Application of EIS to studies in the liquid state. A one hour tour.

CICECO/DEMaC, Universidade de Aveiro, Portugal

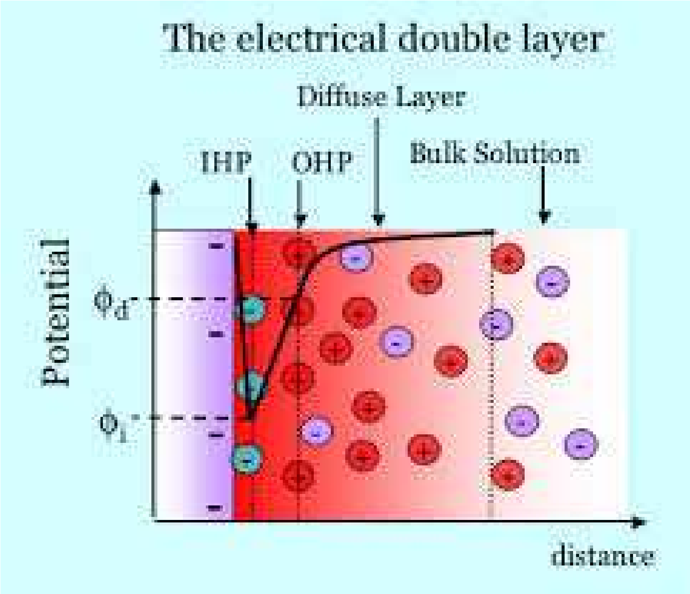
Alexandre Bastos

acbastos@ua.pt

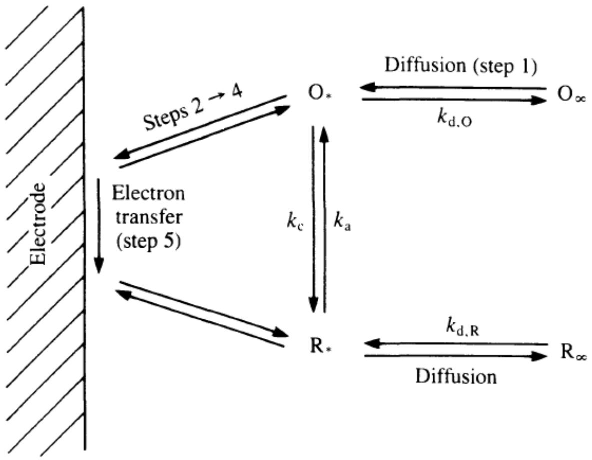
Overview

- Electrochemical kinetics and mechanisms
- Structure of the double layer
- ITIES – Interface between Two Immiscible Electrolyte Solutions
- Impedimetric sensors
- Materials and interfaces
- Corrosion

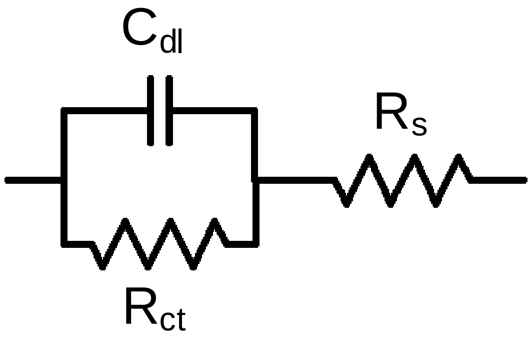
The simplest representation of the electrode-solution interface



4.3 The mechanism of electron transfer



Scheme of electron transfer at an electrode.



$$Z = R_s + \frac{R_{ct}}{1+\omega^2 C_{dl}^2 R_{ct}^2} - j\frac{\omega C_{dl} R_{ct}^2}{1+\omega^2 C_{dl}^2 R_{ct}^2}$$

Some experimental details

Applied DC potential: typically OCP (open circuit potential).

Applied AC perturbation: generally a sinusoidal potential signal of 10 mV rms.

Sinusoidal: other forms of perturbation are possible but this one is easier to handle electronically.
Potential: can also be current (if current bursts are expected during the measurement).
Non electrical quantities are also possible: temperature, light and hydrodynamics (RDE rotation speed).
10 mV: it's nowadays the standard, but the smaller the better. 5 mV or less for bare metals, 30 to 100 mV for high resistance thick organic coatings, up to 1 V or even more for thick dielectrics.
Rms: root mean square. The 10 mV sinusoidal signal has in fact a peak amplitude of $(10 \times \sqrt{2}) = 14.14$ mV
The effective (RMS) of a sinusoidal current of 10 mV delivers the same power as a DC current of 10 mV.

Frequency range: 100 kHz – 1 mHz, 5-10 points per decade with log distribution.

1 MHz: some equipments allow to measure up to 1 MHz but usually no new information comes from that extra frequency range, either because the cables and electronics give response or simply the only signal comes from the uncompensated solution resistance.
1 mHz: because it takes time to achieve this frequency people simply stop at 0.01 Hz or even 0.1Hz, missing valuable information for the mechanistic determination of the systems under study.

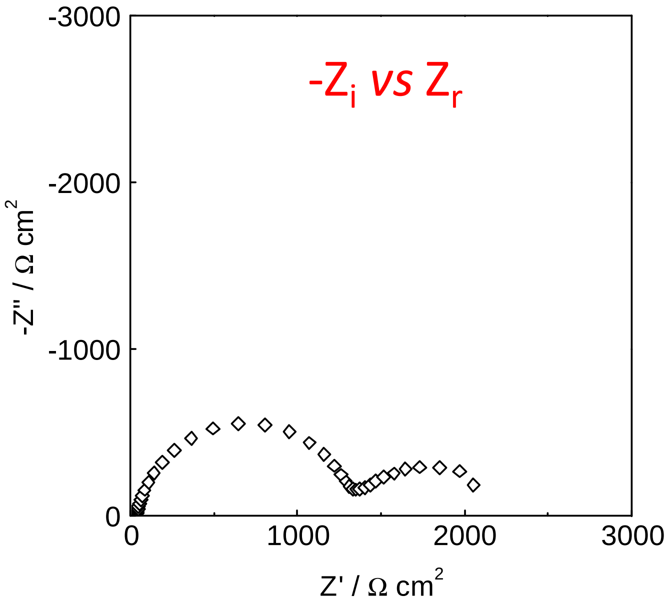
The most common ways to represent EIS results

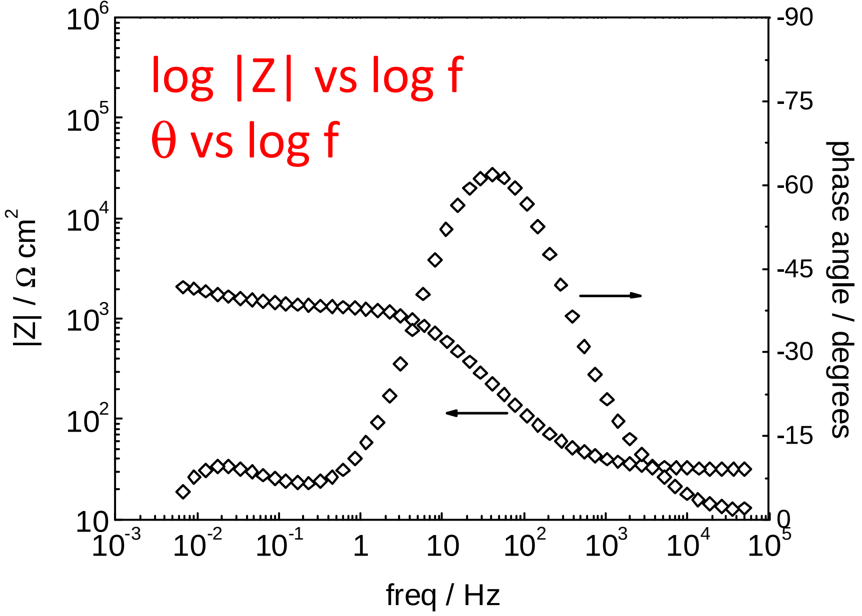
Complex plane plot
Argand diagram
Nyquist plot

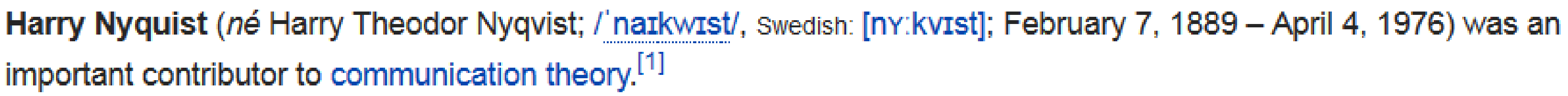
Bode plot

$$|Z| = \sqrt{Z'(\omega)^2 + Z''(\omega)^2}$$

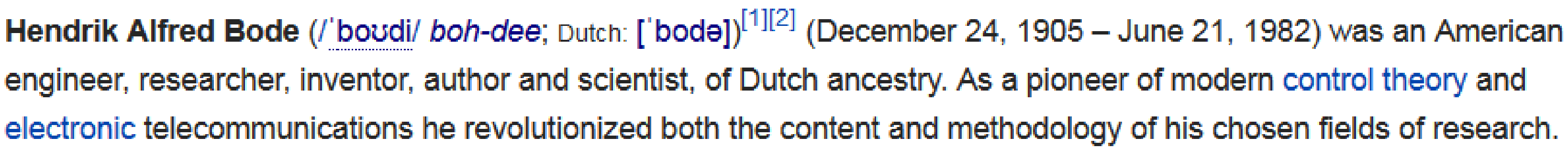
$$\phi = arctg \frac{Z''(\omega)}{Z'(\omega)}$$





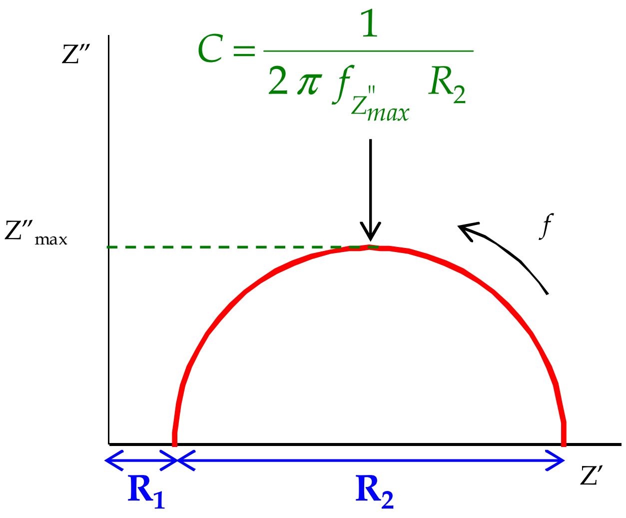


Harry Nyquist (*né* Harry Theodor Nyqvist; /ˈnaɪkwɪst/, Swedish: [nʏːkvɪst]; February 7, 1889 – April 4, 1976) was an important contributor to communication theory.[1]

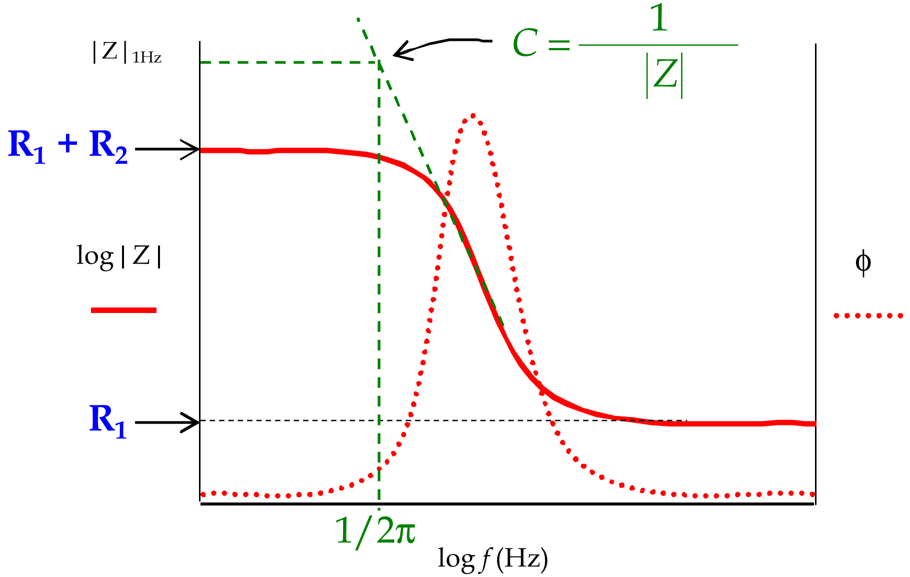


Hendrik Alfred Bode (/ˈboʊdi/ *boh-dee*; Dutch: [ˈbodə])[1][2] (December 24, 1905 – June 21, 1982) was an American engineer, researcher, inventor, author and scientist, of Dutch ancestry. As a pioneer of modern control theory and electronic telecommunications he revolutionized both the content and methodology of his chosen fields of research.

Direct determination of parameters



$$C = \frac{1}{2\pi f_{Z''_{max}} R_2}$$



$$C = \frac{1}{|Z|}$$

$$C = \frac{1}{2\pi f Z''}$$

$$C = \frac{1}{2\pi f |Z|}$$

Try to calculate C using the different equations and compare the results.

Typical resistances

Solution resistance. Resistance of the electrolytic solution between the working electrode and the reference electrode, together with the resistance of cables and instrument. It is also called uncompensated resistance (R_u), electrolyte resistance (R_e) or ohmic resistance (R_Ω).

Charge transfer resistance. Resistance of the faradaic process at the electrode. It's value is an indication of the rate of the electrochemical process.

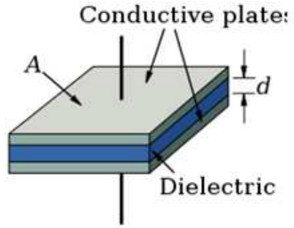
Coating, film, oxide resistance. Various films of different nature can be found at the electrode surface, either deliberately produced of as a consequence of the processes at the electrode: polymers, metal oxides, precipitated inorganic layers. These films may be conductive or insulators. In this last case, the measured resistance is in fact the resistance of the electrolyte solution inside pores and defects of the film.

Typical capacitances

Double layer capacitance. The interface between the metal and the solution is electrified. Charges at the metal and ions from the solution line up, creating the so called double layer, wich can be seen as a capacitor.

Coating, film, oxide capacitance. The films deposited on the electrode's surface can give a capacitive response.The dielectric is the layer itself an the plates are the electrode in one side and the conductive solution on the other side.

Space-charge capacitance. In semi-conductors a separation of charge occurs at the solid boundary, similar to the double layer in solution.



$$C = \frac{\varepsilon \, \varepsilon_0 \, A}{d}$$

ε is the dielectric constant of the medium between the plates, ε_o is the permittivity of free space (8.85419 pF/m), *A* is the surface area of the plates (m^2), and *d* is the thickness of the insulating layer (m).

Tipical capacitance values

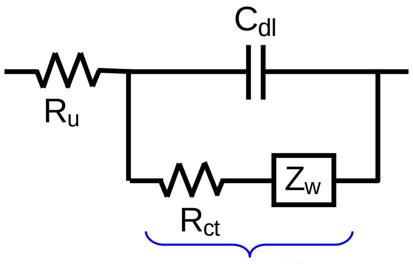
System	ε	d / nm	C / 10^{-6} F cm^{-2}
Double layer	-	-	10-50
Al_2O_3 oxide	6.7	12	0.5
Fe_2O_3 oxide	7	3	2
Ni_2O_5 oxide	42	3	2
Epoxy film	3.6	1-500 x 10^5	10^{-4}-10^{-6}

The capacitance increases as the distance between plates decreases or the dielectric constant of the material increases.

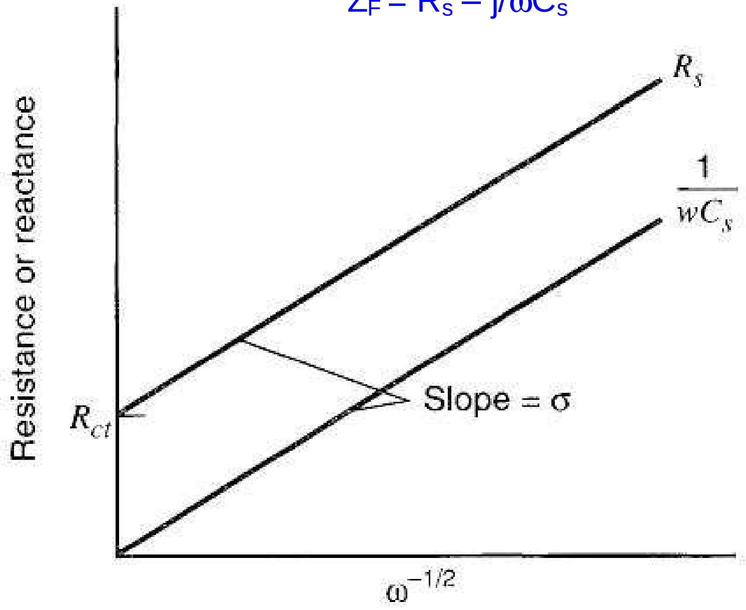
• Electrochemical kinetics and mechanisms

Randles Method.

Method of plotting the resistive, R_s, and the reactive, $1/\omega C_s$, components of the Faradaic impedance, Z_F, versus $\omega^{-1/2}$ to obtain values for charge-transfer resistance, R_{ct} and Warburg diffusion coefficient, σ. ω is angular frequency ($\omega = 2\pi$ f, rad s^{-1}).



$Z_F = R_s - j/\omega C_s$



Dependence of R_s and $1/\omega C_s$ on frequency.

$$R_s = R_{ct} + \sigma/\omega^{1/2}$$

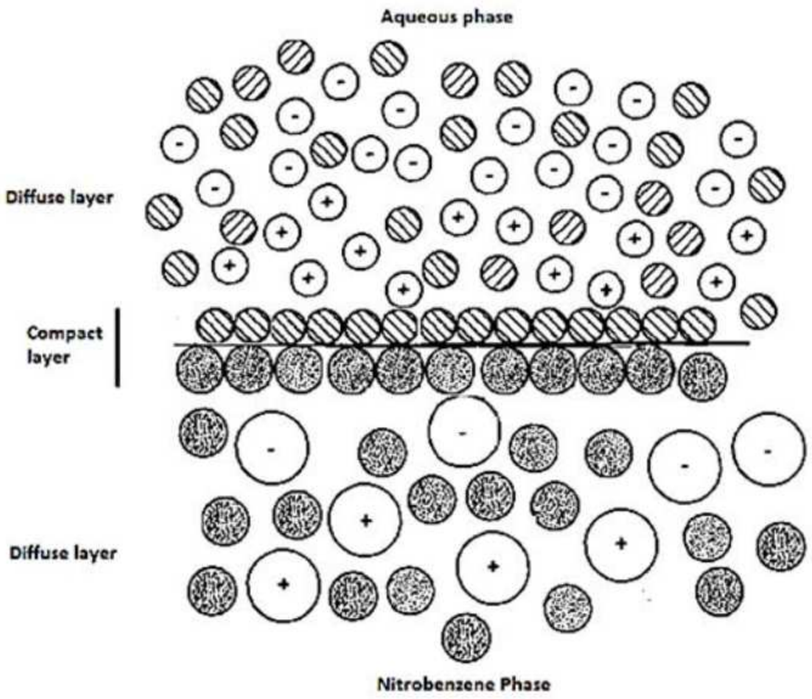
$$C_s = \frac{1}{\sigma\omega^{1/2}}$$

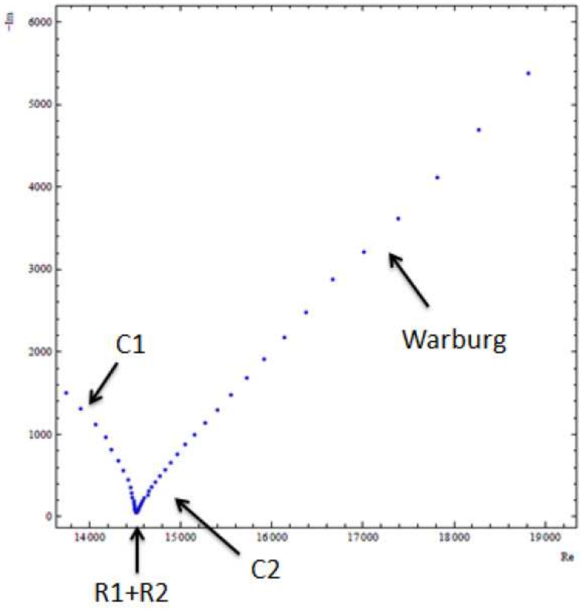
$$R_s - \frac{1}{\omega C_s} = R_{ct} = \frac{RT}{Fi_0}$$

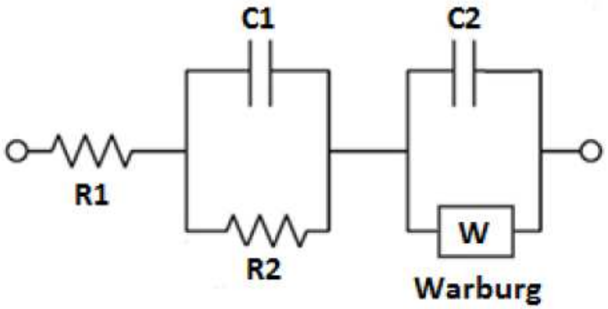
$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}}\left(\frac{1}{D_O^{1/2}C_O^*} + \frac{1}{D_R^{1/2}C_R^*}\right)$$

J. E. B. Randles, *Disc. Far. Soc.* 1 (1947) 11.
Bard, Faulkner, Electrochemical Methods, 2nd Ed, Wiley, 2001, p. 377ss

• ITIES – Interface between Two Immiscible Electrolyte Solutions







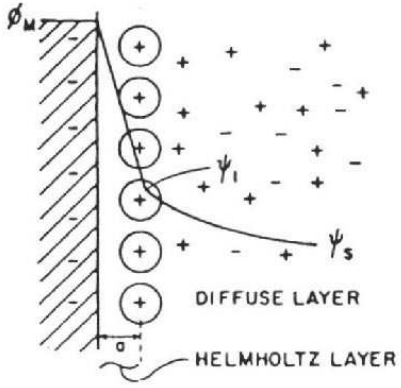
K. van Berlo, Electrical impedance spectroscopy of the water/nitrobenzene interface, Bachelor's thesis, Utrecht University, Netherlands, 2014.

Structure of the double layer

The **integral capacitance** of a simple capacitor is defined by $C = q / E$.

The electrochemical double layer represents a more complicated problem as the capacitance is dependent upon the applied potential. The thickness of the double layer changes with potential: the further the electrode potential is from the potential of zero charge (E_{pzc}) the greater the attraction or repulsion from the electrolyte ions and the smaller are the dimensions of the double layer. This **differential capacitance** can be measured by EIS:

$$C_d = \left(\frac{\partial q^m}{\partial \Delta\phi_{m/s}} \right)_{const.composition}$$



Following the Stern model and in the absence of specific adsorption, the overall double layer capacitance is given by,

$$\frac{1}{C_{dl}} = \frac{1}{C_{OHP}} + \frac{1}{C_{diffuse}}$$

C_{OHP} is the differential capacitance of the outer Helmholtz layer and the second capacitance corresponds to the diffuse region. The smallest capacitance will dominate the C_{dl} response.

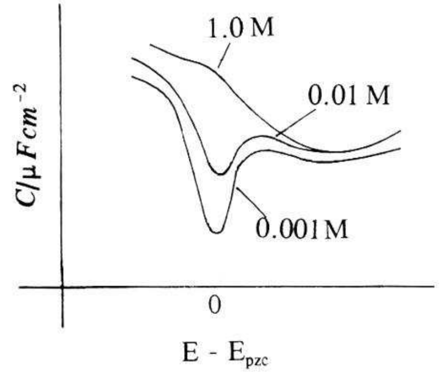
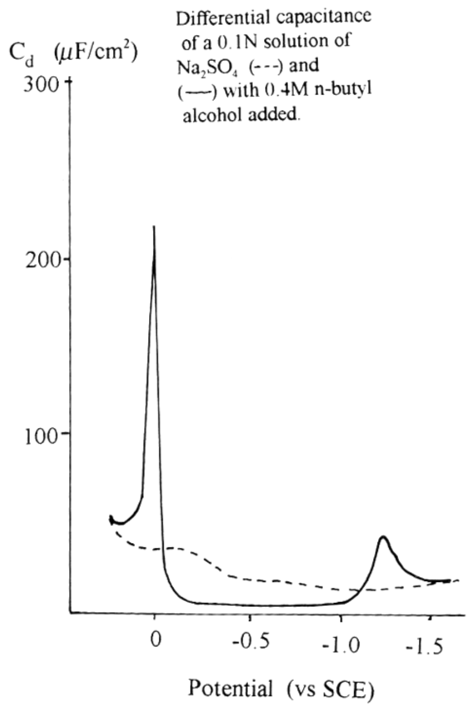


Fig. 4.15 Differential capacitance plots for varying concentrations of NaF.



Differential capacitance of a 0.1N solution of Na_2SO_4 (---) and (—) with 0.4M n-butyl alcohol added.

Fig. 4.16 The influence of organics on the differential capacitance.

A.C. Fischer, Electrode Dynamics, Oxford Chemistry Primers, 1996.

• Impedimetric sensors

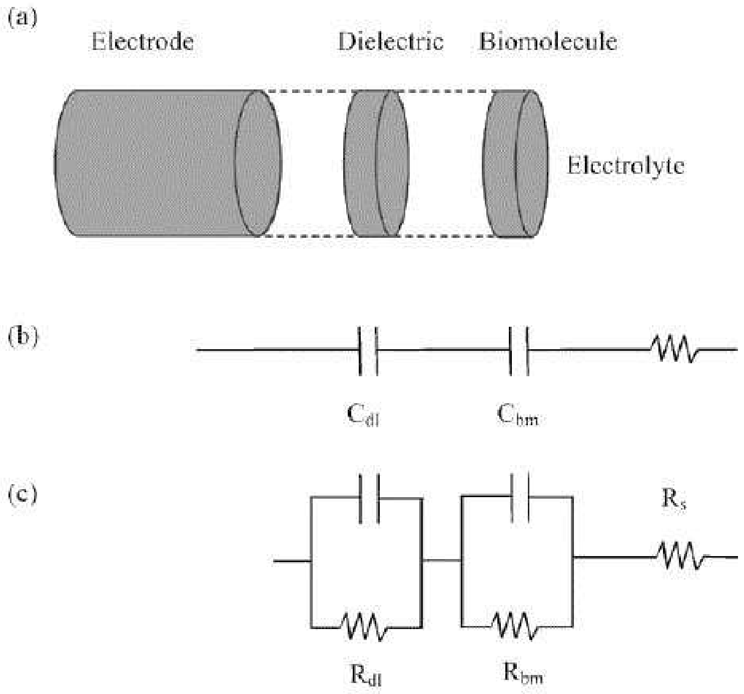
In **capacitive**, or **impedimetric**, **immunosensors** a specific receptor is immobilised on an insulating dielectric material that was previously deposited on the surface of an electrode. The interaction between the receptor and the target species, or analyte, (e.g. antibody-antigen binding) may result in changes in the thickness or dielectric properties of the dielectric layer, charge distribution or even conformational changes on the immobilised biomolecule, which all lead to variations in the measured capacitance.

The electrode (sensor) is considered to be composed by two capacitors, an inner one corresponding to the dielectric layer (C_d) and an outer one corresponding to the biomolecule layer (C_{bm}). Since these capacitors are in series, the total capacitance (C_t) is

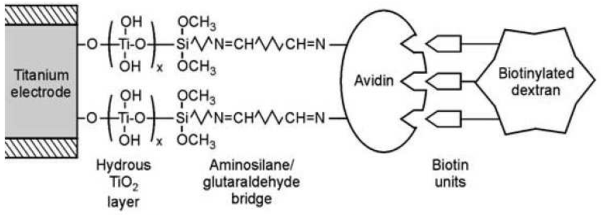
$$\frac{1}{C_t} = \frac{1}{C_d} + \frac{1}{C_{bm}}$$

In a good, sensitive sensor, with a wide dynamic range, the binding of the analyte to the receptor dominates the total capacitance. For this, the dielectric layer should be thin enough and/or have a high dielectric constant. It should have no defects, be stable with time and provide functional groups for the immobilization of the receptor.

M.I. Prodromidis / Electrochimica Acta 55 (2010) 4227–4233



Biosensors Based on Anodically Formed Ti/TiO$_2$ Electrodes



Scheme 1. Schematic representation of the Ti/TiO$_2$/silane/avidin/biotinylated dextran architecture.

Electroanalysis 17 (2005) 1878

- ## Corrosion

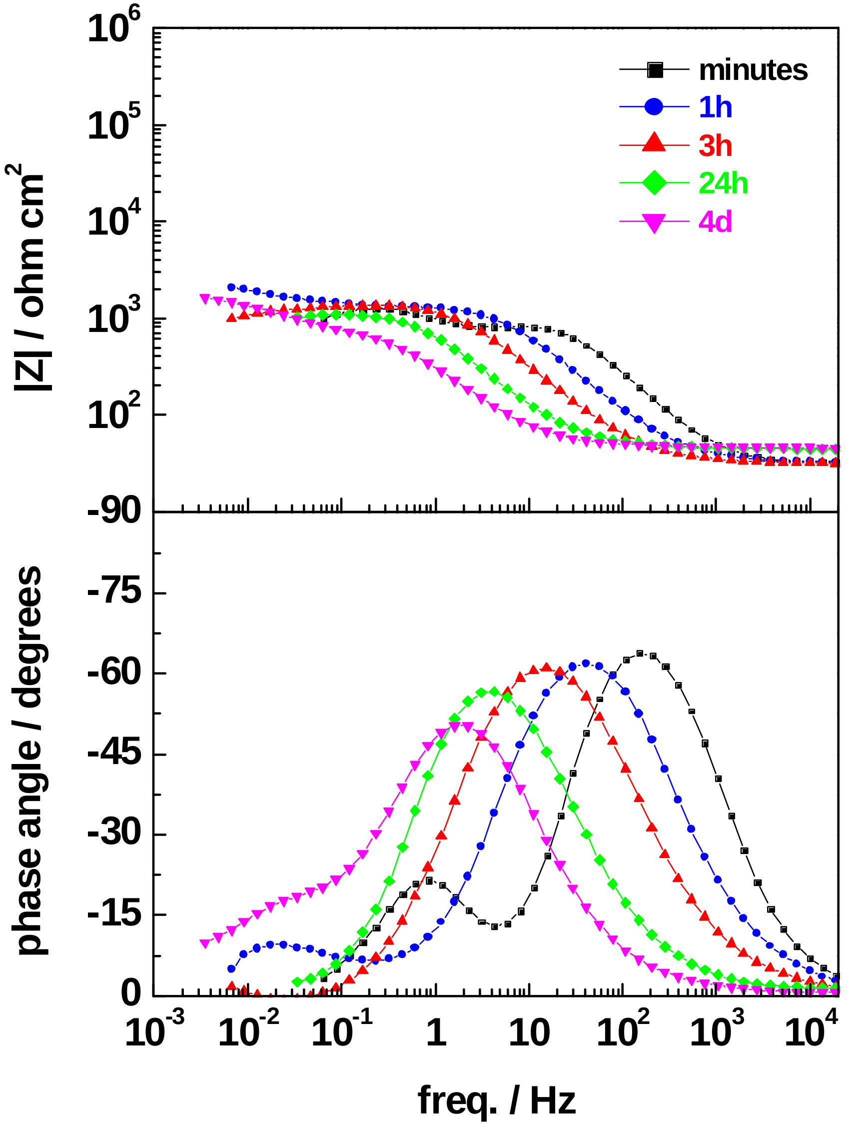
The remaining of this presentation will focus on the application of EIS to corrosion.

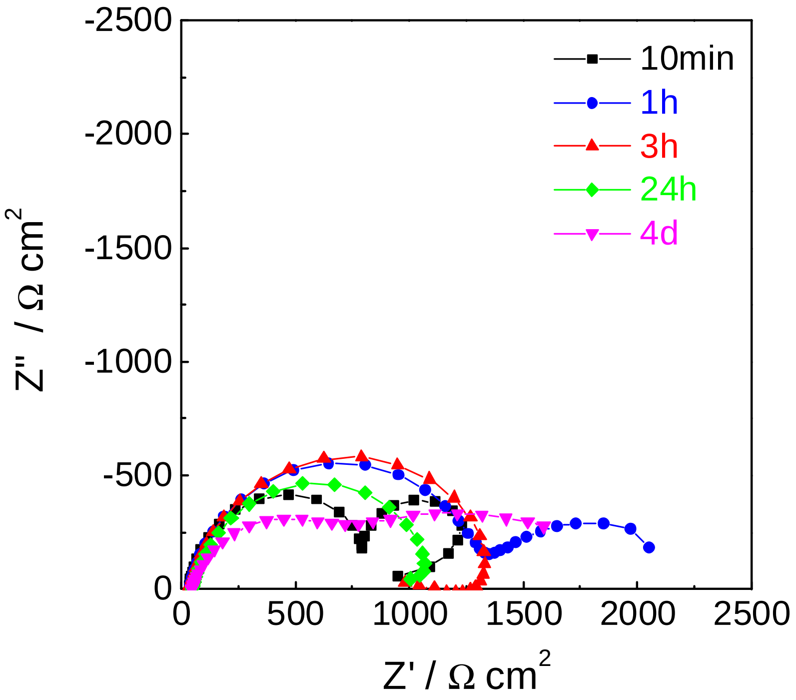
The objective is to keep it simple and illustrative, using the corrosion of zinc as an example and gradually increasing the complexity of the system.

First we analyse the corrosion of zinc in 0.1M NaCl.
Then the effect of corrosion inhibitors in the same medium.
After we'll see the impedance response of an inert layer (phosphate) deposited on the top of zinc (in fact, galvanised steel).
Finally, we'll have the characterisation of a complete system, comprising steel with electroplated zinc, a phosphate treatment and two layers of paint.

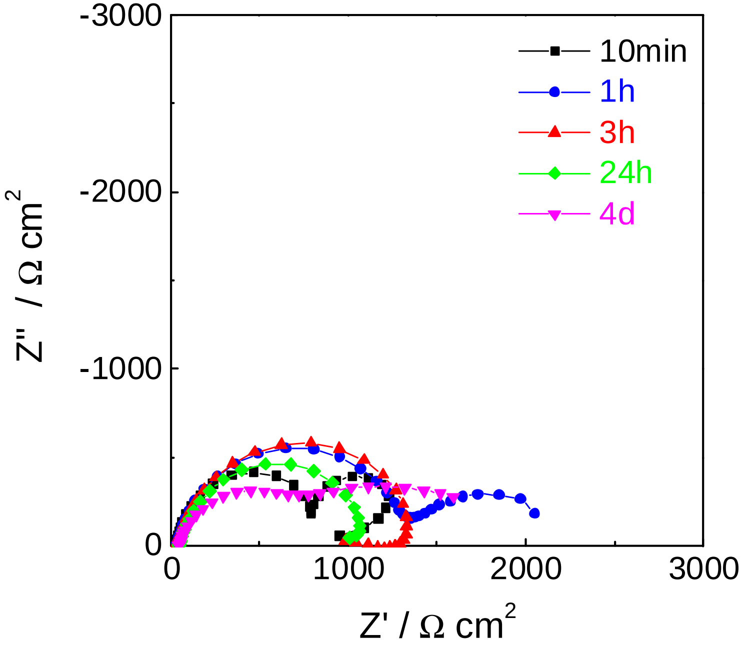
Some information is given on data treatment, reproducibility and influence of experimental conditions and equipment.

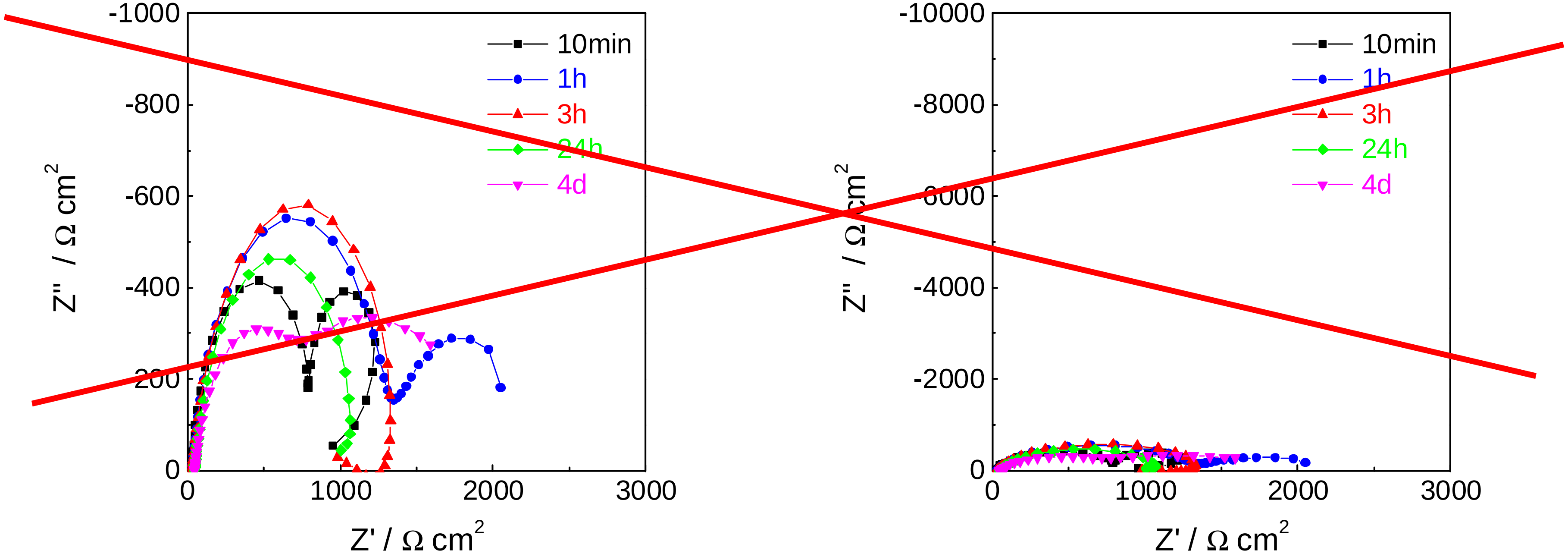
Pure zinc immersed in 0.1M NaCl



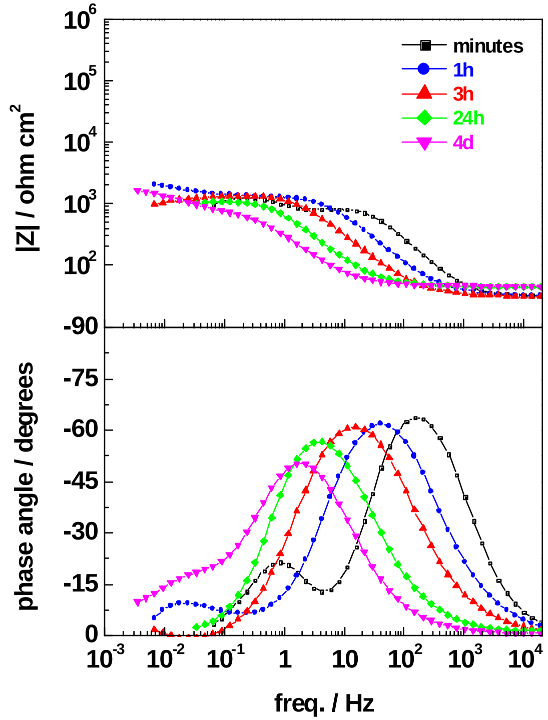


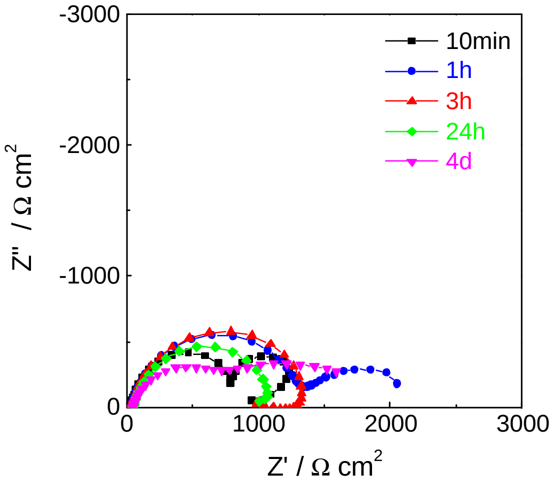
The importance of having orthonormal axis in complex plane (Nyquist) plots





Pure zinc immersed in 0.1M NaCl

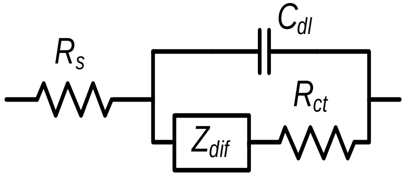




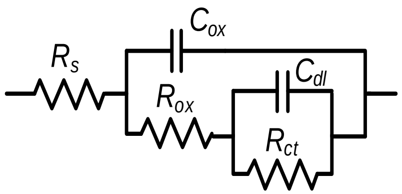
2 time constants!

To what do they correspond?

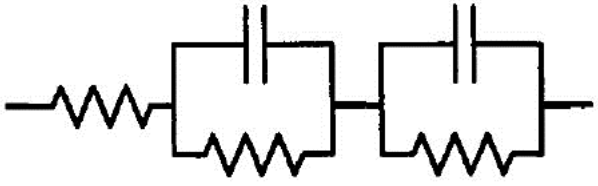
a) C_{dl}/R_{ct} + diffusion process

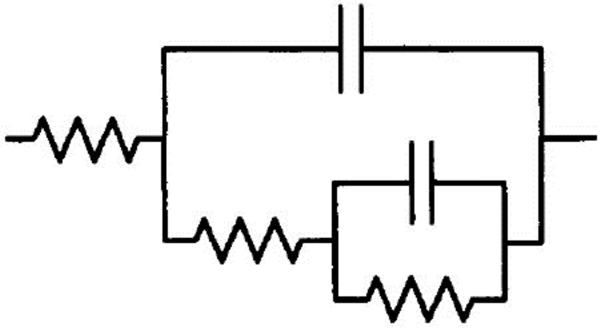


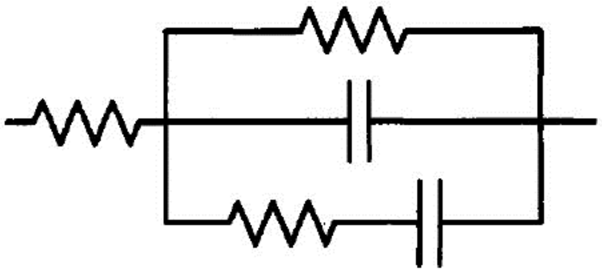
b) R_{ox}/C_{ox} + C_{dl}/R_{ct}



The need for independent confirmation of the elements considered in the circuit


(a)


(b)


(c)

With properly selected values of R and C these circuits will give exactly the same impedance response.

A good fit is necessary but not sufficient.

The circuit must be physically logical.
The values of each parameter must lie inside a valid interval.
Circuits and parameters must evolve coherently with time.

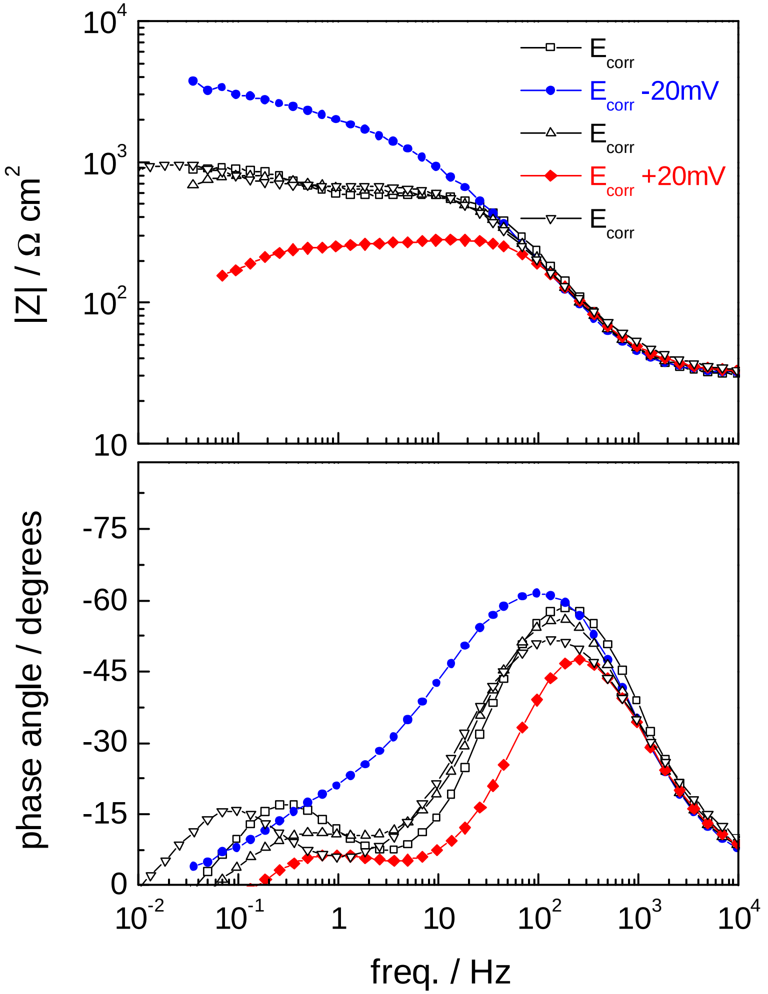
Confirm the existence of circuit elements.

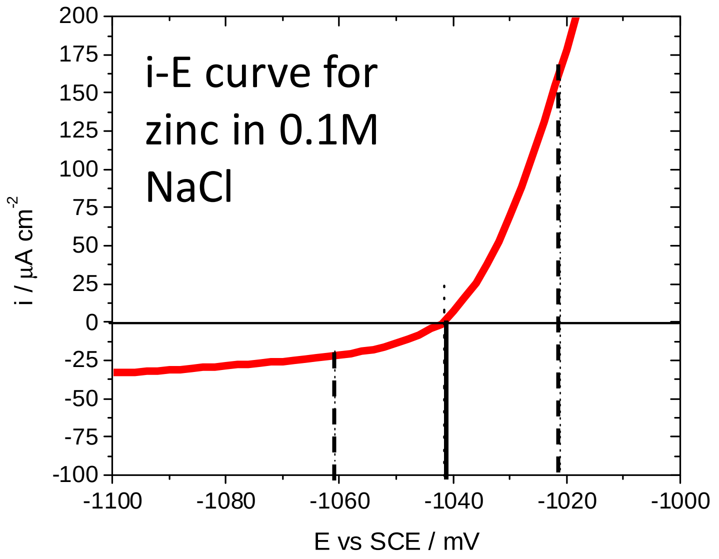
- Are you assuming the presence of a deposit or film?
Prove it using microscopy or surface analysis.
They can give extra information for the model: thickness, uniformity, porosity, defects, etc.

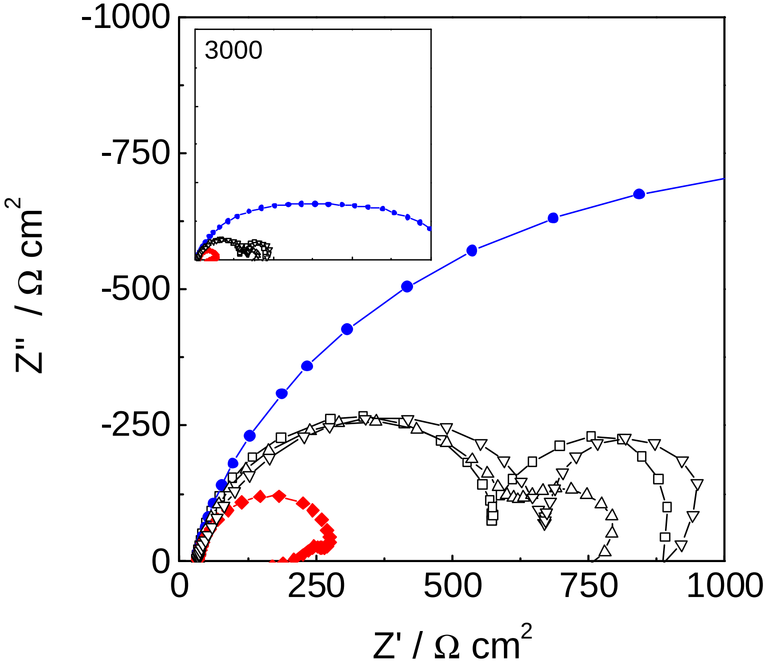
- Is there a strong barrier film? Make a defect on it. The impedance should decrease.

- Polarise the sample. Only the active elements will feel the difference.

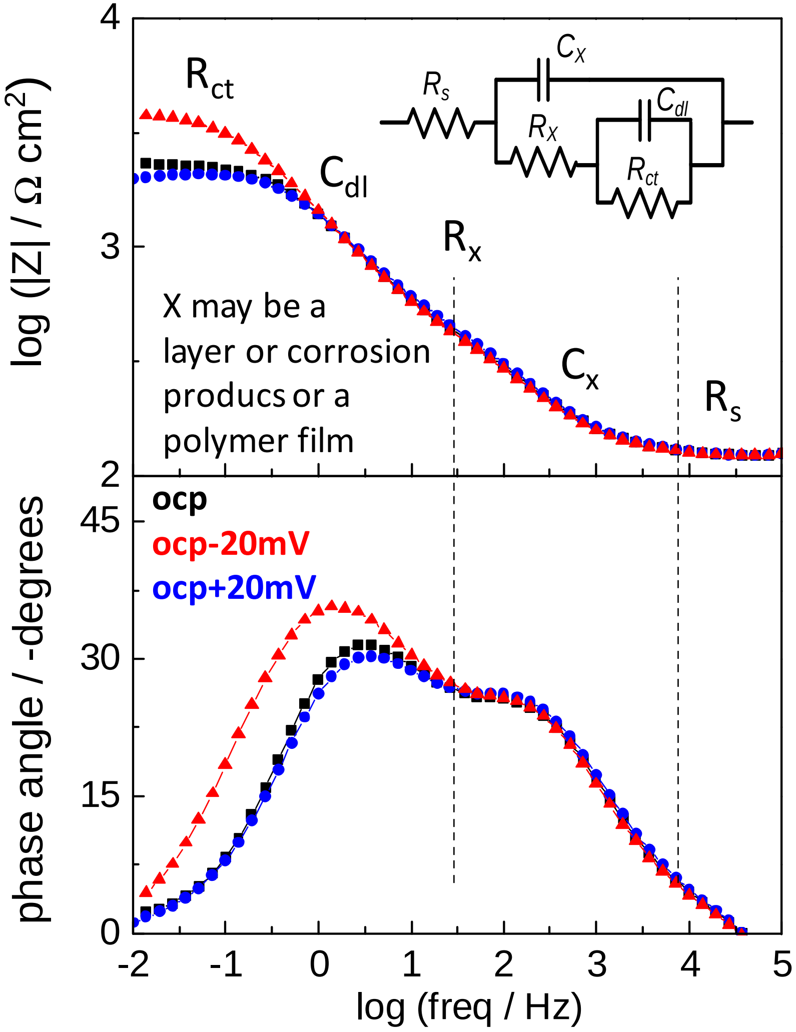
EIS with small DC polarization
to identify the response of
active elements (R_{ct}, C_{dl})



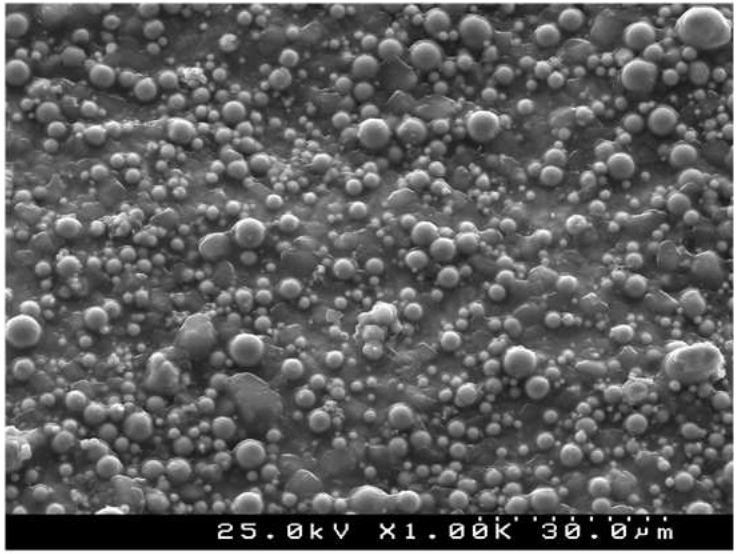

i-E curve for zinc in 0.1M NaCl

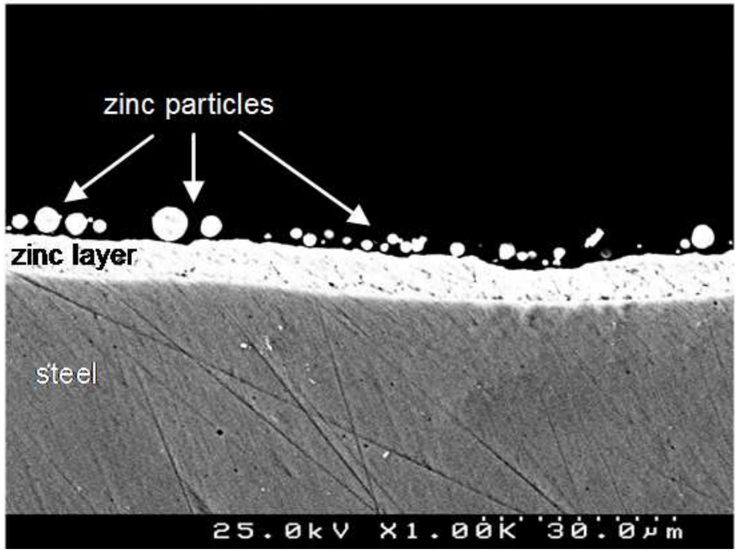


Just an example where the active elements appear at lower frequencies



X may be a layer or corrosion producs or a polymer film





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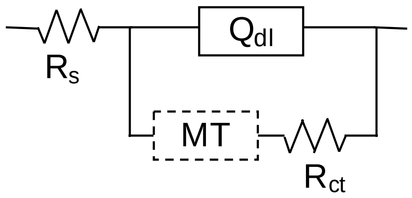
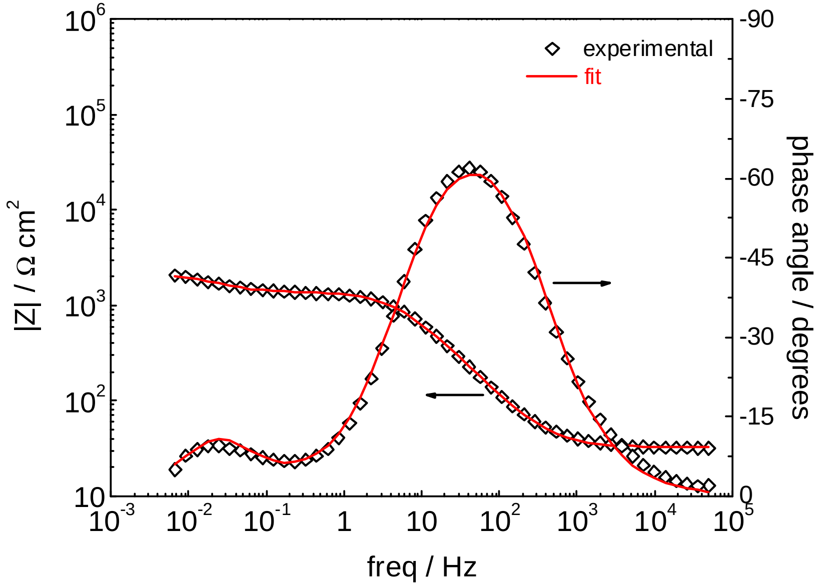
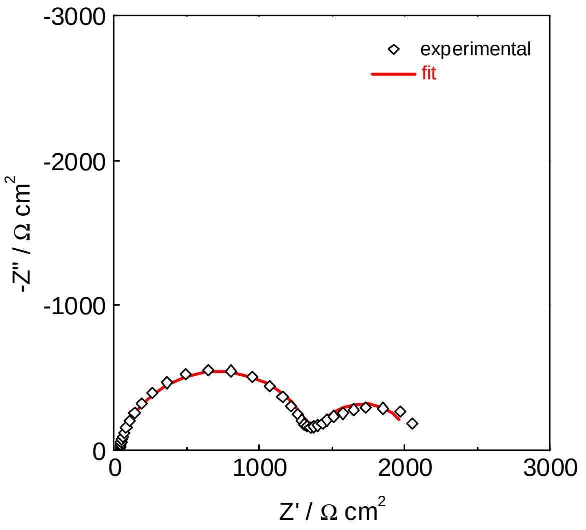
Fit curves for spectra with 1 and 2 time constants

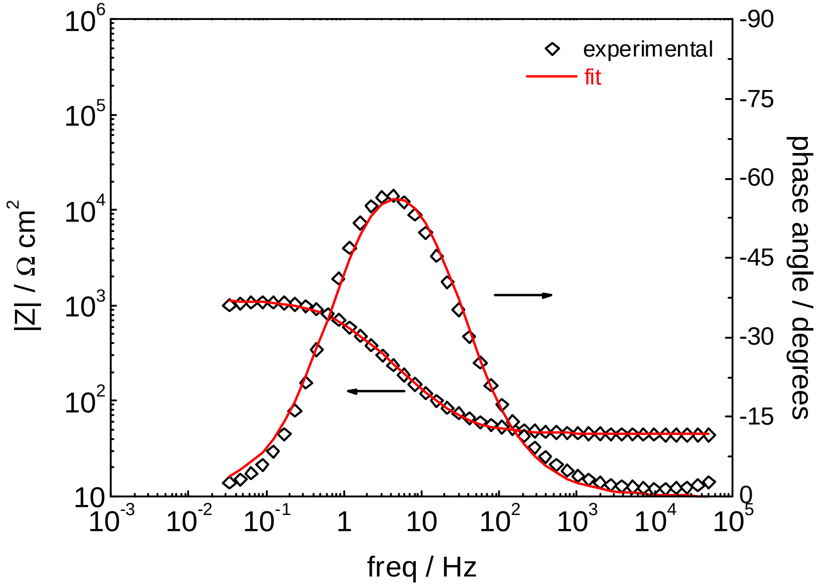


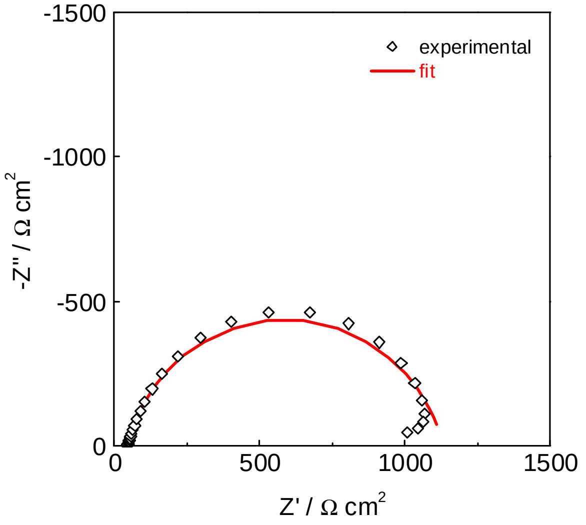
$R_s = 32.4\ \Omega\ cm^2$
$Y_0(Q_{dl}) = 3.78x10^{-5}\ F\ cm^{-2}\ s^{n-1}$
$n(Q_{dl}) = 0.858$
$R_{ct} = 1,36x10^3\ \Omega\ cm^2$
$Y_0(Q_{dif}) = 1.0x10^{-2}\ F\ cm^{-2}\ s^{n-1}$
$n(Q_{dif}) = 0.934$
$R_{dif} = 672\ \Omega\ cm^2$





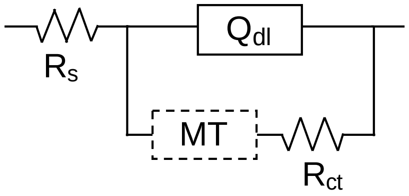
$R_s = 45.1\ \Omega\ cm^2$
$Y_0(Q_{dl}) = 2.45x10^{-4}\ F\ cm^{-2}\ s^{n-1}$
$n(Q_{dl}) = 0.860$
$R_{ct} = 1.08x10^3\ \Omega\ cm^2$

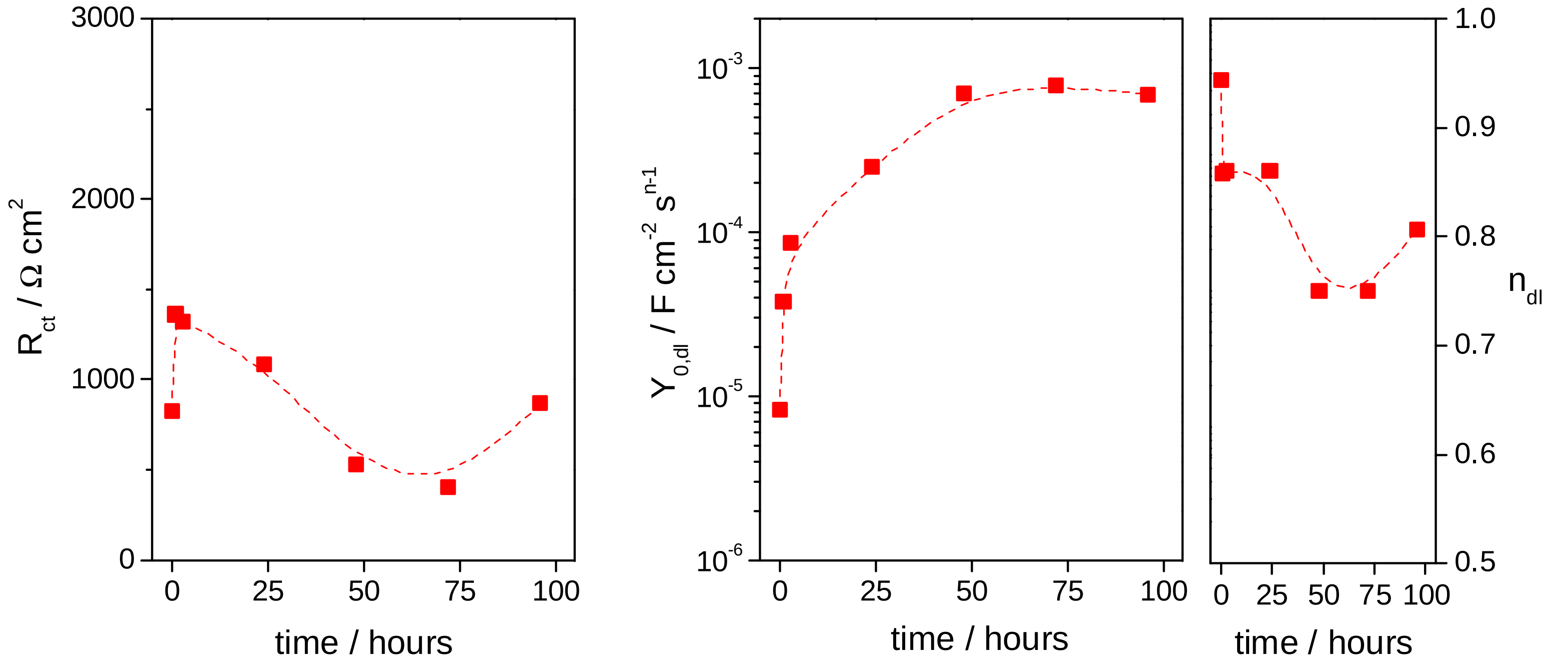




Pure zinc immersed in 0.1M NaCl

Parameters determined by numerical fitting





Time-constant dispersion and the constant-phase-element

Many models assume that the electrode behaves as a uniformly active surface where each physical phenomenon or reaction has a single-valued time constant.

This assumption is generally not valid.

Time-constant dispersions can be observed due to variation along the electrode surface of reactivity or current and potential, resulting in a 2-dimensional distribution (e.g. surface roughness, differences in composition and other heterogeneities). 3-dimensional distributions are also possible, when layers and coatings exist over the electrode, for example.

It became common practice to model the time constant (or frequency) distribution by use of a constant-phase-element (CPE).

$$Z_{CPE} = \frac{1}{Y_0\ (j\omega)^n}$$

Y_0 is the frequency independent admittance
n is the power of Q
$j = \sqrt{-1}$
ω is the angular frequency (in radians).

n = 0 (resistance, $R = 1/Y_0$)

n = 1 (capacitor, $C = Y_0$)

n = 0.5 (Warburg, $\sigma = 1/\sqrt{2}Y_0$)

n = -1 (inductance, $L = Y_0^{-1}$)

Determining C from the CPE

B. Hirschorn, M.E. Orazem, B. Tribollet, V. Vivier, I. Frateur, M. Musiani, *Electrochim. Acta* 55 (2010) 6218.

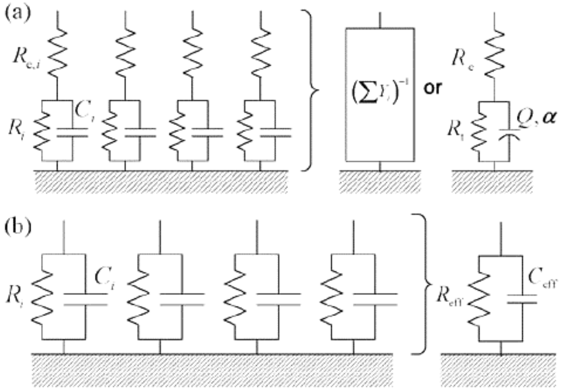


Fig. 1. Schematic representation of a surface distribution of time constants: (a) distribution of time constants in the presence of an Ohmic resistance resulting in a distributed time-constant behavior that, for an appropriate time-constant distribution, may be expressed as a CPE; and (b) distribution of time constants in the absence of an Ohmic resistance resulting in an effective RC behavior. The admittance Y_i shown in (a) includes the local interfacial and Ohmic contributions.

$$C = Y_0^{1/n}(R_1^{-1} + R_2^{-1})^{(n-1)/n}$$

$$C = Y_0^{1/n} \; R_1^{(1-n)/n}$$

G.J. Brug, A.L.G. van den Eeden, M. Sluyters-Rehbach, J.H. Sluyters, J. Electroanal. Chem. 176 (1984) 275.

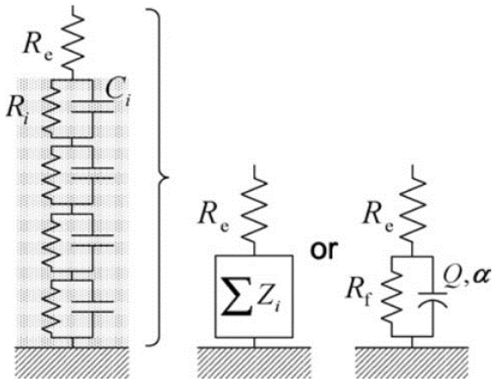


Fig. 2. Schematic representation of a normal distribution of time constants resulting in a distributed time-constant behavior that, for an appropriate time-constant distribution, may be expressed as a CPE.

$$C = Y_0 \left(\omega_{Z''\max}\right)^{n-1}$$

C.H. Hsu, F. Mansfeld, Corrosion 57 (2001) 747.

Determining corrosion rates from R_p (or R_{ct}?)

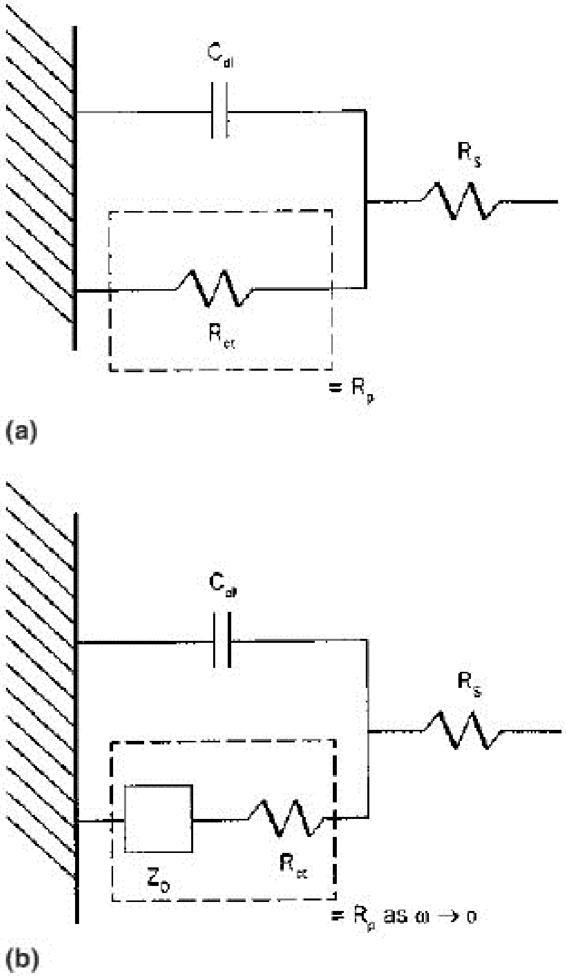


Figure 3 Electrical equivalent circuit model commonly used to represent an electrochemical interface undergoing corrosion. R_p is the polarization resistance, C_{dl} is the double layer capacitance, R_{ct} is the charge transfer resistance in the absence of mass transport and reaction intermediates, R_D is the diffusional resistance, and R_S is the solution resistance. (a) $R_p = R_{ct}$ when there are no mass transport limitations and electrochemical reactions involve no absorbed intermediates and nearly instantaneous charge transfer control prevails. (b) $R_p = R_D + R_{ct}$ in the case of mass transport limitations.

Kelly, Scully, Shoesmith, Buchheit, Electrochemical Techniques in Corrosion Science and Engineering, CRC Press, 2003, p.131.

Determining corrosion rates from R_p (or R_{ct}?)

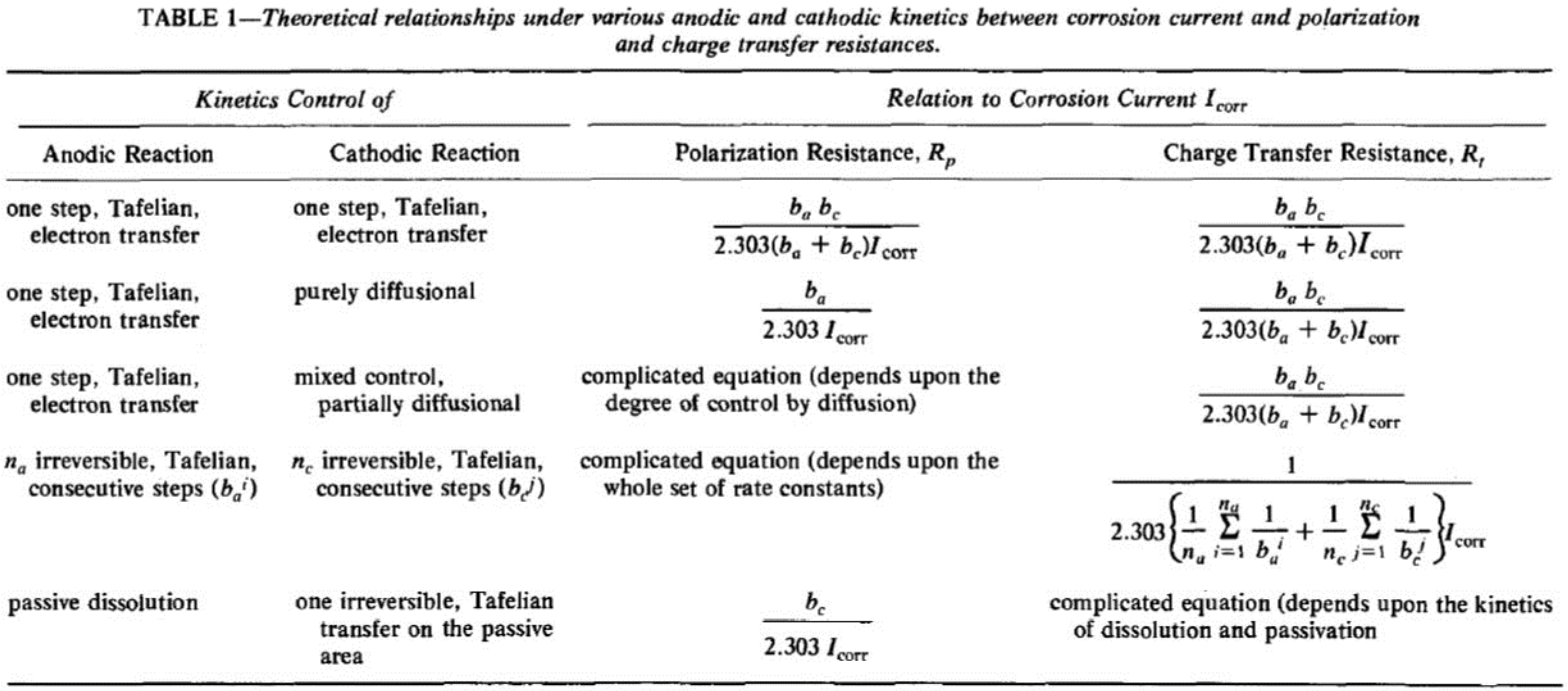


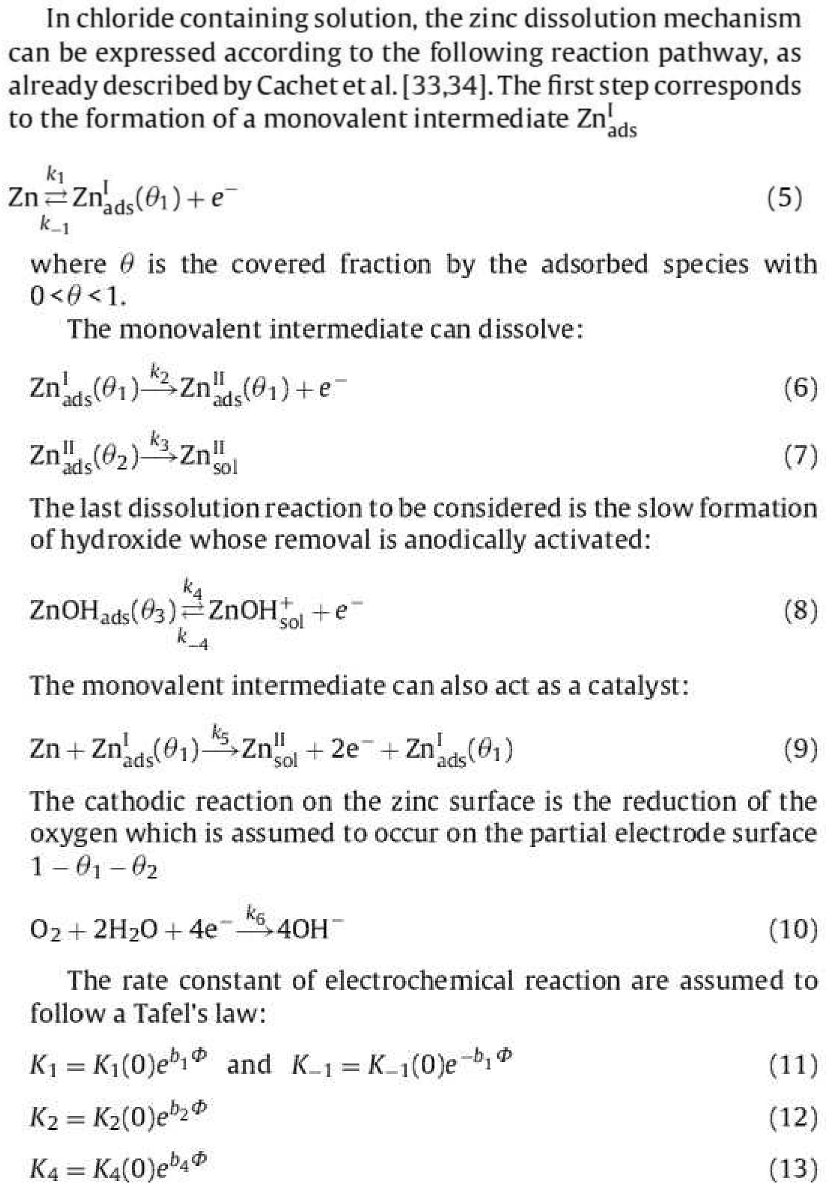
TABLE 1—*Theoretical relationships under various anodic and cathodic kinetics between corrosion current and polarization and charge transfer resistances.*

Kinetics Control of		*Relation to Corrosion Current I_{corr}*	
Anodic Reaction	Cathodic Reaction	Polarization Resistance, R_p	Charge Transfer Resistance, R_t
one step, Tafelian, electron transfer	one step, Tafelian, electron transfer	$\frac{b_a b_c}{2.303(b_a + b_c)I_{corr}}$	$\frac{b_a b_c}{2.303(b_a + b_c)I_{corr}}$
one step, Tafelian, electron transfer	purely diffusional	$\frac{b_a}{2.303\ I_{corr}}$	$\frac{b_a b_c}{2.303(b_a + b_c)I_{corr}}$
one step, Tafelian, electron transfer	mixed control, partially diffusional	complicated equation (depends upon the degree of control by diffusion)	$\frac{b_a b_c}{2.303(b_a + b_c)I_{corr}}$
n_a irreversible, Tafelian, consecutive steps ($b_a{}^i$)	n_c irreversible, Tafelian, consecutive steps ($b_c{}^j$)	complicated equation (depends upon the whole set of rate constants)	$\frac{1}{2.303\left\{\frac{1}{n_a}\sum_{i=1}^{n_a}\frac{1}{b_a^i}+\frac{1}{n_c}\sum_{j=1}^{n_c}\frac{1}{b_c^j}\right\}I_{corr}}$
passive dissolution	one irreversible, Tafelian transfer on the passive area	$\frac{b_c}{2.303\ I_{corr}}$	complicated equation (depends upon the kinetics of dissolution and passivation

I. Epelboin, C. Gabrielli, M. Keddam, H. Takenouti, "Alternating-current impedance measurements applied to corrosion studies and corrosion-rate determination" in Mansfeld, Bertocci (Eds), Electrochemical corrosion Testing, ASTM STP 727, 1981, p. 161.

A different approach to the impedance response of zinc

Electrochimica Acta 88 (2013) 6– 14



In chloride containing solution, the zinc dissolution mechanism can be expressed according to the following reaction pathway, as already described by Cachet et al. [33,34]. The first step corresponds to the formation of a monovalent intermediate Zn^{I}_{ads}

$$Zn \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Zn^{I}_{ads}(\theta_1) + e^- \tag{5}$$

where θ is the covered fraction by the adsorbed species with $0 < \theta < 1$.

The monovalent intermediate can dissolve:

$$Zn^{I}_{ads}(\theta_1) \xrightarrow{k_2} Zn^{II}_{ads}(\theta_1) + e^- \tag{6}$$

$$Zn^{II}_{ads}(\theta_2) \xrightarrow{k_3} Zn^{II}_{sol} \tag{7}$$

The last dissolution reaction to be considered is the slow formation of hydroxide whose removal is anodically activated:

$$ZnOH_{ads}(\theta_3) \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} ZnOH^{+}_{sol} + e^- \tag{8}$$

The monovalent intermediate can also act as a catalyst:

$$Zn + Zn^{I}_{ads}(\theta_1) \xrightarrow{k_5} Zn^{II}_{sol} + 2e^- + Zn^{I}_{ads}(\theta_1) \tag{9}$$

The cathodic reaction on the zinc surface is the reduction of the oxygen which is assumed to occur on the partial electrode surface $1 - \theta_1 - \theta_2$

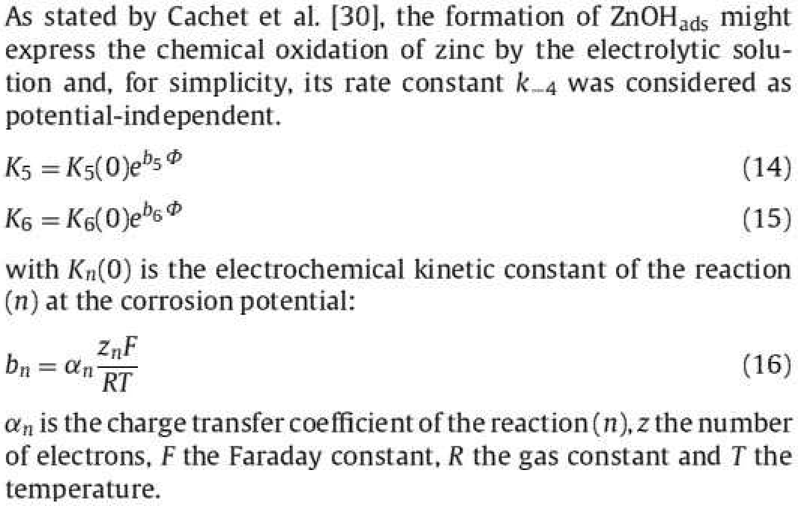
$$O_2 + 2H_2O + 4e^- \xrightarrow{k_6} 4OH^- \tag{10}$$

The rate constant of electrochemical reaction are assumed to follow a Tafel's law:

$$K_1 = K_1(0)e^{b_1\Phi} \quad \text{and} \quad K_{-1} = K_{-1}(0)e^{-b_1\Phi} \tag{11}$$

$$K_2 = K_2(0)e^{b_2\Phi} \tag{12}$$

$$K_4 = K_4(0)e^{b_4\Phi} \tag{13}$$



As stated by Cachet et al. [30], the formation of $ZnOH_{ads}$ might express the chemical oxidation of zinc by the electrolytic solution and, for simplicity, its rate constant k_{-4} was considered as potential-independent.

$$K_5 = K_5(0)e^{b_5\Phi} \tag{14}$$

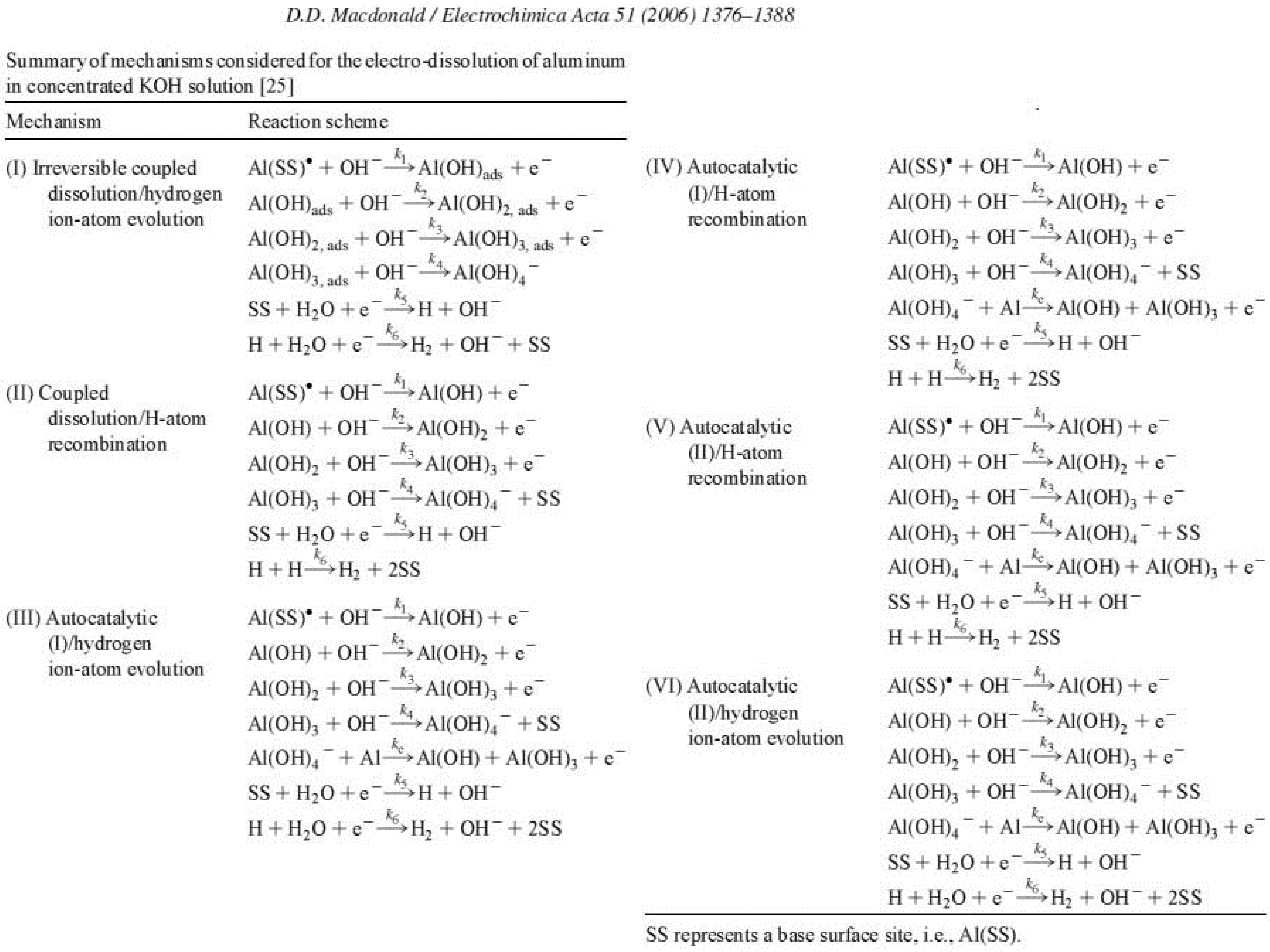
$$K_6 = K_6(0)e^{b_6\Phi} \tag{15}$$

with $K_n(0)$ is the electrochemical kinetic constant of the reaction (n) at the corrosion potential:

$$b_n = \alpha_n \frac{z_n F}{RT} \tag{16}$$

α_n is the charge transfer coefficient of the reaction (n), z the number of electrons, F the Faraday constant, R the gas constant and T the temperature.

...and for the dissolution of Al in 4M KOH



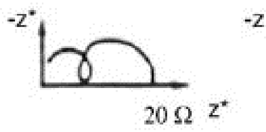
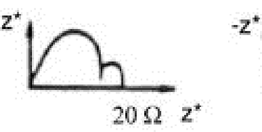
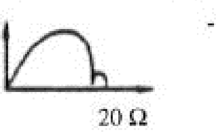
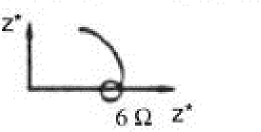
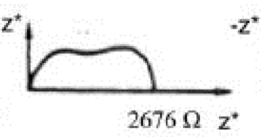
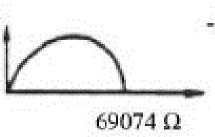
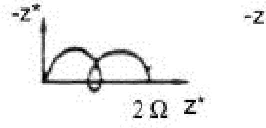
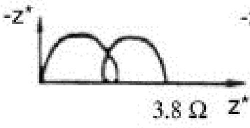
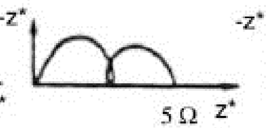
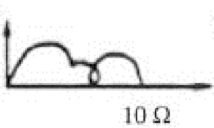
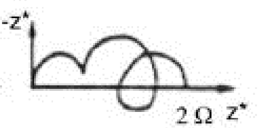
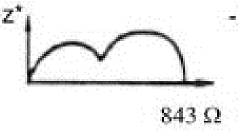
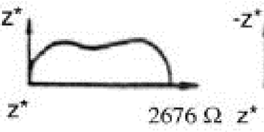
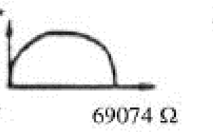
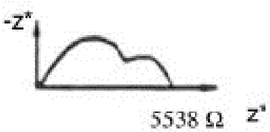
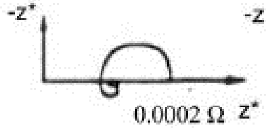
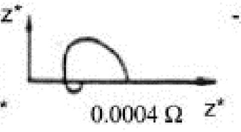
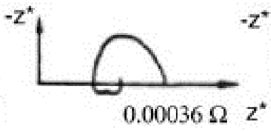
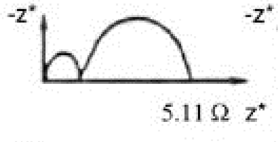
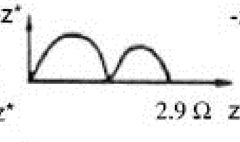
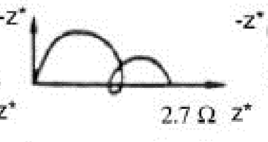
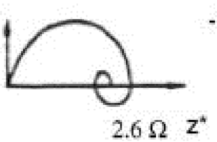
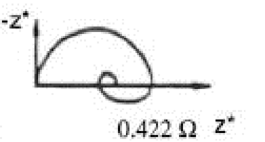
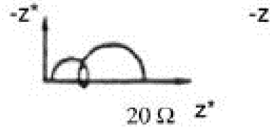
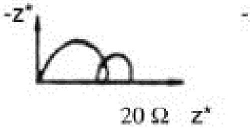
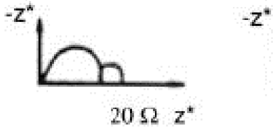
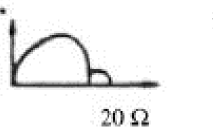
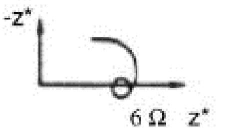
D.D. Macdonald / Electrochimica Acta 51 (2006) 1376–1388

Summary of mechanisms considered for the electro-dissolution of aluminum in concentrated KOH solution [25]

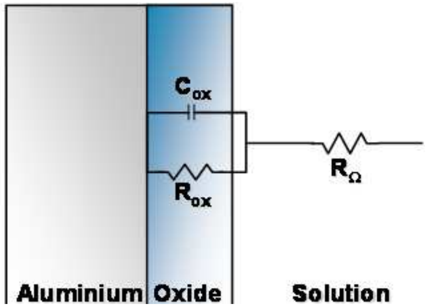
Mechanism	Reaction scheme
(I) Irreversible coupled dissolution/hydrogen ion-atom evolution	$Al(SS)^{\bullet} + OH^- \xrightarrow{k_1} Al(OH)_{ads} + e^-$ $Al(OH)_{ads} + OH^- \xrightarrow{k_2} Al(OH)_{2,\,ads} + e^-$ $Al(OH)_{2,\,ads} + OH^- \xrightarrow{k_3} Al(OH)_{3,\,ads} + e^-$ $Al(OH)_{3,\,ads} + OH^- \xrightarrow{k_4} Al(OH)_4^-$ $SS + H_2O + e^- \xrightarrow{k_5} H + OH^-$ $H + H_2O + e^- \xrightarrow{k_6} H_2 + OH^- + SS$
(II) Coupled dissolution/H-atom recombination	$Al(SS)^{\bullet} + OH^- \xrightarrow{k_1} Al(OH) + e^-$ $Al(OH) + OH^- \xrightarrow{k_2} Al(OH)_2 + e^-$ $Al(OH)_2 + OH^- \xrightarrow{k_3} Al(OH)_3 + e^-$ $Al(OH)_3 + OH^- \xrightarrow{k_4} Al(OH)_4^- + SS$ $SS + H_2O + e^- \xrightarrow{k_5} H + OH^-$ $H + H \xrightarrow{k_6} H_2 + 2SS$
(III) Autocatalytic (I)/hydrogen ion-atom evolution	$Al(SS)^{\bullet} + OH^- \xrightarrow{k_1} Al(OH) + e^-$ $Al(OH) + OH^- \xrightarrow{k_2} Al(OH)_2 + e^-$ $Al(OH)_2 + OH^- \xrightarrow{k_3} Al(OH)_3 + e^-$ $Al(OH)_3 + OH^- \xrightarrow{k_4} Al(OH)_4^- + SS$ $Al(OH)_4^- + Al \xrightarrow{k_c} Al(OH) + Al(OH)_3 + e^-$ $SS + H_2O + e^- \xrightarrow{k_5} H + OH^-$ $H + H_2O + e^- \xrightarrow{k_6} H_2 + OH^- + 2SS$
(IV) Autocatalytic (I)/H-atom recombination	$Al(SS)^{\bullet} + OH^- \xrightarrow{k_1} Al(OH) + e^-$ $Al(OH) + OH^- \xrightarrow{k_2} Al(OH)_2 + e^-$ $Al(OH)_2 + OH^- \xrightarrow{k_3} Al(OH)_3 + e^-$ $Al(OH)_3 + OH^- \xrightarrow{k_4} Al(OH)_4^- + SS$ $Al(OH)_4^- + Al \xrightarrow{k_c} Al(OH) + Al(OH)_3 + e^-$ $SS + H_2O + e^- \xrightarrow{k_5} H + OH^-$ $H + H \xrightarrow{k_6} H_2 + 2SS$
(V) Autocatalytic (II)/H-atom recombination	$Al(SS)^{\bullet} + OH^- \xrightarrow{k_1} Al(OH) + e^-$ $Al(OH) + OH^- \xrightarrow{k_2} Al(OH)_2 + e^-$ $Al(OH)_2 + OH^- \xrightarrow{k_3} Al(OH)_3 + e^-$ $Al(OH)_3 + OH^- \xrightarrow{k_4} Al(OH)_4^- + SS$ $Al(OH)_4^- + Al \xrightarrow{k_c} Al(OH) + Al(OH)_3 + e^-$ $SS + H_2O + e^- \xrightarrow{k_5} H + OH^-$ $H + H \xrightarrow{k_6} H_2 + 2SS$
(VI) Autocatalytic (II)/hydrogen ion-atom evolution	$Al(SS)^{\bullet} + OH^- \xrightarrow{k_1} Al(OH) + e^-$ $Al(OH) + OH^- \xrightarrow{k_2} Al(OH)_2 + e^-$ $Al(OH)_2 + OH^- \xrightarrow{k_3} Al(OH)_3 + e^-$ $Al(OH)_3 + OH^- \xrightarrow{k_4} Al(OH)_4^- + SS$ $Al(OH)_4^- + Al \xrightarrow{k_c} Al(OH) + Al(OH)_3 + e^-$ $SS + H_2O + e^- \xrightarrow{k_5} H + OH^-$ $H + H_2O + e^- \xrightarrow{k_6} H_2 + OH^- + 2SS$

SS represents a base surface site, i.e., Al(SS).

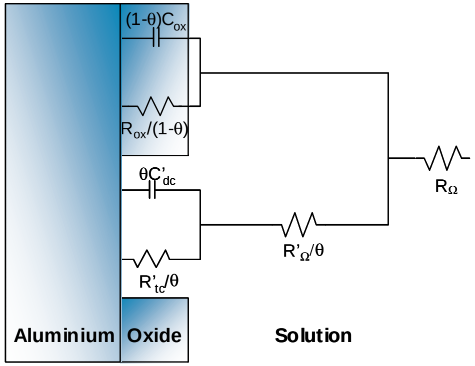
Summary of model spectra and experimental data for Al in 4 M KOH at 25 °C (after Macdonald et al. [25])

	POTENTIAL (vs. SHE)				
Description	-1.50	-1.64 V	-1.70 v	-1.88	-1.95
Mechanism I					
Mechanism II					
Mechanism III					
Mechanism IV					
Mechanism V					
Mechanism VI					
Experimental					

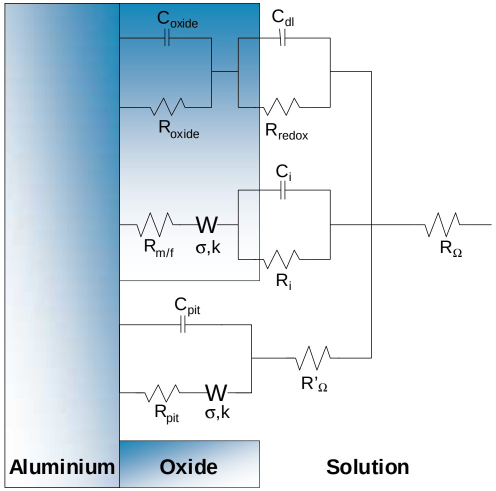
Circuits for pitting of aluminium

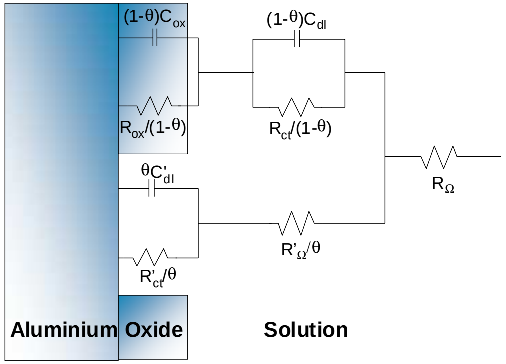


K. Jüttner, *Electrochimica Acta*, **35** (1990), 1501

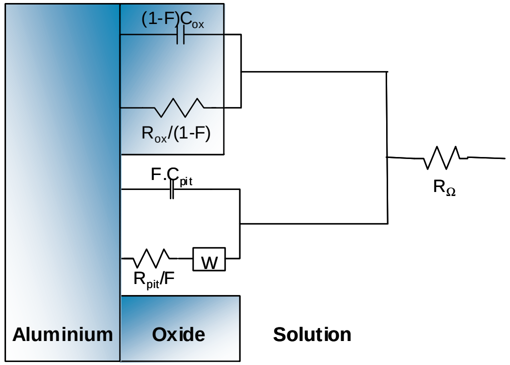


F. Mansfeld, *Electrochimica Acta*, **35** (1990), 1533

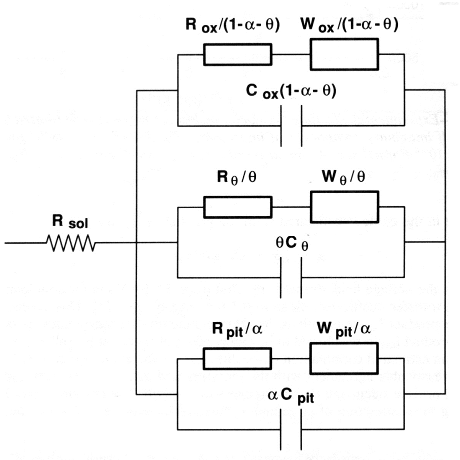




G.R.T. Schueller, S.R. Taylor and E.E. Hajcsar, *J. Electrochem. Soc.*, **139** (1992), 2799



R. Oltra e M. Keddam, *Corros. Sci.*, **28** (1988), 1

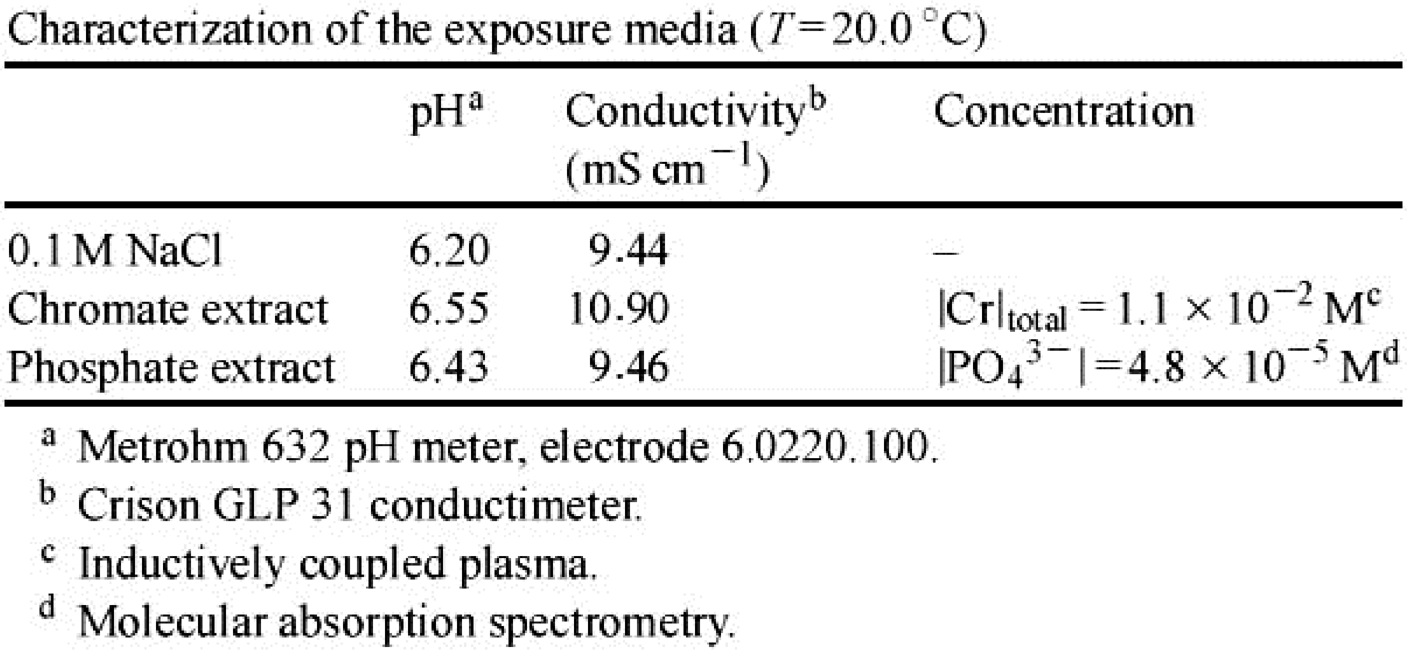


Scully, J.R., “Characterization of the Corrosion of Aluminium Thin Films Using Electrochemical Impedance Methods”, in Electrochemical Impedance: Analysis and Interpretation, ASTM STP 1188, J.R. Scully, D.C. Silverman and M.W. Kendig Eds., ASTM (1993), pp. 276-296

Credits of this slide to Prof J. Salvador Fernandes from IST Lisbon

Returning to zinc...

The effect of addition of corrosion inhibitors to the 0.1M NaCl solution



Characterization of the exposure media ($T = 20.0$ °C)

	pH[a]	Conductivity[b] (mS cm^{-1})	Concentration
0.1 M NaCl	6.20	9.44	–
Chromate extract	6.55	10.90	$\lvert Cr \rvert_{total} = 1.1 \times 10^{-2}$ M[c]
Phosphate extract	6.43	9.46	$\lvert PO_4^{3-} \rvert = 4.8 \times 10^{-5}$ M[d]

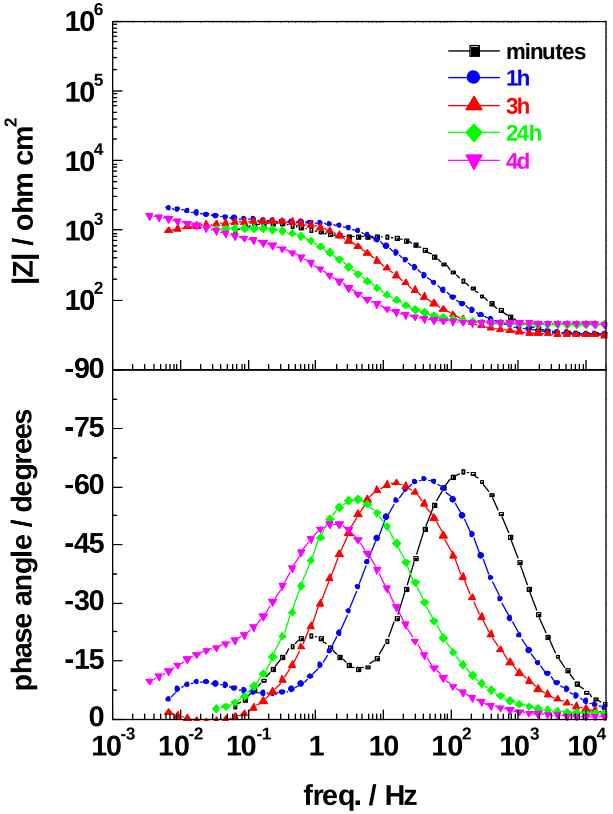
[a] Metrohm 632 pH meter, electrode 6.0220.100.

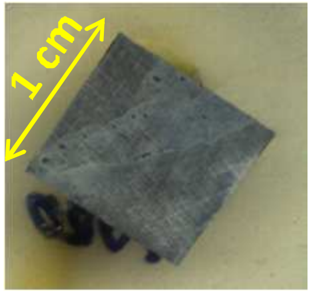
[b] Crison GLP 31 conductimeter.

[c] Inductively coupled plasma.

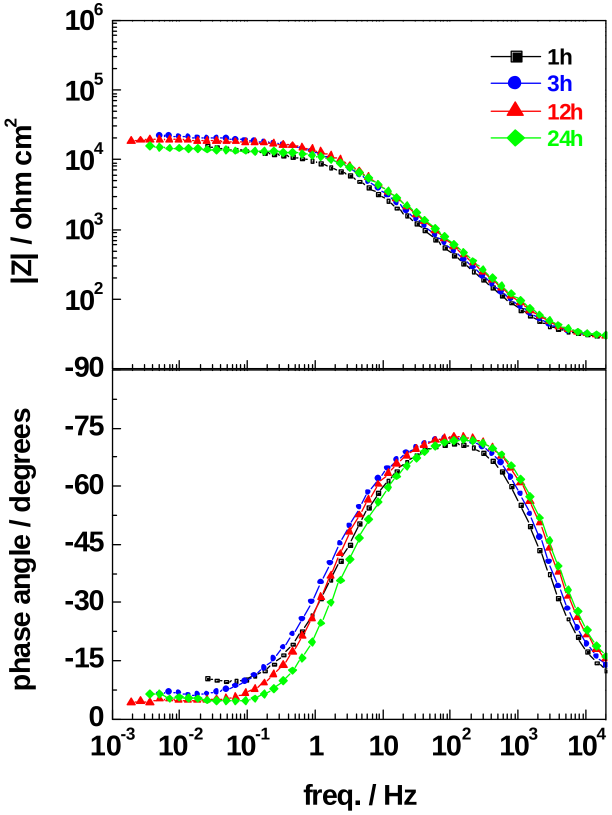
[d] Molecular absorption spectrometry.

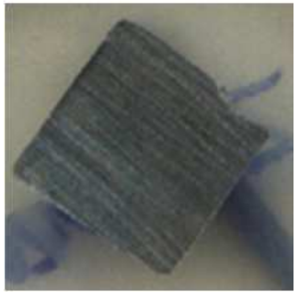
Zn in 0.1M NaCl



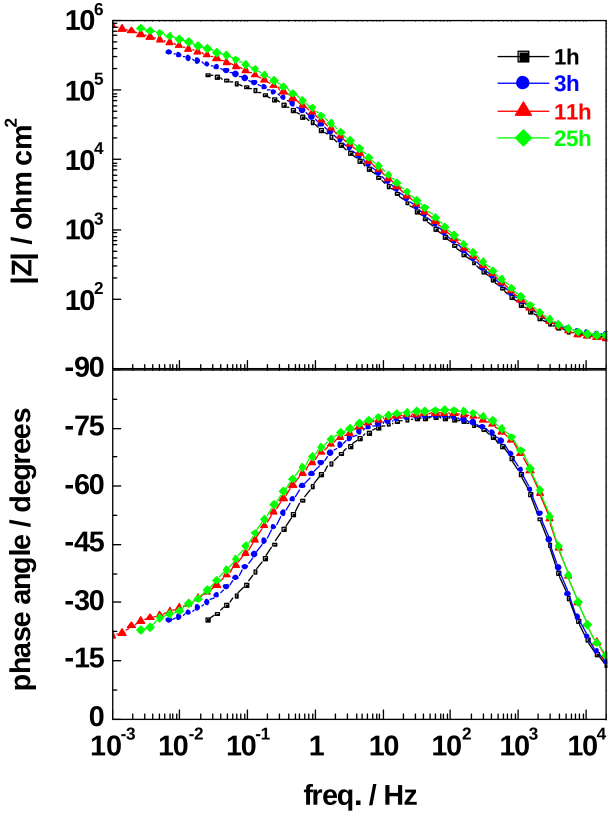


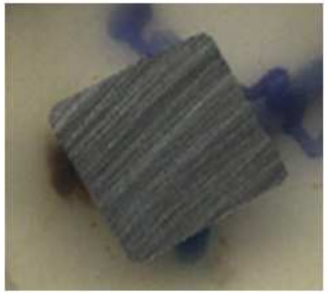
phosphate extract in 0.1M NaCl





chromate extract in 0.1M NaCl





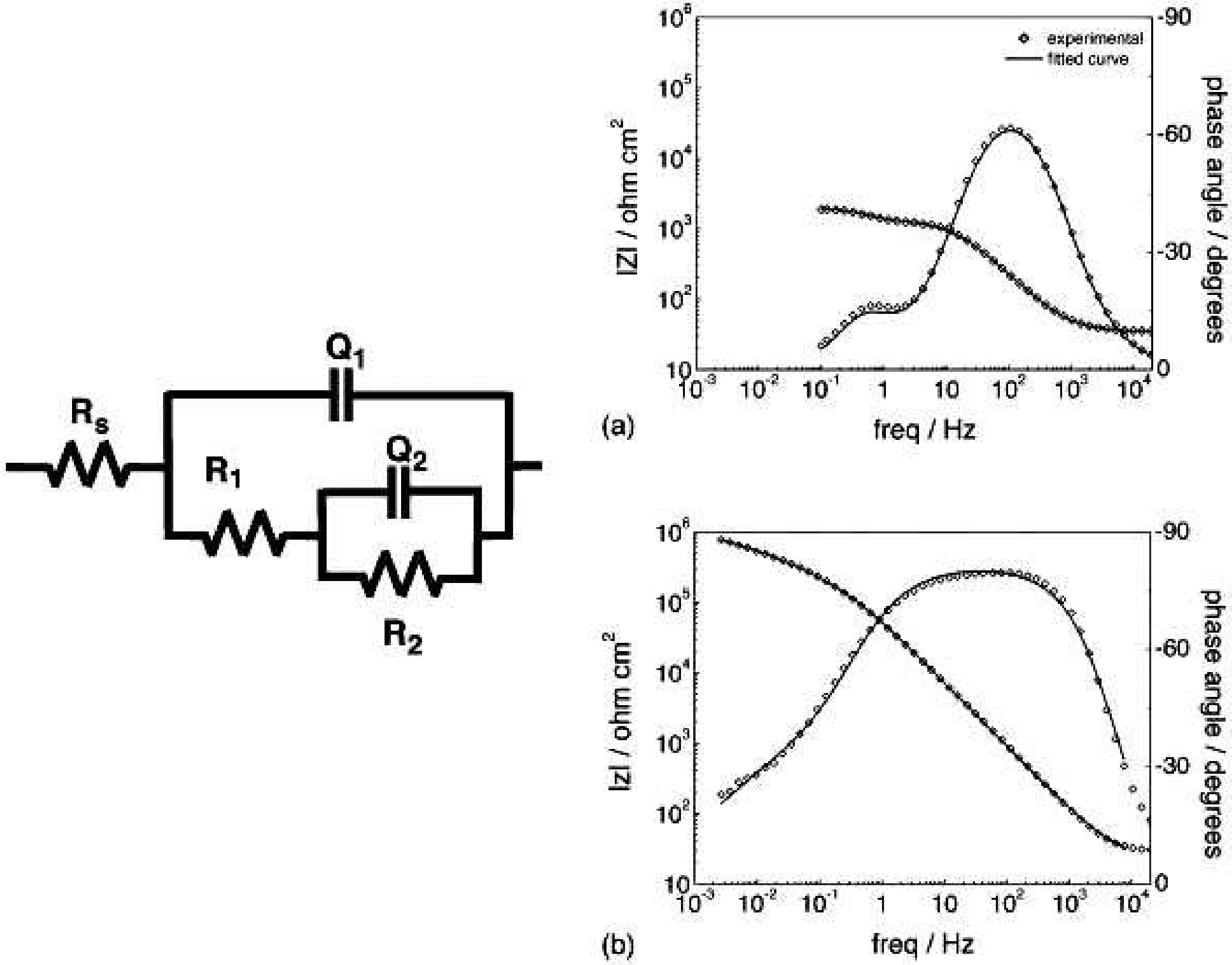
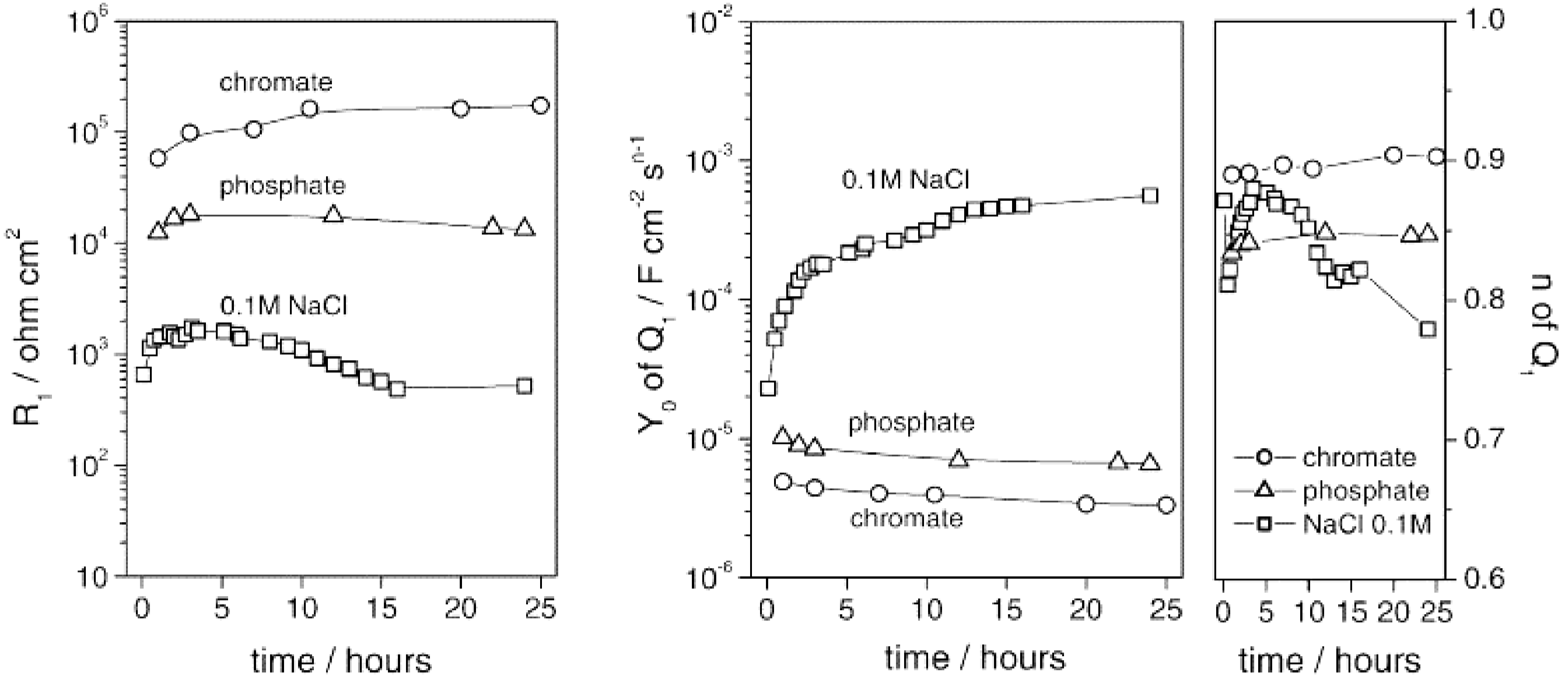


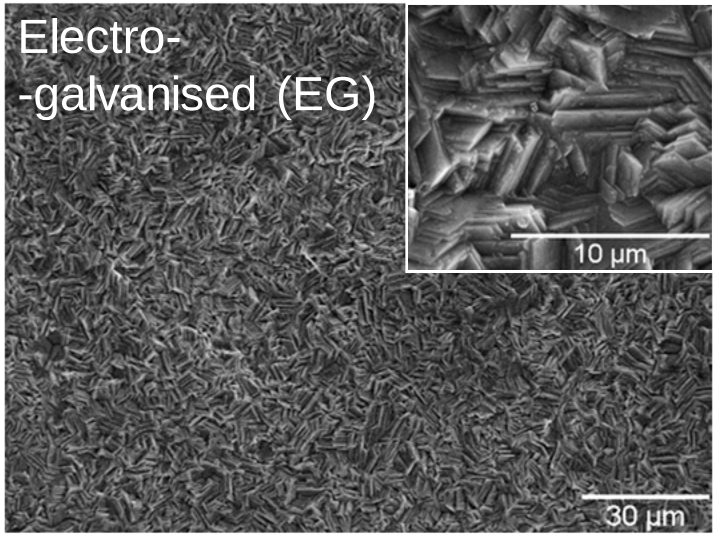
Fig. 5. General equivalent circuit and fittings for pure zinc in 0.1 M NaCl without inhibitor (a) and with zinc chromate extract (b). Fitting parameters for (a) $R_s = 34.4\,\Omega\,\mathrm{cm}^2$; $Y_0(Q_1) = 1.62 \times 10^{-5}\,\mathrm{F\,cm^{-2}\,s^{n-1}}$; $n(Q_1) = 0.872$; $R_1 = 1.31 \times 10^3\,\Omega\,\mathrm{cm}^2$; $Y_0(Q_2) = 6.06 \times 10^{-4}\,\mathrm{F\,cm^{-2}\,s^{n-1}}$; $n(Q_2) = 1$; $R_2 = 631\,\Omega\,\mathrm{cm}^2$; $\chi^2 = 3.9 \times 10^{-4}$. Fitting parameters for (b) $R_s = 26.2\,\Omega\,\mathrm{cm}^2$; $Y_0(Q_1) = 3.31 \times 10^{-6}\,\mathrm{F\,cm^{-2}\,s^{n-1}}$; $n(Q_1) = 0.903$; $R_1 = 1.74 \times 10^5\,\Omega\,\mathrm{cm}^2$; $Y_0(Q_2) = 6.51 \times 10^{-6}\,\mathrm{F\,cm^{-2}\,s^{n-1}}$; $n(Q_2) = 0.500$; $R_2 = 1.14 \times 10^6\,\Omega\,\mathrm{cm}^2$; $\chi^2 = 1.0 \times 10^{-3}$.

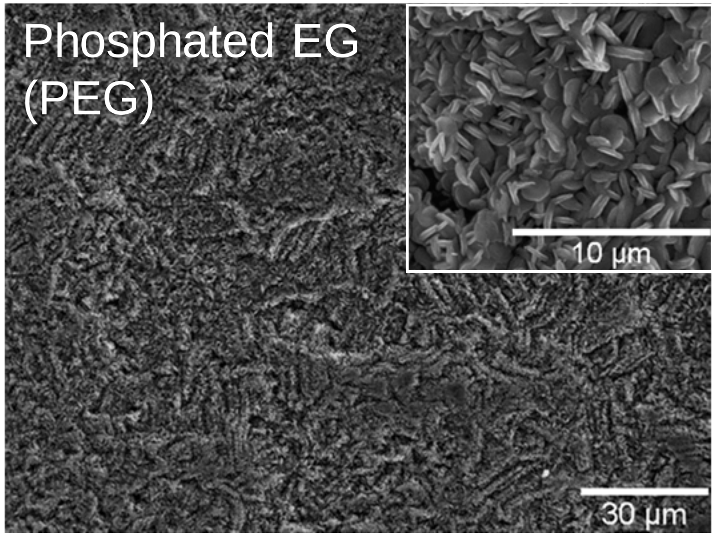
Evolution of fit parameters with time of immersion



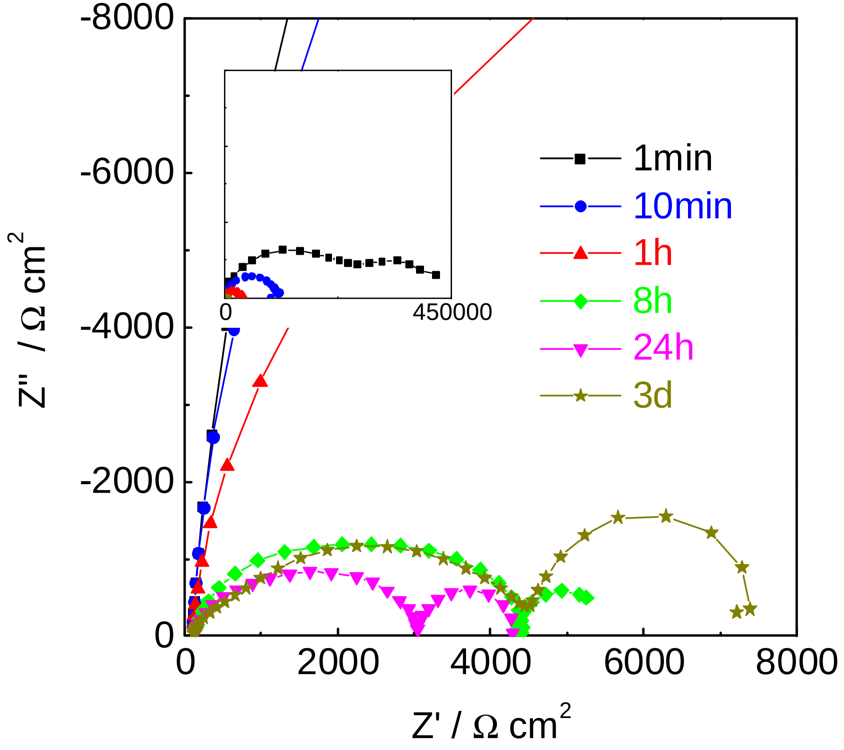
Zinc surface covered by an inert layer

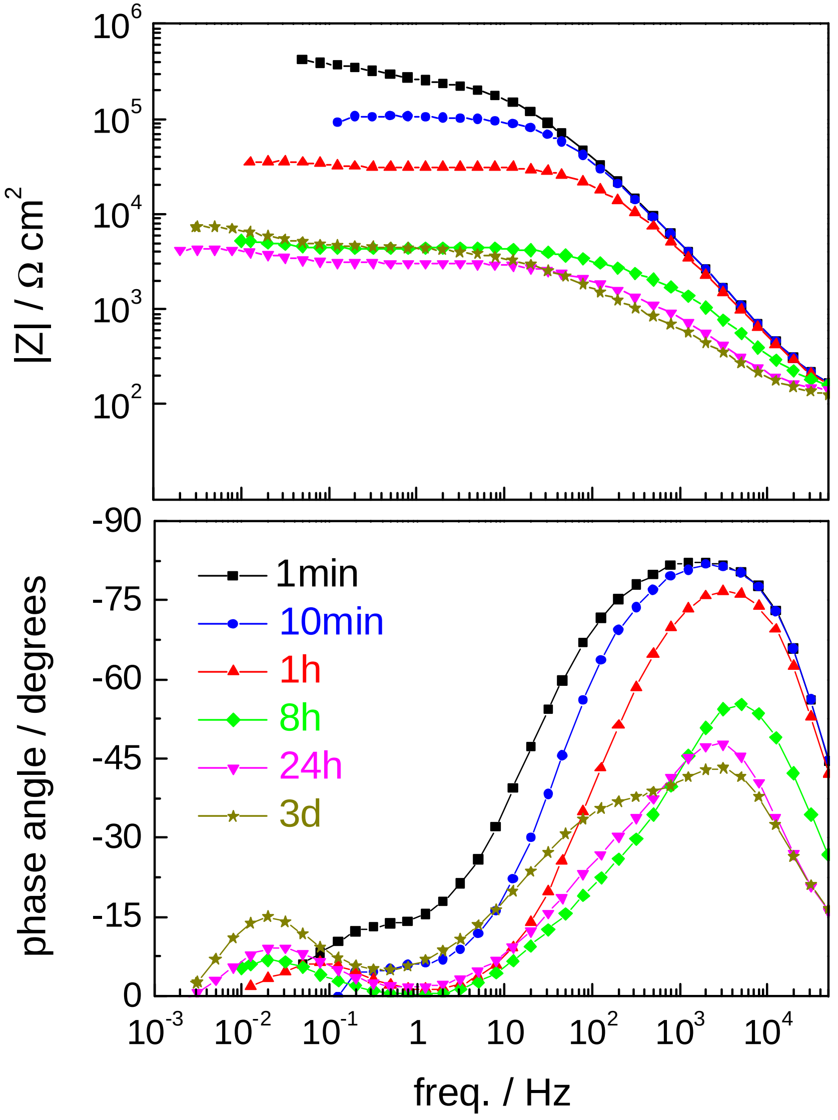
Phosphated electrogalvanised steel (PEG)



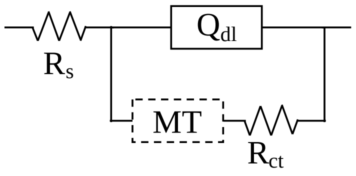


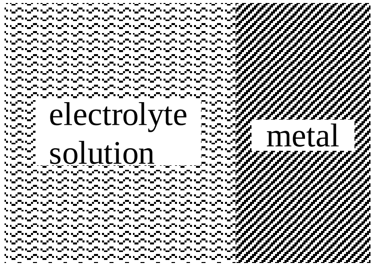
Impedance response of phosphated galvanised steel

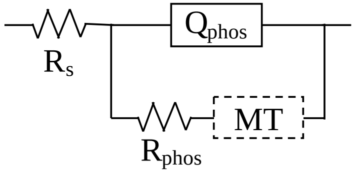


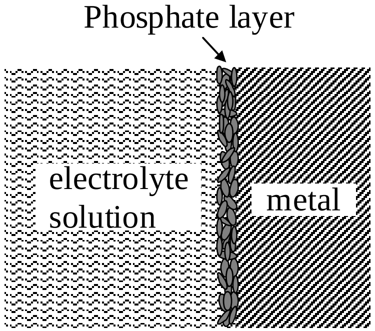


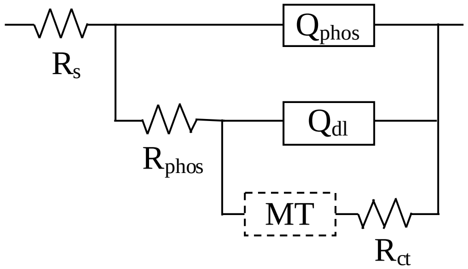
Circuits for the impedance response of PEG

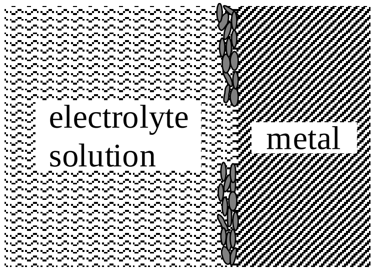


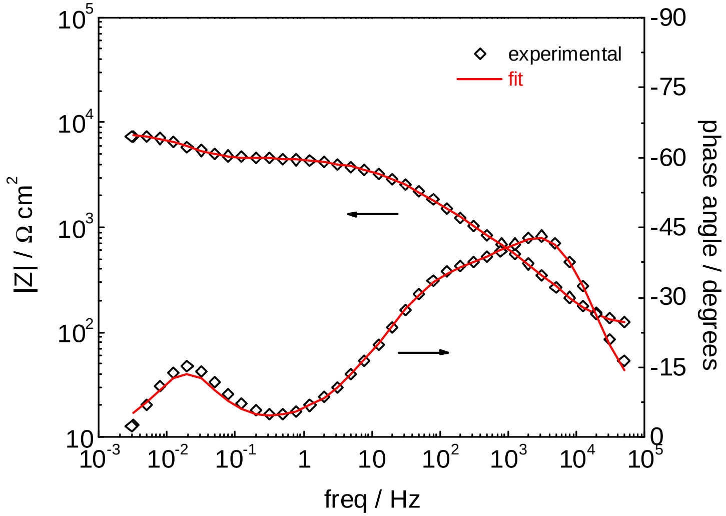


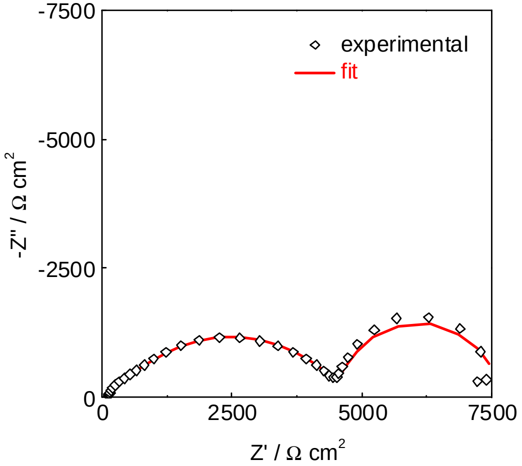






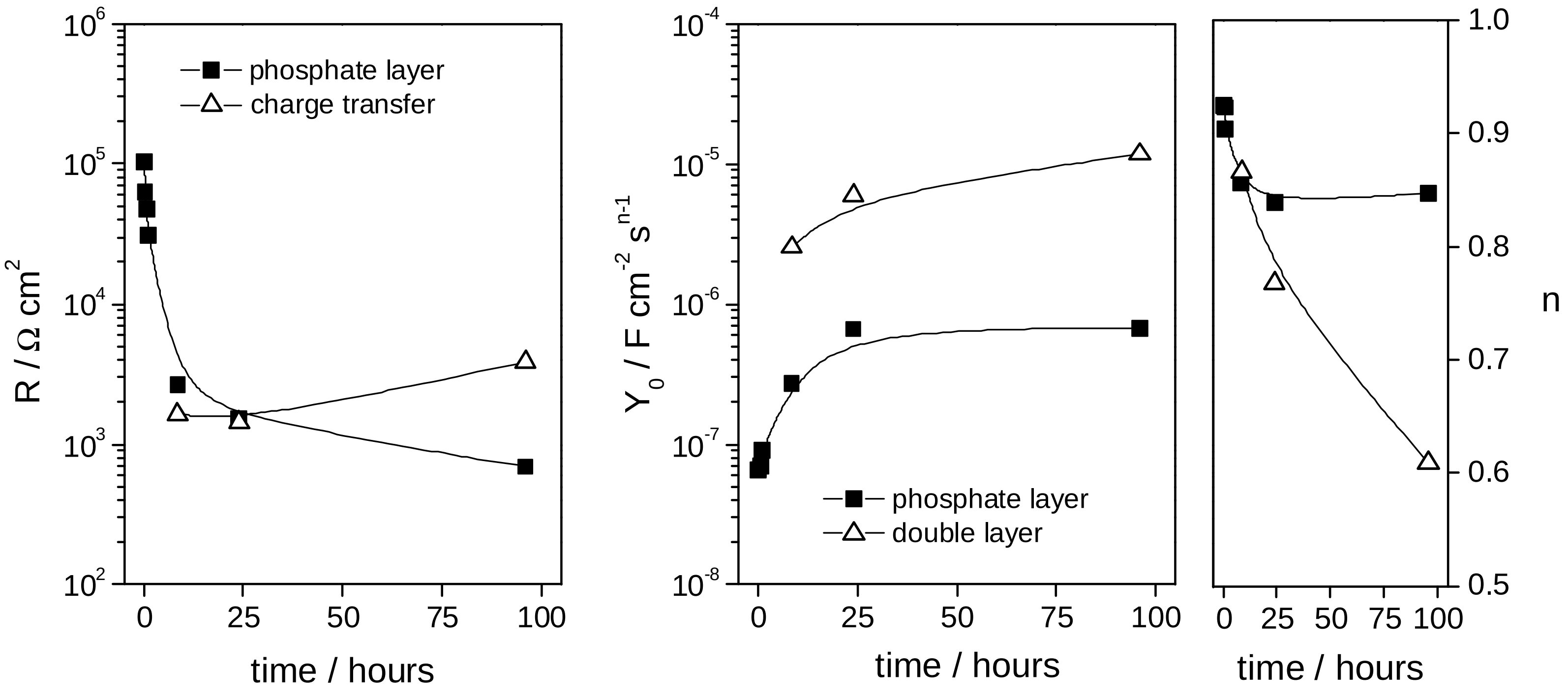




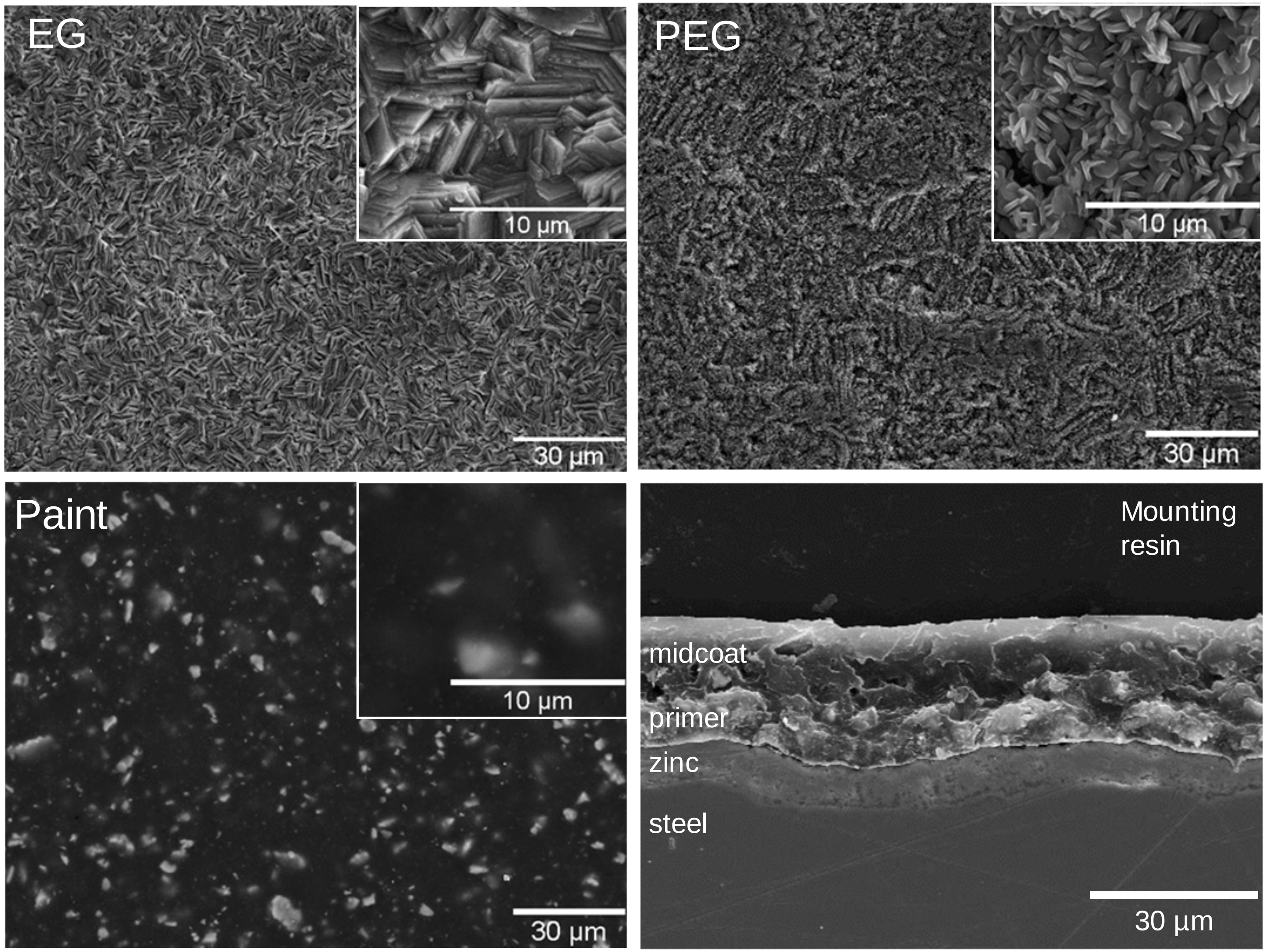


R_s = 126 Ω cm^2; $Y_0(Q_{phos})$ = 6,64x10^{-7} F cm^{-2} s^{n-1}; $n(Q_{phos})$ = 0.839; R_{phos} = 1,51x10^3 Ω cm^2; $Y_0(Q_{dl})$ = 5,93x10^{-6} Fcm^{-2} s^{n-1}; $n(Q_{dl})$ = 0,768; R_{ct} = 1,44x10^3 Ω cm^2; $Y_0(Q_{dif})$ = 5,52x10^{-3} F cm^{-2} s^{n-1}; $n(Q_{dif})$ = 0,975; R_{dif} = 1,25x10^3 Ω cm^2.

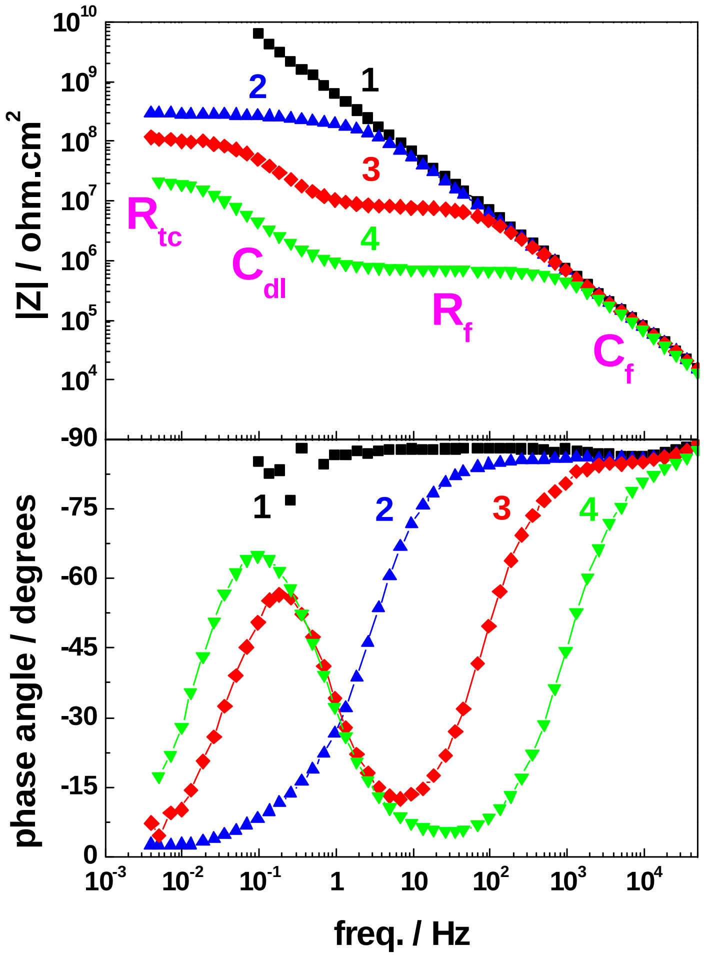
Evolution of fit parameters with time of immersion



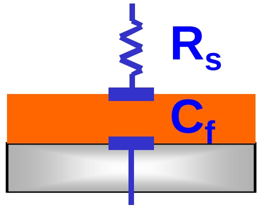
A more complex system: steel + zinc + phosphate + paint



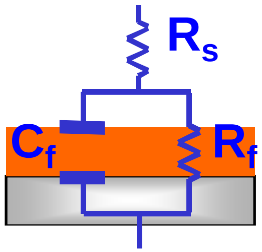
Evolution of the impedance of a painted metal while it degrades



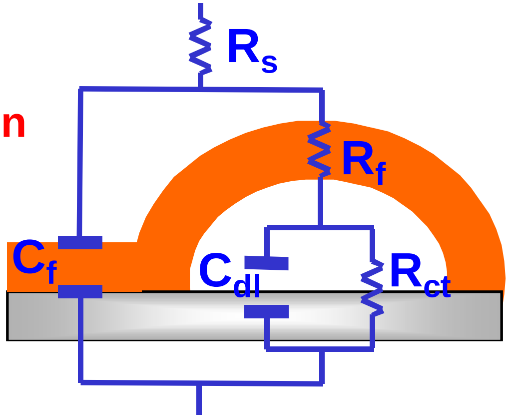
1. Intact film



2. Conductive pathways through the film



3, 4 corrosion



R_s – solution resistance
R_f – paint (pore) resistance
C_f – paint film capacitance
R_{ct} – charge transfer resistance
C_{dl} – double layer capacitance

Parameters

Solution resistance, R_s

This is the uncompensated resistance between the working electrode and the reference electrode, plus the internal resistance of electrodes and electrical cables, being these, in general, negligible compared to the former.

Paint film resistance, R_f

Corresponds to the resistance of the solution inside pores and defects in the matrix. It decreases with the increase of number and size of pores, which is a consequence of the paint’s degradation. For this reason it is used as an indication of the paint degradation.

Paint film capacitance, C_f

When immersed in aqueous solution, a paint applied to a metal can be considered to be the dielectric between the plates of a capacitor, where one plate is the metal-paint interface and the other is the paint-solution interface. The increase of capacitance with time is an indication of water absorption by the paint film.

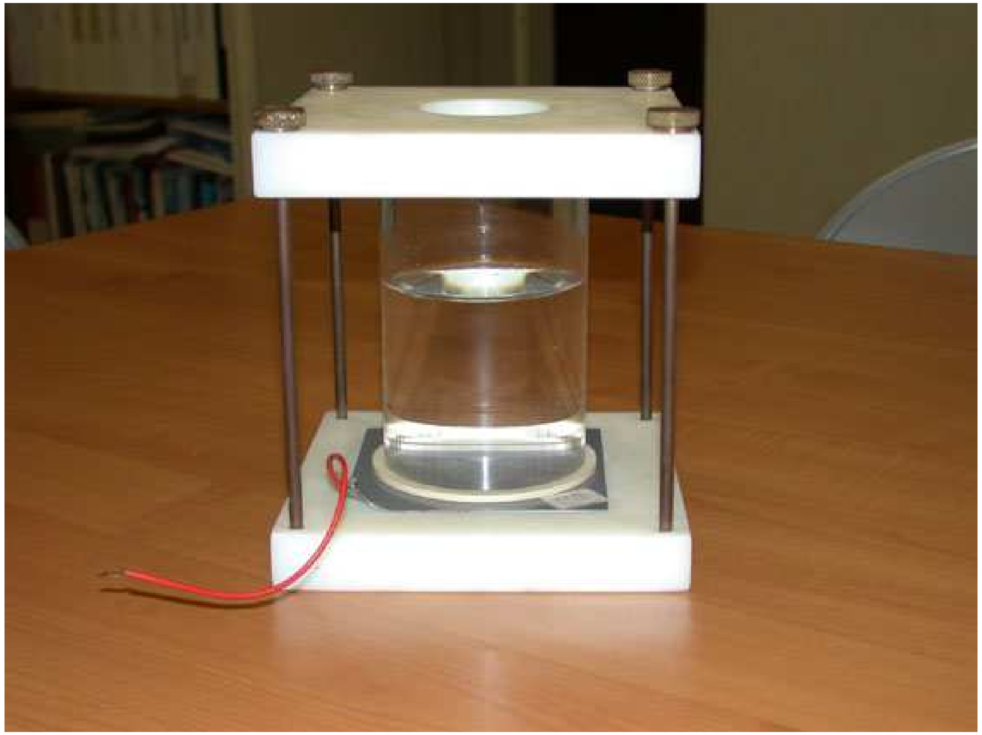
Double layer capacitance, C_{dl}

This is the capacitance that is established on the metal-solution interface and can be considered to be a capacitor with parallel plates. For painted metals, it’s assumed that its response is detected only when the solution reaches the metal surface and the increase reveals degradation, being it proportional to the wetted area, that is, the area where the paint delaminated from the metal substrate.

Charge transfer resistance, R_{ct}

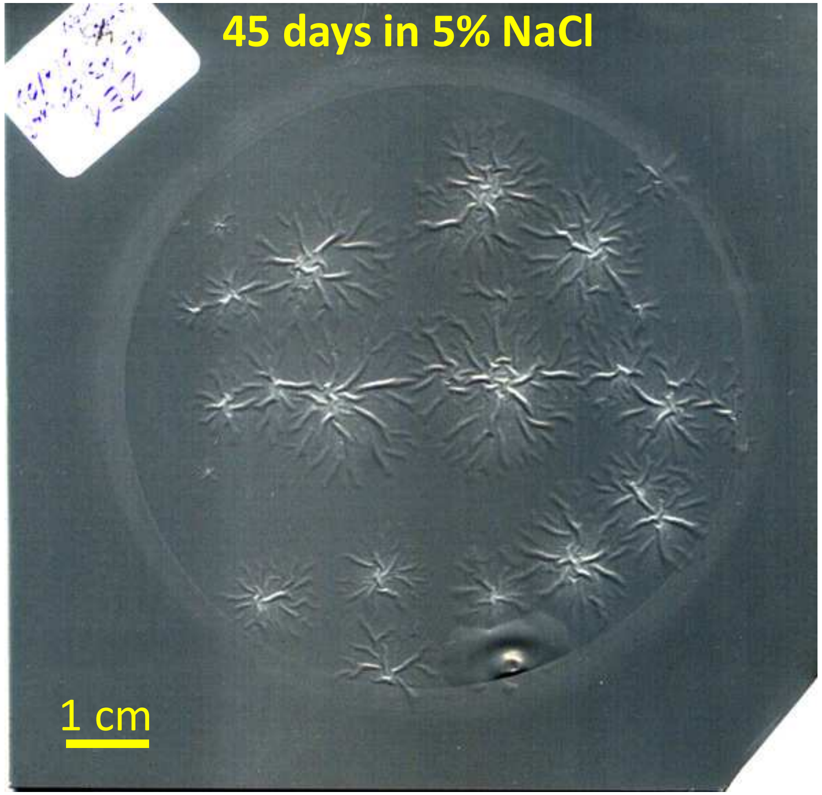
This parameter is, in many circumstances, similar to the polarization resistance, allowing the determination of corrosion rate through the Stern-Geary equation.

Typical electrochemical cells

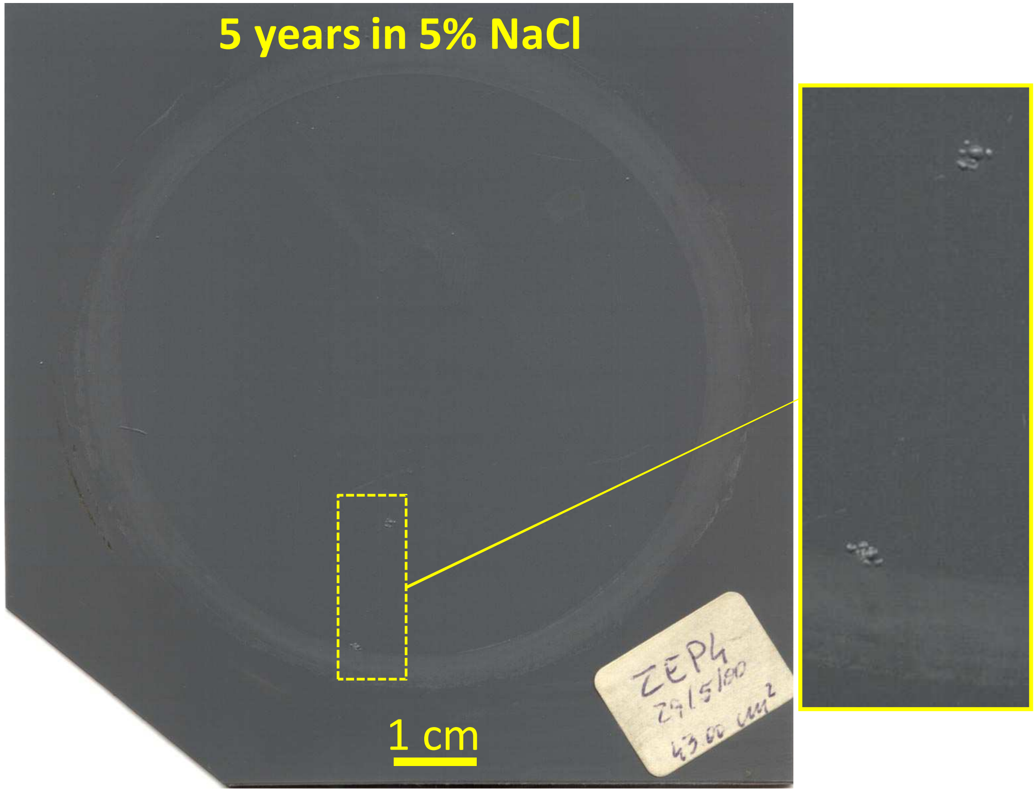


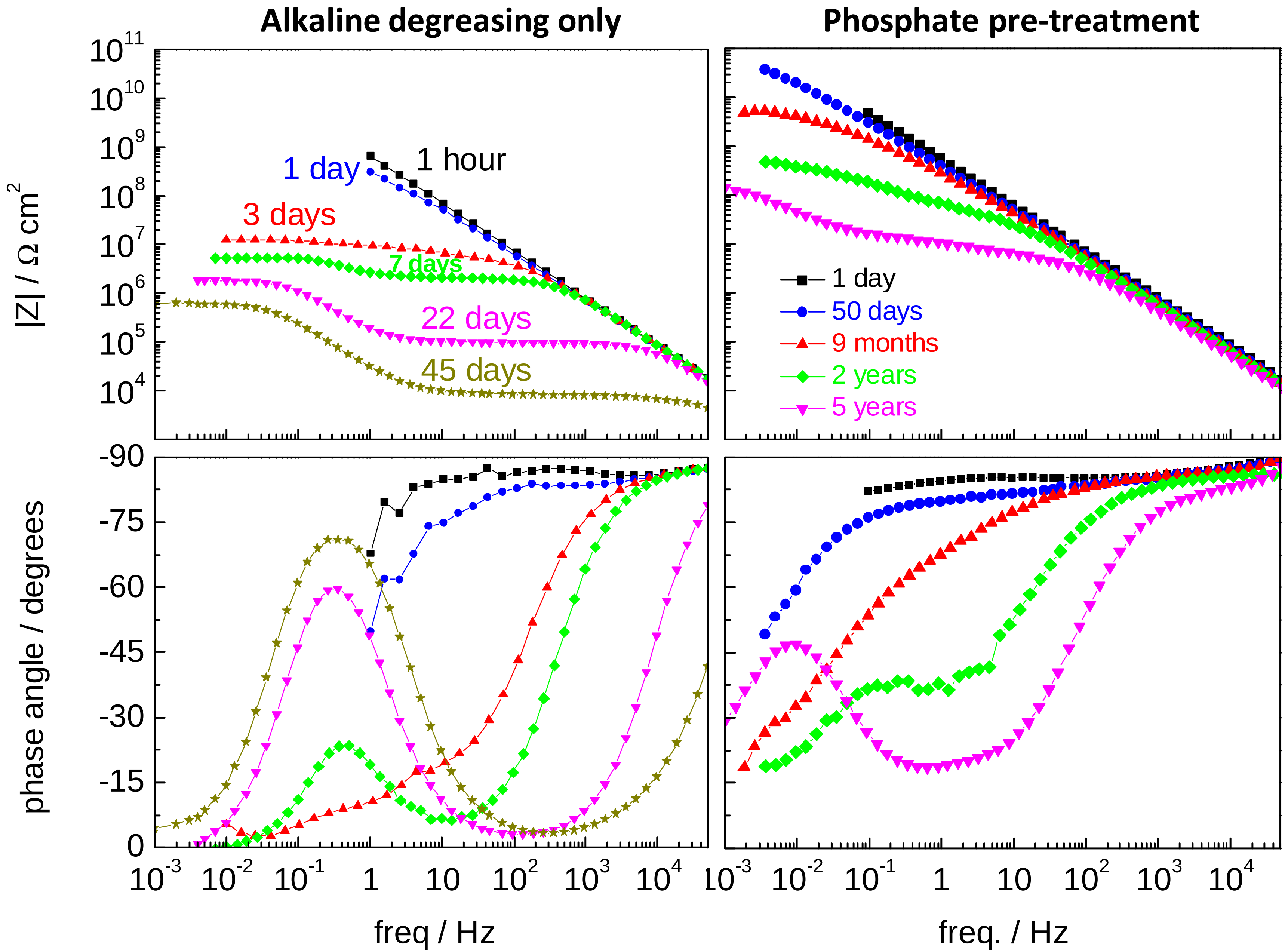
Effect of pre-treatment on painted metal substrates

Galvanised steel with alkaline degreasing before painting



Galvanised steel with phosphating pretreament before painting




Alkaline degreasing only
Phosphate pre-treatment
|Z| / Ω cm^2
10^{11}
10^{10}
10^9
10^8
10^7
10^6
10^5
10^4
1 day
1 hour
3 days
7 days
22 days
45 days
1 day
50 days
9 months
2 years
5 years
phase angle / degrees
-90
-75
-60
-45
-30
-15
0
10^{-3}
10^{-2}
10^{-1}
1
10
10^2
10^3
10^4
freq / Hz
freq. / Hz

A.C. Bastos, A.M.P. Simões / Progress in Organic Coatings 65 (2009) 295–303

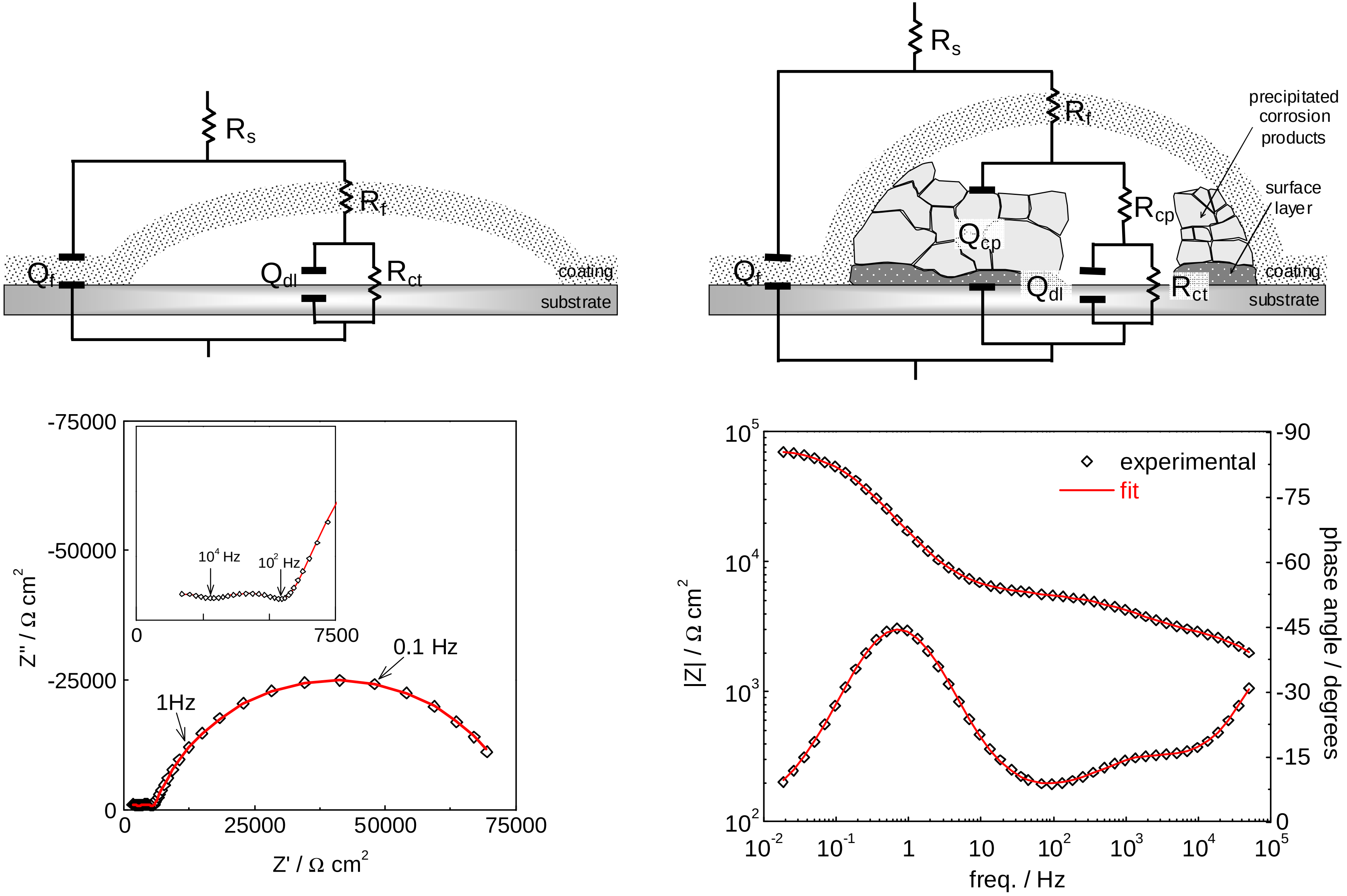
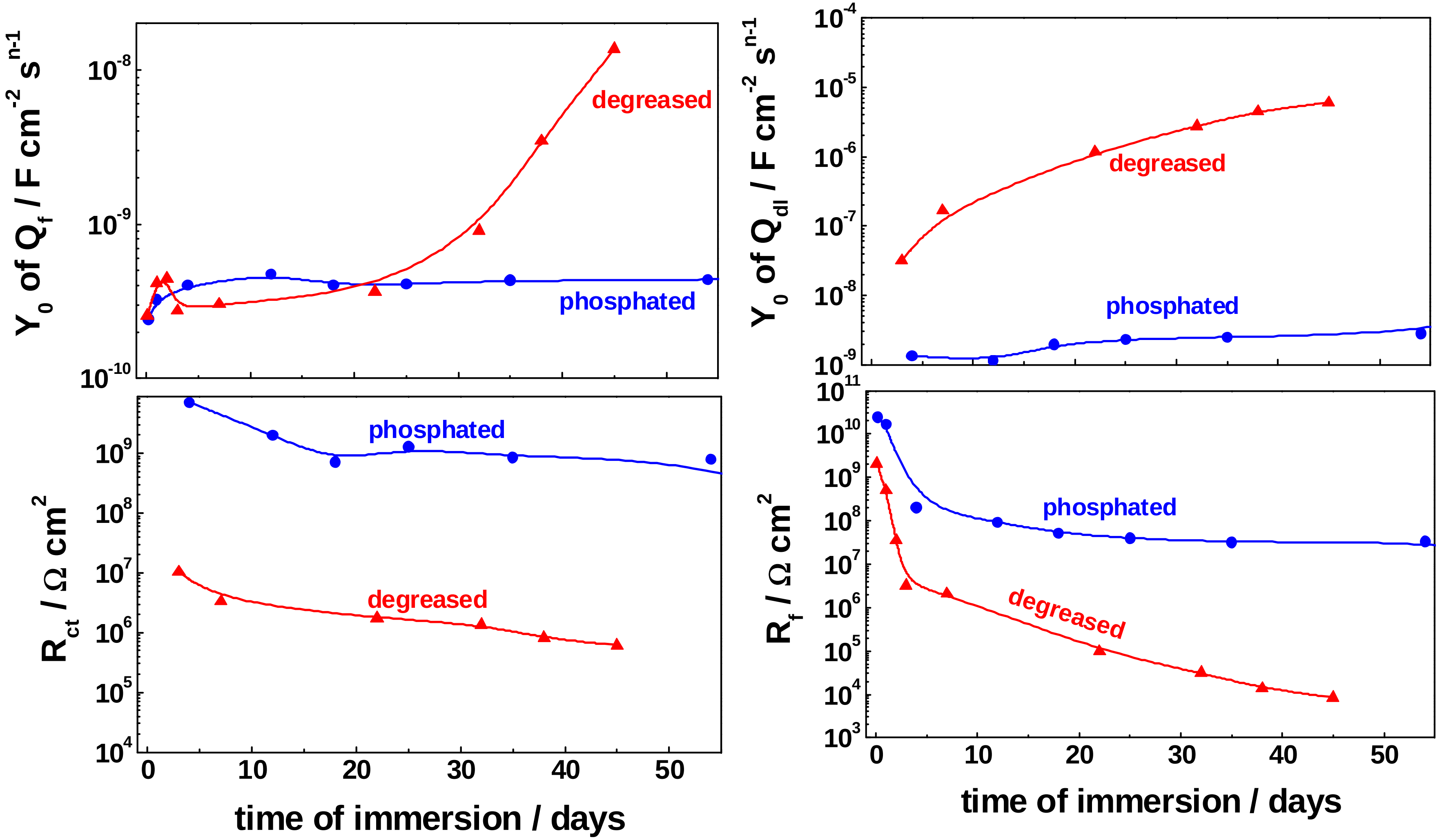


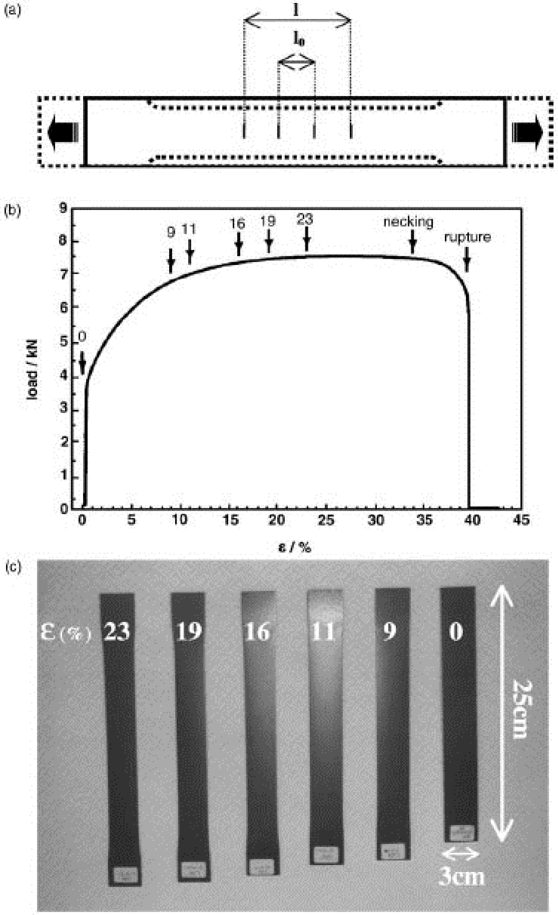
Fig. 14. Equivalent circuits used to fit the EIS results, (a) and (b); fit of spectrum obtained on a formed sample without pre-treatment after 37 days of immersion in 5% NaCl (c). Parameters: $R_s = 573\ \Omega\,\mathrm{cm}^2$; $Y_0(Q_f) = 3.33 \times 10^{-9}\ \mathrm{F\,cm^{-2}\,s^{n-1}}$; $n(Q_f) = 0.924$; $R_f = 2.16 \times 10^3\ \Omega\,\mathrm{cm}^2$; $Y_0(Q_{ox}) = 1.14 \times 10^{-6}\ \mathrm{F\,cm^{-2}\,s^{n-1}}$; $n(Q_{ox}) = 0.656$; $R_{ox} = 3.24 \times 10^3\ \Omega\,\mathrm{cm}^2$; $Y_0(Q_{dl}) = 1.49 \times 10^{-5}\ \mathrm{F\,cm^{-2}\,s^{n-1}}$; $n(Q_{dl}) = 0.797$; $R_{ct} = 7.01 \times 10^4\ \Omega\,\mathrm{cm}^2$, $\chi^2 = 3 \times 10^{-5}$.

Evolution of fit parameters with time of immersion



A word about reproducibility

Influence of temperature



Black 0%

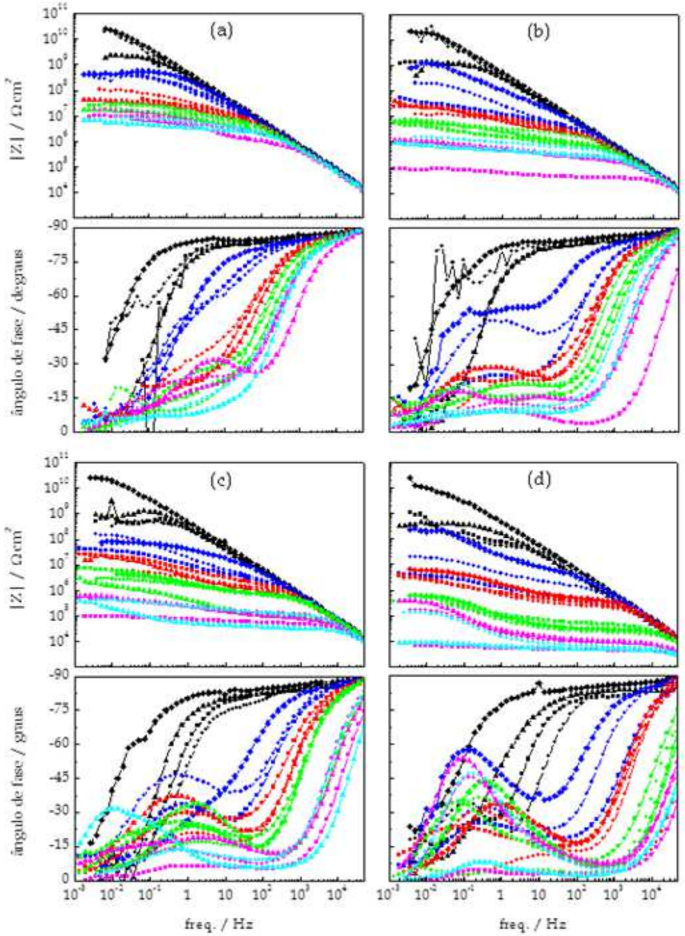
Blue 9%

Red 11%

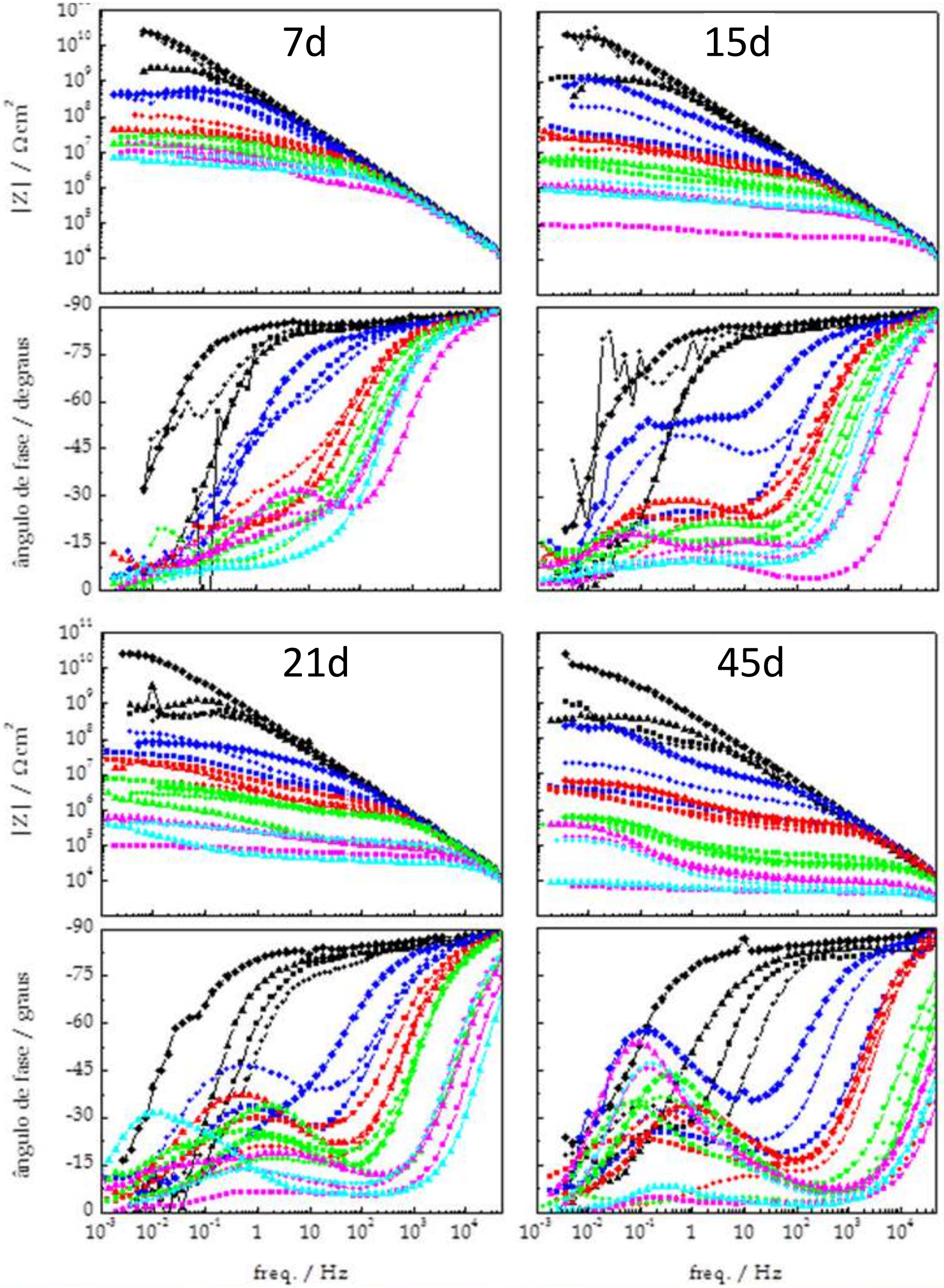
Green 16%

Cyan 19%

Magenta 23%



Jan	Fev	Mar	Abr	Mai	Jun	Jul	Ago	Set	Out	Nov	Dez
18-26	17-24	21-24	21-23	23-26	23-27	24-28	24-28	23-27	23-28	20-22	19-22
									Serie 1 (●)		
Série 2 (♦)											
					Série 3 (■)						
					Série 4 (▲)						



Black 0%
Blue 9%
Red 11%
Green 16%
Cyan 19%
Magenta 23%

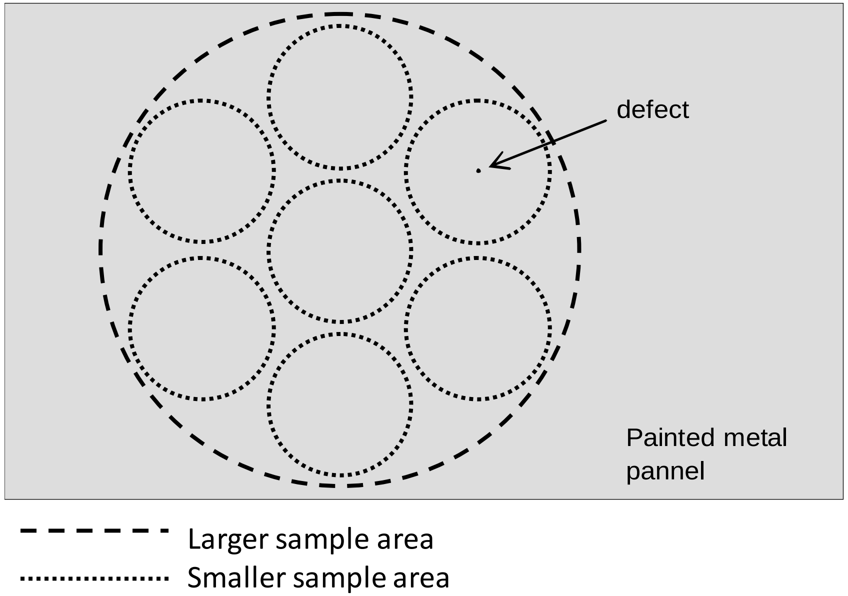
The samples measured on warmer periods showed lower impedance.

The temperature variation was not large - less than 10 Celsius degrees - yet diferences were easily detected in EIS spectra.

In this case the variation did not affect the ranking of samples.

However, in the presence of larger temperature variations or more susceptible materials, erroneous conclusions could be drawn, just by a deficient temperature control of ignorance of its possible effect.

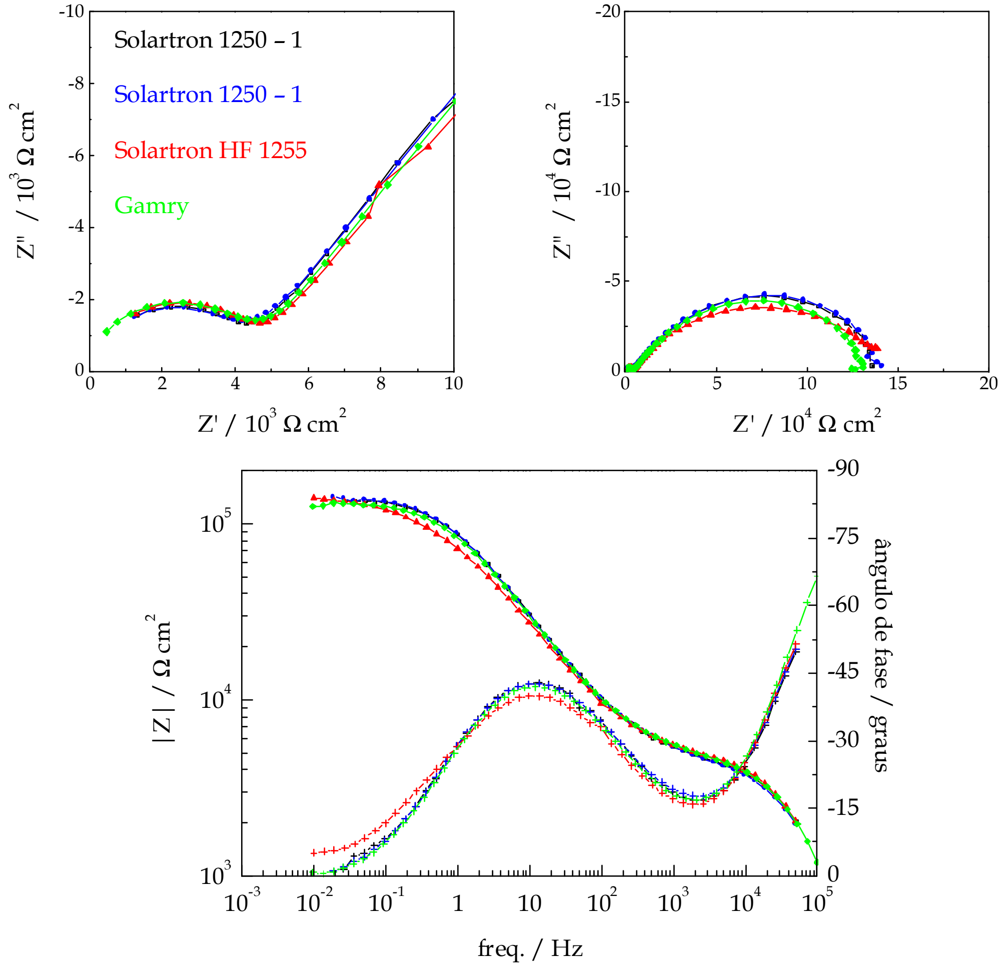
Influence of the sample’s area



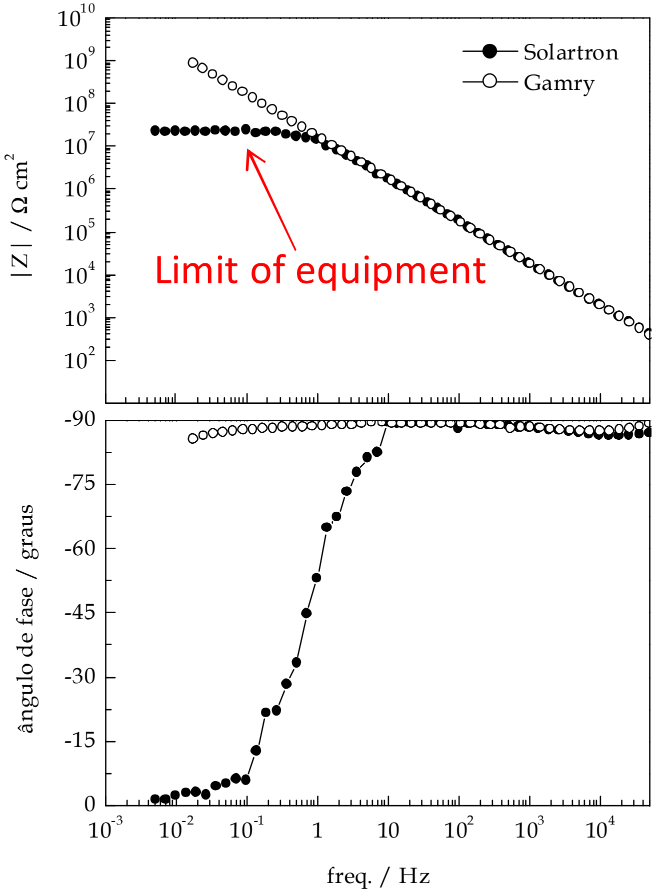
In this example, using a sample with larger area, a defect is present and lower impedance is measured. If smaller areas were prefered, only one sample out of seven would show the lower impedance, with a great probability of being discarded as an outlier. This is a clear example of how sampling can influence the conclusions extracted from the experimental data.

Influence of the measuring equipment

4 different measuring devices, same sample. No difference.



But for higher impedances...



Limit of equipment

Electrochimica Acta 135 (2014) 133–138

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Analysis and mitigation of the artefacts in electrochemical impedance spectroscopy due to three-electrode geometry

Alberto Battistel*,[1], Mu Fan[1], Jelena Stojadinović[1], Fabio La Mantia*,[1]

Zentrum für Elektrochemie, Ruhr-Universität Bochum, DE–44801 Bochum, Germany

LEIS
Localised Electrochemical Impedance Spectroscopy

V.M. Huang et al. / Electrochimica Acta 56 (2011) 8048–8057

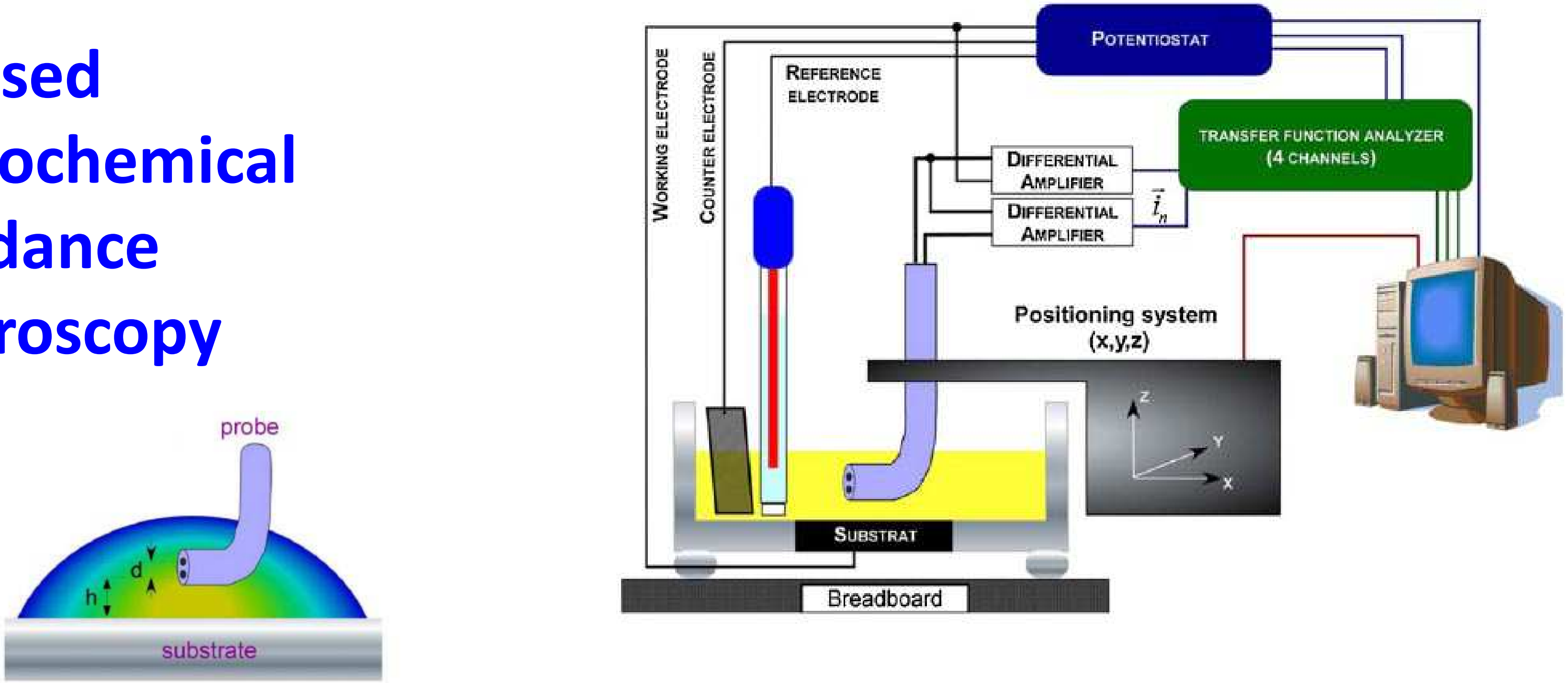

Fig. 1. (a) Block diagram of the LEIS setup; (b) zoom on the microprobe close to the substrate. The probe-to-sample distance is *h* and the distance between the two microreference electrodes is *d*.

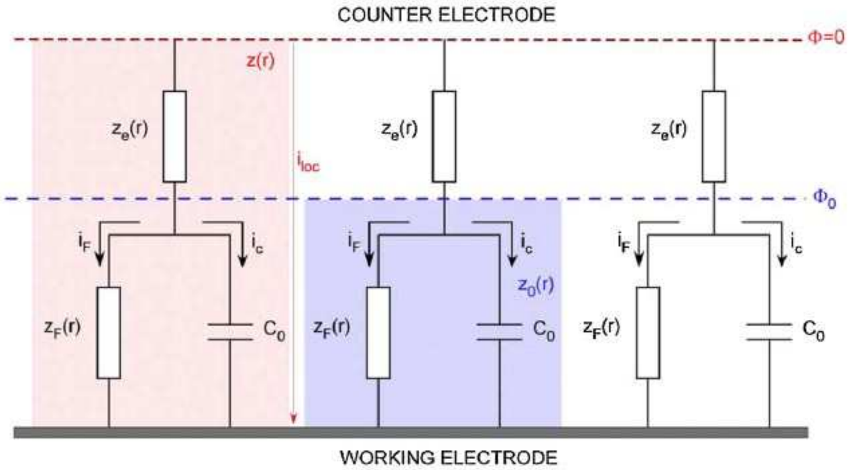

Fig. 2. Electrical equivalent representation of the electrochemical cell.

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