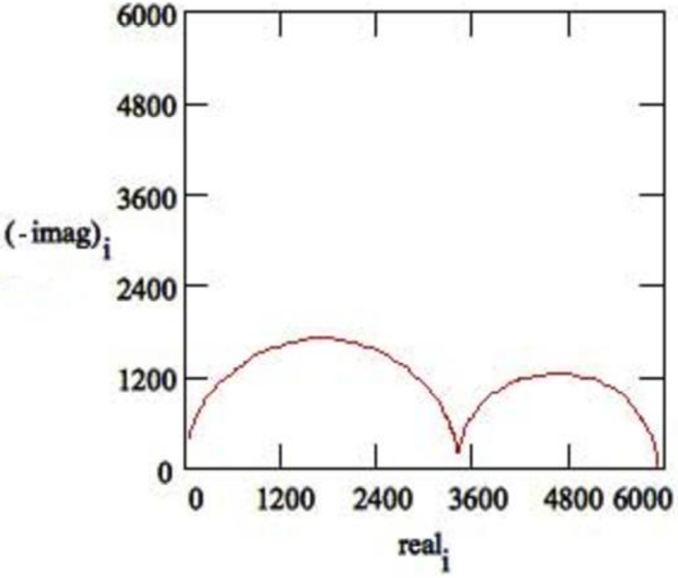
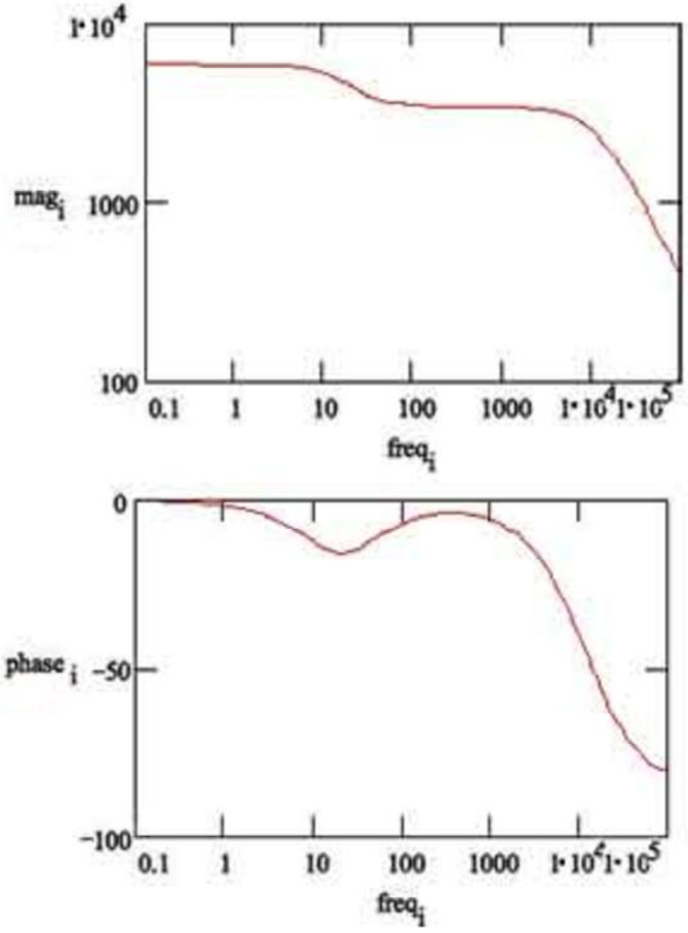


Fig. 9 Impedance spectra for diffusion-limited behavior (a) semi-infinite diffusion; (b) finite diffusion with unhindered ion transfer at the far end of the diffusion region; and (c) finite diffusion with blocked ion transfer at the far end of the diffusion layer.

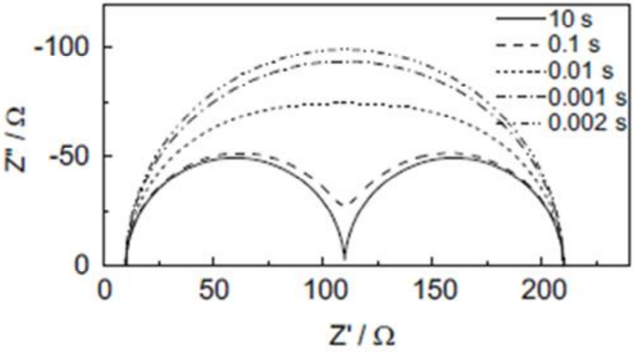
Coatings or corrosion products

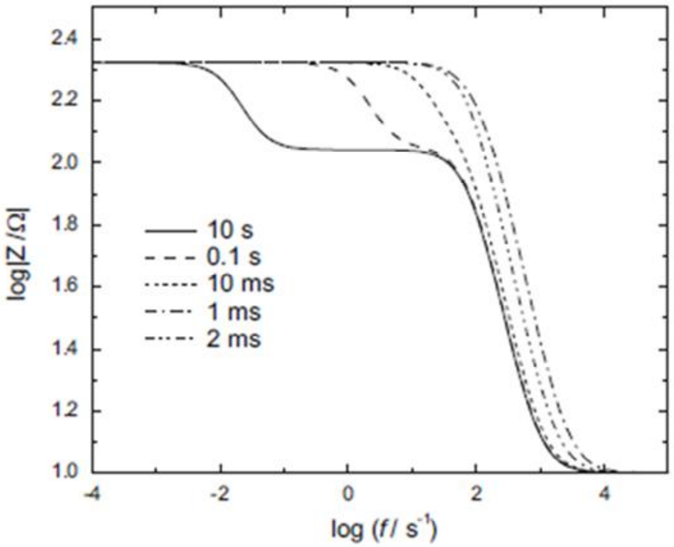


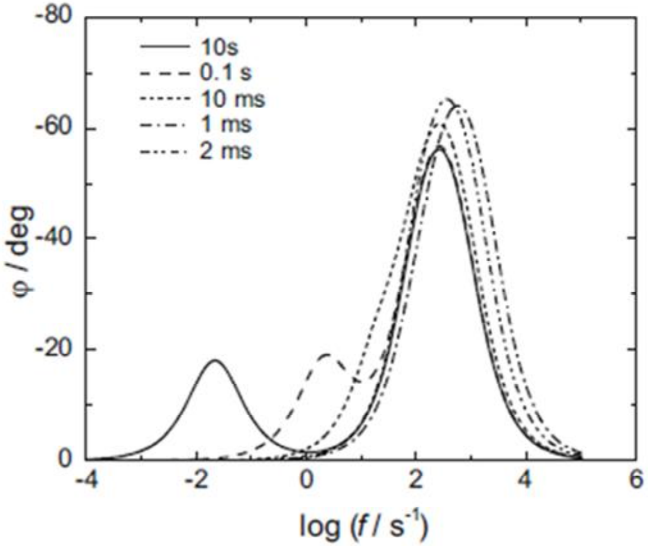




Coatings or corrosion products







Other circuits

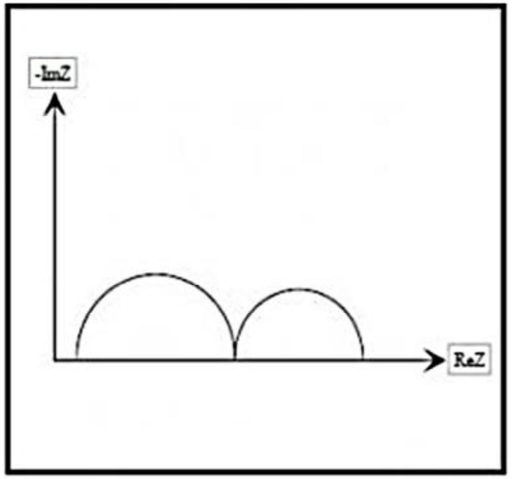


Figure Two Time Constant Spectrum

This spectrum can be modeled by any of the equivalent circuits shown

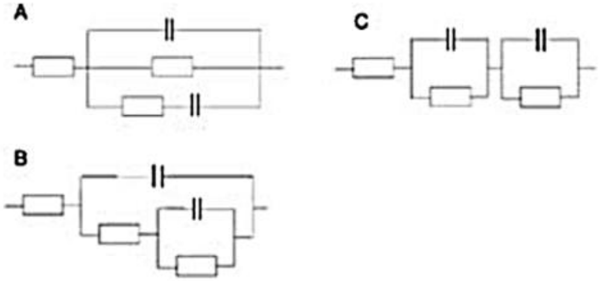


Figure Equivalent Circuit Models with Two Time Constants

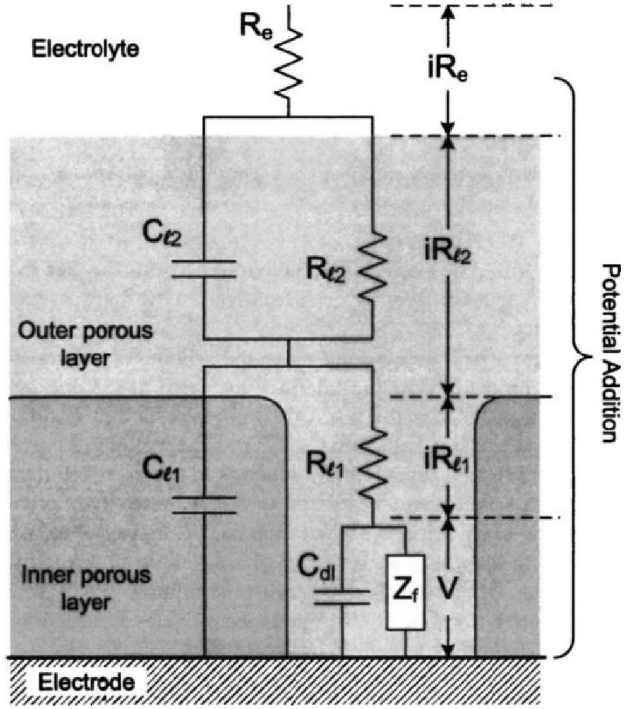
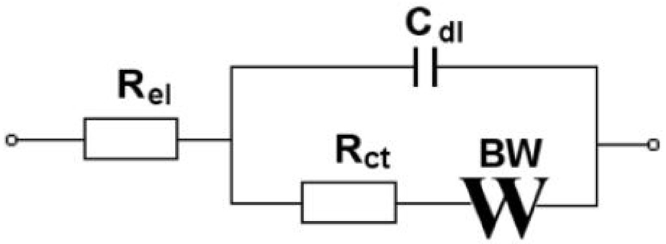
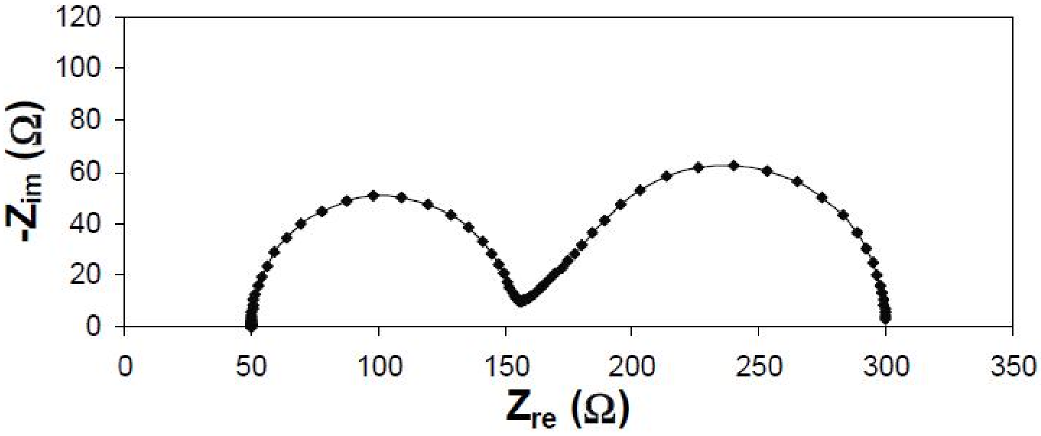


Figure 9.5: Equivalent electrical circuit of the impedance for a electrode coated by two superimposed porous layers.



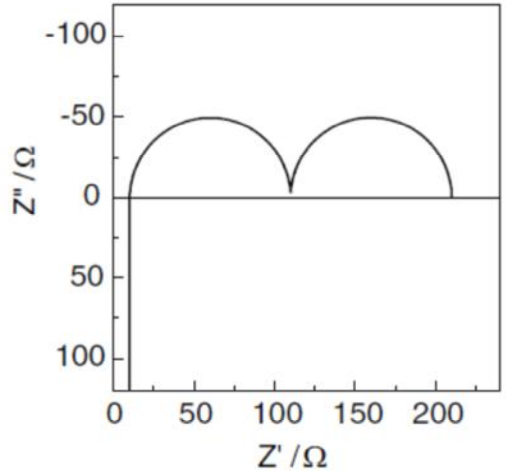
a

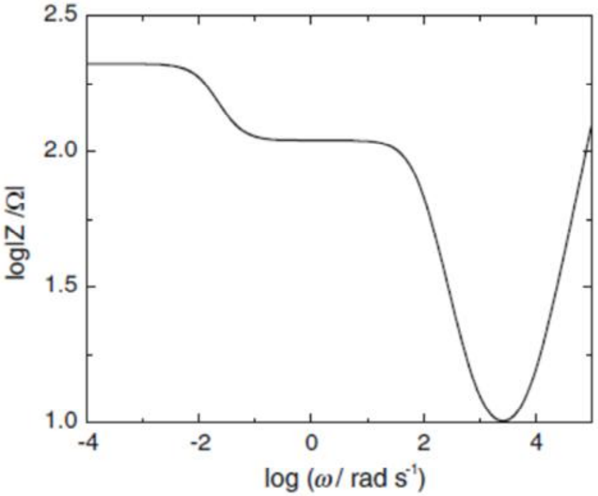


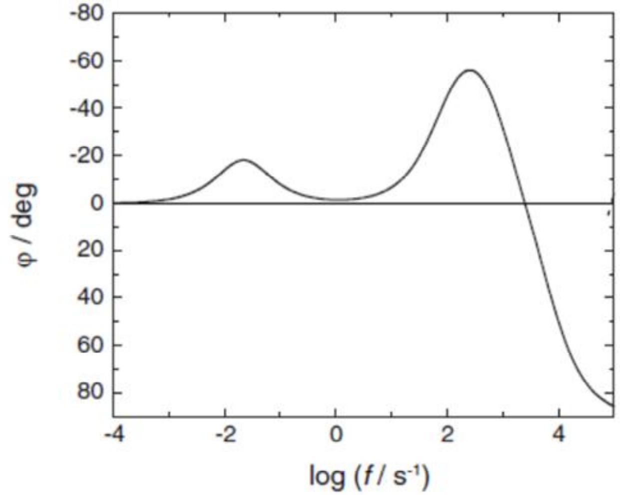
b

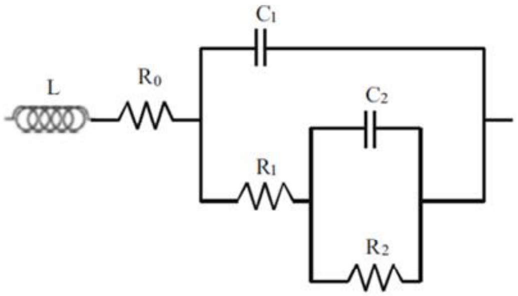
Figure 4.18. *a* Modified Randles cell having a bounded Warburg in series with R_{ct} (Model D17); *b* Nyquist plot of modified Randles cell having a bounded Warburg element in series with R_{ct}, over the frequency range 1 MHz to 1 mHz (Model D17: $R_{el} = 50\ \Omega$, $R_{ct} = 100\ \Omega$, $C_{dl} = 0.00001$ F, $\sigma = 50\ \Omega s^{-1/2}$, $R_0 = 150\ \Omega$)

Other circuits

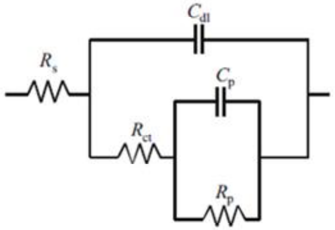


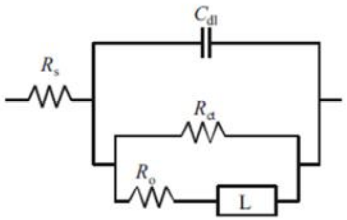


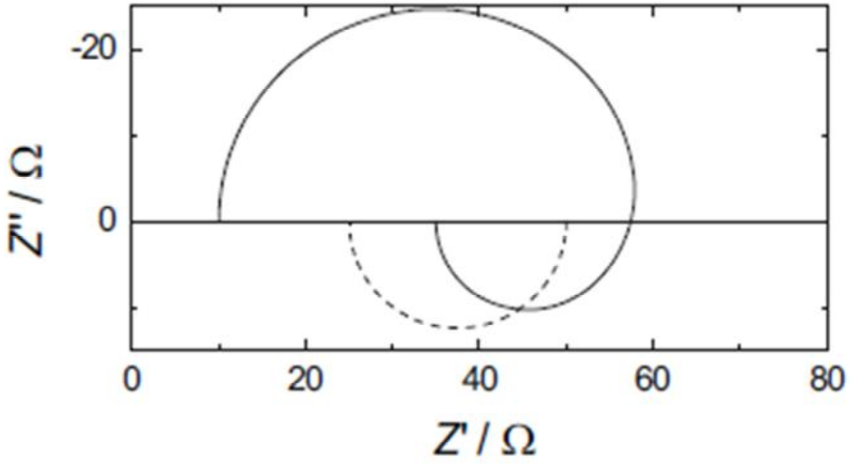




Other circuits

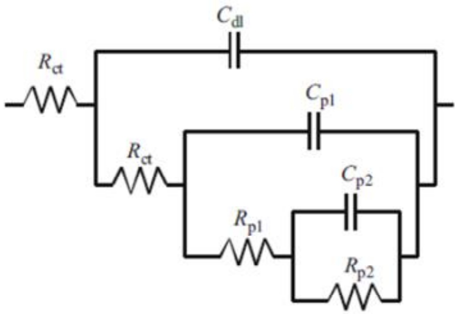


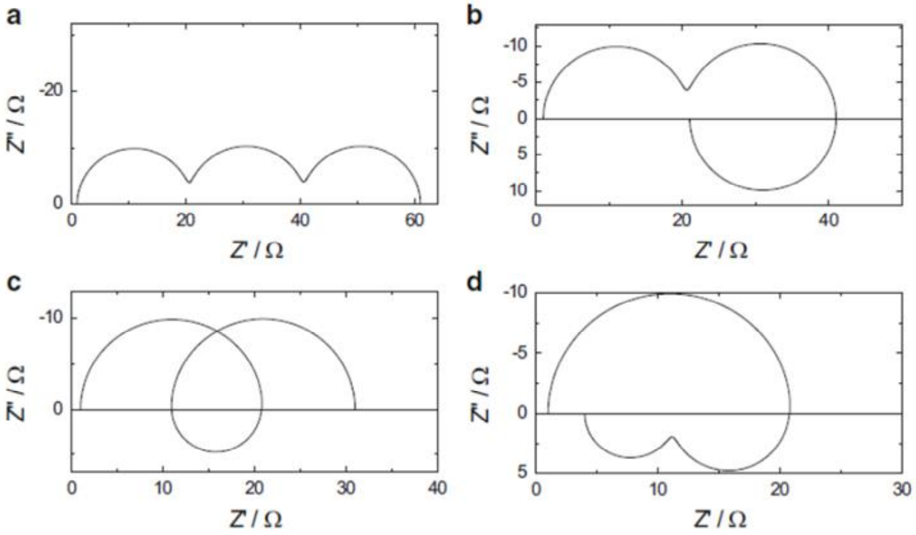




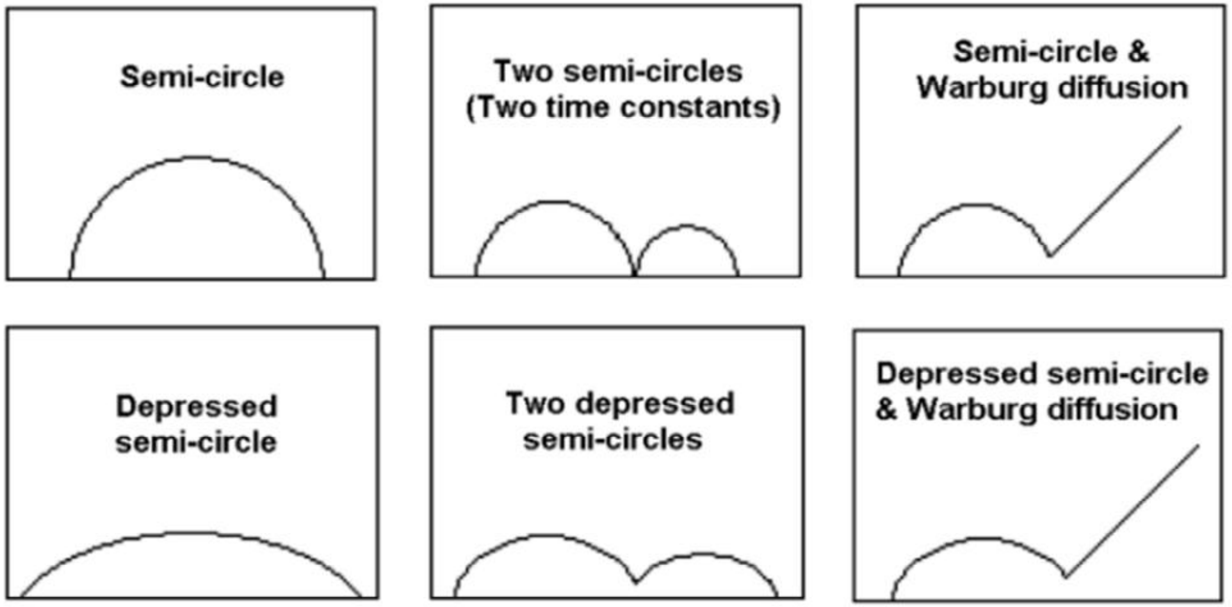
Other circuits

Example of
electrical equivalent circuit
obtained in case of two
adsorbed species





Examples of complex plane plots obtained in presence of two adsorbed species assuming the following parameters: $R_s = 1\ \Omega$, $C_{dl} = 20\ \mu F$, $R_{ct} = 20\ \Omega$; **(a)** $R_{p1} = R_{p2} = 20\ \Omega$, $C_{p1} = 0.02$ F, $C_{p2} = 2$ F; **(b)** $R_{p1} = 20\ \Omega$, $R_{p2} = -20\ \Omega$, $C_{p1} = 0.02$ F, $C_{p2} = -2$ F; **(c)** $R_{p1} = -10\ \Omega$, $R_{p2} = 20\ \Omega$, $C_{p1} = -0.02$ F,$C_{p2} = 2$ F; **(d)** $R_{p1} = -10\ \Omega$, $R_{p2} = -7\ \Omega$, $C_{p1} = -0.02$ F, $C_{p2} = -2$ F



Typical Nyquist plots for electrochemical systems

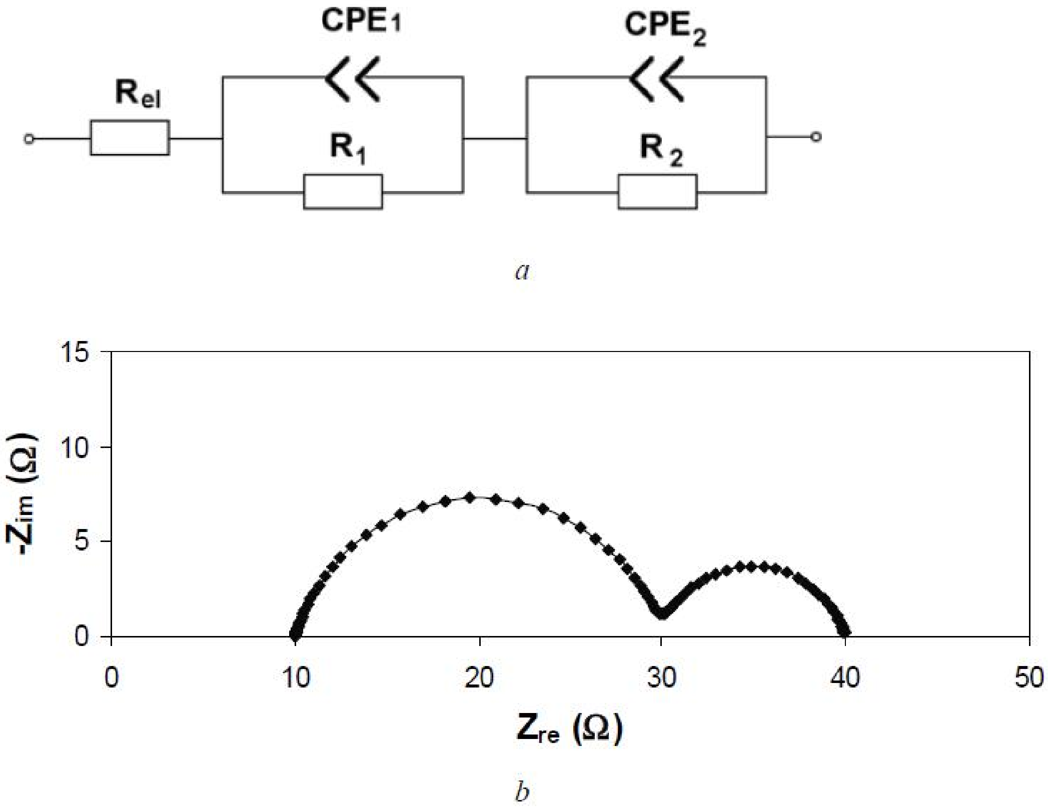
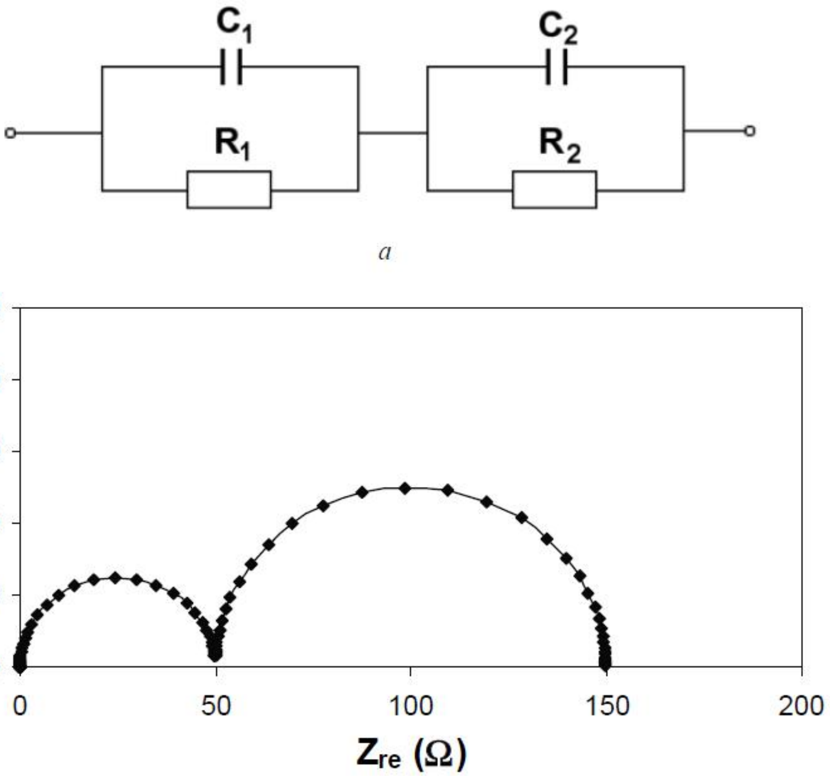


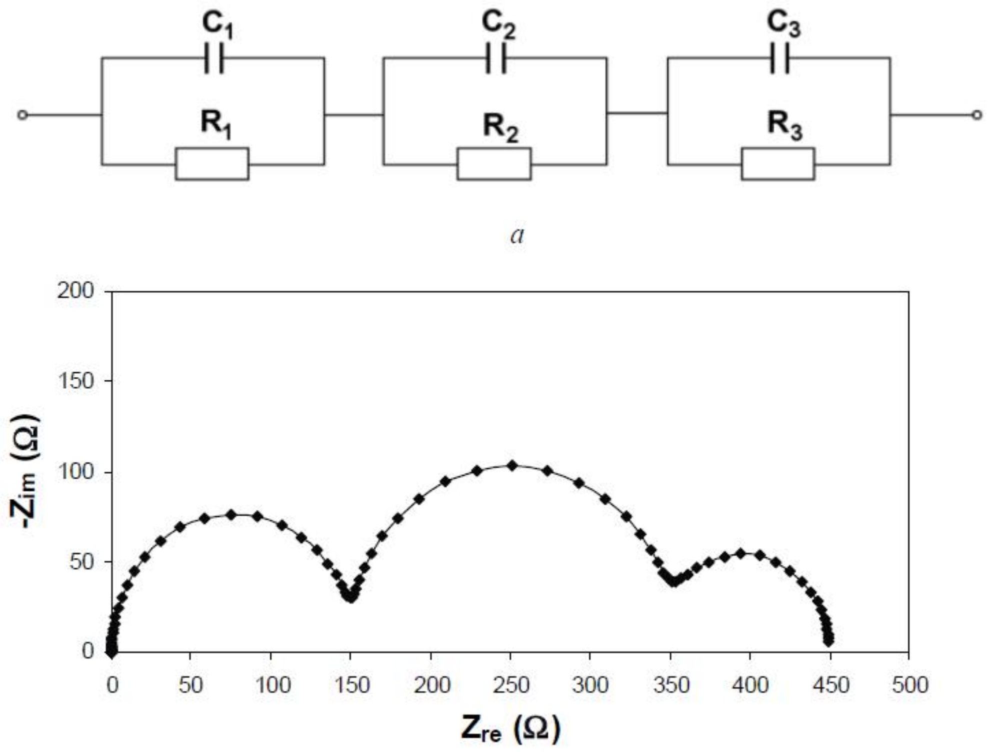
Figure 4.29. *a* Resistor and Voigt structure in series, with capacitors replaced by CPE (Model D25); *b* Nyquist plot of the modified Voigt structure over the frequency range 1 MHz to 1 mHz (Model D25: $R_{el} = 10\ \Omega$, $R_1 = 20\ \Omega$, $R_2 = 10\ \Omega$, $Q_1 = 0.0001\ \Omega^{-1}s^{0.8}$, $Q_2 = 0.1\ \Omega^{-1}s^{0.8}$, $n_1 = 0.8$, $n_2 = 0.8$)



a

b

Figure 4.24. *a* Voigt structure with two RC in series (Model D21); *b* Nyquist plot of Voigt structure with two RC in series, over the frequency range 1 MHz to 1 mHz (Model D21: $R_1 = 50\ \Omega$, $R_2 = 100\ \Omega$, $C_1 = 0.00001$ F, $C_2 = 0.01$ F)



a

b

Figure 4.25. *a* Voigt structure with three RC in series (Model D22); *b* Nyquist plot of Voigt structure with three RC in series, over the frequency range 1 MHz to 1 mHz (Model D22: $R_1 = 150\ \Omega$, $R_2 = 200\ \Omega$, $R_3 = 100\ \Omega$, $C_1 = 0.00001$ F, $C_2 = 0.001$ F, $C_3 = 0.1$ F)

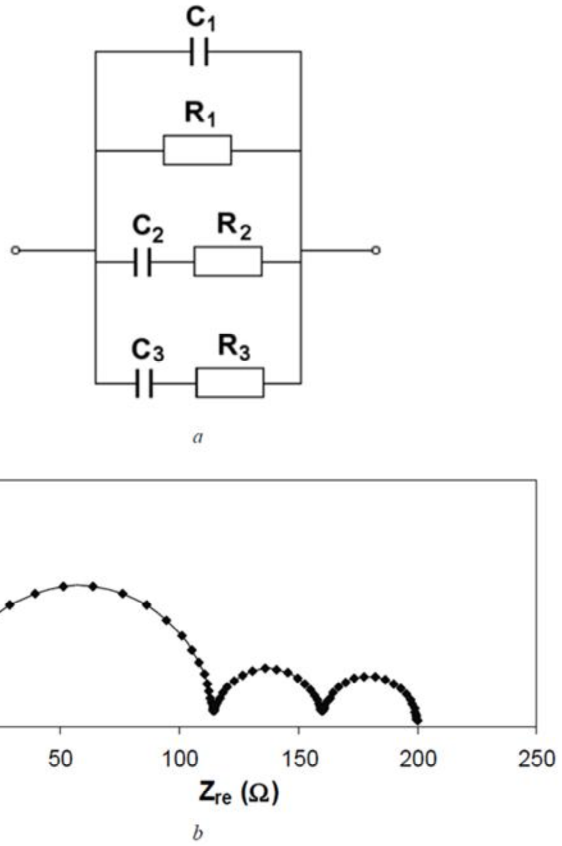


Figure 4.22. *a* Simple example of Maxwell's structure with two parallel processes (Model D20); *b* Nyquist plot of a simple Maxwell structure over the frequency range 1 MHz to 1 mHz (Model D20: $R_1 = 200\ \Omega$, $C_1 = 0.000001$ F, $R_2 = 400\ \Omega$, $C_2 = 0.0001$ F, $R_3 = 800\ \Omega$, $C_3 = 0.01$ F)

Most of the material displayed in this lecture is taken from:
http://www.gamry.com/App_Notes/EIS_Primer/EIS_Primer.htm