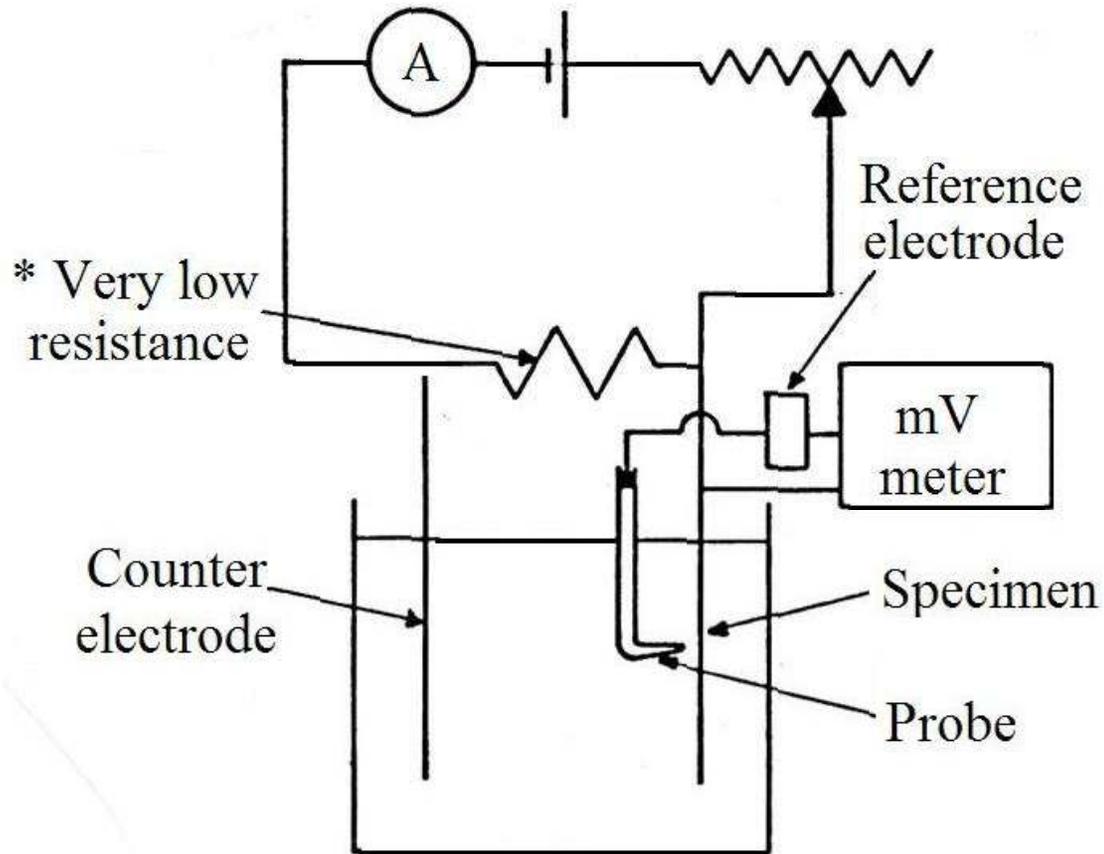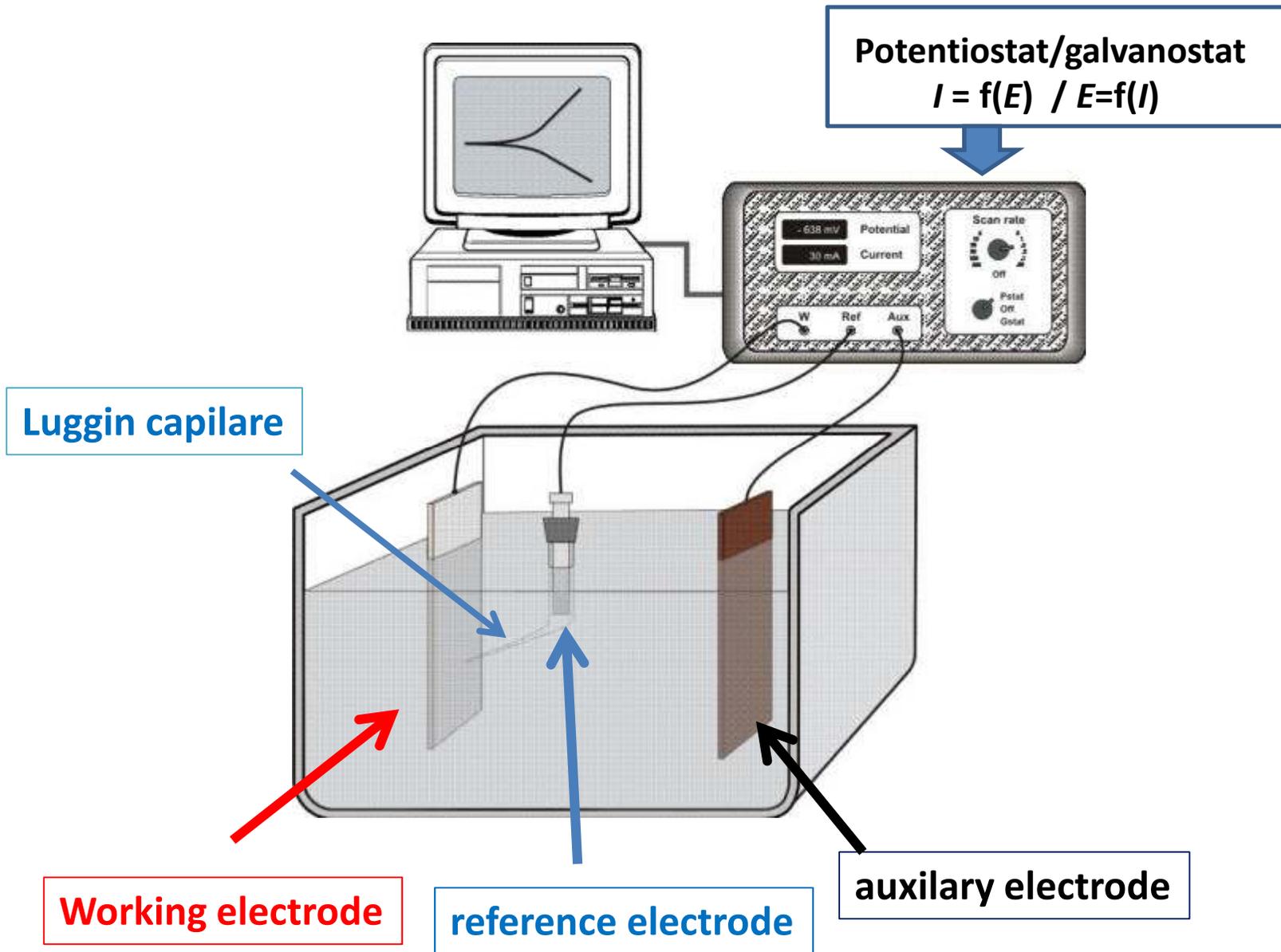# Electrochemical measuremenst in corrosion testing

## Jacek Banaś

# Polarization Measurements



The simple potentiostat for applying a fixed potential (relative to a reference electrode) and measuring the current (flowing from the working electrode to the counter or auxiliary electrode)

# Polarisation measurements

Potentiostat/galvanostat
$I = f(E)$ / $E = f(I)$

- 638 mV  Potential

- 30 mA  Current

Scan rate

Off

Pstat
Off
Gstat

W    Ref    Aux

Luggin capilare

Working electrode

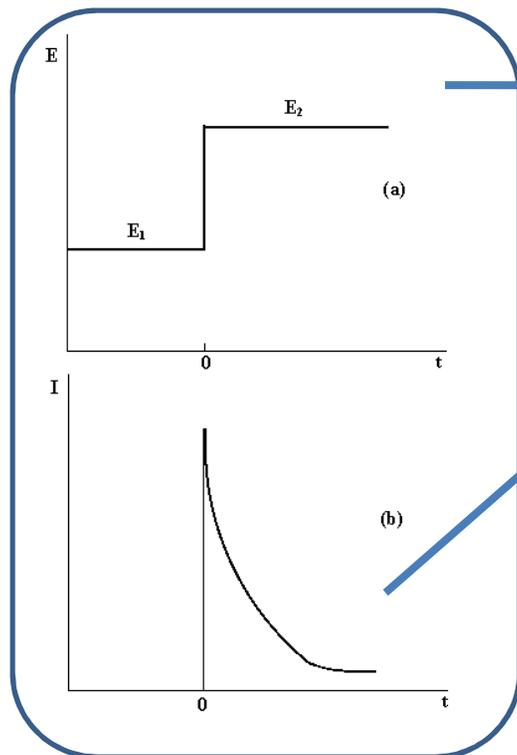reference electrode
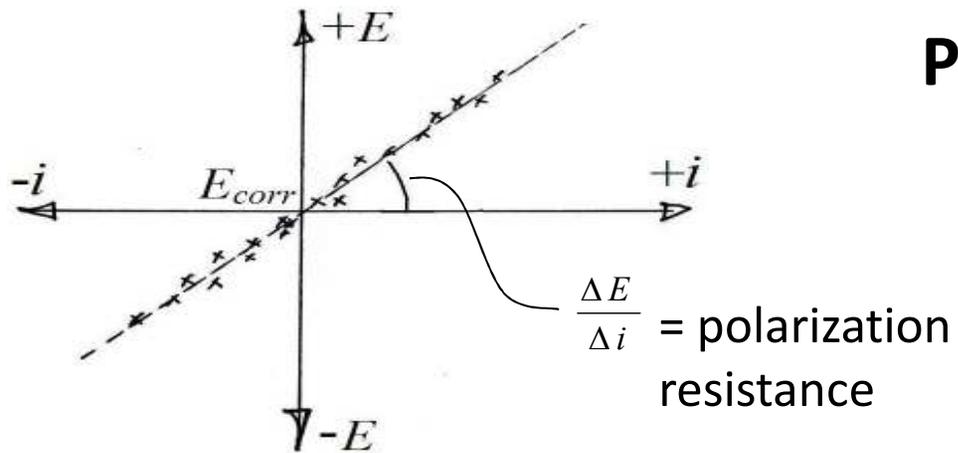
auxilary electrode

# Corrosion Examples on Evans Diagrams (from Fontana)
## Velocity Effects
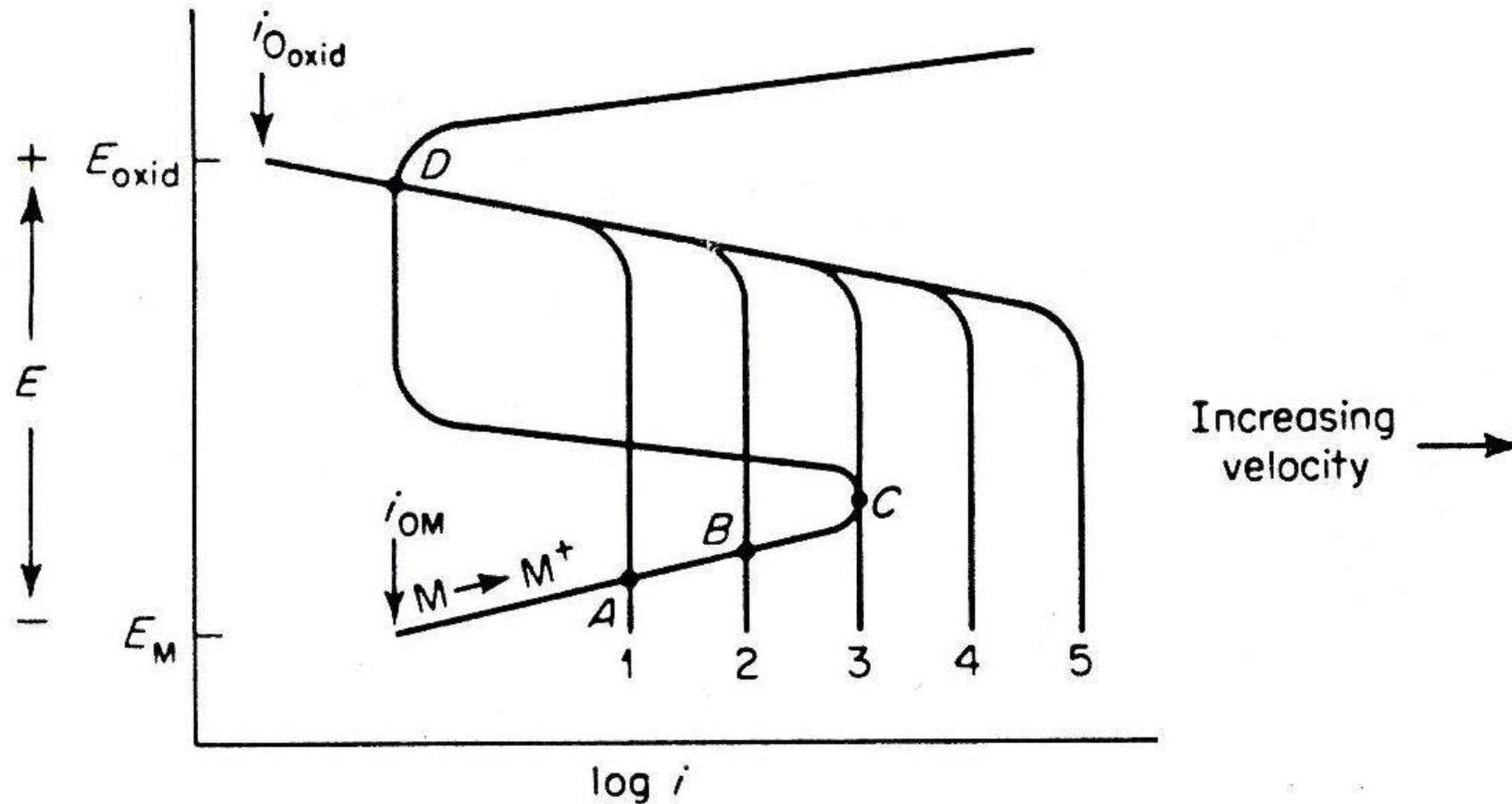


Effect of velocity on the electrochemical behavior of an active-passive metal corroding under diffusion control.

# Polarization resistance

$$\frac{\Delta E}{\Delta i} = \text{polarization resistance}$$

$$R_p = \frac{\Delta E}{\Delta i_{\Delta E \to 0}} = \frac{b_a \cdot b_k}{2{,}303 \cdot i_{kor} \cdot (b_a + b_k)}$$

$$v_{kor} = \frac{\Delta m}{\Delta t} = \frac{M}{nF} i_{kor}$$

The "corrosion current" .. $i_{corr}$ .. related to amount of metal corroded by Faraday's law…

$$i_{corr}t = \frac{nFw}{M}$$

$n$ = no. electrons involved in metal dissolution ($\rightarrow$ valency);

$F$ = Faraday constant (96,500 coulomb/mol);

$w$ = mass corroded metal;

$M$ = molecular weight of metal.

Note: there may be more than one cathodic reaction (i.e., more than one "$i_c$") and more than one anodic reaction (i.e., more than one "$i_a$"..e.g. for alloy);

$$i_{corr} = \sum i_a = -\sum i_c$$

# Electrochemical method of corrosion monitoring

## Linear polarization method (LPR):

$$R_p = \frac{\Delta E}{\Delta i_{\Delta E \to 0}} = \frac{b_k b_a}{2,303 i_{kor}(b_k + b_a)} = \frac{B}{i_{kor}}$$

$$B = \frac{b_k b_a}{2,303(b_k + b_a)} = 0,026$$
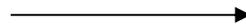
$$i_{kor} = B \frac{\Delta i}{\Delta E}$$



ZE SF 2 38 dni

Electrochemical method of corrosion monitoring

St37 ←

20H12M1F →

# EIS - ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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.
Electrochemical Impedance is normally measured using a small excitation signal of 10 to 50 mV. In a linear (or pseudo-linear) system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase.
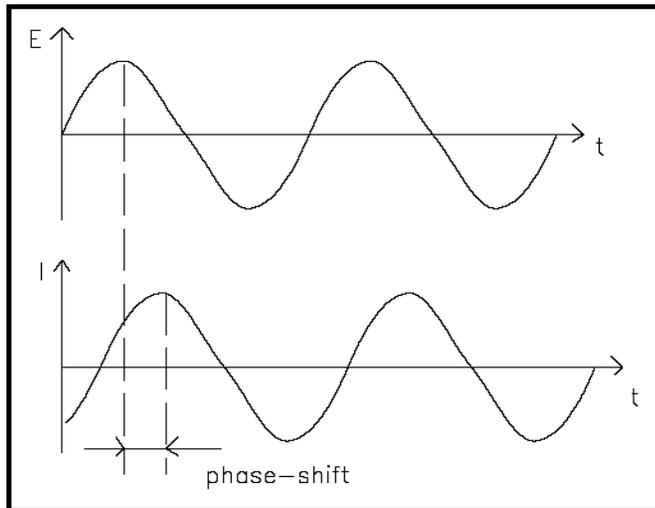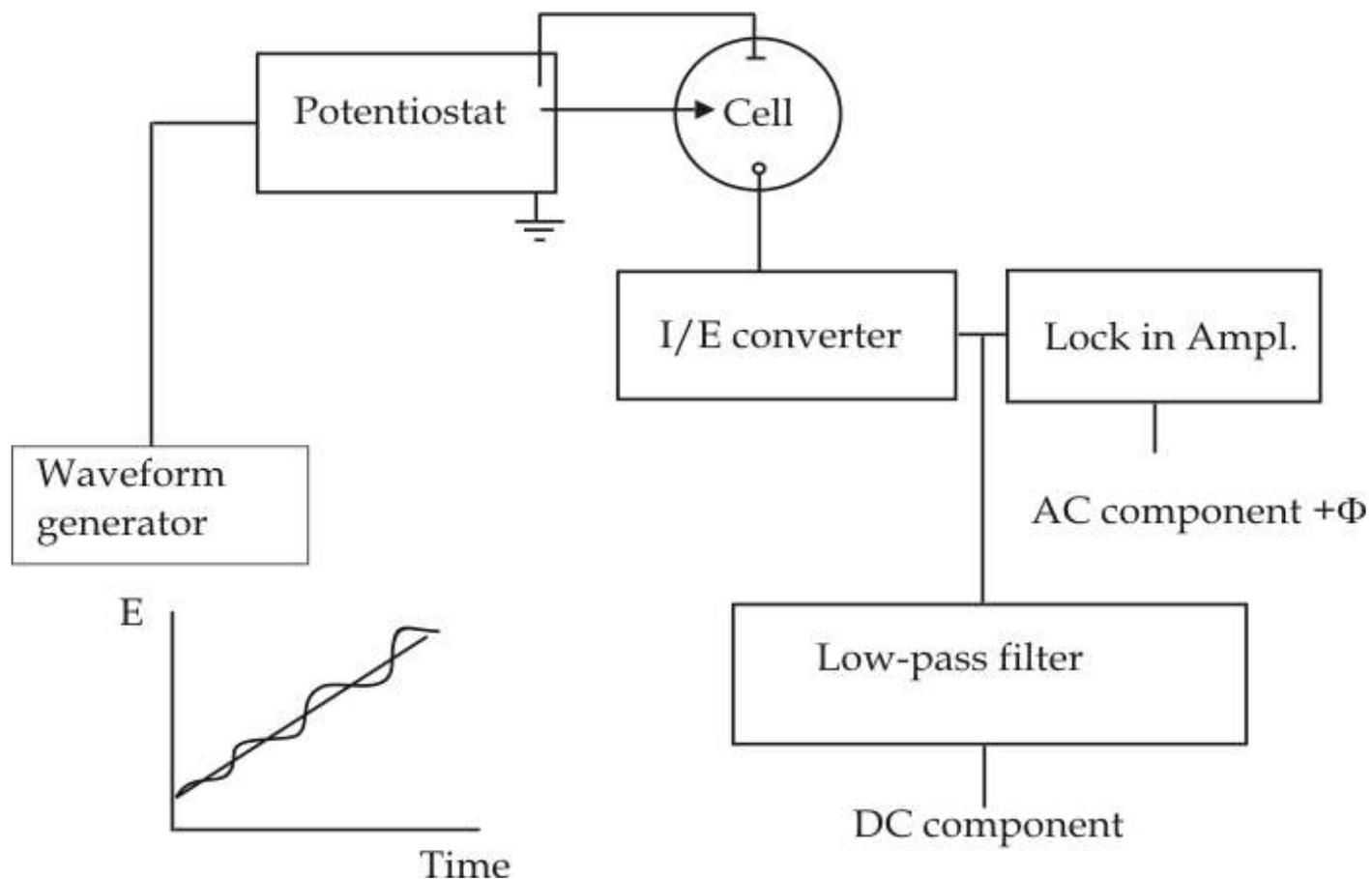


$$E_t = E_0 \sin(\omega t)$$

$$\omega = 2\pi f$$

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

Sinusoidal Current Response in a Linear System

# EIS - ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY



**Schematic diagram of apparatus for AC voltammetric experiments**

An expression analogous to Ohm's Law allows us to calculate the impedance of the system as:

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

The impedance is therefore expressed in terms of a magnitude (modulus) $|Z|$, and a phase shift, $\varphi$. 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, $\quad E_t = E_0 \exp(j\omega t)$

and the current response as, $\quad I_t = I_0 \exp(j\omega t - \phi)$

The impedance is then represented as a complex number:

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

# EIS Data Presentation

The expression for Z(ω)

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

is composed of a real and an imaginary part. If the real part is plotted on the Z axis and the imaginary part on the Y axis of a chart, we get a "Nyquist plot". Notice that in this plot the y-axis is negative and that each point on the Nyquist plot is the impedance at one frequency.
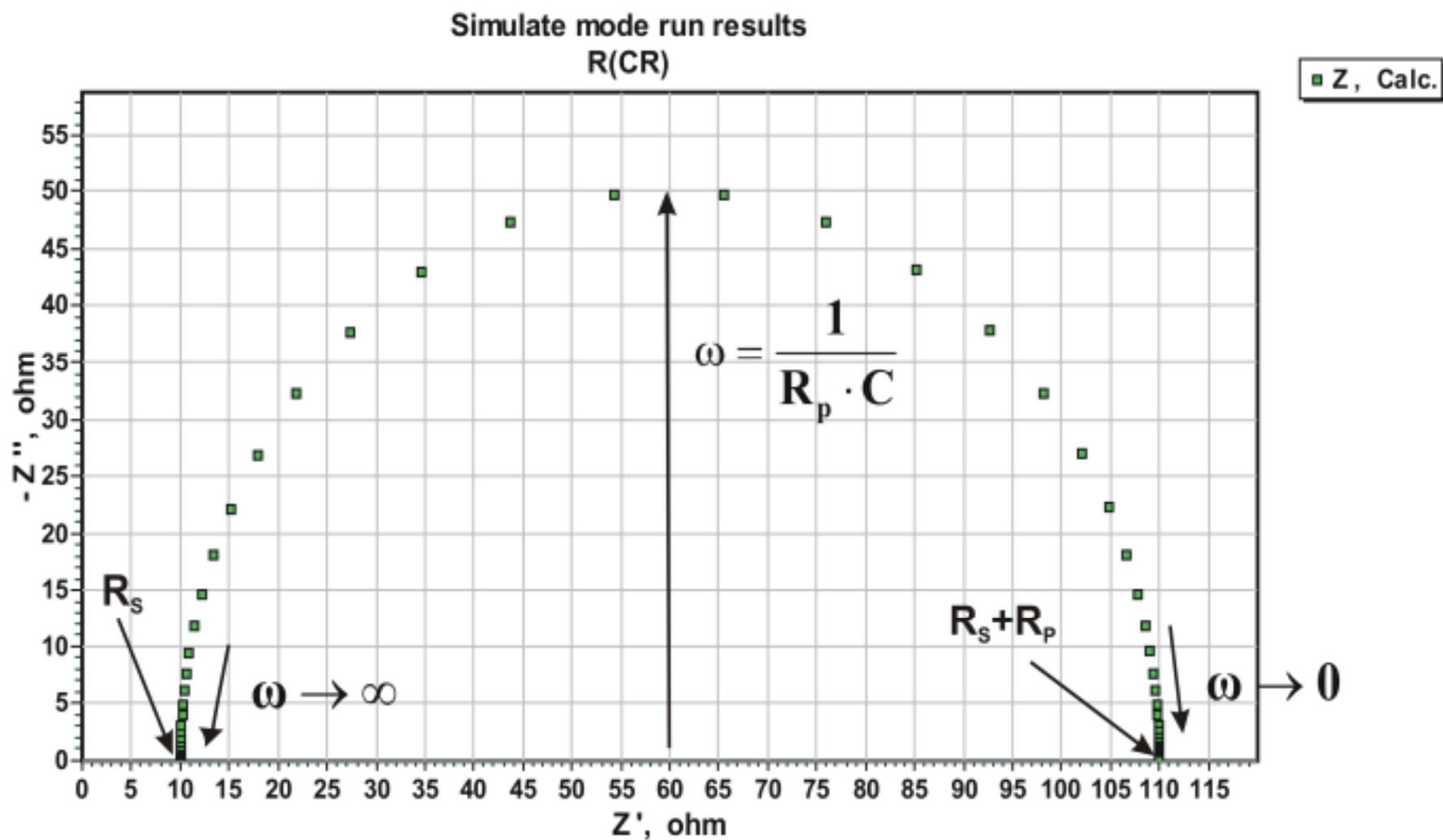
Nyquist Plot with Impedance Vector

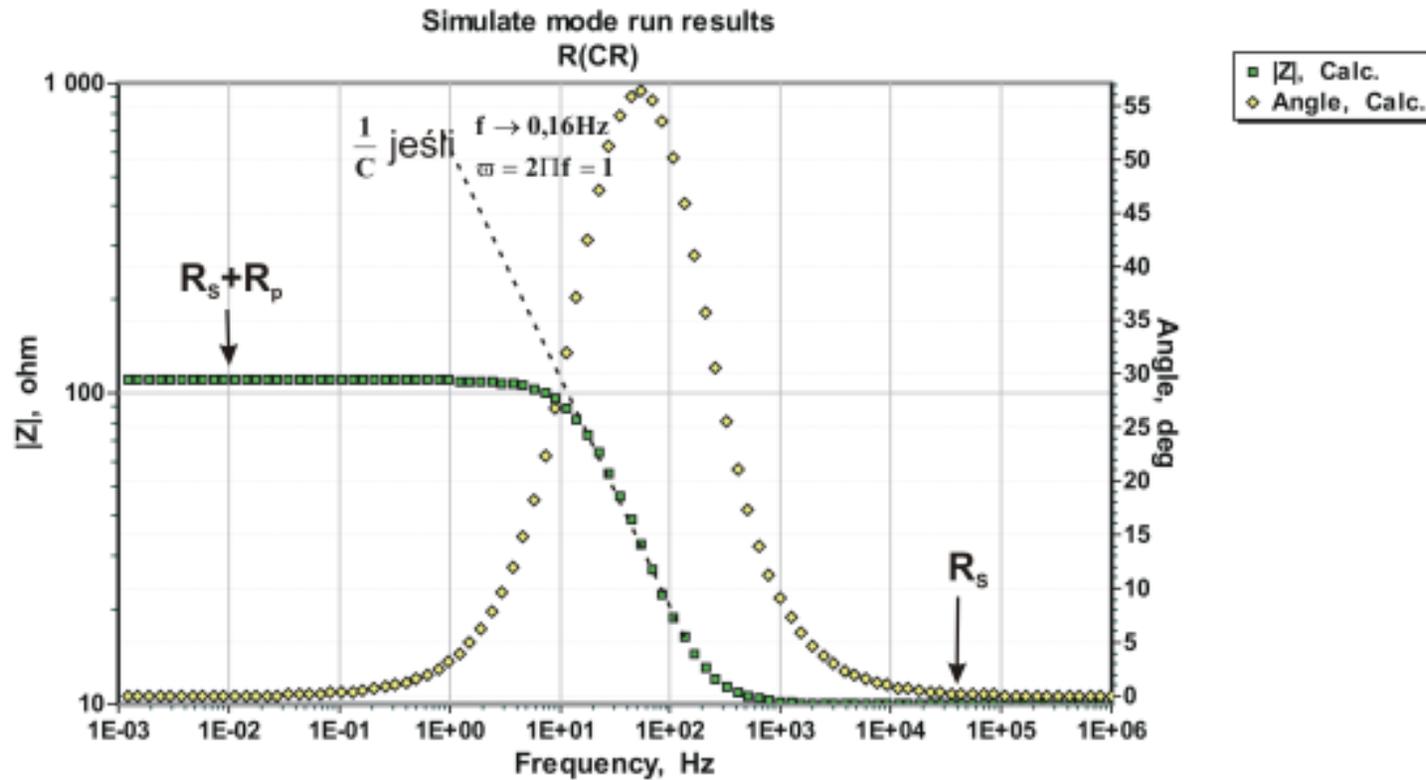# Equivalent circuit of an electrochemical cell.



**Kapilara Ługgina**

$M^{n+} \longleftarrow M$
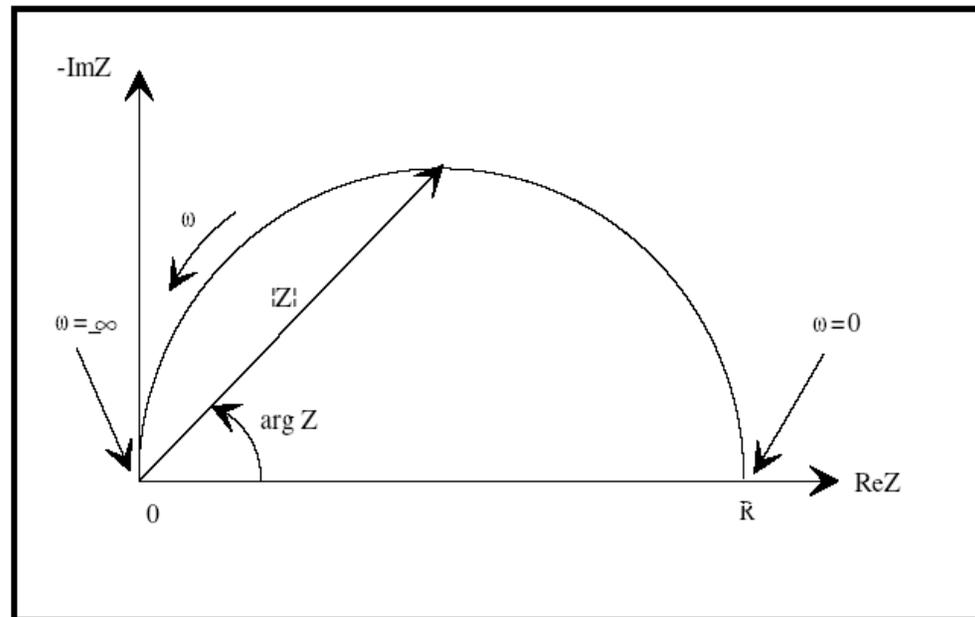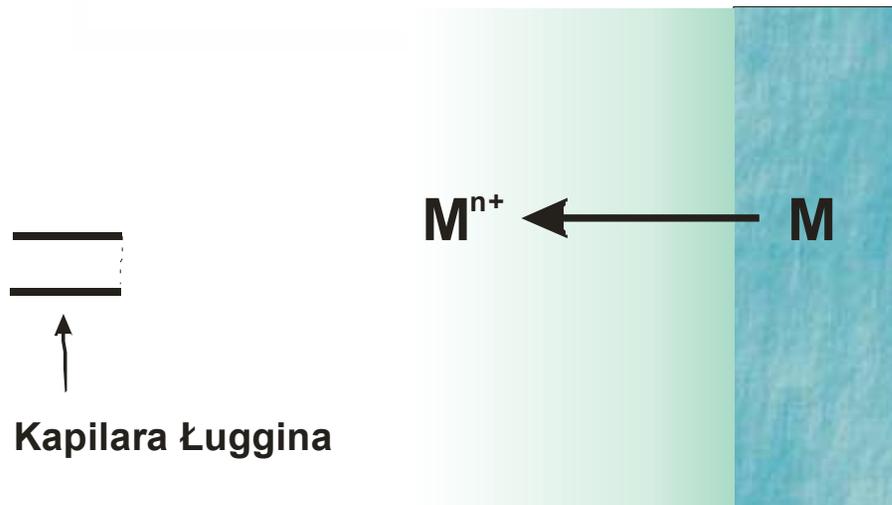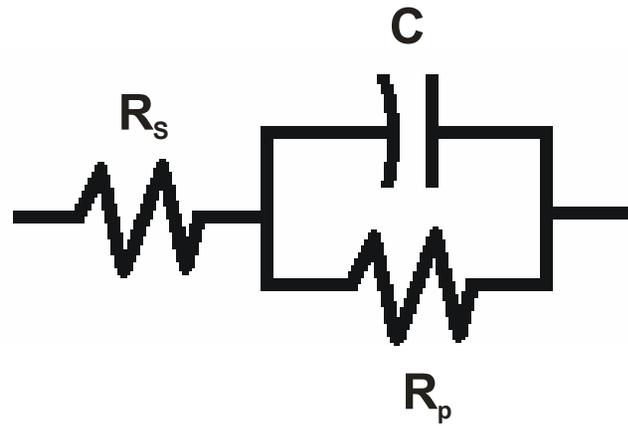
Randles circuit describes simple charge transfer reaction

# Nyquist diagram for R(RC) ( $R_s$ = 10Ω, $R_p$ = 100Ω i C = 0,0001F)



Simulate mode run results
R(CR)

$$\omega = \frac{1}{R_p \cdot C}$$

$R_s$

$R_s + R_p$

$\omega \rightarrow \infty$
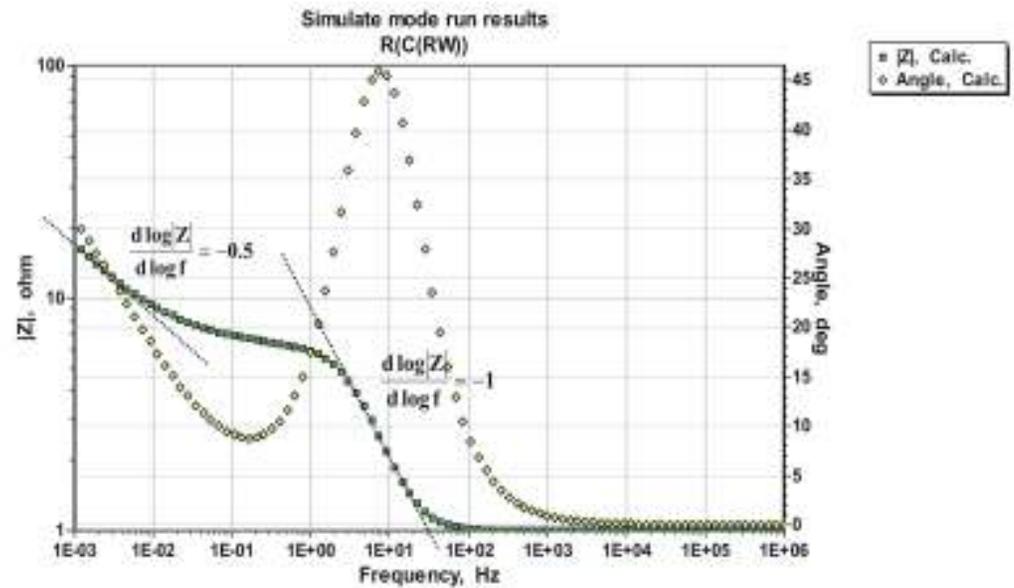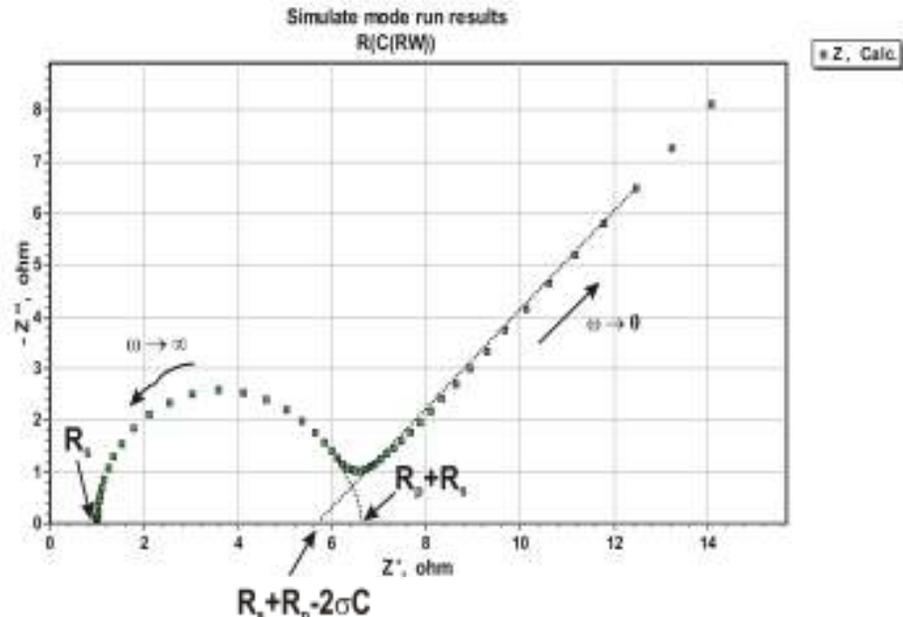
$\omega \rightarrow 0$

- Z'', ohm

Z', ohm

■ Z, Calc.

**Bode diagram for R(RC) ( $R_s = 10\Omega$, $R_p = 100\Omega$ i C = 0,0001F)**



Simulate mode run results
R(CR)

$\frac{1}{C}$ jeśli    f → 0,16Hz
$\varpi = 2\Pi f = 1$

$R_s + R_p$

$R_s$

■ |Z|, Calc.
◇ Angle, Calc.

$|ZI| = Z_{re}^2 + Z_{im}^2$

For  φ = 0  $|ZI| = Z_{re}$    for  φ = 0

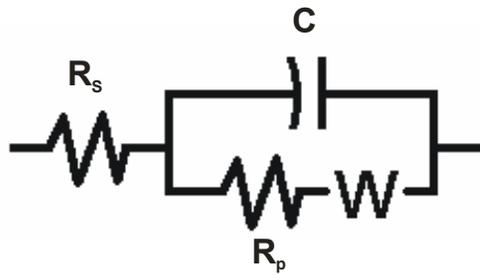# Charge transfer coupled with diffusion of reagents( $R_s = 1\Omega$, $R_p = 5\Omega$ i C = 0,01F, W=1 )

C

$R_s$

W

$R_p$

$M^{n+}$ $M^{n+} \leftarrow M$

Kapilara Ługgina
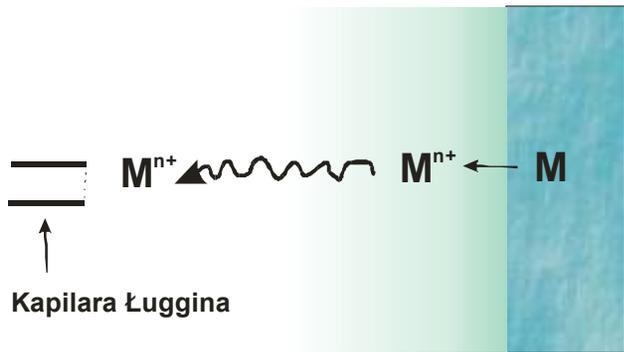
Warburg impedance:

$$W = Z_W = \sigma(\omega)^{-\frac{1}{2}}(1-j)$$

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



Simulate mode run results
R(C(RW))

- Z, Calc.

$\omega \to \infty$ $\omega \to 0$

$R_s$

$R_p + R_s$

$R_s + R_p - 2\sigma C$

-Z'', ohm

Z', ohm



Simulate mode run results
R(C(RW))

- |Z|, Calc.
- Angle, Calc.

$\frac{d\log|Z|}{d\log f} = -0.5$

$\frac{d\log|Z|}{d\log f} = -1$

|Z|, ohm

Angle, deg

Frequency, Hz

# Model of interface with charge transfer reaction coupled with formation of barrier layer( $R_s = 1\Omega$, $R_p = 5\Omega$ i C = 0,01F, T=1, B=10 )



Kapilara Ługgina

$M^{n+}$ ← M
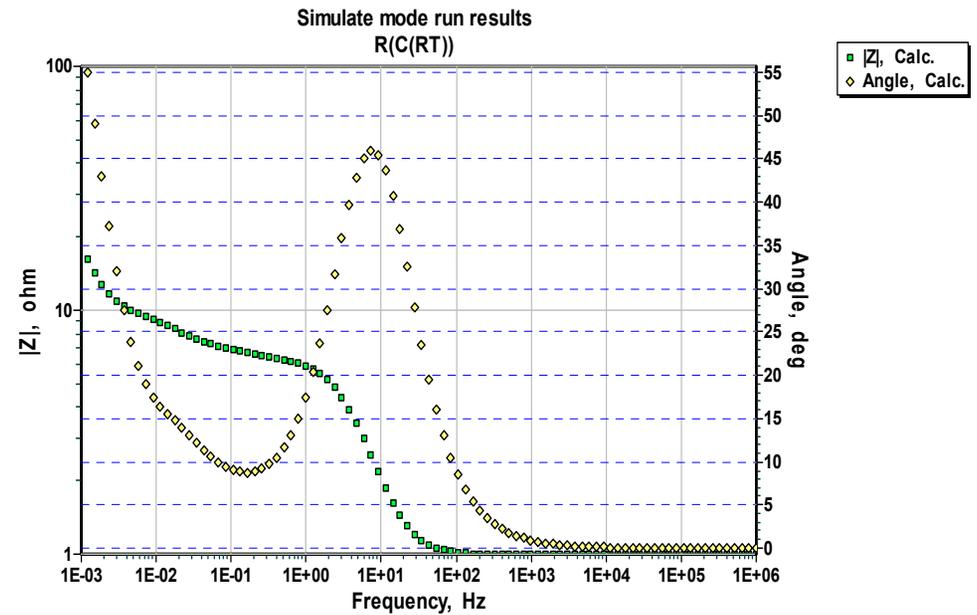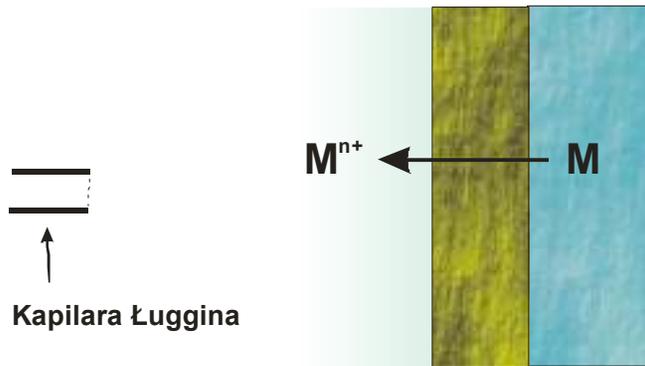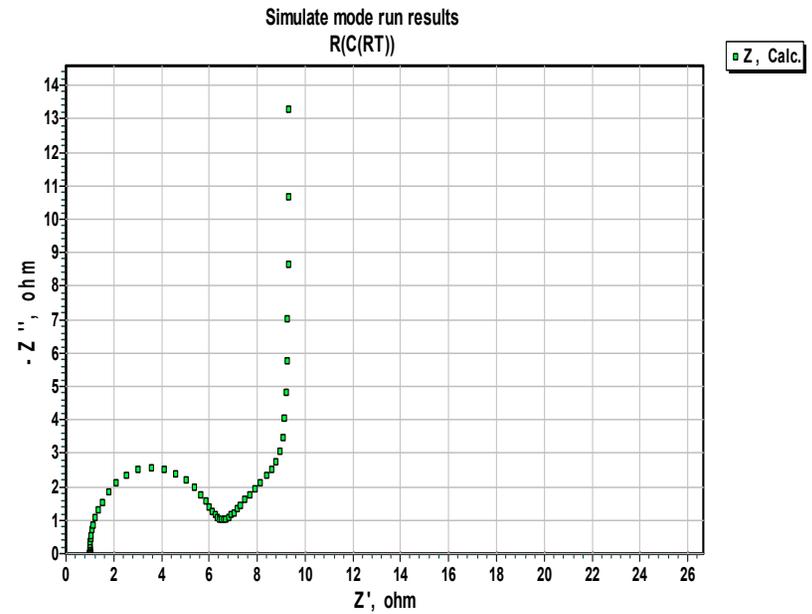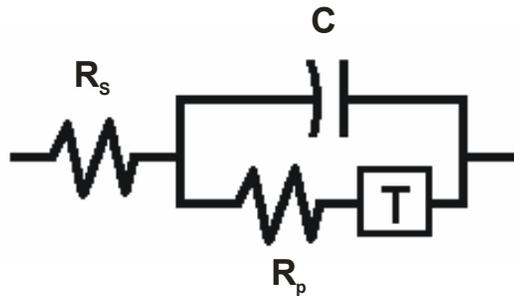
## Two Time Constant Spectrum
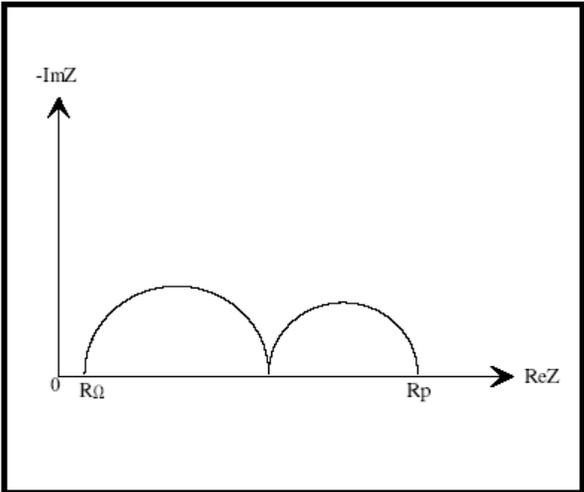


## Equivalent Circuit Models with Two Time Constants
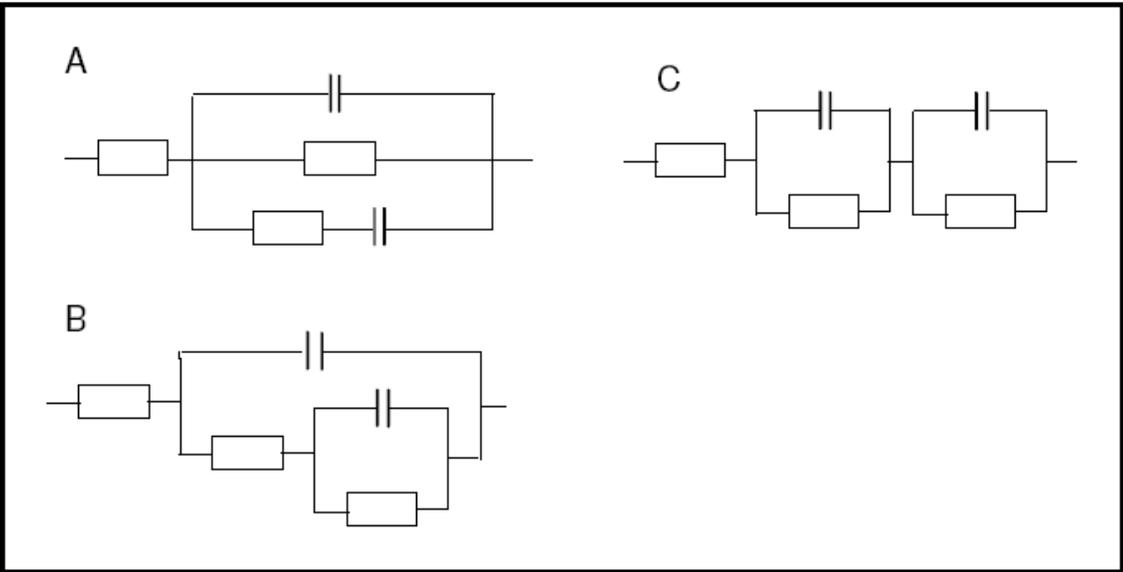
# Common Electrical Elements

| Component | Current Vs.Voltage | Impedance |
|-----------|--------------------|-----------|
| resistor | $E = IR$ | $Z = R$ |
| inductor | $E = L\, di/dt$ | $Z = j\omega L$ |
| capacitor | $I = C\, dE/dt$ | $Z = 1/j\omega C$ |

**Impedances in Series**
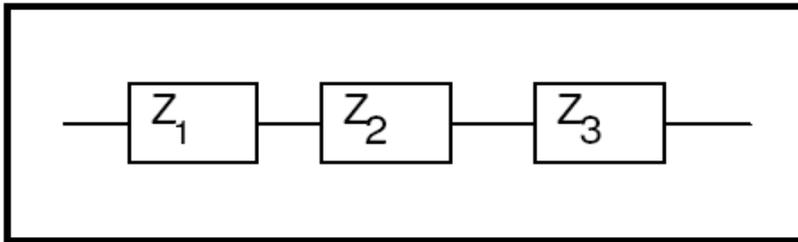


$$Z_{eq} = Z_1 + Z_2 + Z_3$$

**Impedances in Parallel**



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

**Literature**

1. Impedance Spectroscopy; Theory, Experiment, and Applications, 2nd ed. , E. Barsoukov, J.R. Macdonald, eds., Wiley Interscience Publications, 2005.
2. Electrochemical Methods; Fundamentals and Applications, A.J. Bard, L.R. Faulkner, Wiley Interscience Publications 2000.
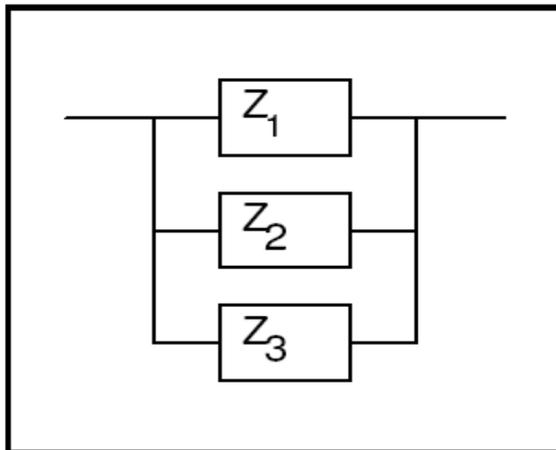3. Electrochemical Impedance: Analysis and Interpretation, J.R. Scully, D.C. Silverman, and M.W. Kendig, editors, ASTM, 1993.
4. Physical Chemistry, P.W. Atkins, Oxford University Press ,1990.
5. Signals and Systems, A.V. Oppenheim and A.S. Willsky, Prentice-Hall, 1983.
6. Comprehensive Treatise of Electrochemistry; Volume 9 Electrodics: Experimental Techniques; E. Yeager, J.O'M. Bockris, B.E. Conway, S. Sarangapani, Chapter 4 "AC Techniques", M. Sluyters-Rehbach, J.H. Sluyters, Plenum Press, 1984.
7. Mansfeld, F., "Electrochemical Impedance Spectroscopy (EIS) as a New Tool for Investigation Methods of Corrosion Protection", Electrochimica Acta, 35 (1990), 1533.
8. Walter, G.W., "A Review of Impedance Plot Methods Used for Corrosion Performance Analysis of Painted Metals", Corrosion Science, 26 (1986) 681.
9. Kendig, M., J. Scully, "Basic Aspects of Electrochemical Impedance Application for the Life Prediction of Organic Coatings on Metals", Corrosion, 46 (1990) 22.
10. Fletcher, S., "Tables of Degenerate Electrical Networks for Use in the Equivalent-Circuit Analysis of Electrochemical Systems", J. Electrochem. Soc., 141 (1994) 1823.

**Equivalent circuit of an electrochemical cell.**
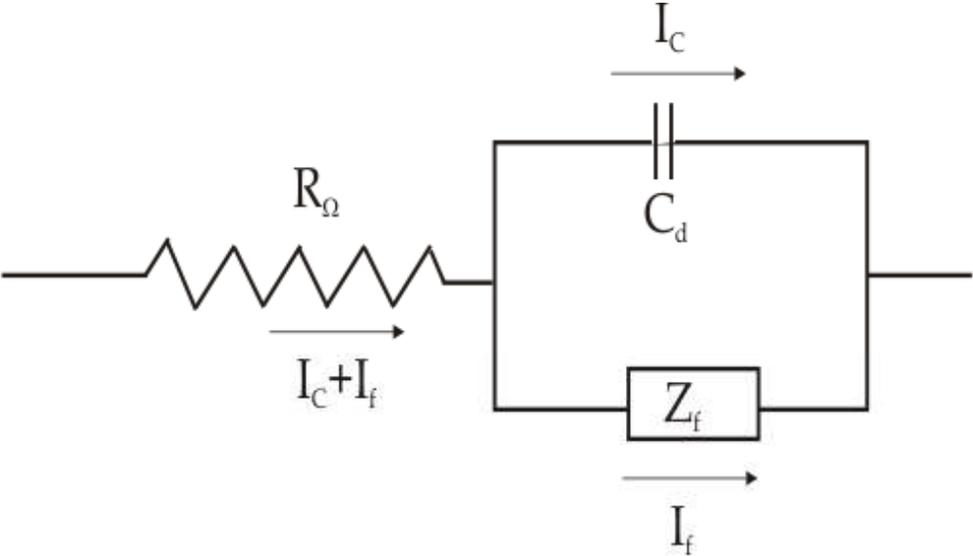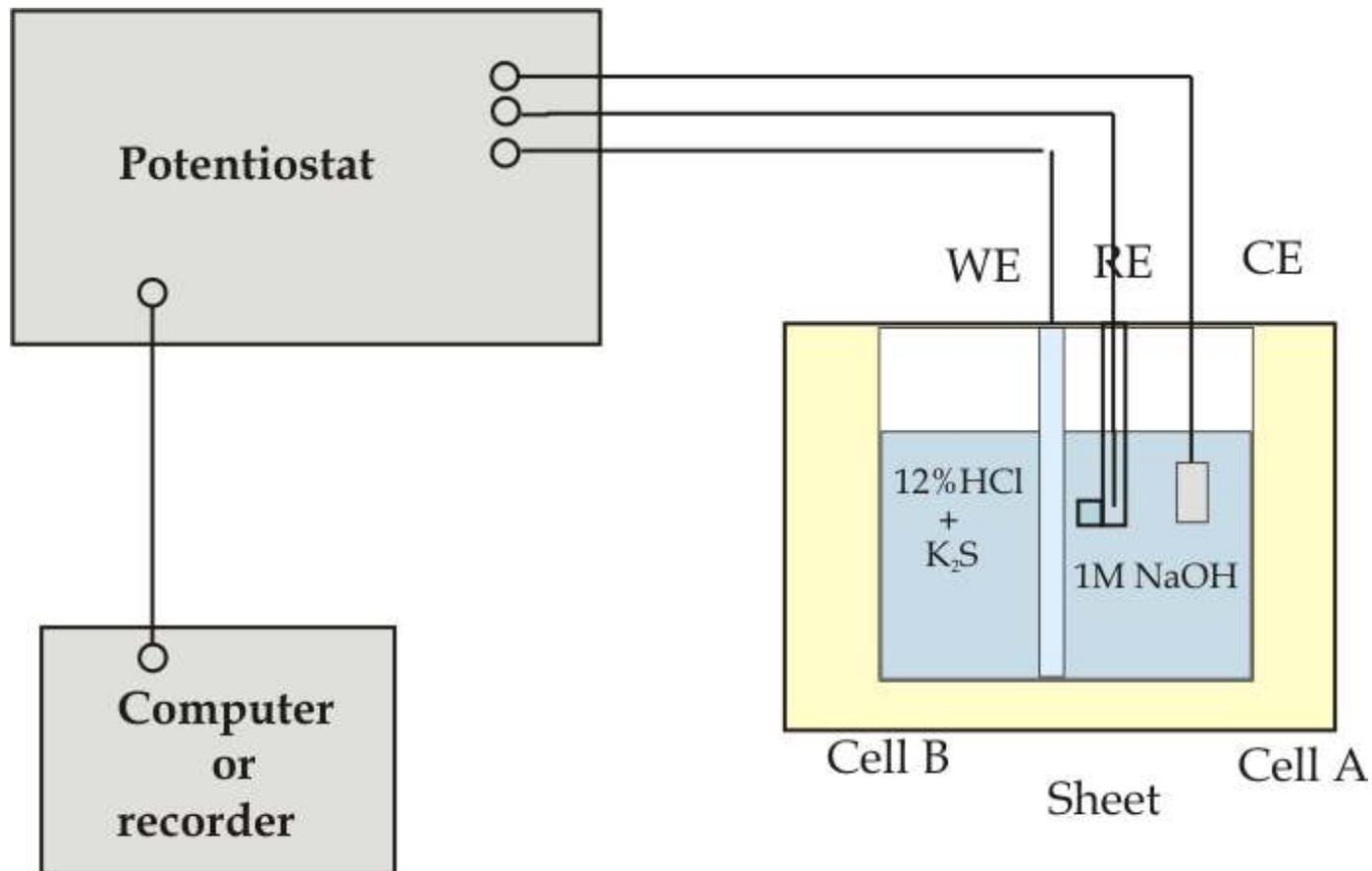
**Experimental arrangement and circuit for measuring hydrogen permetation through steel.**

# Corrosion monitoring in low conductivity media

The following conditions can be accepted for organic solvents characterized by a very low conductivity and absence of basic electrolyte (dissolved ionic substances):

1.  The capacitance of double layer should be the same for both: cathode and anode region, as it is responsible for the adsorption and orientation of solvent particles on practically the same material which the metal surface is.

2.  The internal resistance of corrosion microcell $R_\Omega$ is related with the conductivity of an electrolyte, and in pure organic solvent it may be of the same order as a resistance of the exchange reaction $R_p$ and thus it may determine the corrosion rate.

3.  The resistances $R_\Omega$ and $R_p$ depend to a great degree on the properties of a solvent, that is, on the ionic conductivity and dielectric constant.

# Methods of corrosion testing in low conductivity media

Corrosion of metals in these media is very low and usually of a local character (non uniform corrosion). This creates serious problems in evaluation of the corrosion resistance of materials used for performance in these environments.

In our laboratory three methods are used for the evaluation of corrosion rate:

chemical analysis of corrosion medium,
electrochemical method,
computer image analysis.

# Corrosion monitoring in low conductivity media

Corrosion current in a microcell will be given by the equation:
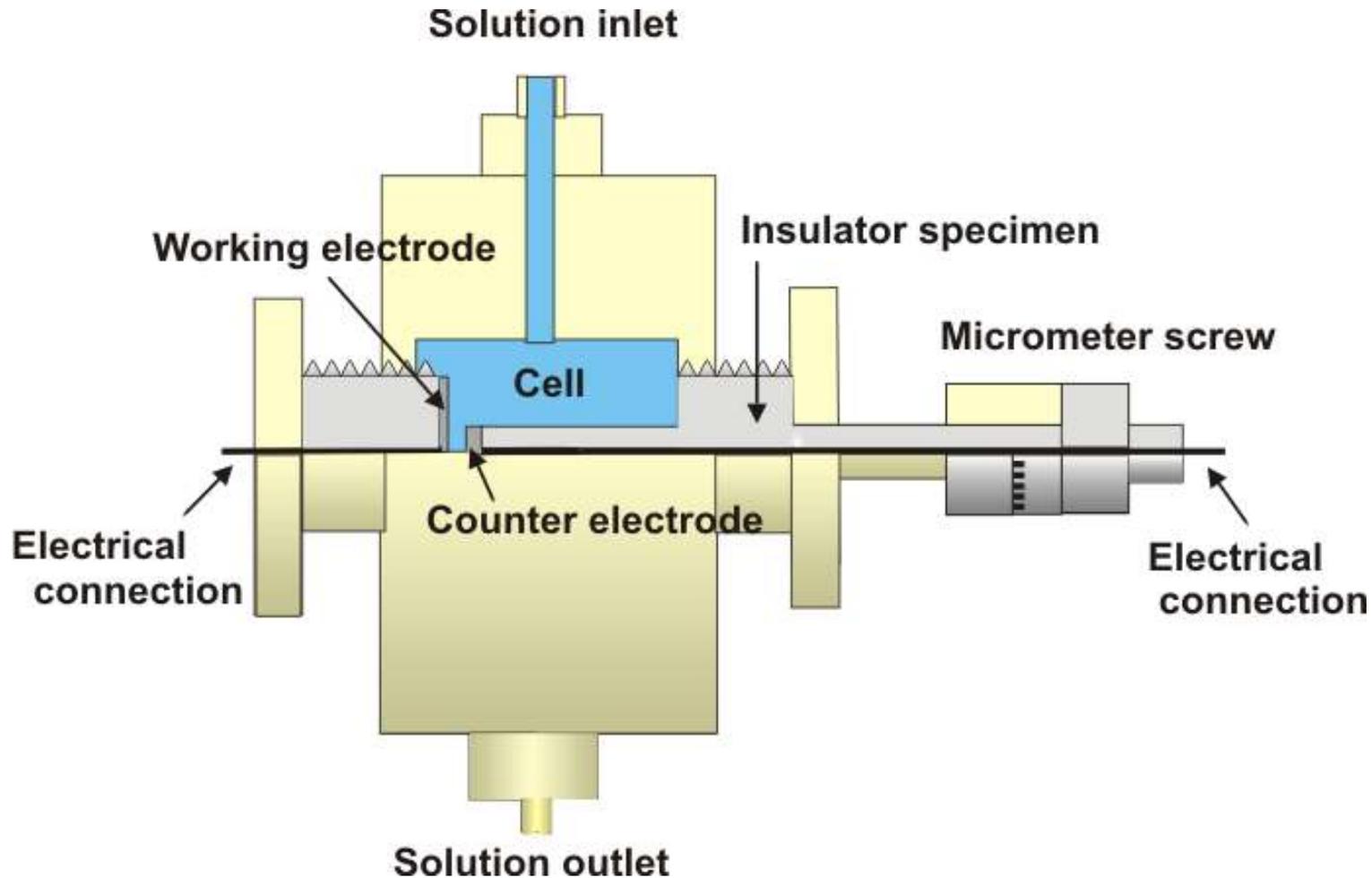
$$I_{corr} = \frac{E_A - E_C}{R_\Omega + R_P^A + R_P^C}$$

For $R_\Omega >> R_P^A, R_P^C$ we have:

$$I_{corr} = \frac{\Delta E \cdot \kappa}{k}$$

Where:

$\Delta E$ is constant value for a given metal, related with differences in energy on the metal surface,

$\kappa$ is the coductivity of a corrosion medium,

k is a coefficient related with the configuration of local cathodes and anodes, and hence with the metal microstructure.

# Corrosion monitoring in low conductivity media (electrochemical methods)



Solution inlet

Working electrode

Insulator specimen

Micrometer screw

Cell

Counter electrode

Electrical connection

Electrical connection

Solution outlet

**It has been assumed that the stationary current obtained in measurements with application of the impulses of constant voltage is measure of the corrosion rate of the examined anode.**

# Corrosion monitoring in low conductivity media



Relation anodic current - corrosion rate for Zn-4%Al alloy exposed in petrol
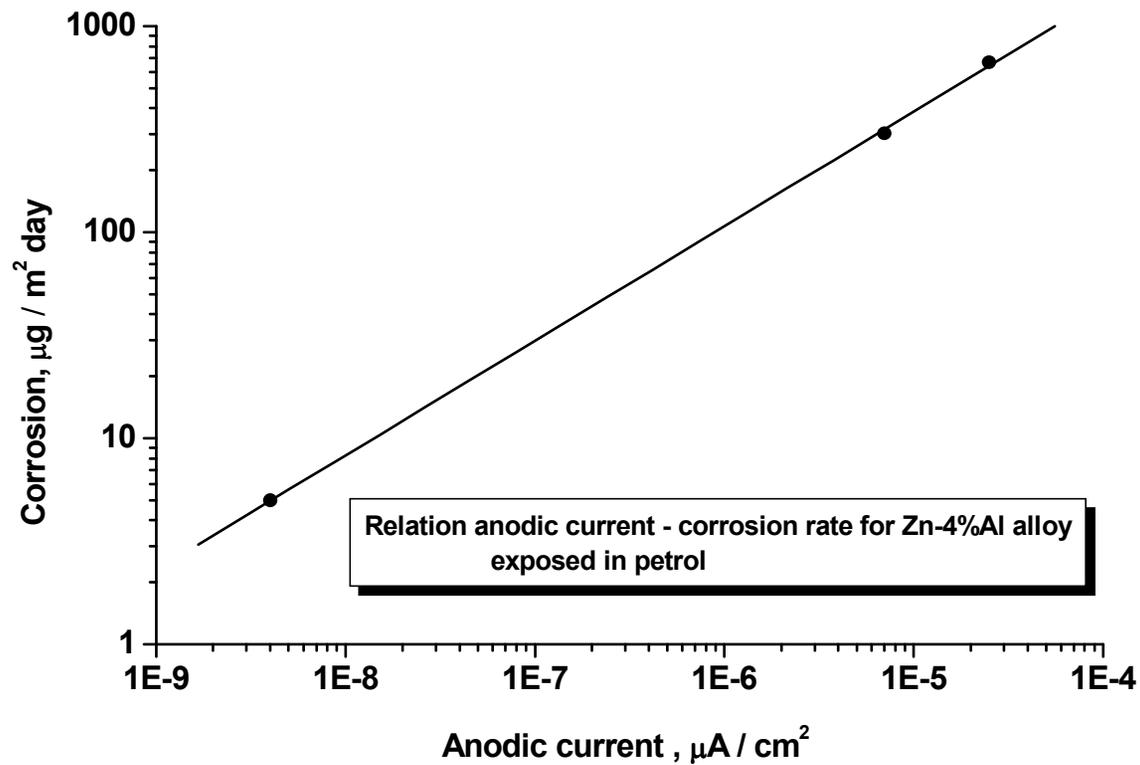
# Corrosion monitoring in low conductivity media

It has been assumed that the stationary current obtained in measurements with application of the impulses of constant voltage is measure of the corrosion rate of the examined anode. The table presents the corrosion measurements for Zn-4%Al.

| Petrol | Permittivity $\varepsilon$ | Resistivity $\rho$, $\Omega \cdot cm$ | Anodic current | Corrosion $\mu g$ /m$^2 \cdot$day |
|---|---|---|---|---|
| Ref. petrol | 2.27 | $3.3 \cdot 10^9$ | 4 nA | 5 |
| Ethanol 3% Isobutanol 3% Water0,159% DAC 4303 | 3.31 | $5.9 \cdot 10^7$ | 7 $\mu A$ | 302 |
| Ethanol 5% Water 0,102% | 3,68 | $5.6 \cdot 10^5$ | - | 297 |
| Methanol 3% Isobutanol 2% Water 0,03% | 2,83 | $5,9 \cdot 10^7$ | 25 | 666 |

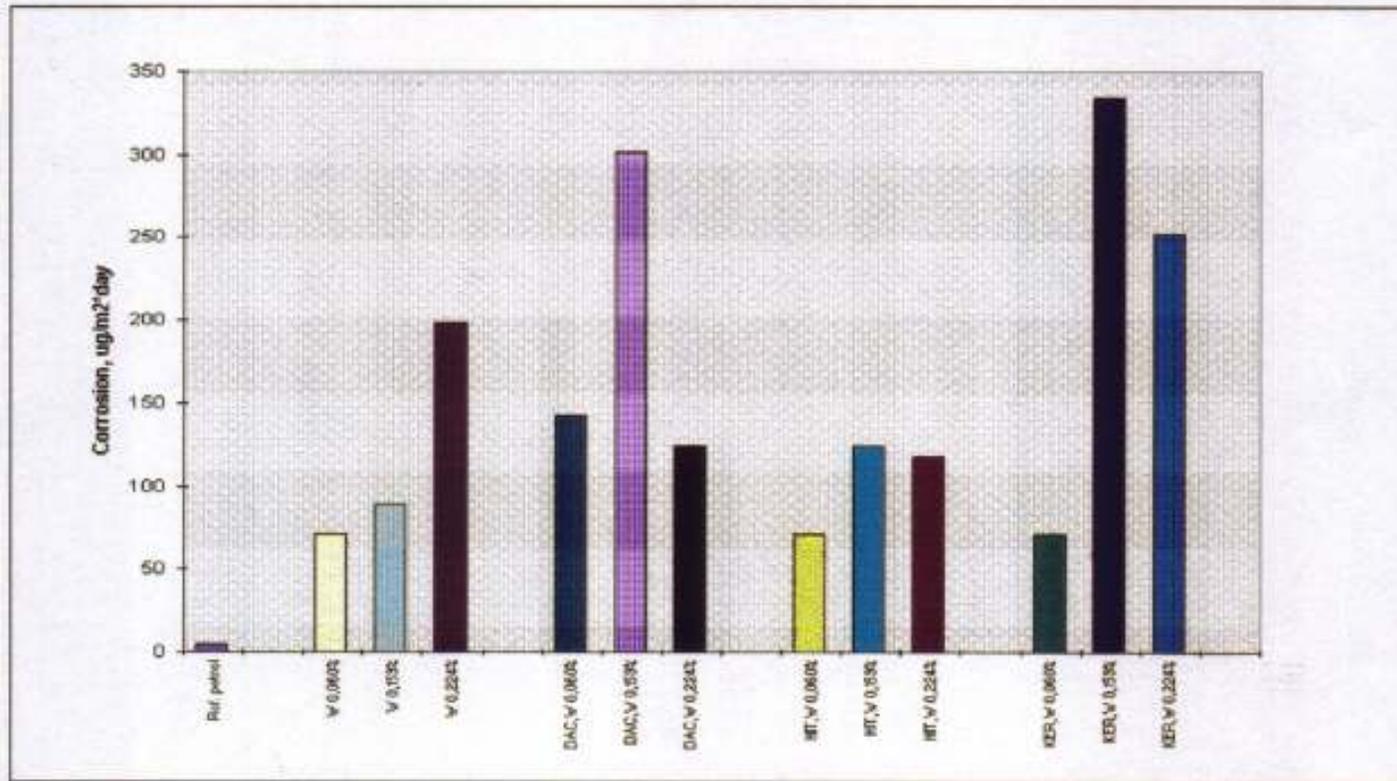# Corrosion monitoring in low conductivity media



Fig.4. Effect of water concentration and of the additives of DAC 4303, HITEC, KEROPUR on corrosion rate of Zn 4 % Al alloy in petrol containing 5% ethanol and 3% iso-butanol. W - water.

# Surface image analysis

The image of microstructure was processed into an analogue signal. Further processing of the signal consisted in its transformation to a digital form using a Qualys ver.1.5 computer program. The results of corrosion tests were processed by a statistical program Statgraphics 5.0 made by STSC.

Computer image analysis (the black level) has been based on an assumption that the elements of the grey level 255 are black elements, while all the white elements have a conventionally accepted value 0.

In the measurements a constant grey level equal to 255 was used; it was obtained from the grey profile of a standard, i.e. The calibration plate.

The plate in the form of a metallographic specimen made from a „Uranus" type steel (22%Cr,24%Ni,4%Mo,Ti,Cu) was used as a reference standard for calibration (the measurement of the quantity of pits and of the corrosion area) within a predetermined system of coordinates.
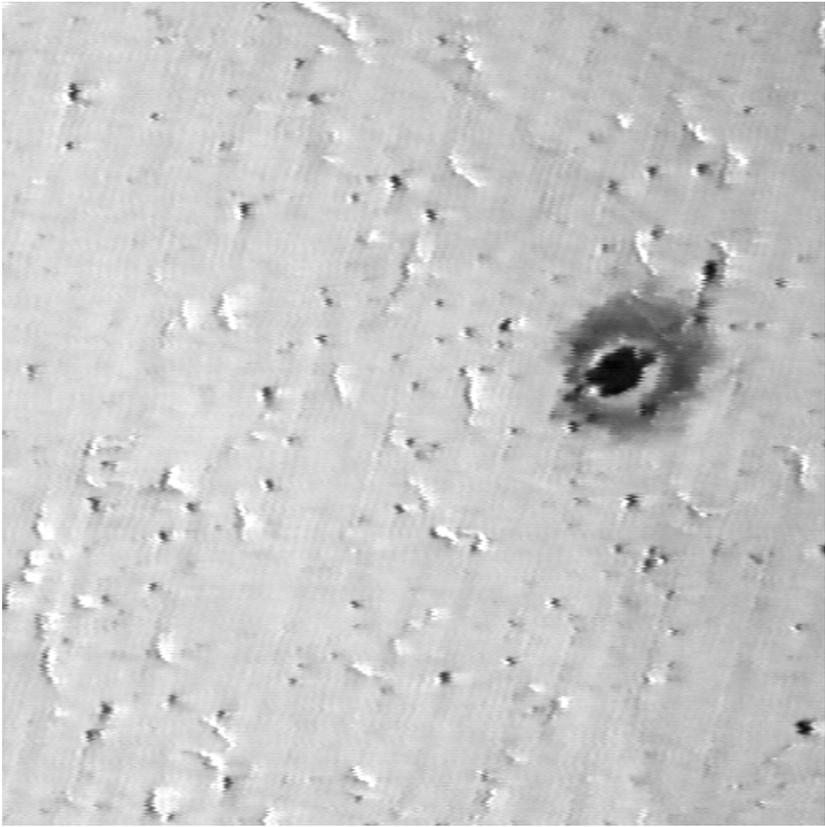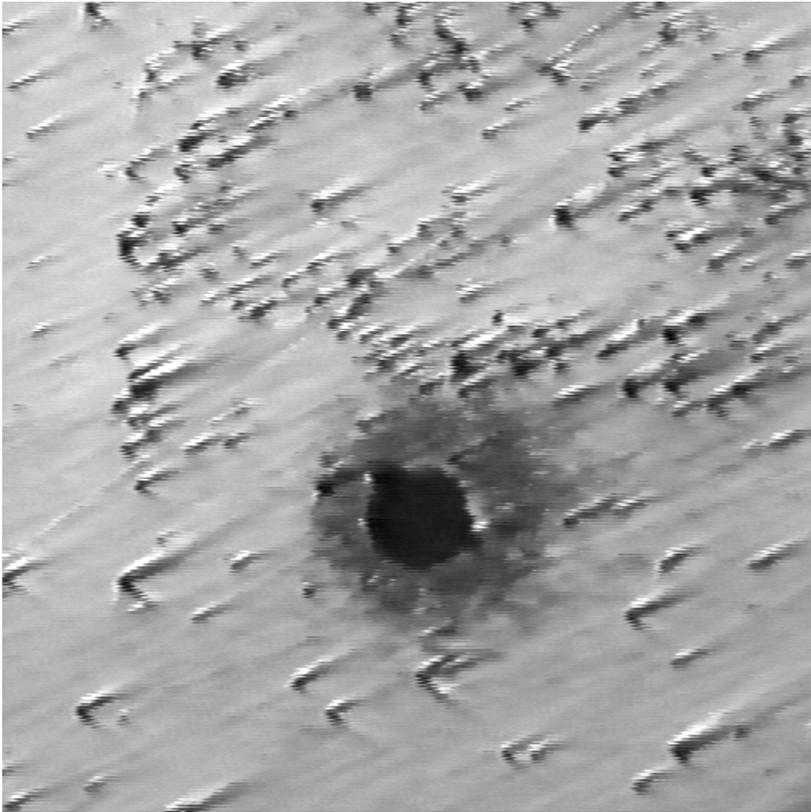
To compare the degree of corrosion an area of 1,13 mm$^2$ selected at random from 25 different places of three specimens was examined.

Corrosion of iron and zinc in N-dimethylformamide-formamide solvent
(DMF-FA, iron-80 days, zinc-5 days, 20C)
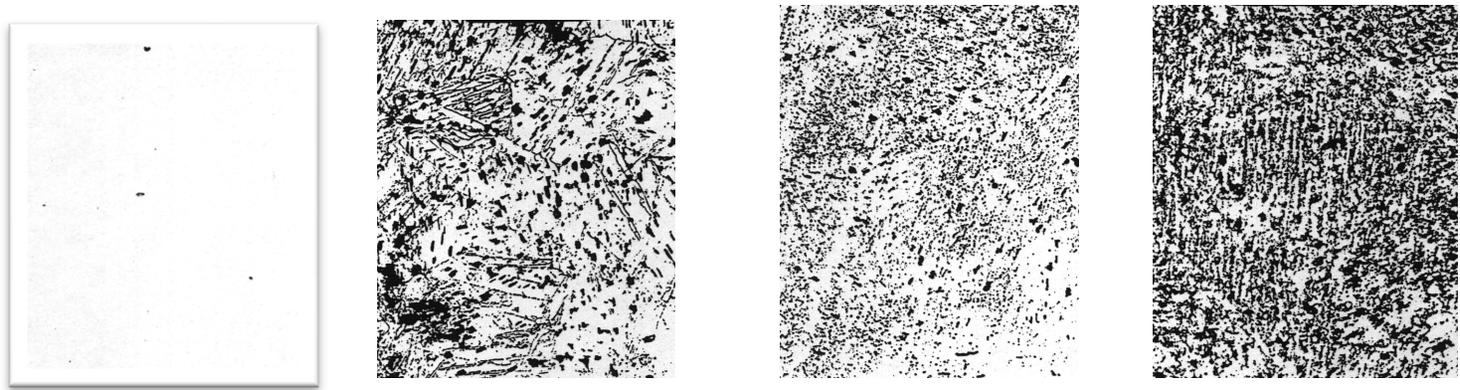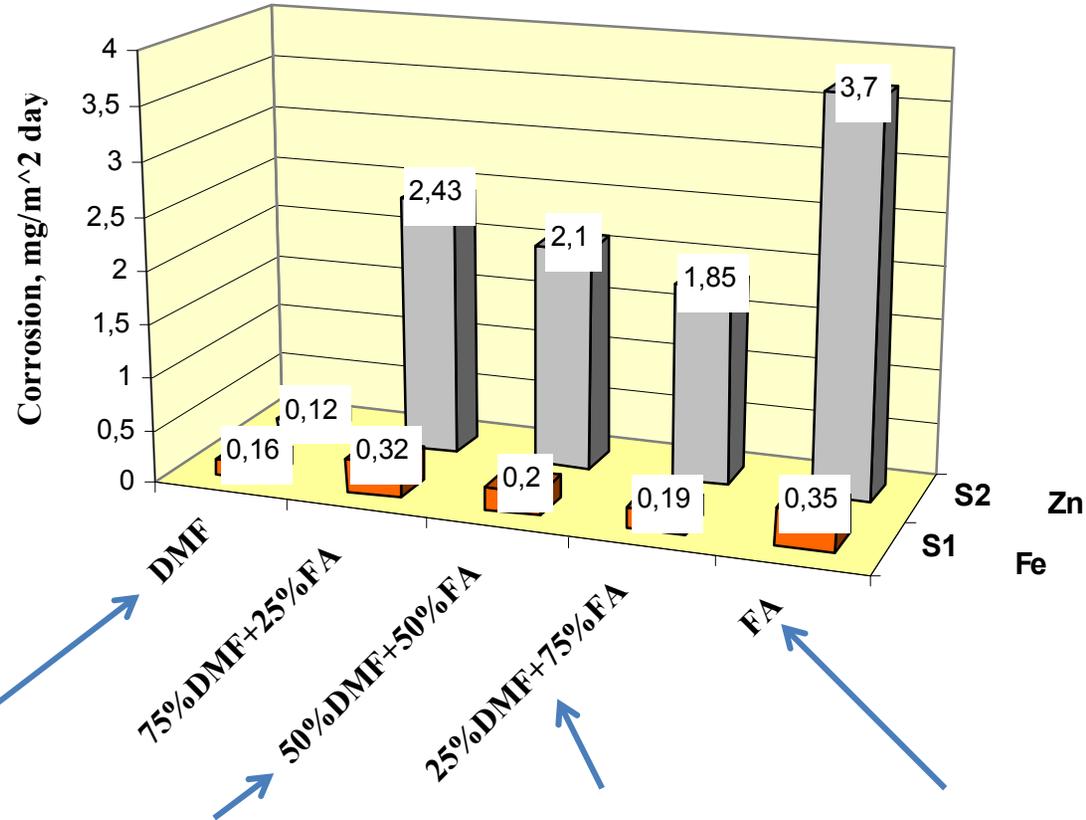
Surface morphology of Zn in N-dimethylformamide-formamide mixtures (20⁰C, 5 days)

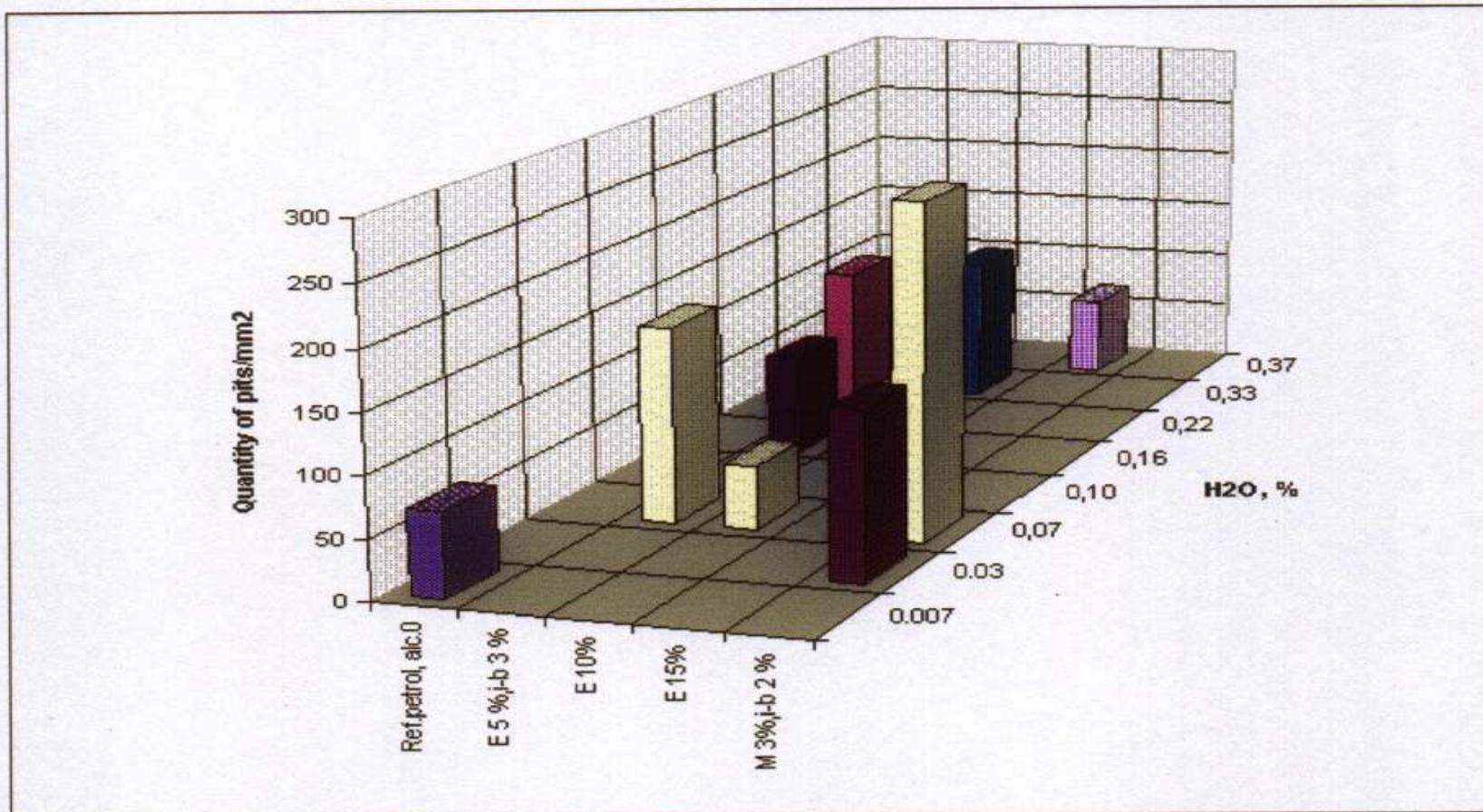# Corrosion attack on Armco Iron in gasoline

**Fig.5a: Effect of water concentration in petrol with alcohol on progress in pitting corrosion (quantity of pits/mm$^2$) of carbon steel. E - ethanol, M - methanol, i-b - iso-butanol.**
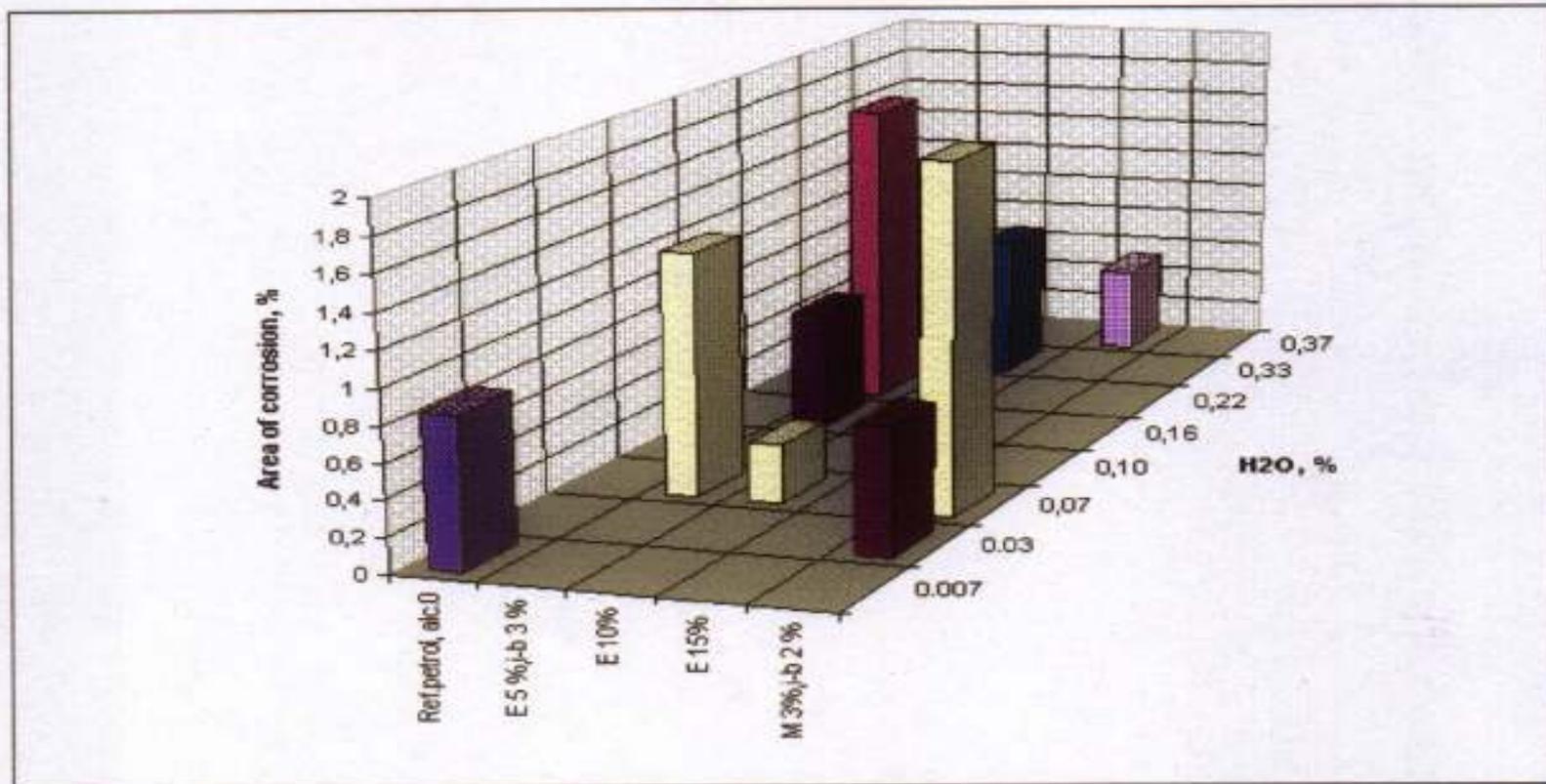
**Fig.5b:** Effect of water concentration in petrol with alcohol on progress in pitting corrosion (area of corrosion, %) of carbon steel. E - ethanol, M - methanol, i-b - iso-butanol.