ELECTROCHEMICAL CORROSION

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Types of corrosion

Uniform corrosion is characterized by corrosive attack proceeding evenly over the **entire surface** area, or a large fraction of the area of the metal under attack. Uniform corrosion results in loss of material until failure (most widespread form of corrosion

Pitting Corrosion is considered to be **more dangerous** than uniform corrosion damage because it is more difficult to predict and design against. Corrosion products often cover the pits making the detection often very difficult.

Crevice Corrosion occurs in the presence of stagnant solution **in a small (micro) crevice**. Local chemistry changes in crevices (*shielded areas*) such as those formed under gaskets, washers, insulation material, fastener heads, surface deposits, unbonded coatings, threads, lap joints and clamps, can result in crevice corrosion.

Types of corrosion

Galvanic Corrosion

refers to corrosion damage induced when two dissimilar materials are coupled in a corrosive electrolyte (into electrical contact under water) - one of the metals in the couple becomes the **anode** and corrodes **faster** than it would all by itself, while the other becomes the **cathode** and corrodes **slower** than it would alone. Either (or both) metal in the couple may or may not corrode by itself (themselves) in seawater.
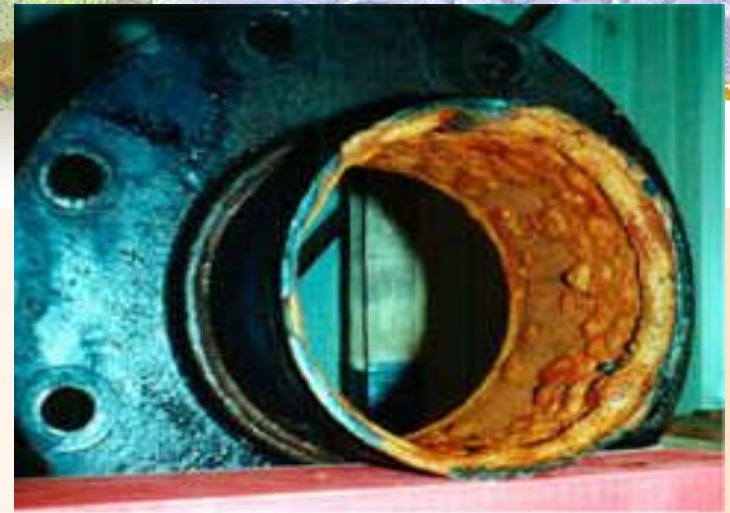
Microbiologically Induced Corrosion *(MIC)* refers to corrosion caused by **biological organisms or microbes**. These microbes are categorized by common characteristics such as their by-products (i.e., sludge producing) or compounds they effect (i.e. sulfur oxidizing). They all fall into one of two groups based upon their oxygen requirements; one being **aerobic (requires oxygen)** such as sulfur oxidizing bacteria, and the other being **anaerobic, (requires little or no oxygen),** such as sulfate reducing bacteria.
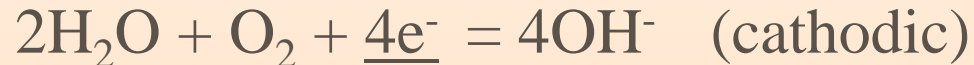
The process of corrosion of metals

➢ **deterioration** or **degradation** of metal

➢ the formation of **rust** on steel

➢ most corrosion phenomena are of **electrochemical nature**

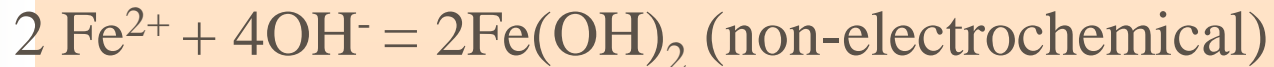➢ consist of at least **two reactions** on the surface of the corroding metal

1) the oxidation (*e.g.*, dissolution of iron)

$$Fe = Fe^{2+} + \underline{2e^-} \qquad \text{(anodic)}$$

2) the reduction (*e.g.*, reduction of oxygen)

$$2H_2O + O_2 + \underline{4e^-} = 4OH^- \quad \text{(cathodic)}$$

1) and 2) :

$$\mathbf{2Fe + 2H_2O + O_2 = 2Fe(OH)_2}$$

$$2\,Fe^{2+} + 4OH^- = 2Fe(OH)_2 \text{ (non-electrochemical)}$$

Electrochemical characterisation

LSV
- Linear sweep voltammetry

EIS
- Electrochemical impedance spectroscopy

ECN
- Electrochemical noise with FFT

Measurement of corrosion rates

Weight loss measurements

- as a function of time
- no simple way to extrapolate the results to predict the lifetime of the system under investigation

Electrochemical Tests

- to characterize corrosion mechanisms
- to predict corrosion rates

Calculation of corrosion rate

➢ The corrosion rate depends on the kinetics of both anodic (oxidation) and cathodic (reduction) reactions.

➢ According to Faraday's law, there is a linear relationship between the metal dissolution rate or corrosion rate, R_M, *and the corrosion* current i_{corr}:

$$v_{corr} = \frac{M}{nF\rho} i_{corr}$$

M is the atomic weight of the metal, ρ is the density, n is the charge number which indicates the number of electrons exchanged in the dissolution reaction, the ratio M/n is also referred to as equivalent weight.

Calculation of corrosion currents

Calculation of corrosion rates requires the calculation of corrosion currents.
When reaction mechanisms for the corrosion reaction are known, the
corrosion currents can be calculated using **Tafel Slope Analysis**.

$$i = i_{corr}\left[\exp(2.303\frac{\eta}{b_a} + \exp(-2.303\frac{\eta}{b_c}\right] \qquad \eta = E - E_{corr}$$

E_{corr} is the open circuit potential of a corroding metal, b_a, , b_c Tafel constants

For large anodic overpotentials **($\eta / b_a >> 1$)** the **Butler Volmer equation**
simplifies to the **Tafel equation** for the anodic reaction.
$\eta = log\ i_{corr} + b_a\ log\ i$
For large cathodic overpotentials **($\eta / b_c << -1$)**
$\eta = = log\ i_{corr} - b_c\ log\ |i|$
Tafel equations predict a straight line for the variation of the logarithm of
current density

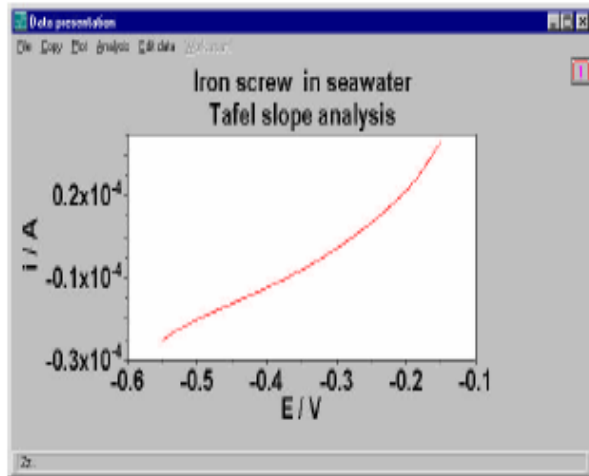**Figure 1:** Current potential curve for iron screw immersed in seawater.

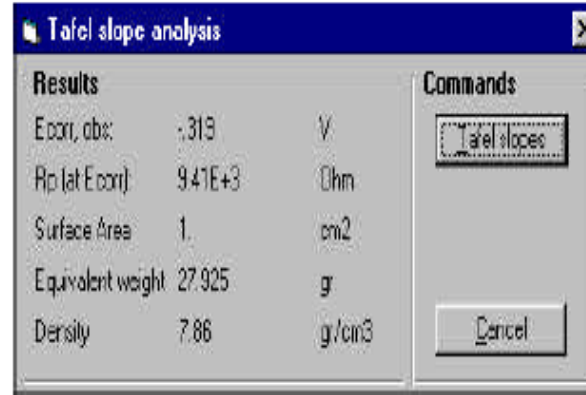**Figure 3:** GPES window for specifying the parameters required for Tafel analysis.

Figure 5: GPES window for showing the results of Tafel analysis.

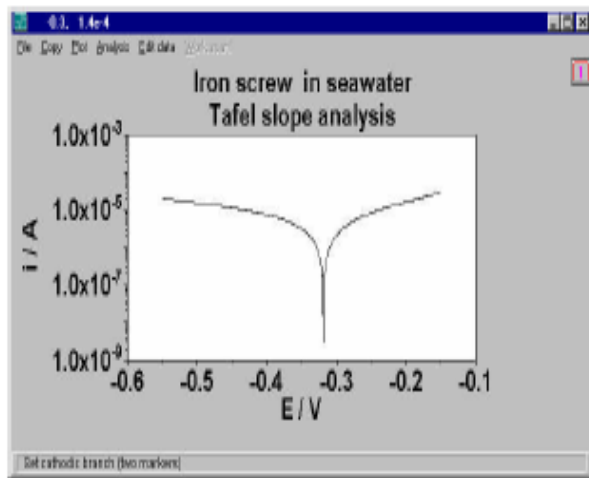**Figure 2:** Tafel plot for iron screw immersed in seawater.

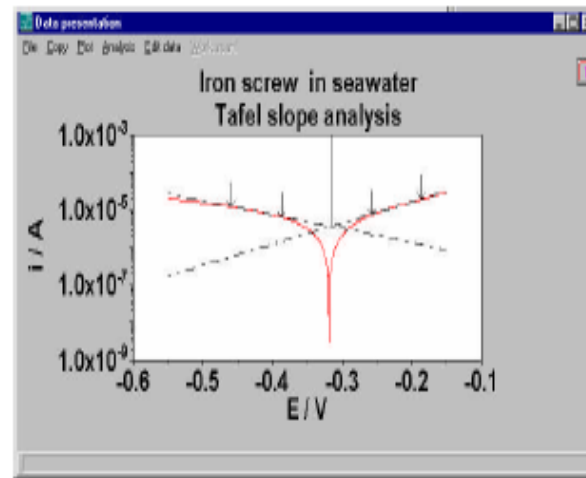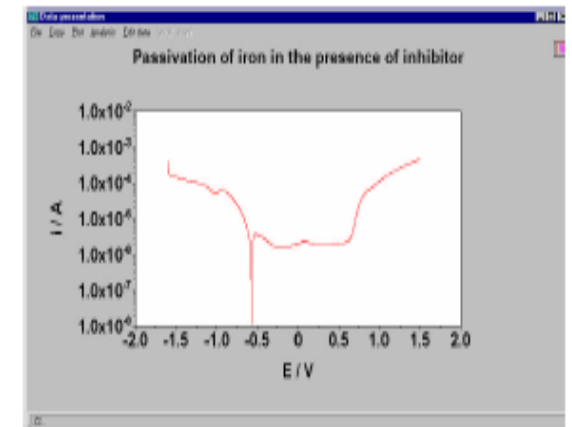**Figure 4:** GPES window for the specification of Tafel regions with the help of markers.
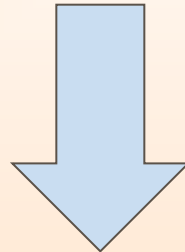

Figure 6: Tafel plot showing passivation of iron in the presence of inhibitor.

Calculation of corrosion rate

the assumption that

➤ **the corrosion reactions were under charge transfer control (activation overpotential)**

➤ **the mechanisms of the reactions were known**

Polarization resistance - R_p

Measurement of polarization resistance

$$R_p = \left. \frac{\Delta E}{\Delta I} \right|_{\Delta E \to 0}$$

ΔE polarization voltage
ΔI polarization current

$$i = i_{corr} \left[\exp(2.303 \frac{\eta}{b_a} + \exp(-2.303 \frac{\eta}{b_c} \right]$$

For small η, i.e. for potentials close to corrosion potentials, the above equation can be reduced to:

$$i_{corr} = 2.303 \frac{b_a b_c}{b_a + b_c} \left(\frac{1}{R_p} \right)$$

$$R_p = 2.303 \frac{b_a b_c}{b_a + b_c} \left(\frac{1}{i_{corr}} \right)$$

If the Tafel slopes are not known (e.g. when corrosion mechanism is not known), the R_p can still be used as a quantitative parameter to compare the corrosion resistance of metals under various conditions.

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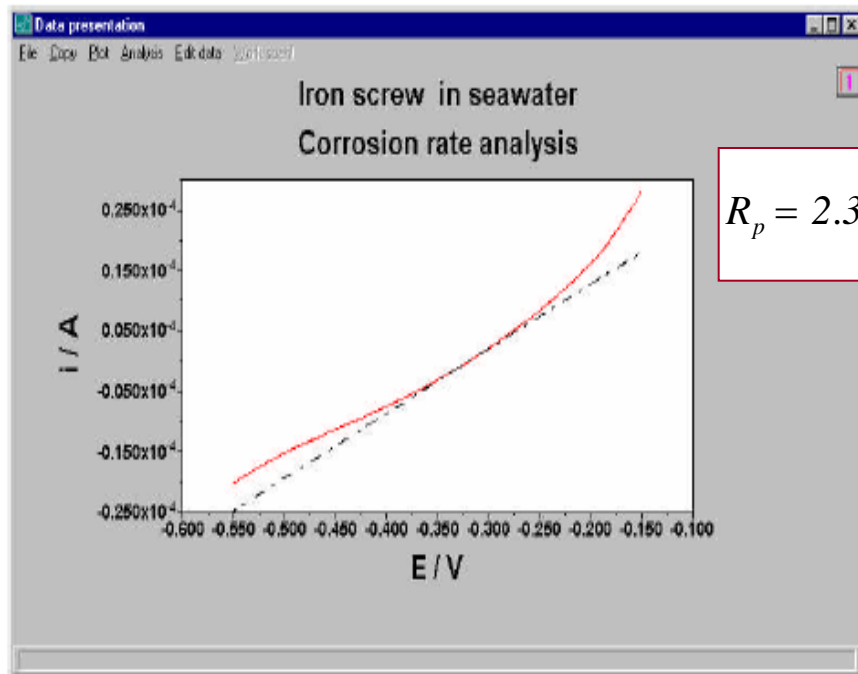
Measurement of R_p

LSV
- Linear sweep voltammetry

EIS
- Electrochemical impedance spectroscopy

Figure 1: LSV data for corrosion of iron screw immersed in seawater.

Randles circuit　　**CPE – Constant Phase Element**

Iron screw in seawater
Corrosion rate analysis

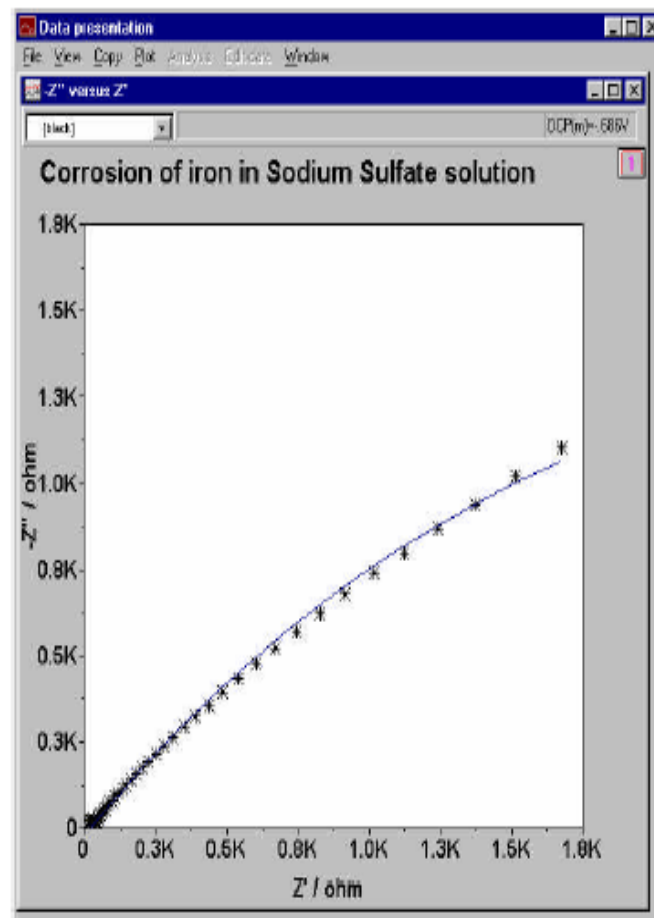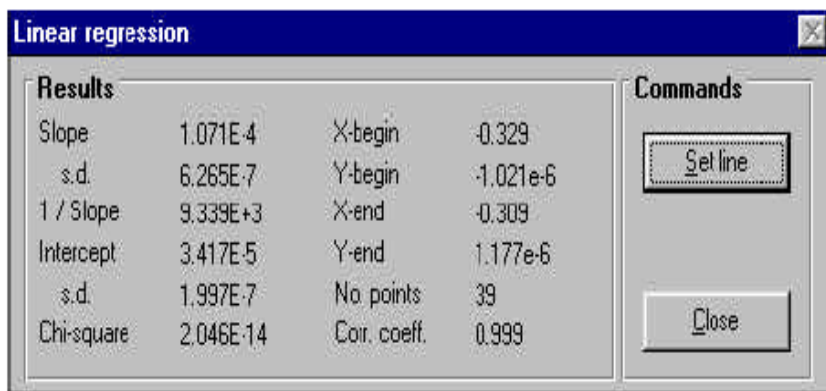$$R_p = 2.303 \frac{b_a b_c}{b_a + b_c} \left(\frac{1}{i_{corr}} \right)$$
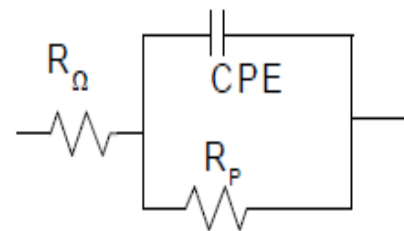
Figure 4: Estimation of R_p for corrosion of iron is sulfate solution using EIS

Figure 2: Estimation of R_p for corrosion of iron screw immersed in seawater.

Linear regression

| Results				Commands
Slope	1.071E-4	X-begin	-0.329	Set line
s.d.	6.265E-7	Y-begin	-1.021e-6	
1 / Slope	9.339E+3	X-end	-0.309	
Intercept	3.417E-5	Y-end	1.177e-6	
s.d.	1.997E-7	No. points	39	Close
Chi-square	2.046E-14	Cor. coeff.	0.999	

Corrosion of iron in Sodium Sulfate solution

Electrochemical impedance spectroscopy EIS

corrosion
electrodeposition,
electrodissolution, passivity
SAM
diffusion of ions across
membranes semiconductor
interfaces

The fundamental approach of all
impedance methods is to apply a
**small amplitude
sinusoidal excitation signal**
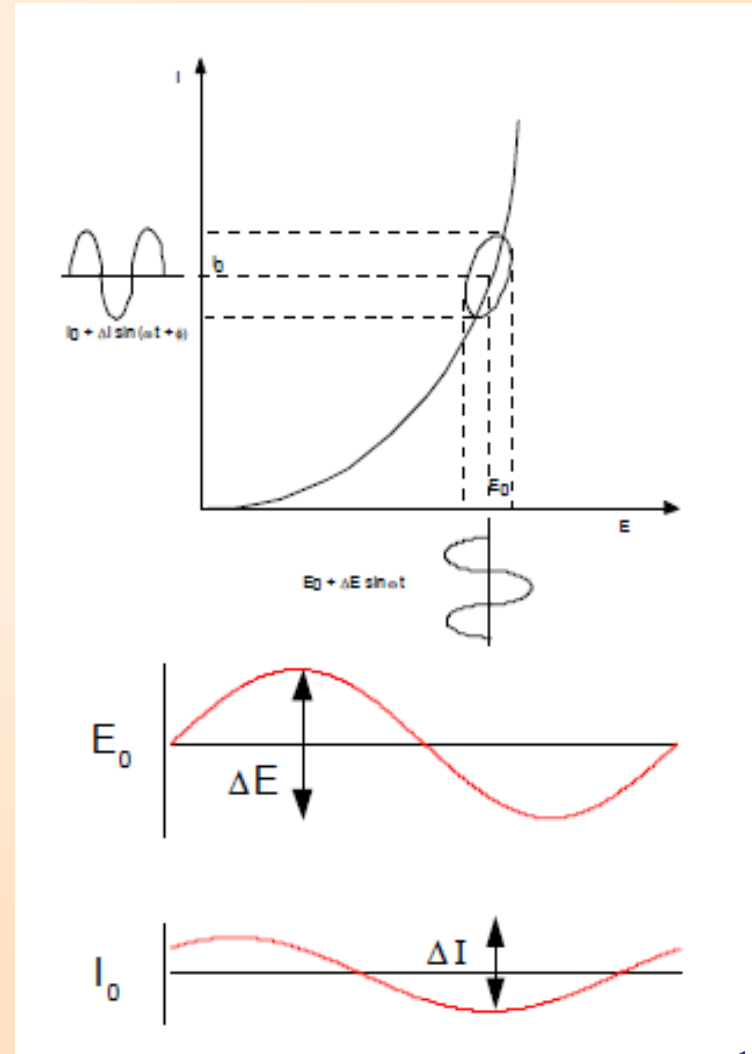
Principles of EIS measurements

Taylor series expansion for the current is given by

$$\Delta I = \left(\frac{dI}{dE} \right)_{E_0, I_0} \Delta E + \frac{1}{2} \left(\frac{d^2 I}{dE^2} \right)_{E_0, I_0} \Delta E^2 + ...$$

If the magnitude of the perturbing signal ΔE is small, then the higher order terms can be assumed to be negligible. The impedance of the system can then be calculated using Ohm's law:

$$Z(\omega) = \frac{\Delta E(\omega)}{\Delta I(\omega)}$$

$Z(\omega)$ is impedance $= f(\omega)$

frequency range of 100kHz – 0.1Hz

The impedance of a resistor

The current through a resistor will be in phase with the potential drop and the impedance will thus be given by a vector lying on the real axis i.e. $Z_R = R + i*0$

The current through a capacitor with the capacity C can be calculated by help of the capacitor equation: $Q = C*U$:

$$I = \frac{dQ}{dt} = C \cdot \frac{dU}{dt}$$

$$Z(\omega) = \frac{\Delta E(\omega)}{\Delta I(\omega)} = \frac{\Delta U(\omega)}{\Delta I(\omega)}$$

If a sine current, $U = U_0 \sin(\omega t)$, is used:

90°

$$I = -\omega \cdot C \cdot U_0 \cdot \cos(\omega \cdot t) = \omega \cdot C \cdot U_0 \cdot \sin\left(\omega \cdot t - \frac{\pi}{2}\right)$$

This shows that the impedance has the magnitude $1/\omega C$ and will be phase shifted by 90° negative in relation to the potential drop. The impedance can therefore be expressed as:

The impedance of a capacitor

$$Z_C = 0 - i \cdot \frac{1}{\omega \cdot C}$$

Similarly the impedance of an inductor can be shown to be:

The impedance of an inductor

$$Z_L = 0 + i \cdot \omega \cdot L$$

where L is the inductance. Only very few electrochemical reactions contains inductive elements in particular auto catalytic reactions.

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EIS: data analysis

Summary of equivalent circuit elements

Circuit Element	Impedance
R, Resistance	R
C, Capacitance	$\dfrac{1}{j\omega C}$
L, Inductance	$j\omega L$
CPE, Constant Phase Element, ☺	$\dfrac{1}{(j\omega C)^{\alpha}}$
W, Warburg Impedance Infinite diffusion length	$\dfrac{R}{\sqrt{j\omega}}$
W, Warburg Impedance Finite diffusion length	$R\dfrac{\tanh\sqrt{j\omega\tau}}{\sqrt{\tau}}$

$$Z = R\frac{\tanh\sqrt{j\omega\tau}}{\sqrt{\tau}}$$

$$\tau = \frac{\delta^2}{D}$$

R is the diffusion resistance
τ is the diffusion time constant
δ is the diffusion layer thickness
D is the diffusion coefficient

Constant phase element - CPE

$$Z = \frac{1}{(j\omega C)^{\alpha}}$$

$\alpha = 1$, CPE acts as an ideal capacitor
$\alpha = 0$, CPE acts as an ideal resistor

Principles of EIS measurements

The double layer capacity

This double layer capacity, C_{dl}, gives rise to an alternative path for the current across the electrode/electrolyte interface and will therefore operate in parallel with the charge transfer reaction:

C_{dl}

R_{ct}
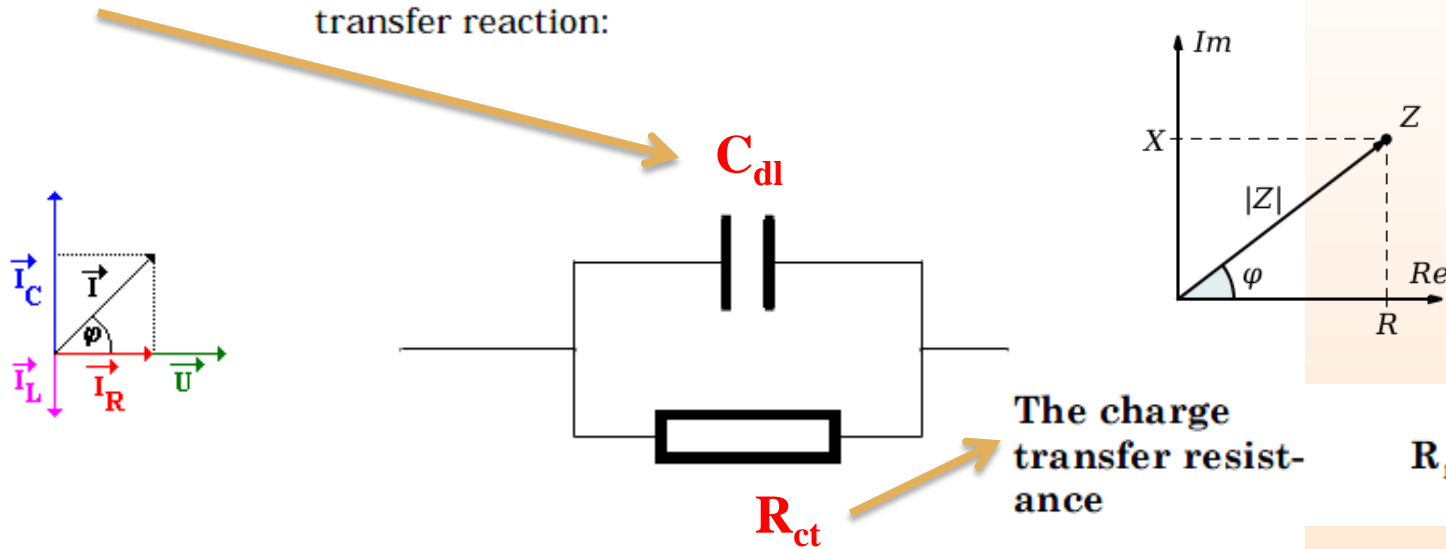
The charge transfer resistance

$$R_{react} = \frac{RT}{nFi_o}$$

The impedance of the parallel combination can be found from:

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

The impedance of a parallel combination

$$Z = \frac{R}{1 + C^2\omega^2R^2} - i \cdot \frac{R^2\omega C}{1 + C^2\omega^2R^2}$$

Principles of EIS measurements

$$\frac{1}{Z} = \frac{1}{R_{ct}} + \frac{1}{1/j\omega C_{dl}} = \frac{1}{R_{ct}} + j\omega C_{dl}$$

$$Z = \frac{R_{ct}}{1 + j\omega C_{dl}R_{ct}}$$

$$Z = R_e + \frac{R_{ct}}{1 + j\omega C_{dl}R_{ct}}$$

$$Z_{real} = R_e + \frac{R_{ct}}{1 + \omega^2 C_{dl}^2 R_{ct}^2}$$

$$Z_{im} = \frac{R_{ct}^2 C_{dl}\omega}{1 + \omega^2 C_{dl}^2 R_{ct}^2}$$

The impedance of a parallel combination
$$Z = \frac{R}{1 + C^2\omega^2 R^2} - i \cdot \frac{R^2\omega C}{1 + C^2\omega^2 R^2}$$

Electrical Analogues

charging current

C_{dl}

Ohmic Resistance

R_e

Faradaic current

R_{ct}
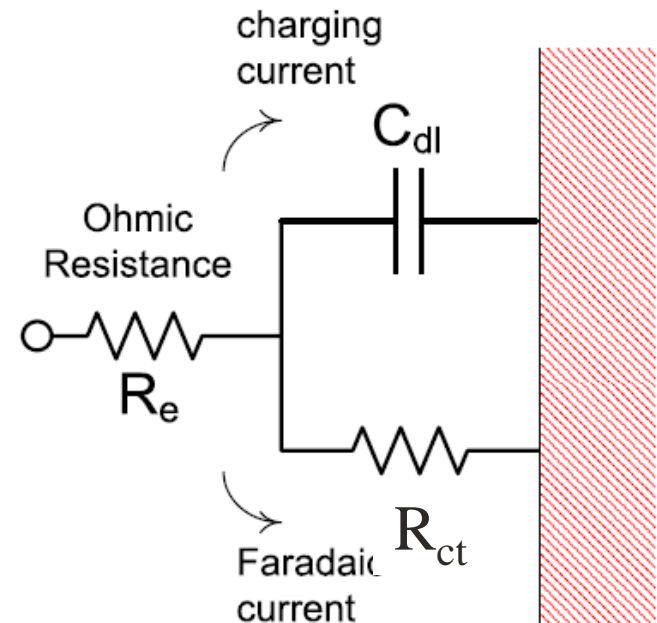
Principles of EIS measurements

In cartesian co-ordinates $Z(w) = Z_r(w) + jZ_j(w)$

In polar co-ordinates $Z(\omega) = |Z(\omega)| e^{\phi\omega}$

magnitude of the
impedance

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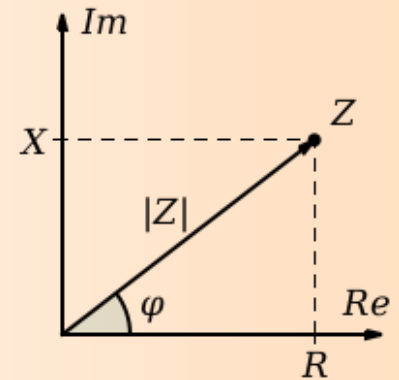
$$Z(t) = \frac{E(t)}{I(t)} = \frac{E_0 \cos(\omega t)}{I_0 \cos(\omega t - \phi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \phi)}$$

The plot of the imaginary part against the real part of impedance - **Nyquist plot.**
The shape of the curve is important in making qualitative interpretations of the data.
The disadvantage of the Nyquist representation is that one loses the frequency
dimension of the data. One way of overcoming this problem is by labelling
the frequencies on the curve. The absolute value of impedance and the phase shifts
are plotted as a function of frequency in two different plots giving a **Bode plot.** The
relationship between the two ways of representing the data is as follows:

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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
The absolute value of Z and the phase shifts are plotted as a function of frequency in two different plots giving a **Bode plot**

Nyquist and Bode plot

Data presentation
File View Copy Plot Analysis Edit data Window

-Z" versus Z'
[black]

$$|Z|^2 = (\mathrm{Re}\,Z)^2 + (\mathrm{Im}\,Z)^2$$

$$tg\phi = \frac{\mathrm{Im}\,Z}{\mathrm{Re}\,Z}$$

10 Hz ↓

-Z" / ohm
Z' / ohm

Bode plot
[black]

$$(\mathrm{Re}\,Z) = |Z|\cos\phi$$

$$(\mathrm{Im}\,Z) = |Z|\sin\phi$$

log(Z)(o)
-phase / deg(*)
log(f)

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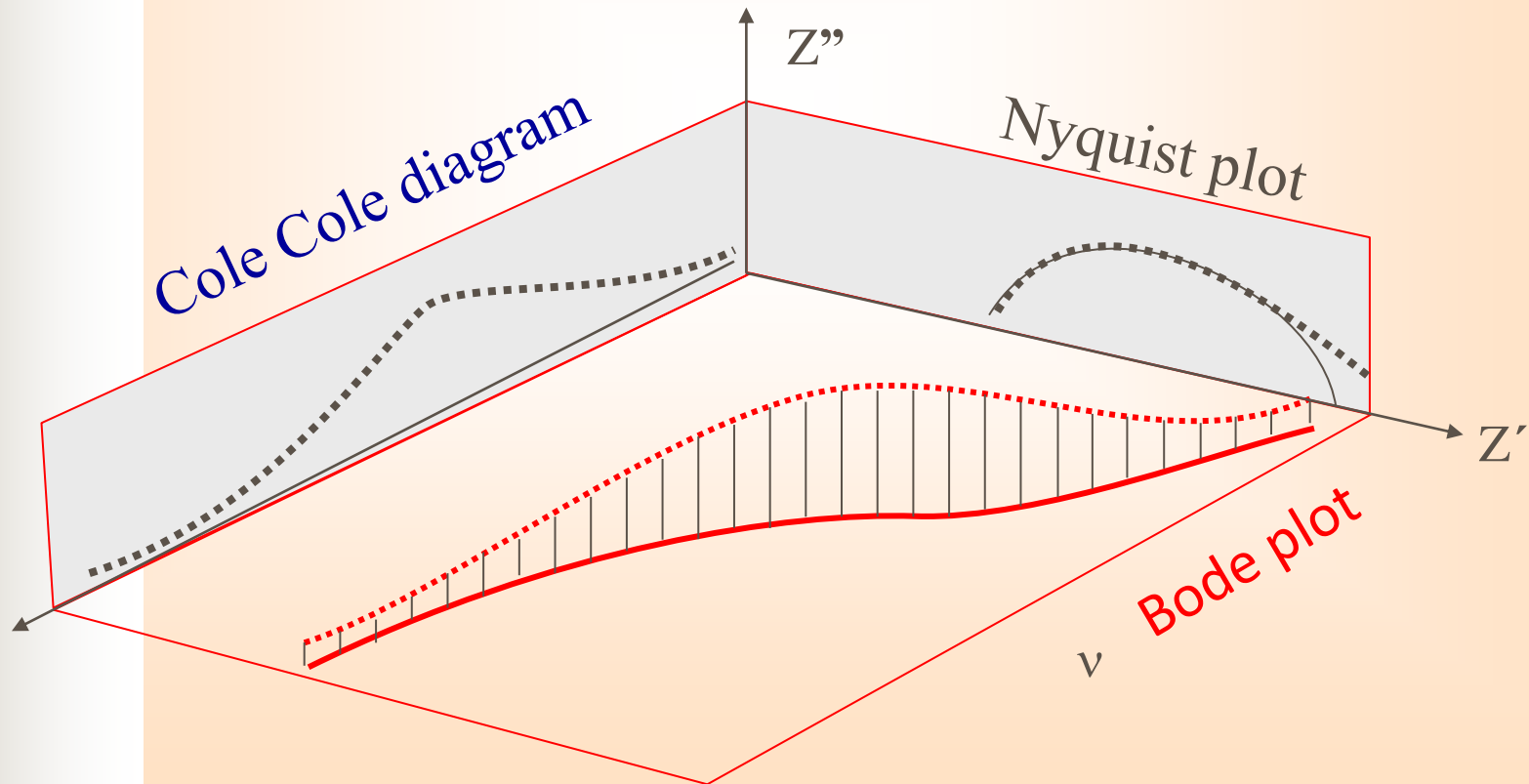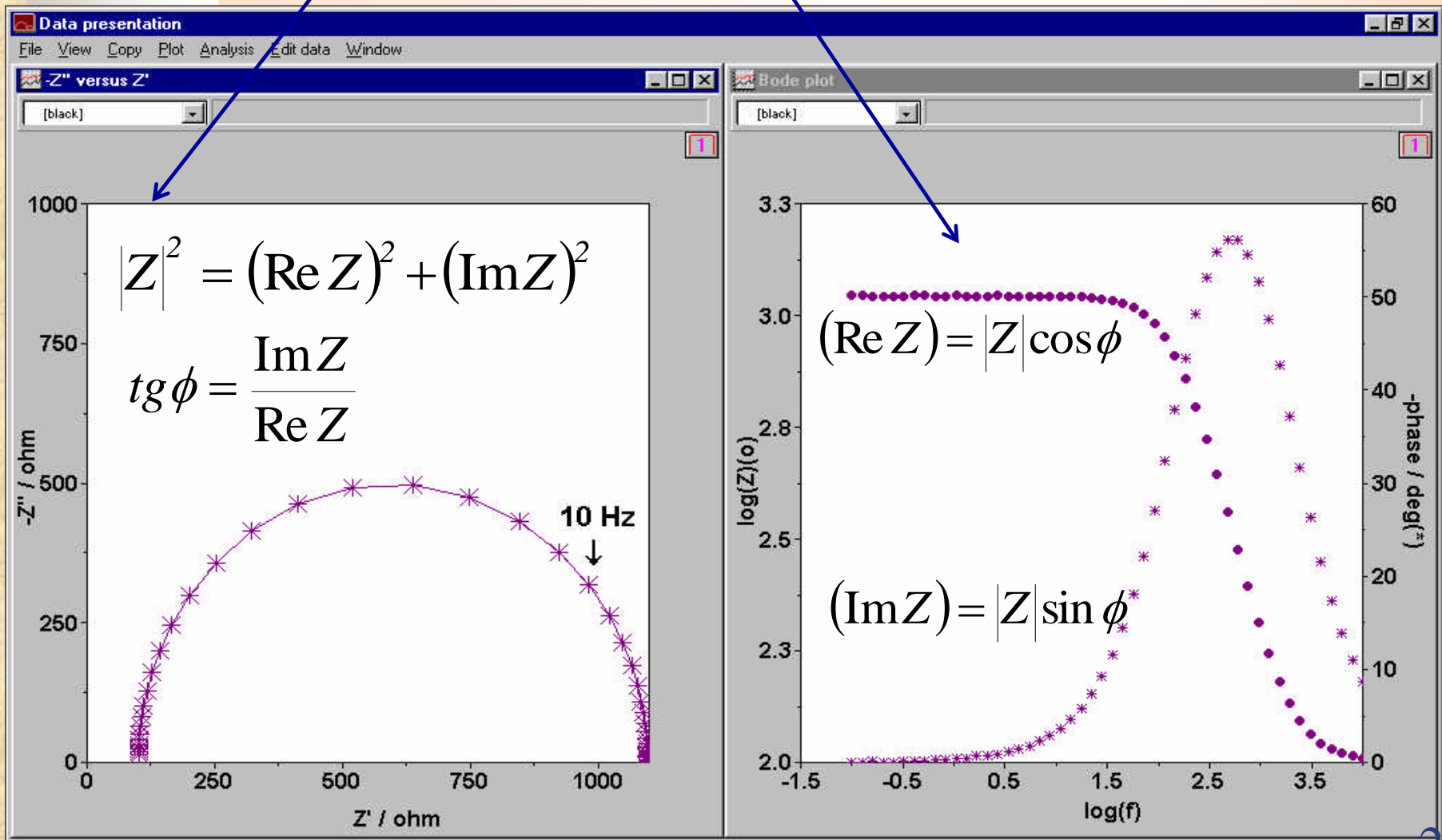
EIS: Experimental set-up

potentiostat/galvanostat, a frequency response analyser (FRA modul)

2 electrode cell
3 electrode cell
4 electrode cell

4 electrode cell
- between two measuring electrodes separated by a membrane, the WE and the CE enable current flow.
This kind of a cell is usually used :
➢ to study ion transport through a membrane,
➢ to perform electron or ion conductivity measurements
➢ to measure low impedance where the influence of contact and wire resistance should be minimal.
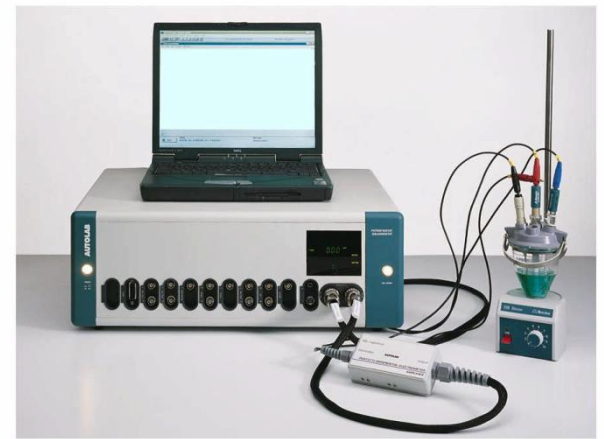
EIS: experiment parameters

potentiostat/galvanostat   FRA modul

Potentiostatic or galvanostatic mode

at a fixed DC potential   at a fixed DC current

DC potential or current

typical current potential curve for a corrosion of iron in passivating solution

- Open circuit potential (OCP), corrosion potential or zero current
- Potential or current in the active region
- Potential or current in the passive region
- Potential or current in the limiting current plateau region
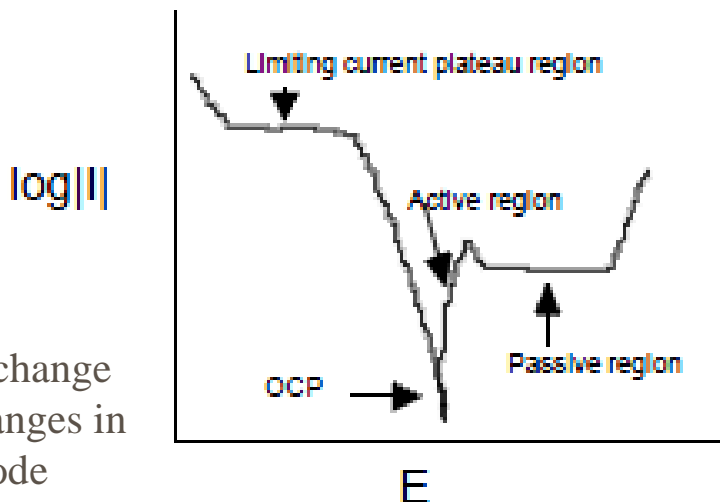
OCP can change due to changes in the electrode surface

it is desirable that OCP is measured dynamically at each frequency or the measurements are done under galvanostatic control at zero current

EIS: experiment parameters

FRA parameters or settings

1. *AC mode (single sine or multi sine)*
2. *perturbation (sine wave) amplitude (10 mV)*
3. *integration time*
4. *wait for steady state*
5. *frequency range (100kHz – 0.1Hz)*
6. *frequency distribution* (linearly, <u>logarithmically</u> or with a square root distribution)

EIS: **equivalent circuit models**

Model 2

A resistance, a capacitance and an inductance in series

$$R_\Omega \quad C \quad L$$
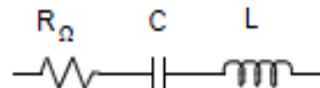
Model 2 can be used to model the response of a supercapacitor.

Model 1

A resistance and a capacitance in series

$$R_\Omega \quad C$$
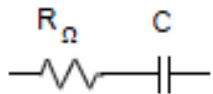
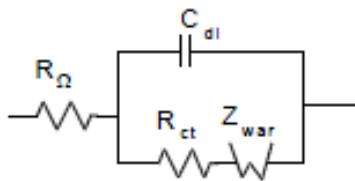Model 1 can be used, for example, to model a metal with an undamaged high impedance coating.
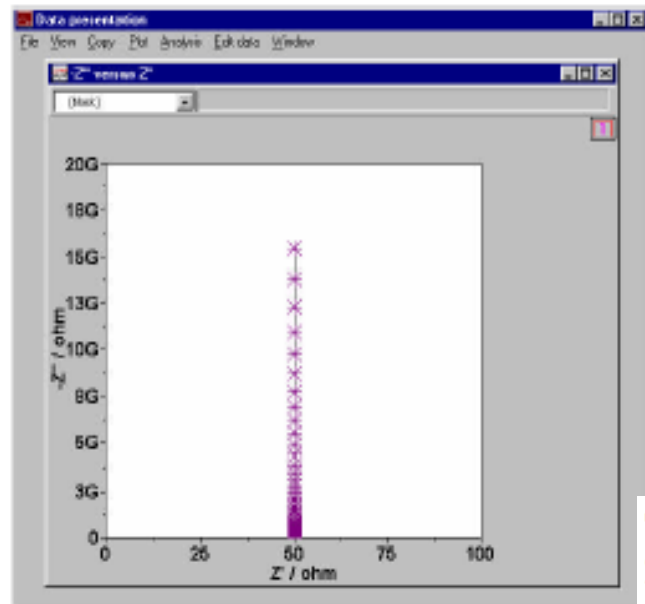
Model 3

A resistance and a capacitance in parallel (Randles circuit)

$$R_\Omega \quad C \text{ or } CPE \quad R_{ct}$$

The Randles circuit is one of the simplest and most common cell models. It includes a solution resistance, a double layer capacitor or a CPE and a polarization resistance. It is used to model corrosion processes and is often the starting point for other more complex models.

The impedance of a parallel combination

$$Z = \frac{R}{1 + C^2 \omega^2 R^2} - i \cdot \frac{R^2 \omega C}{1 + C^2 \omega^2 R^2}$$
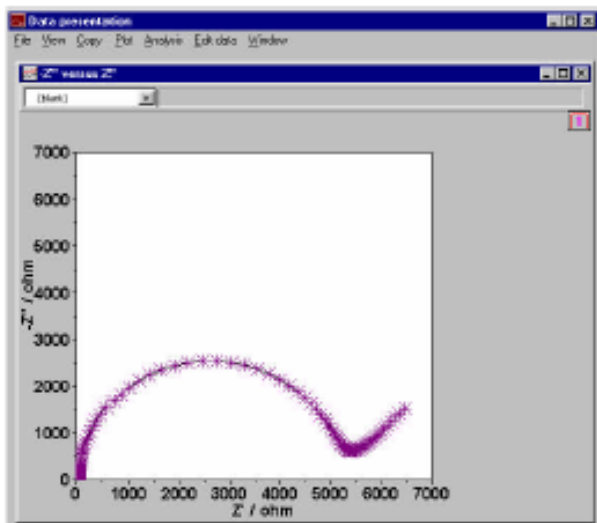
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EIS: **equivalent circuit models**

Model 4

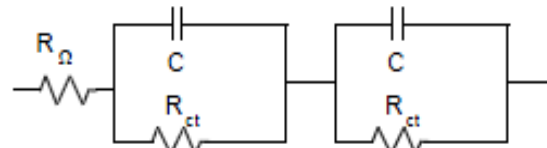Mixed kinetic and diffusion control

Model 4 can be used to describe electrode processes when both kinetics and diffusion are important.
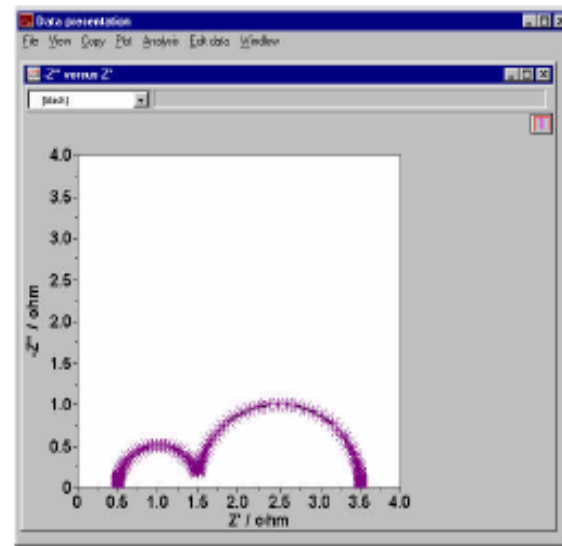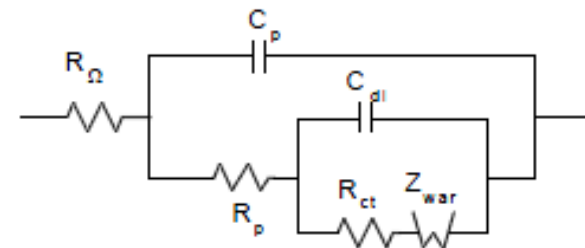

Model 5

Two Randles circuits in series

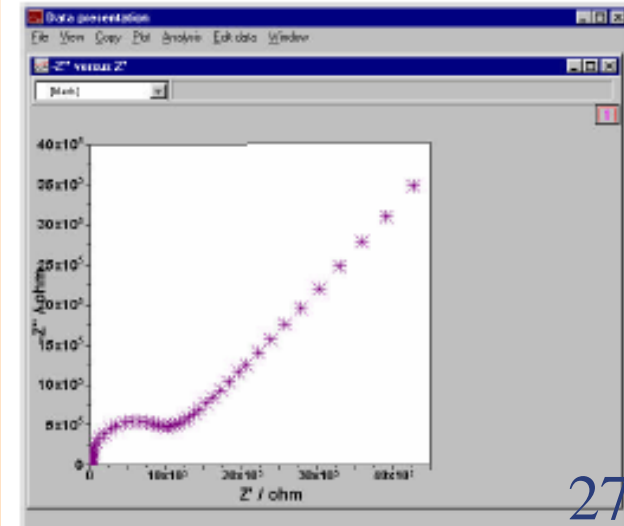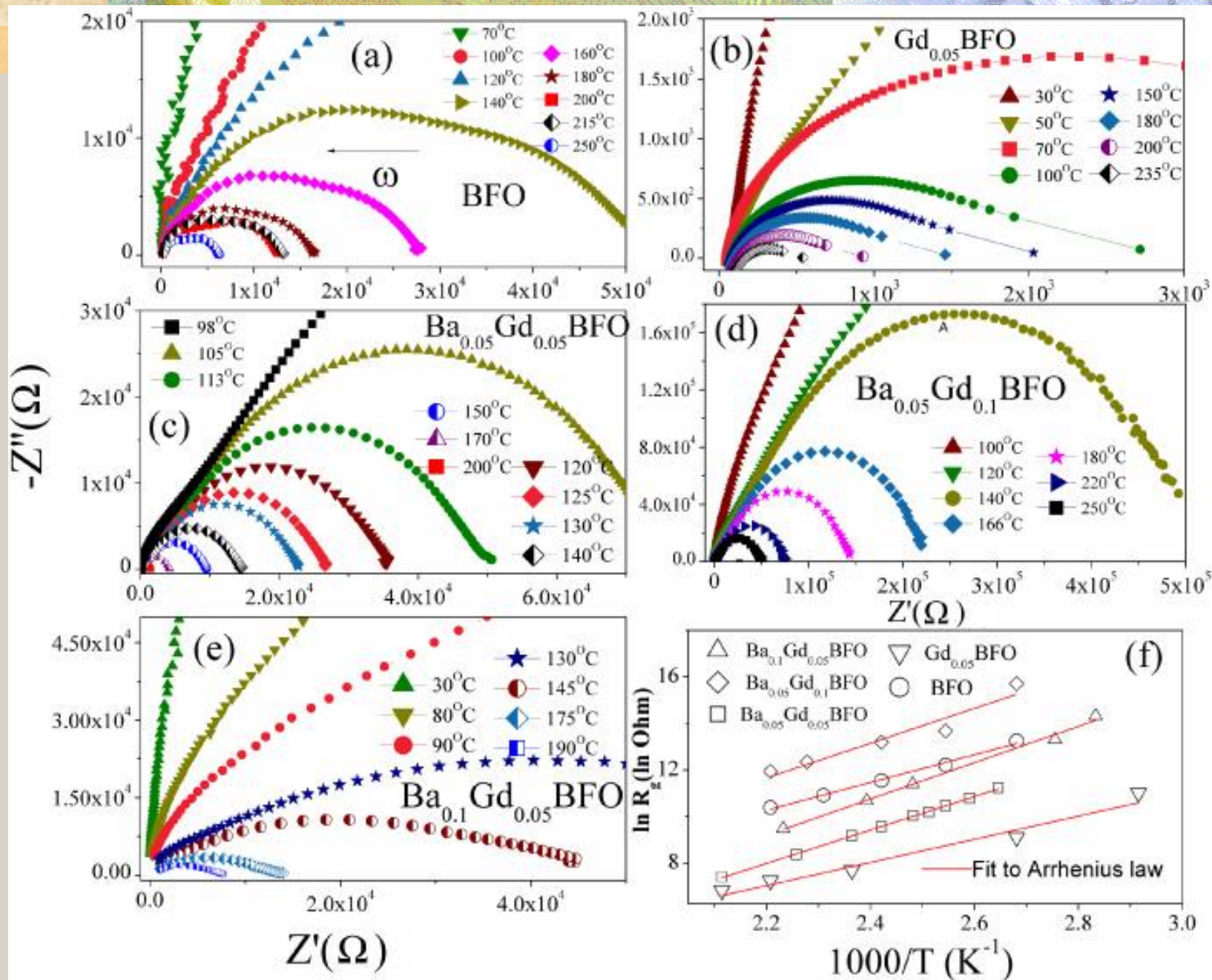Model 5 can be used, for example, to model the response of batteries.
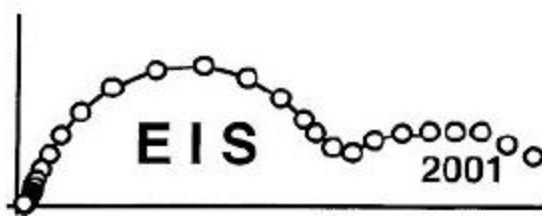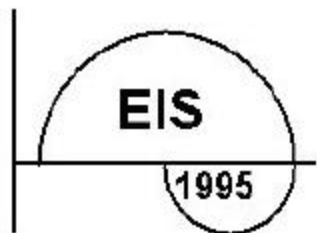

Model 6

A complex circuit

Model 6 can be used, for example, to describe the impedance of an organic coating on a metal substrate in contact with an electrolyte.

EIS 1989

EIS 2001

1992 – no logo

EIS 1995

2004 EIS

2007 EIS

Applications

- Electrochemical systems
  - **Corrosion**
  - **Electrodeposition**
  - **Human Skin**
  - **Batteries**
  - **Fuel Cells**
- Materials

Physical Description

- Electrode-Electrolyte Interface
  - **Electrical Double Layer**
  - **Diffusion Layer**
- Electrochemical Reactions
- Electrical Circuit Analogues

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