
**Corrosion of metals and alloys — Test
method for corrosion of materials
by electrochemical impedance
measurements**

*Corrosion des métaux et alliages — Méthode d'essai pour la corrosion
des matériaux par des mesures électrochimiques d'impédance*

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 156, *Corrosion of metals and alloys*.

Corrosion of metals and alloys — Test method for corrosion of materials by electrochemical impedance measurements

1 Scope

This Technical Report describes basic principles of electrochemical impedance spectroscopy (EIS), specially focusing on the corrosion of metallic materials. It also deals with how to use electrochemical apparatus, set up and connect electrical instruments, present measured data, and analyse results. However, a more detailed description of this methodology can be found in ISO 16773-1 and ISO 16773-2.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 16773-1, *Paints and varnishes — Electrochemical impedance spectroscopy (EIS) on high-impedance coated specimens — Part 1: Terms and definitions*

ISO 16773-2, *Paints and varnishes — Electrochemical impedance spectroscopy (EIS) on high-impedance coated specimens — Part 2: Collection of data*

ISO 16773-3, *Paints and varnishes — Electrochemical impedance spectroscopy (EIS) on high-impedance coated specimens — Part 3: Processing and analysis of data from dummy cells*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 16773-1 and the following apply.

3.1

bode plot

phase angle and the logarithm of the impedance magnitude $|Z|$ plotted versus the logarithm of the applied frequency

3.2

constant phase element

CPE

equivalent circuit component that models the behaviour of an imperfect capacitor representing a constant phase shift through the whole frequency range

Note 1 to entry: A capacitor has a phase shift of -90° ; for a CPE, the absolute value is smaller.

3.3

counter electrode

inert electrode in the electrochemical cell through which the current passes from or to the working electrode

Note 1 to entry: The counter electrode is also called auxiliary electrode.

**3.4
dummy cell**

printed circuit board with mounted electrical components according to the equivalent circuit with connection points to the measuring instrument

**3.5
double-layer capacitance**

C_{dl}
capacitance values in the equivalent circuit representing the metal-electrolyte interface characteristics

**3.6
impedance**

frequency-dependent, complex-valued proportionality factor, $\Delta E/\Delta I$, between the applied potential (or current) and the response current (or potential) in an electrochemical cell

Note 1 to entry: This factor becomes the impedance when the perturbation and response are related linearly (the factor value is independent of the perturbation magnitude) and the response is caused only by the perturbation. The value can be related to the corrosion rate when the measurement is made at the corrosion potential.

**3.7
magnitude of the impedance**

$|Z|$
magnitude modulus
square root of the sum of squares of the real and imaginary component of impedance

Note 1 to entry: This is given by the formula below.

$$|Z| = \left[(Z')^2 + (Z'')^2 \right]^{1/2}$$

where

- Z is the complex impedance;
- Z' is the real part of impedance;
- Z'' is the imaginary part of impedance.

**3.8
Nyquist plot**

real component of impedance Z' plotted versus the negative of the imaginary component of impedance Z'' in rectangular coordinate values

**3.9
phase angle**

phase difference between the periodically recurring voltage and the current of the same frequency, expressed in angular measure

**3.10
polarization resistance**

R_p
slope (d_e/d_i) at the corrosion potential of a potential (e) versus current density (i) curve

Note 1 to entry: For a simple corroding system, charge transfer resistance, R_{ct} , is used.

**3.11
potentiostat**

electronic instrument for automatically maintaining the working electrode in an electrolyte at a controlled potential with respect to a reference electrode, and for measuring the resulting current between the working and counter electrodes

3.12**reference electrode**

electrode which allows the measurement of an electrode potential

Note 1 to entry: This electrode has to present a thermodynamically stable potential versus the standard hydrogen electrode.

3.13**solution resistance**
 R_s

resistance of the solution between the working electrode and the tip of Luggin capillary connected to the reference electrode

Note 1 to entry: This term is not defined in ISO 16773-1.

3.14**working electrode**

test or specimen electrode in an electrochemical cell

Note 1 to entry: This definition is different from the definition in ISO 16773-1.

3.15**Kramers-Kronig relation**

mathematical relation connecting the real and imaginary parts of any complex function which is analytic in the upper half-plane

Note 1 to entry: These relations are often used to relate the real and imaginary parts of response functions in physical systems because causality implies that the analyticity condition is satisfied, and conversely, analyticity implies causality of the corresponding physical system.

4 Principles**4.1 Simple corroding system**

Simple corrosion systems, which are under charge transfer control resulting in uniform corrosion on homogeneous surface, can be described by a simple equivalent circuit shown in [Figure 1](#). The use of electrochemical impedance spectroscopy (EIS) on corroding metals requires that the measured system do not react in such a way that the measured system change during the measurement time, steady-state should be maintained. A metal immersed in the solution may corrode by anodic and cathodic reactions at the metal/solution interface, as shown in [Figure 1](#).

A simple corroding system in an electrolyte is represented by an anodic and cathodic reaction:



where

n is the number of electrons e^- ;

Me is the metal.

Metal 1 has less nobility than metal 2.

The equivalent circuit represents the metal/solution interface of the metal surface which consists of a polarization resistance, R_p , also commonly noted charge transfer resistance, R_{ct} , in parallel with an electric double-layer capacitance, C_{dl} , which is in series with a solution resistance, R_s .

A metal sample in immersion develops an electric double layer at the interface. The double layer is represented by a capacitance in EIS. It is not a true capacitive value measured by EIS and the double layer is, therefore, represented by a constant phase element (CPE) to compensate the deviation from the true capacitive value. The elements CPE and R_p are not always dependent on corrosion resistance but can reflect the overall electrical resistance and dielectric properties of passive film oxides. For example, a passive film growth depends on the transport of cations and anions or their vacancies across the oxide film. If defects such as pores, channels, or cracks are present in the passive film, the electrolyte will penetrate the film and impair its resistance. In addition, a surface oxide film might exhibit capacitive behaviour due to a dielectric nature of the oxide.

The CPE is a component of the equivalent circuit for modelling the behaviour of an electrical double layer, an imperfect capacitor. The impedance of a CPE is given by $1/Z_{CPE} = Q^\circ(j\omega)^n$. The Q° is the constant corresponding to the electric double-layer capacitance qualitatively. The factor n ranges from 0 to 1 as follows:

- $n = 1$ represents an ideal capacitor;
- $n = 0$ represents a pure resistor.

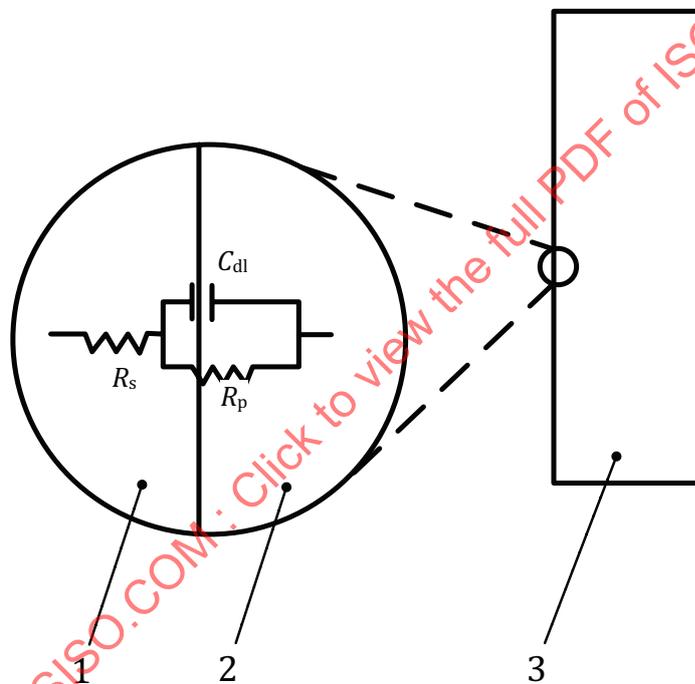


Figure 1 — Schematic representation of a metal in solution and the equivalent circuit representing the metal/solution interface

Key

R_s solutions resistance	1 solution
C_{dl} double layer capacitance	2 metal
R_p polarization resistance	3 corroding metal

For a simple corroding metal, the value of C_{dl} is generally proportional to the actual surface area of the working electrode. When the anodic and cathodic reactions are controlled by the charge transfer step

around the corrosion potential, the current flowing through the working electrode, I_w , is represented by Formula (1).

$$I_w = I_{\text{cor}} \left\{ \exp \left[\frac{2,303(E - E_{\text{cor}})}{\beta_a} \right] - \exp \left[\frac{-2,303(E - E_{\text{cor}})}{\beta_c} \right] \right\} \quad (1)$$

where

I_{cor} is the corrosion current;

β_a and β_c are Tafel constants (V/decade) in anodic and cathodic regions, respectively.

The R_p and I_{cor} have the following relation:

$$R_p = \frac{K}{I_{\text{cor}}} \quad (2)$$

where

$$K = \frac{\beta_a \beta_c}{2,303(\beta_a + \beta_c)} \quad (3)$$

The value of K is dependent upon the type of specimen material and the environment, and the I_{cor} can be obtained from R_p theoretically.

When a semicircle of the impedance is depressed indicating an untrue capacitance in the Nyquist plot, the constant phase element (CPE) may be incorporated in the equivalent circuit instead of C_{dl} . The outline of CPE is revealed in [Annex B](#). The theoretical relationship in Formula (3) might not hold for the corrosion system with a CPE because other electrochemical reactions than simple metallic corrosion might be involved in the system. It is recommended that the correlation between R_p values and I_{cor} values from weight-loss measurements be used to determine K values.

4.2 Presentation of impedance by a complex number

The impedance Z is represented by the complex number with real part Z' and imaginary part Z'' .

$$Z = Z' - j Z'' \quad (4)$$

The relation of Z' and Z'' on the complex plane is depicted in [Figure 2](#). The magnitude impedance, $|Z|$, and phase shift φ (in degrees) or θ (in radians) of Z are related by

$$|Z| = \sqrt{(Z')^2 + (Z'')^2} \quad (5)$$

$$\varphi = \arctan \left(\frac{-Z''}{Z'} \right) \quad (6)$$

$$\theta = \frac{180}{\pi} \varphi \quad (7)$$

The phase angle of vector Z is presented in φ (degrees) on the complex plane, as in [Figure 2](#).

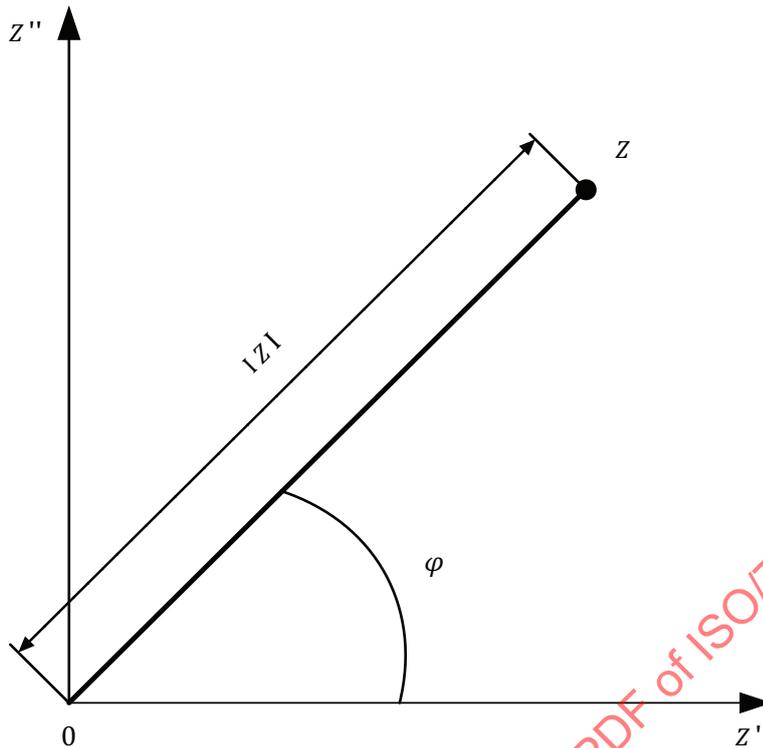


Figure 2 — Impedance Z presented on the complex plane

4.3 Impedance spectra of circuit elements

4.3.1 The impedance spectra of circuit elements, R and C , and their combinations can be presented in Bode and Nyquist plots. Bode plots of impedance spectra of each circuit element and their combination are shown in [Figure 3](#).

4.3.2 The impedance of a resistor R is represented by a simple formula $Z = R$. The magnitude $|Z|$ and phase shift φ have a constant value of R and zero, respectively, through the whole frequency range, as shown in [Figure 3 a](#)).

4.3.3 The impedance of a capacitor C is represented by the formula $Z = 1/j\omega C$. The magnitude of $\log |Z|$ decreases with the increase in $\log f$ with a slope of -1 , as is represented by the relationship: $\log |Z| = -\log f - \log (2\omega C)$. The phase shift φ is -90° for a capacitor and the value of $\log |Z|$ is equal to $\log (1/C)$ at $f = 1/2\omega$ (Hertz), as shown in [Figure 3 b](#)).

4.3.4 For a serial RC circuit, the magnitude of $\log |Z|$ decreases with the increase in $\log f$, and the slope is -1 in the low frequency range because $R \ll 1/\omega C$, and φ is -90° in the low frequency range. The magnitude of $\log |Z|$ takes a constant value in the high frequency range because $R \gg 1/\omega C$, and φ is 0° in the high frequency range, as shown in [Figure 3 c](#)).

4.3.5 For a parallel RC circuit, the $\log |Z|$ takes a constant value, and φ is 0° in the low frequency range because $R \ll 1/\omega C$ where the current flows through the resistor. The magnitude of $\log |Z|$ decreases with the increase in $\log f$ with the slope of -1 , and φ is -90° in the high frequency range, because $R \gg 1/\omega C$ where the current flows through the capacitor, as shown in [Figure 3 d](#)).

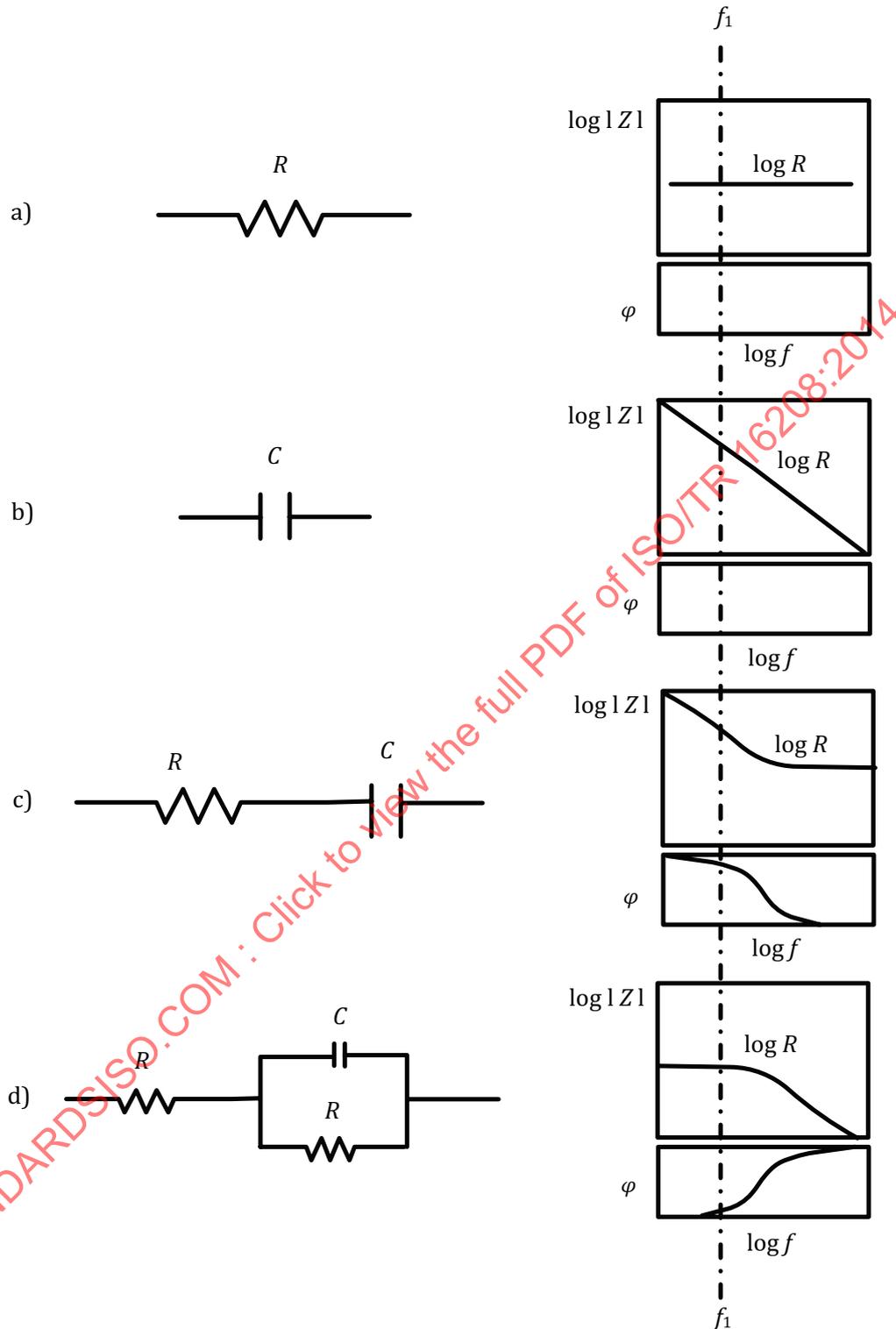


Figure 3 — Circuit elements and their Bode plots

4.4 Presentation of a simple corroding system

The Bode plot for the equivalent circuit for a simple corrosion system in [Figure 4 a\)](#) is shown in [Figure 4 b\)](#). In the low frequency range, the $\log |Z|$ has a constant value, which is approximately $R_s + R_p$ with φ of 0° because $1/\omega C_{dl}$ is large. In the middle frequency range, the $\log |Z|$ decreases with the increase in

frequency with the slope of -1 because $R \gg 1/\omega C$ in the electrochemical circuit due to the combined effect from the large capacitance and higher frequency. The $\log |Z|$ is approximated to be R_s with φ of 0° when $1/\omega C$ becomes negligibly small in the high frequency range.

The magnitude of real and imaginary parts of Z for an equivalent circuit in [Figure 4 a\)](#) is given by Formula (8):

$$Z' = R_s + \frac{R_p}{1 + \omega^2 R_p^2 C_{dl}^2} \tag{8}$$

$$Z'' = \frac{\omega^2 R_p^2 C_{dl}^2}{1 + \omega^2 R_p^2 C_{dl}^2} \tag{9}$$

The Nyquist plot for the equivalent circuit in [Figure 4 a\)](#) is shown in [Figure 4 c\)](#). The locus of Z is a semicircle with a diameter R_p . The low and high frequency limits converge to $R_s + R_p$ and R_s respectively, on the real axis. The frequency at the top of the semicircle f_{max} has the following relationship with the time constant $R_p C_{dl}$:

$$f_{max} = \frac{1}{2\pi R_p C_{dl}} \tag{10}$$

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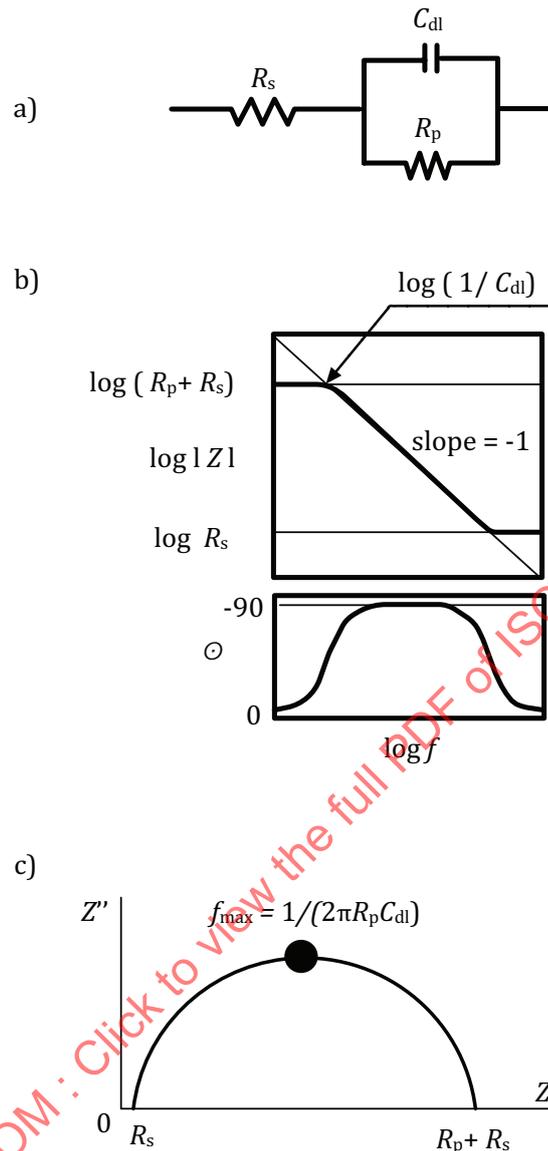


Figure 4 — A simple corroding system: a) equivalent circuit, b) the Bode plot, and c) the Nyquist plot

5 Apparatus

5.1 General

The measurement system consists of an electrochemical cell connected to instrumentation and software for the characterization of materials using precision electrical measurement techniques.

NOTE 1 Guidance is given in ISO 17474.

The measurement procedure in electrochemical impedance spectroscopy is to take the frequency spectrum with logarithmic data point spacing. Therefore, it is also necessary to apply the number of data points within each decade of frequency points. It is advised to take at least 5 points per decade to provide a minimum data point resolution. This resolution is needed to allow accurate equivalent circuit modelling onto the data after the experiment.

The perturbation amplitude is the potential sine wave that is applied through the potentiostat as a polarization voltage to the working electrode. Its amplitude is defined mostly in millivolts and should be as small as possible. This way perturbation of the electrode is minimal. This is necessary to prevent the electrode surface from being permanently changed by too high polarization during the measurement. It should be applied within the linear response window of the electrode. Due to this small polarization, the resulting currents will also be very small.

The EIS system shall be capable of measuring and extracting the values of the resistors and capacitors in the dummy cell (see [Annex A](#)). Deviations of the fitted values of the electronic components from the real values should not exceed the accuracy limits of the components used in the dummy cells. Excessive errors in the values indicate experimental problems with the EIS system or inaccurate operation of the system.

NOTE 2 Guidance is given in ISO 16773-2.

The potentiostat used to apply the potential signal from an AC generator to FRA should be capable of controlling the electrode potential within ± 1 mV of a preset value. The potentiostat should have outputs in the form of voltage versus ground for both potential and current, and have sufficient bandwidth for minimal phase shift up to at least 100 000 Hz. The terminals to measure the potential difference between the working and reference electrodes should have a high input impedance of the order of $10^{11} \Omega$ to $10^{14} \Omega$ to minimize current drawn from the system during measurement. The sensitivity of current-measurement should have maximum error of less than 0,5 %.

5.2 Test cell

The cell should be constructed of materials that will not corrode, deteriorate, or contaminate the solution. The cell should be leak-proof to ensure that the geometrical surface of the sample does not change with time.

The cell should be constructed to allow the following items to be inserted into the solution chamber: the working electrode, the reference electrode, the counter electrode, a thermometer (temperature control), and gas inlet/outlet tubes to modify the oxygen content. When using an inert gas, a gas scrubber should be used. The cell needs attention regarding formation of crevice between the cell and the test material when the test solution contains halides. Crevice-free setup or cells are to be recommended for corrosion measurements of materials properties.

The test cell should be large enough to contain the electrolyte, working electrode, and a reference electrode and counter electrode. The test cell can incorporate inlet and outlet gas ports and a port for insertion of a temperature-measuring device. The test cell shall be constructed of a material which is inert in the environment at the temperature of testing. The counter electrode is recommended to be separated from the main cell of the working electrode by a fritted disc to avoid contamination of the main cell by reaction products generated at the counter electrodes.

The reference electrode may be inserted directly into the main cell if there is no risk for contamination or deterioration by a corrosive electrolyte. To avoid mutual contamination, a double-junction reference electrode may be used. The reference electrode may also be located in a separate chamber and linked to the main cell by a salt bridge. The tip of the capillary probe (Luggin capillary) shall be positioned so that it is at a distance from the working electrode of about, but not closer than, 2 times the diameter of the tip.

5.3 Electrode holder

The counter and working electrodes shall be mounted in such a way that the holder and mounting material have no influence on the measurement. A special precaution should be exercised to prevent crevice attack for certain applications.

5.4 Electrode material

The working electrode is prepared from the test material of interest, usually in the form of a rod or sheet. The counter electrode is commonly prepared from high-purity platinum. Other materials can be

used, provided they are inert. The counter electrode may be constructed in the form of a sheet or rod, or in the form of gauze supported on a glass frame with the test specimen located centrally. The area of the counter electrode should be at least the area of the working electrode. Graphite can be used as a counter electrode but care shall be taken to avoid contamination; desorption of species retained in the graphite might be necessary prior to usage.

5.5 Reference electrode

The type of reference electrode used will depend on the application, e.g. temperature and environment. A commonly used reference electrode is the saturated KCl silver/silver chloride electrode (SSE). The type of reference electrode should be documented as well as the standard solution concentration for the electrode.

5.6 Electrolyte

The resistance of the test solution should be low in comparison to the impedance of the investigated system. Different types of electrolyte can be used but the electrolyte should be conductive enough to reflect the measured system rather than the solutions resistance.

6 Specimen preparation

6.1 The specimen shall be cleaned, degreased, rinsed, and dried. The specimen can be mill-finished as delivered surface. If a specific surface is preferred, it should preferably be a well-defined surface finish according to the application. In most cases, an R_a value less than $1\ \mu\text{m}$ is desirable to limit the possibility of enhanced reaction in grooves induced by grinding.

6.2 The time elapsed between grinding and immersion can have an influence on the impedance values measured. The elapsed time selected will depend on the purpose of the test but should be standardized for a particular set of tests. Little variation in surface-film thickness occurs after 24 h and, hence, a minimum elapsed time of 1 d is often useful. The specimens should be cleaned and degreased (e.g. using alcohol or acetone) and stored in a desiccated cabinet.

7 Solution preparation

The solutions shall be prepared from analytical reagent-grade chemicals and high-purity water (with a conductivity less than $1\ \mu\text{S} \cdot \text{cm}$), unless testing takes place in the actual service fluid.

8 Dummy cell

In addition to the confidence tests described in ISO 16773-2 and ISO 16773-3, Annex A provides a procedure for check of the overall experimental arrangement. The dummy cell is mounted separately.

9 Procedure

9.1 Measure the difference in potential between the reference electrode and two other validation electrodes. These electrodes should be traceable to the standard hydrogen electrode and used and maintained solely for purpose of validation. If the potential is different by greater than 3 mV, the test electrode should be rejected.

9.2 Measure the exposed surface area of the specimen.

9.3 Assemble the cell with the counter electrode, reference electrode, and Luggin capillary.

9.4 Prepare the test solution in sufficient amount to be added to the electrochemical cell.

9.5 Depending on the type of cell, the sample is mounted before or after the addition of the test solution. For a crevice-free flush port cell, the test sample is mounted before addition of the test solution. For the use of ordinary electrochemical glass cell with a lid, the test solution may be added before the mounting of the test sample in the cell.

9.6 Add the test solution to the cell.

9.7 When purging with gas, the solution should be purged with the appropriate gas for 60 min or longer to achieve equilibrium. When testing in aerated solutions, either an air pump or a cylinder of compressed air can be used to ensure constancy of conditions.

9.8 Control the temperature to ± 1 °C by using temperature sensors or by using a double-wall electrochemical cell controlling the temperature with a water bath circulation. Alternatively, immerse the exterior of the test cell in a controlled-temperature water bath or by other convenient means.

9.9 Adjust the Luggin probe tip so that it is at a distance from the working electrode of about, but not closer than, 2 times the diameter of the tip.

9.10 Record the open-circuit potential of the working electrode, i.e. the corrosion potential changing with time after immersion. The period of exposure at open circuit prior to polarization will depend on the purpose of the experiment. In some applications, it can be useful to allow the open-circuit potential to attain a steady value. Otherwise, a period of 60 min should be allowed.

9.11 Run the impedance experiment at the corrosion potential, E_{cor} , or the polarized potential, depending on the purpose of the test. The amplitude of the superimposed AC potential should be from 5 mV to 10 mV. The frequency is scanned logarithmically between a minimum 10 000 Hz (10 kHz) and, typically, 0,01 Hz (10 mHz).

10 Data analysis

Impedance data are mainly represented in Bode plot or Nyquist diagrams. The diagrams can be used for visual evaluation comparing treatments or exposure tests. Corrosion as well as passivity can be investigated and followed by impedance diagrams. Parameters to follow by impedance measurements at different occasions can be changes in the passive oxide film or start of corrosive reaction, rather than evaluation of the equivalent circuit.

Electrochemical impedance data can be analysed by fitting to an equivalent circuit. The electrical elements included in the equivalent circuit (resistor, capacitor, inductor, etc.) should be identified to corresponding physical characteristics of the corroding or passive metal. The Kramers-Kronig (K-K) test can be used to check whether the measured system is linear and stable in time during the uptake of spectra. If the system investigated changes with time during these measurements, for example through temperature changes or a state of non-equilibrium, the test fails.

Electrochemical impedance spectra for actual corrosion systems can be more complicated than that described in this Technical Report. The interpretation and identification of different chemical and corrosion processes can be difficult.

For example, as shown in [Figure 5](#), active dissolution, i.e. corrosion of a passive metal in sulfuric acid and sodium chloride, might include adsorption and desorption reactions in combination with corrosion. The adsorption and desorption reactions might introduce inductive loops in the spectra.[\[13\]](#) [\[14\]](#)

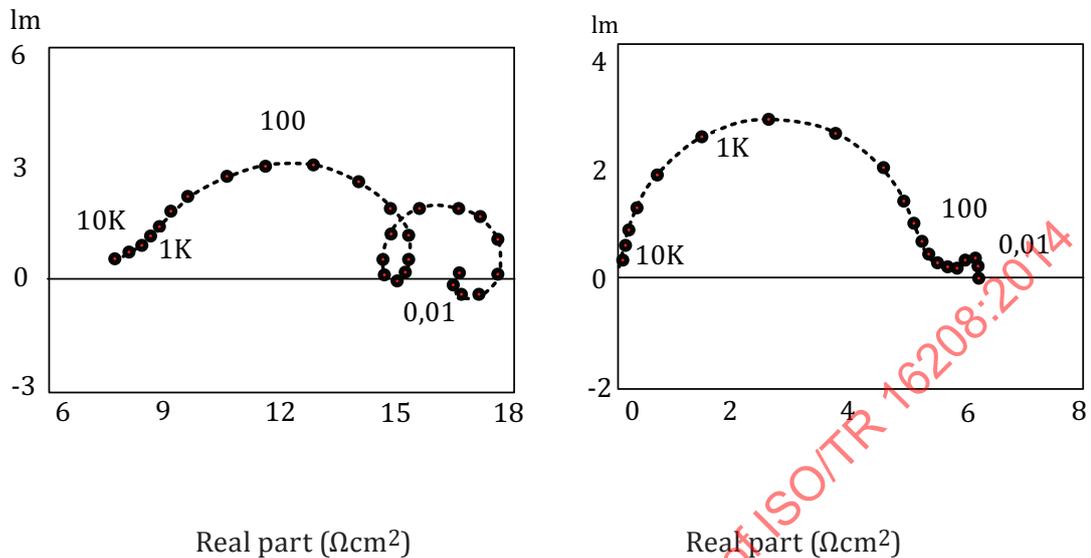


Figure 5 — Measured electrode impedance of Fe17Cr in 0,5 M H₂SO₄ with addition of chloride[\[13\]](#)

It is necessary to begin the interpretation of data with establishing equivalent circuit models through deliberate considerations based upon electrochemical principles. Meaningful parameters shall be obtained using the model of which adequacy is demonstrated.

Since it is difficult to cover entire corrosion systems by stipulations dealing only with some simple models, revisions of this Technical Report can ensue to expand the scope toward more complicated cases. However, examples are provided in the literature on interpretation of more complex corrosion such as, for example, the impedance of pitting processes of aluminium-based materials.[\[15\]](#) [\[16\]](#) [\[17\]](#) A proposed electrochemical circuit model for the impedance of pitting processes of aluminium-based materials is presented in the literature. EIS analysis and an example of an equivalent circuit of aluminium alloy suffering from pitting corrosion in chloride solution is shown in [Figure 6](#).

The component W is referred to as a Warburg impedance related to diffusion processes. It is, however, almost impossible to simulate this circuit element and realistic modelling is necessary to interpret impedance data.

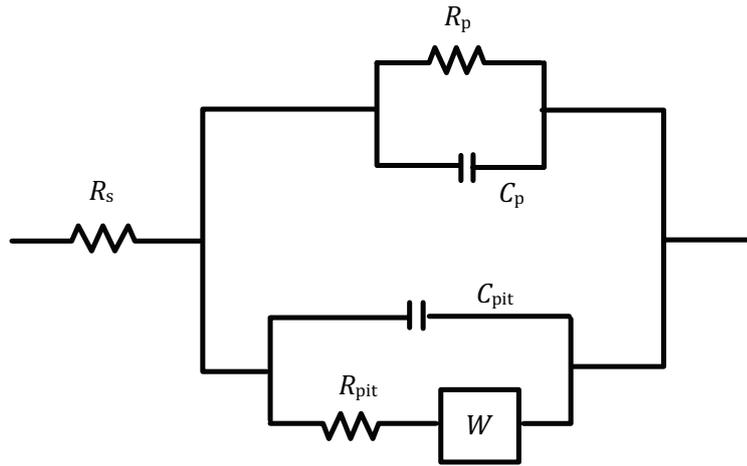


Figure 6 — Equivalent circuit model considered for the impedance of pitting process of aluminium-based materials [15] [16] [17]

11 Test report

The test report shall include the following information:

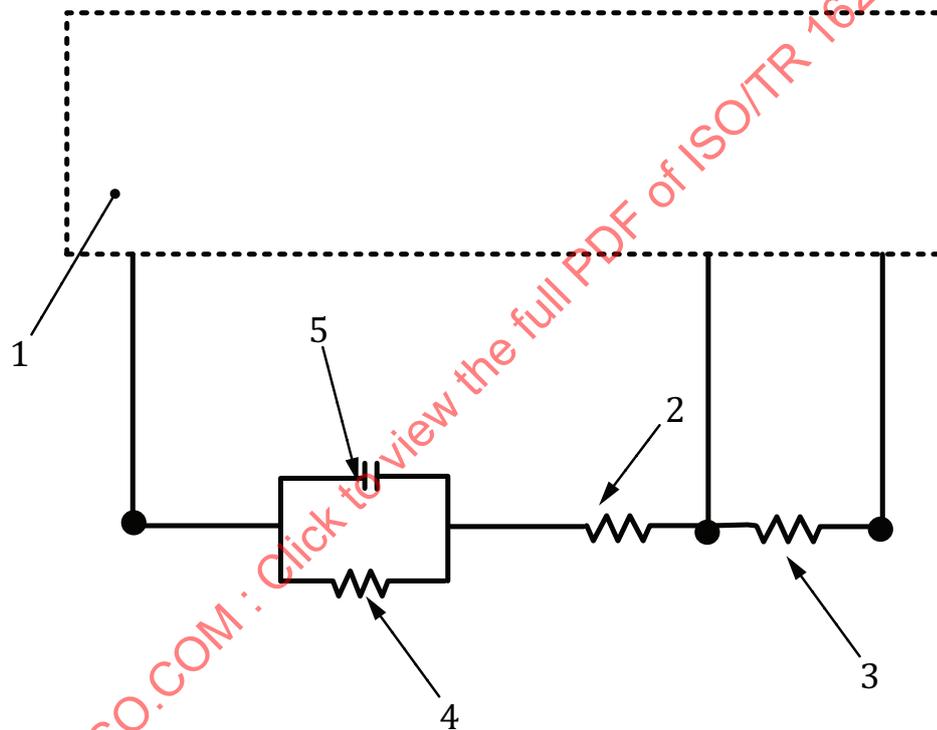
- a) a reference to this Technical Report (i.e. ISO/TR 16208:2013);
- b) a full description of the test material from which the specimens were taken, composition, heat treatment, and type of product;
- c) method of manufacture of the specimens and details of the surface preparation;
- d) the solution composition, pH, volume, temperature, and any variations with time;
- e) the type of reference electrode used in the measurements;
- f) the area of the specimen exposed to the test solution;
- g) the description of the cell and electrodes used;
- h) the time of immersion prior to measurement;
- i) the open-circuit potential before and after measurements and whether this was steady;
- j) the amplitude of the AC voltage, frequency range scanned, and steps per frequency decade;
- k) plots of the resulting frequency response in Nyquist format (the negative of the imaginary impedance versus the real impedance) and/or Bode format (impedance modulus and phase angle versus frequency).

Annex A (informative)

Dummy cell

A.1 Dummy cell

The dummy cell is used to check the equipment for electrochemical impedance measurement. The cell is a circuit with two resistors ($R_{s\text{Dummy}}$ and $R_{c\text{Dummy}}$) in series connected to a parallel combination of a resistor ($R_{p\text{Dummy}}$) and a capacitor ($C_{dl\text{Dummy}}$), as in [Figure A.1](#).



Key

- 1 electrochemical measurements system
- 2 $R_{s\text{Dummy}}$
- 3 $R_{c\text{Dummy}}$
- 4 $R_{p\text{Dummy}}$
- 5 $C_{dl\text{Dummy}}$

Figure A.1 — Circuit diagram for dummy cell and the connections with the electronic instruments

A.2 Procedure for checking the equipment

A.2.1 Connect the cell to the potentiostat as in [Figure A.1](#). Use of 10 Ω to 100 Ω resistor for $R_{s\text{Dummy}}$, 100 Ω to 1000 Ω resistor for $R_{c\text{Dummy}}$, 100 Ω to 1 000 Ω resistor for $R_{p\text{Dummy}}$, and 10 Ω to 100 Ω for $C_{dl\text{Dummy}}$ can be appropriate for most cases.

A.2.2 Record the frequency response at the potential set to 0,0 V. Collect the data with AC voltage (typically an amplitude of 10 mV) between 10 000 Hz (10 kHz) and 0,01 Hz (10 mHz) using from 5 steps per frequency decade to 10 steps per frequency decade.

A.2.3 Plot the data in Nyquist or Bode format and determine the $R_{s\text{Dummy}}$, $R_{p\text{Dummy}}$, and $C_{dl\text{Dummy}}$. Compare the obtained values with the nominal values in the dummy circuit in [Figure A.1](#). The difference should be within $\pm 0,5\%$ of the nominal value.

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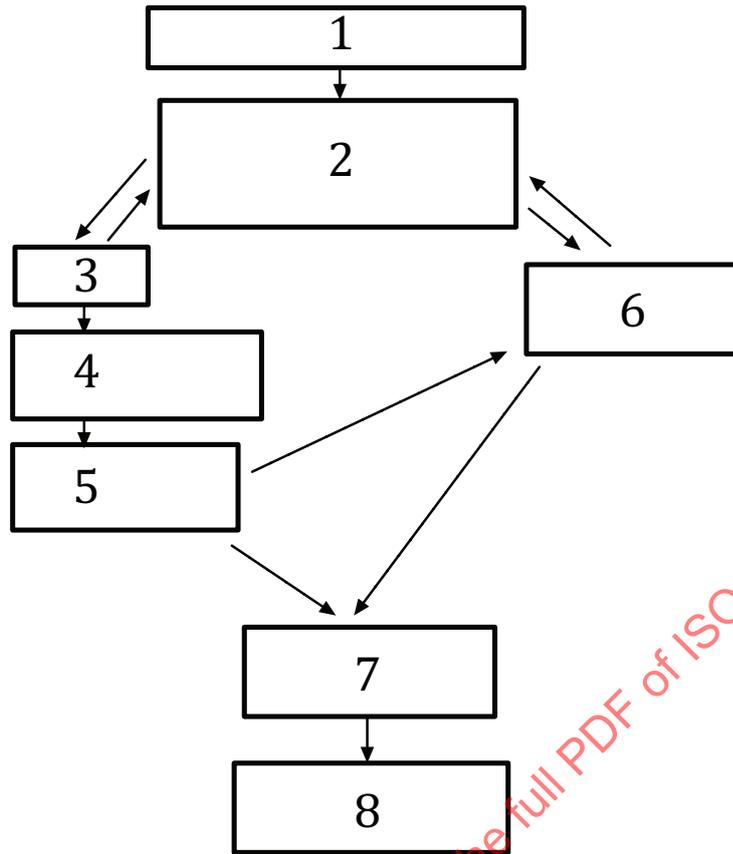
Annex B (informative)

Data analysis

B.1 EIS representation

Depending on the obtained results, the analysis of the impedance spectra needs to start with the identification of physical reactions or properties represented by the EIS spectra. There are occasions when there are great difficulties in identifying an equivalent circuit representing the mathematical model and physical model, but changes in the spectra depending on exposure can indicate instable material. Other instances for identifying EIS data are to maintain passivity in a metallic surface, and evaluation by an equivalent circuit might not be necessary.

Information from the two types of diagrams provides additional information of the metal surface which is not revealed in DC polarization measurements (for example, the resistivity of a passive film). [Figure B.1](#) shows an overview of the evaluation process in electrochemical impedance spectroscopy.



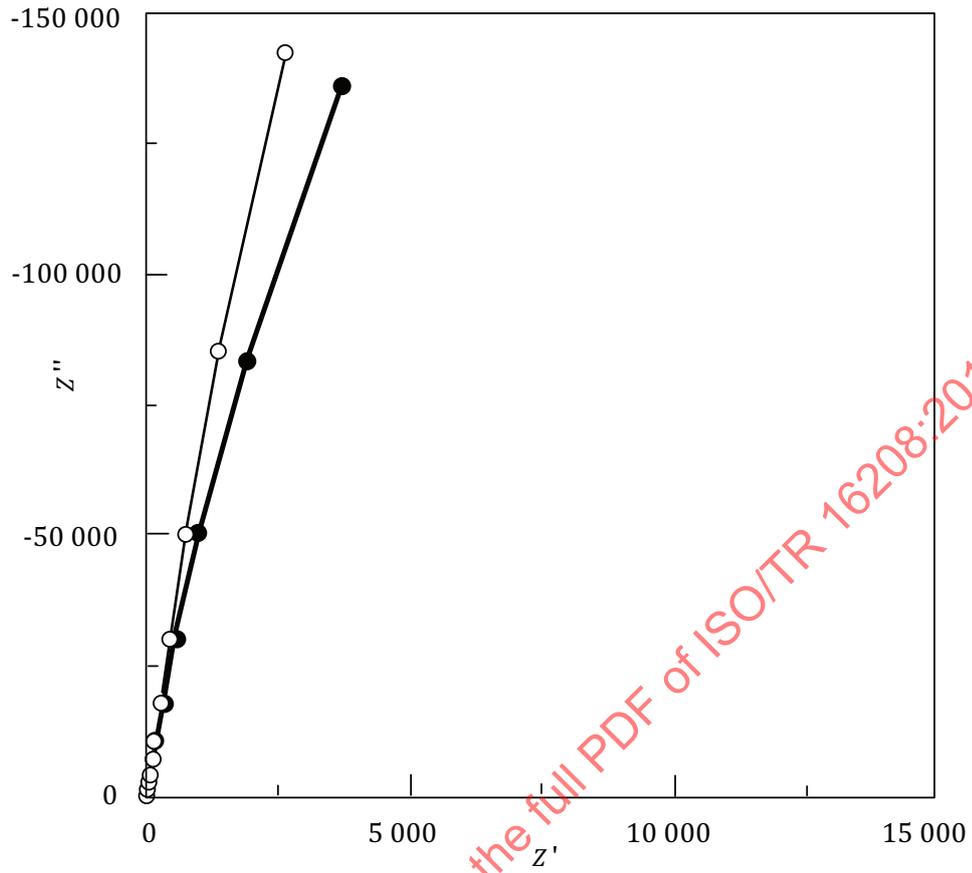
Key

- | | | | |
|---|--|---|--------------------------------|
| 1 | material–electrode system | 5 | mathematical model |
| 2 | EIS experiment measurement values, $Z(\omega)$ | 6 | equivalent circuit |
| 3 | theory | 7 | fit analysis, error analysis |
| 4 | suitable physical model | 8 | characterization of the system |

Figure B.1 — Overview of the evaluation process in EIS

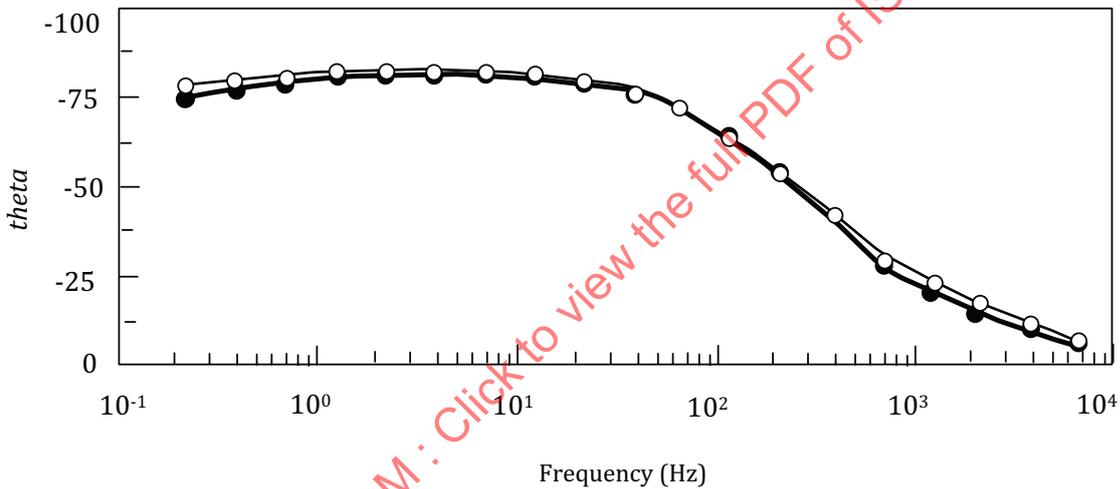
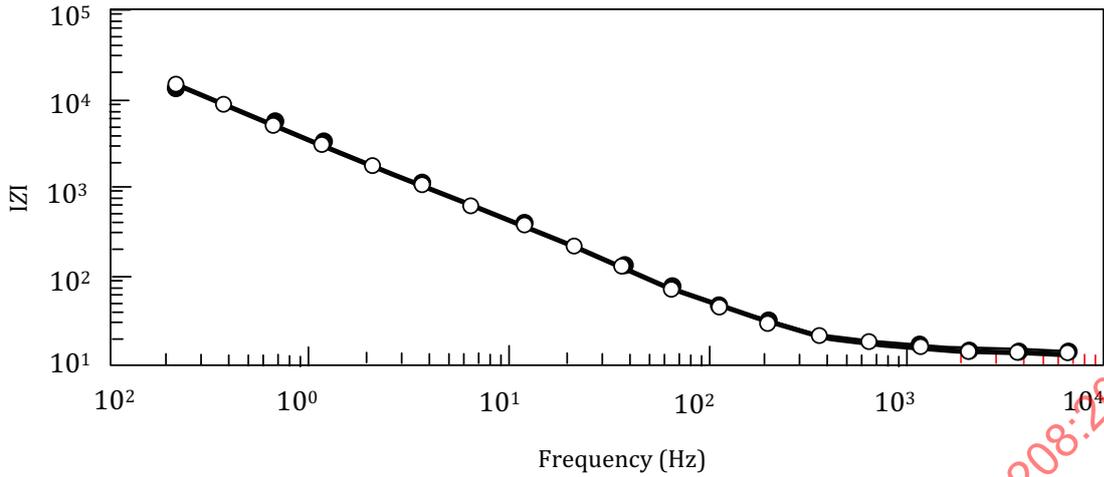
Evaluation by deification of an equivalent circuit can, in some simple cases, be possible by the knowledge of EIS spectra from the different electrical components in the equivalent circuit. It is vital to keep the number of components as low as possible and to use error analysis in combination with the evaluation in equivalent circuits. Some simple examples are shown below.

[Figure B.2 a\)](#) shows EIS measurements typically of a passive metal surface represented by a Nyquist plot and [Figure B.2 b\)](#) shows the Bode plot of the same EIS measurements.



a) Nyquist representation at different times

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b) Bode plot at different times

- Key
- time 1
 - time 2

Figure B.2 — EIS measurements of a metallic passive surface

A surface oxide film exhibits a capacitive behaviour due to the dielectric nature of the oxide. In an ideal scenario, the exponential factor of n is equal to 1 and the CPE acts like a capacitor. Heterogeneous surfaces that contain examples of surface roughness or porosity contribute to a deviation from the ideal capacitive behaviour. By registering the capacitive measurements, the contribution attributable to the