TECHNICAL REPORT

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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

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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.

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

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:

Anode: $Me_1 \rightarrow Me_1^{n+} + ne^-$

Cathode: $Me_2^{n+} + ne^- \rightarrow Me_2$

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 $1/Z_{CPE} = Q°(j\omega)^n$. 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.

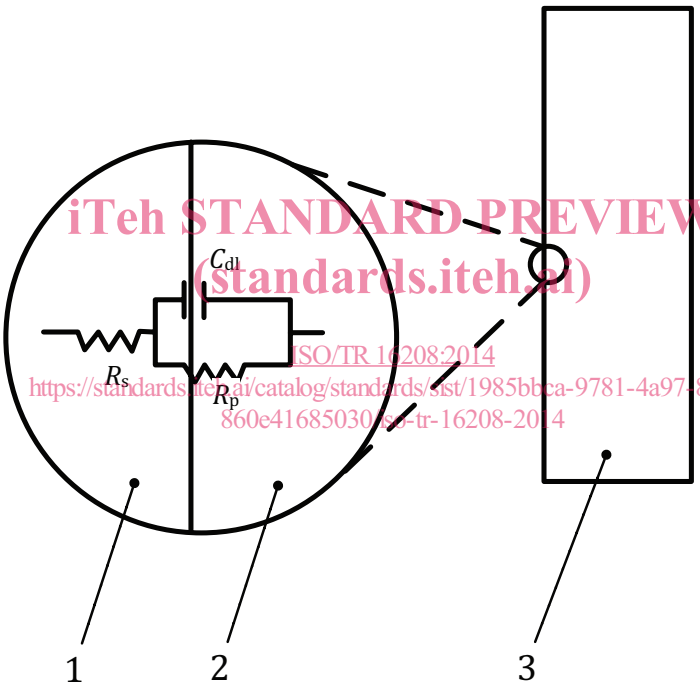

Figure 1 — Schematic representation of a metal in solution and the equivalent circuit representing the metal/solution interface

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).

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

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:

$$R_p = \frac{K}{I_{cor}} \tag{2}$$

where

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

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''.

$$Z = Z' - j\,Z'' \tag{4}$$

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

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

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

$$\theta = \frac{180}{\pi}\varphi \tag{7}$$

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

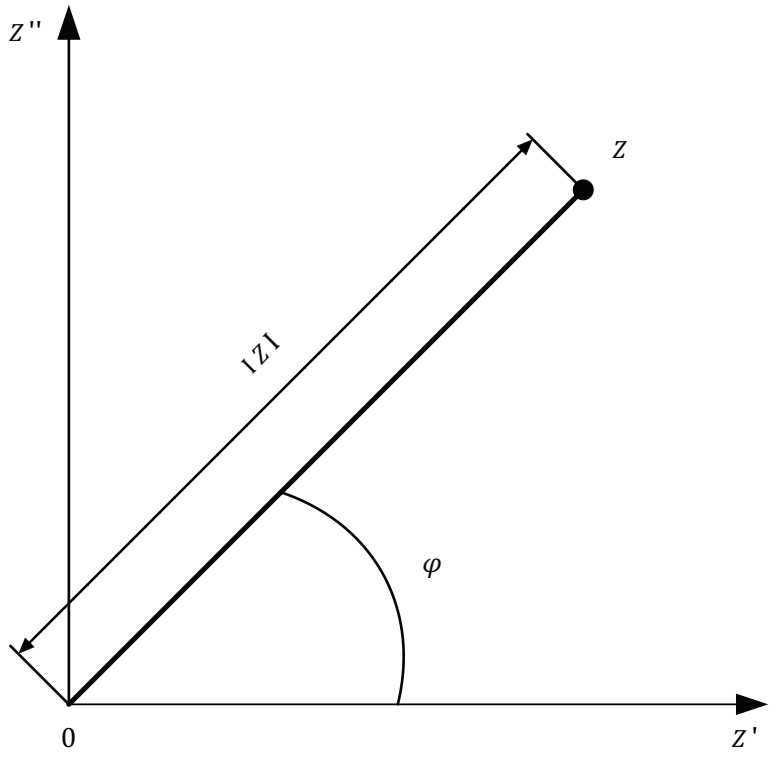

Figure 2 — Impedance Z presented on the complex plane

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).

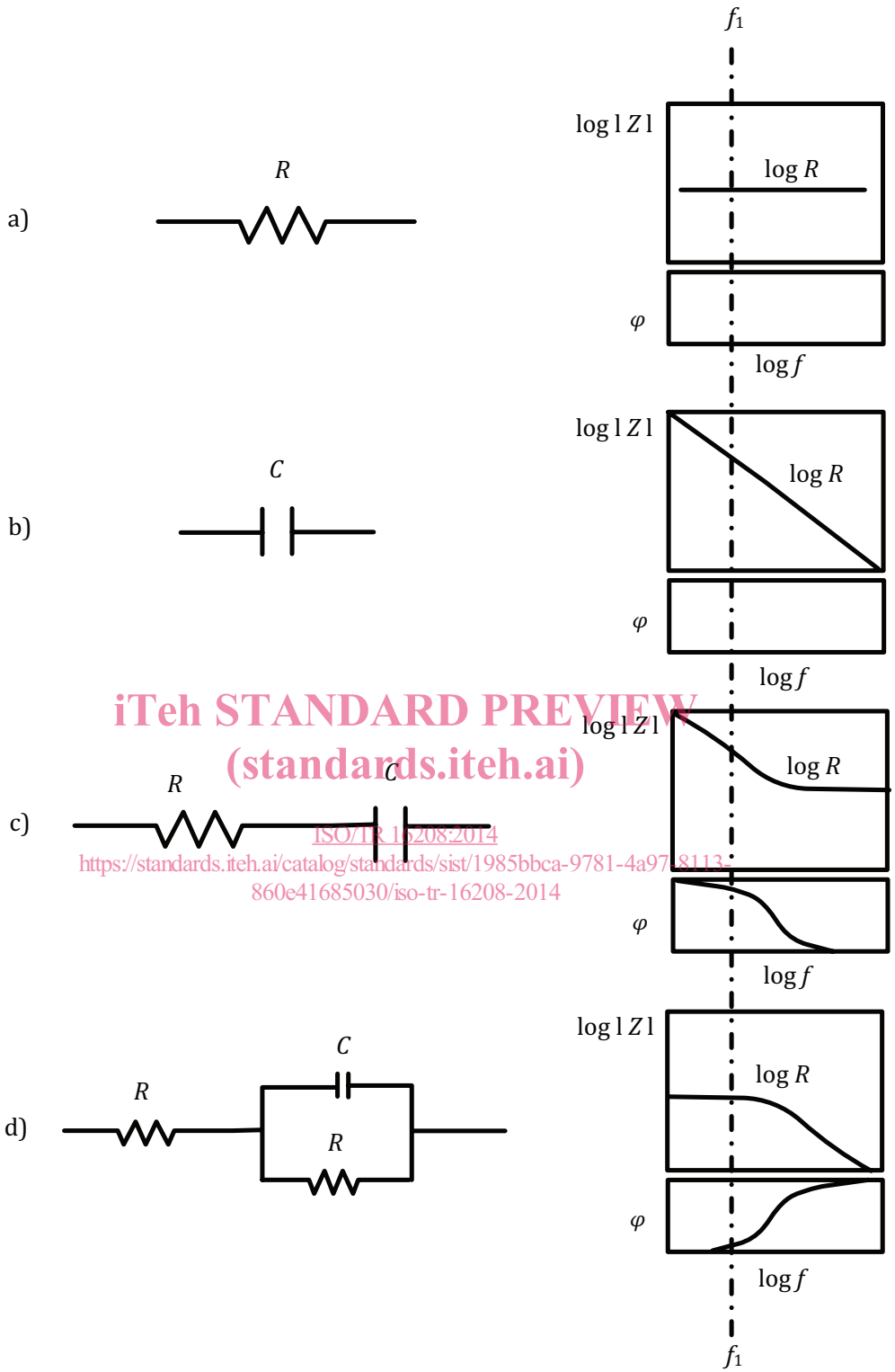

Figure 3 — Circuit elements and their Bode plots

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 $R_p C_{dl}$:

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

