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Corrosion of metals and alloys — Conventions applicable to electrochemical measurements in corrosion testing

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National foreword

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**Corrosion of metals and alloys —
Conventions applicable to
electrochemical measurements in
corrosion testing**

*Corrosion des métaux et alliages — Conventions applicables aux
mesures électrochimiques lors des essais de corrosion*





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Foreword

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ISO 17474 was prepared by Technical Committee ISO/TC 156, *Corrosion of metals and alloys*.

Introduction

Electrochemical test methods are useful for studying corrosion, because it is one particular phenomena of electrochemistry. They can provide quantitative data such as electrode potential, electrochemical current, electrochemical impedance, etc. This International Standard describes how these data are presented, being derived from basic methodology in ASTM G3-89^[1].

Corrosion of metals and alloys — Conventions applicable to electrochemical measurements in corrosion testing

WARNING — This International Standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard is intended to provide conventions for reporting and displaying electrochemical corrosion data. Conventions for potential, current density and electrochemical impedance, as well as conventions for graphical presentation of such data, are included.

2 Normative references

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

ISO 8044, *Corrosion of metals and alloys — Basic terms and definitions*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 8044 apply.

4 Significance and use

This practice provides guidance for reporting, displaying and plotting electrochemical corrosion data and includes recommendations on signs and conventions. Use of this practice will result in the reporting of electrochemical corrosion data in a standard format, facilitating comparison between data developed at different laboratories or at different times. The recommendations outlined in this International Standard may be utilized when recording and reporting corrosion data obtained from electrochemical tests, such as potentiostatic and potentiodynamic polarization, polarization resistance, electrochemical impedance, galvanic corrosion, and open-circuit potential measurements.

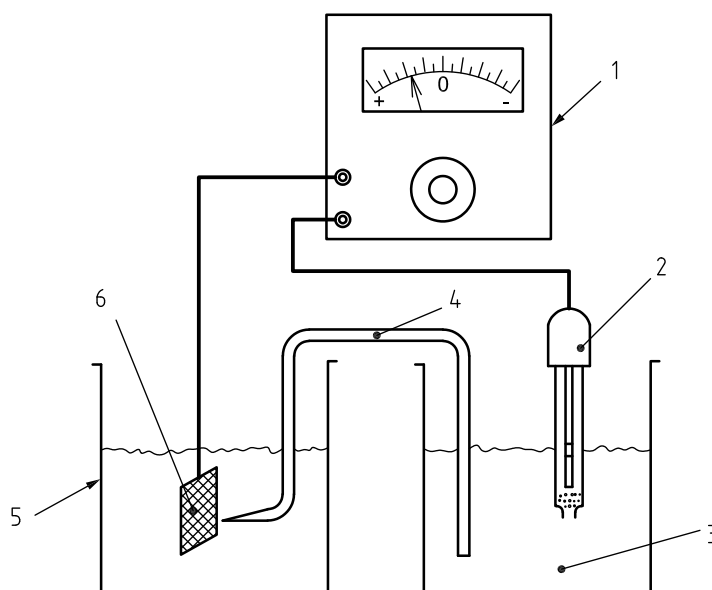
5 Sign convention for electrode potential

5.1 In this convention, the positive direction of electrode potential implies an increase in oxidizing condition at the electrode in question. The positive direction also denotes a noble direction because the corrosion potentials of most noble metals, such as platinum, are more positive than the other non-passive base metals. On the other hand, the negative direction is associated with an increase in the reducing condition, and also denotes an active direction since corrosion potentials of active metals, such as potassium, are more negative than the other metals used. This convention was adopted unanimously by the 1953 International Union of Pure and Applied Chemistry^[1] as the standard for electrode potential.

5.2 To measure a potential of a specimen electrode in an aqueous electrolyte, an experimental set-up may be composed of an electrometer, a reference electrode, an electrochemical cell, the electrolyte, etc. as shown in Figure 1. If the electrometer reads on scale in the negative range, the specimen electrode potential is negative to the reference electrode. Conversely, if the electrometer reads on scale in the positive range, the specimen potential is positive to the reference electrode.

In cases where the polarity of a measuring instrument is in doubt, a simple verification test can be performed as follows: connect the measuring instrument to a dry cell with the lead previously on the reference electrode to the negative battery terminal, and the lead previously on the specimen electrode to the positive battery terminal. The meter deflection shall be in the direction of positive potential. The corrosion potential of magnesium or zinc shall be negative in a 1 N NaCl solution if measured against, for example, a KCl-saturated silver/silver chloride electrode (KCl (sat.)/AgCl/Ag: sat. SSCE).

For accuracy, an input impedance of the electrometer should be more than $10^{11}\Omega$.



Key

- 1 electrometer
- 2 reference electrode
- 3 electrolyte
- 4 salt bridge
- 5 electrochemical cell
- 6 specimen electrode

Figure 1 — Schematic diagram of an apparatus to measure electrode potential of a specimen

6 Sign convention for current and current density

A convention for the sign of current and current density, in which anodic and cathodic values are designated as positive and negative, respectively, is recommended. When the potentials are plotted against the logarithm of the current densities, only the absolute values of the latter can be plotted. In such plots, the values which are cathodic should be clearly differentiated from the anodic values, if both are present.

7 Conventions for displaying polarization data

7.1 Sign conventions

The standard mathematical practice for plotting graphs is recommended for displaying electrochemical corrosion data. In this practice, positive values are plotted above the origin on the ordinate (y axis) and to the right of the origin on the abscissa (x axis). In logarithmic plots, the abscissa value increases from left to right and the ordinate value increases from bottom to top.

7.2 Current density-potential plots

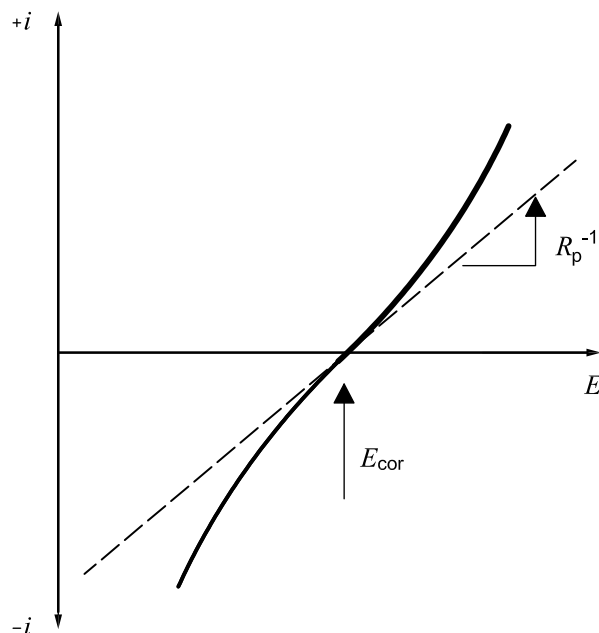
A convention for plotting current density vs. potential data, in which current density is plotted along the ordinate and potential along the abscissa, is recommended. In current density/potential plots, the current density may be plotted on either linear or logarithmic axes. In general, logarithmic plots are used to incorporate wide ranges of current density data and to demonstrate Tafel relationships. Linear plots are used for studies in case the current density or potential range is small, or in case the region of the current density change from anodic to cathodic is assessed. Linear plots are also used for the determination of the polarization resistance R_p , which is defined as the inverse of the slope of a potential-current density plot at the corrosion potential E_{cor} . The relationship between the polarization resistance R_p and the corrosion current density i_{cor} is as follows (References [2][3]):

$$\left[\frac{d(\Delta E)}{di} \right]_{\Delta E=0} = R_p = \frac{b_a b_c}{2,303 (b_a + b_c) i_{\text{cor}}} \quad (1)$$

where

b_a is the anodic Tafel slope;

b_c is the cathodic Tafel slope.



Key

- E potential
- i current density
- E_{cor} corrosion potential
- R_p polarization resistance

Figure 2 — Linear polarization plot

The solid line in Figure 2 is a plot of current density i versus potential E around the corrosion potential E_{cor} , from which the polarization resistance R_p may be determined as an inverse of the slope of the same curve at the potential E_{cor} .

7.3 Potential reference point

In plots where electrode potentials are displayed, some indication for conversion from the displayed values to the standard hydrogen electrode scale (SHE) shall be shown. Expressing the used reference electrode in such a way as ' $E(V)$ vs. 1M KCl (1M KCl/AgCl/Ag)' is recommended. The electrode potential may be plotted on the abscissa, at the bottom of which is the scale against the reference electrode used, together with that at the top with the converted scale against the standard hydrogen electrode (SHE). If the latter is not shown, a relationship such as the following may be used for the conversion according to Annex A.

$$E \text{ vs. SHE} = E \text{ vs. 1M KCl/AgCl/Ag} + 0,235 \text{ V} \tag{2}$$

where

E vs. SHE represents the electrode potential, in volts, against the standard hydrogen electrode;

$E(V)$ vs. 1M KCl/AgCl/Ag represents the electrode potential, in volts, measured against the silver/silver chloride electrode in 1M KCl.

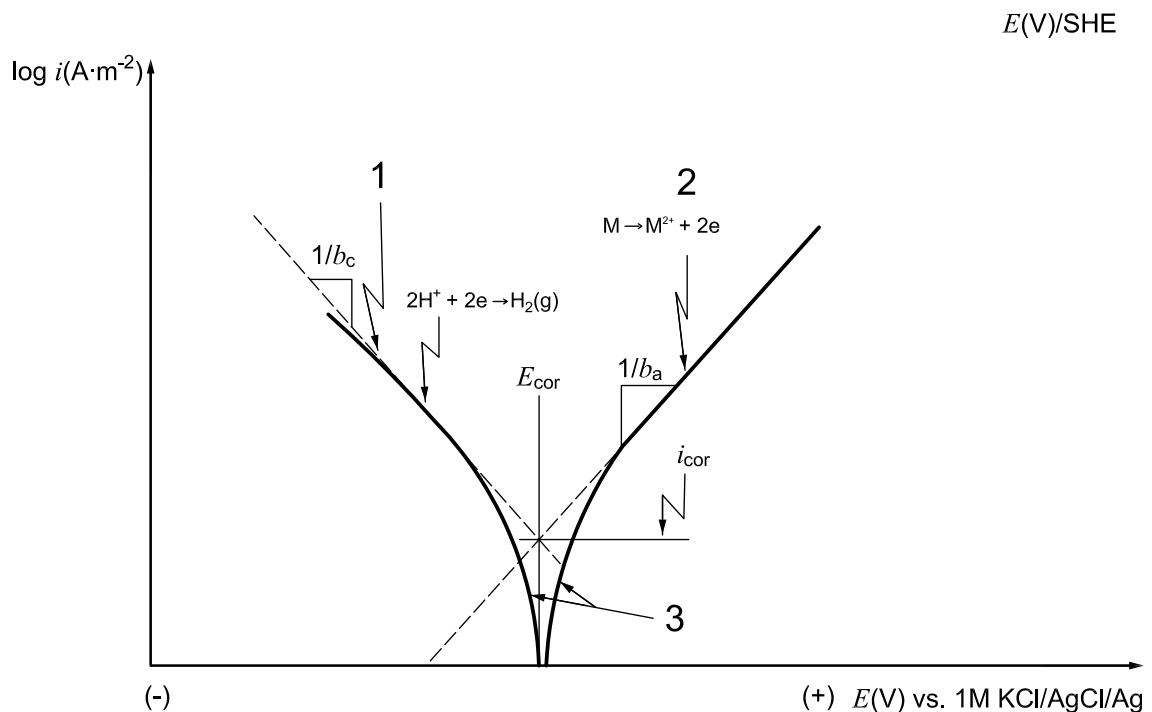
NOTE A table of potentials for various common reference electrodes is given in Annex A.

7.4 Units

The recommended unit of potential is volt (V). If only small potential ranges are covered, millivolts (mV) or microvolts (μV) may be used. The SI units for current density are amperes per square metre ($\text{A}\cdot\text{m}^{-2}$) or amperes per square centimetre ($\text{A}\cdot\text{cm}^{-2}$). Units expressed in milli-amperes per square centimetre ($\text{mA}\cdot\text{cm}^{-2}$), and microamperes per square centimetre ($\mu\text{A}\cdot\text{cm}^{-2}$) are still in use.

7.5 Sample polarization curves

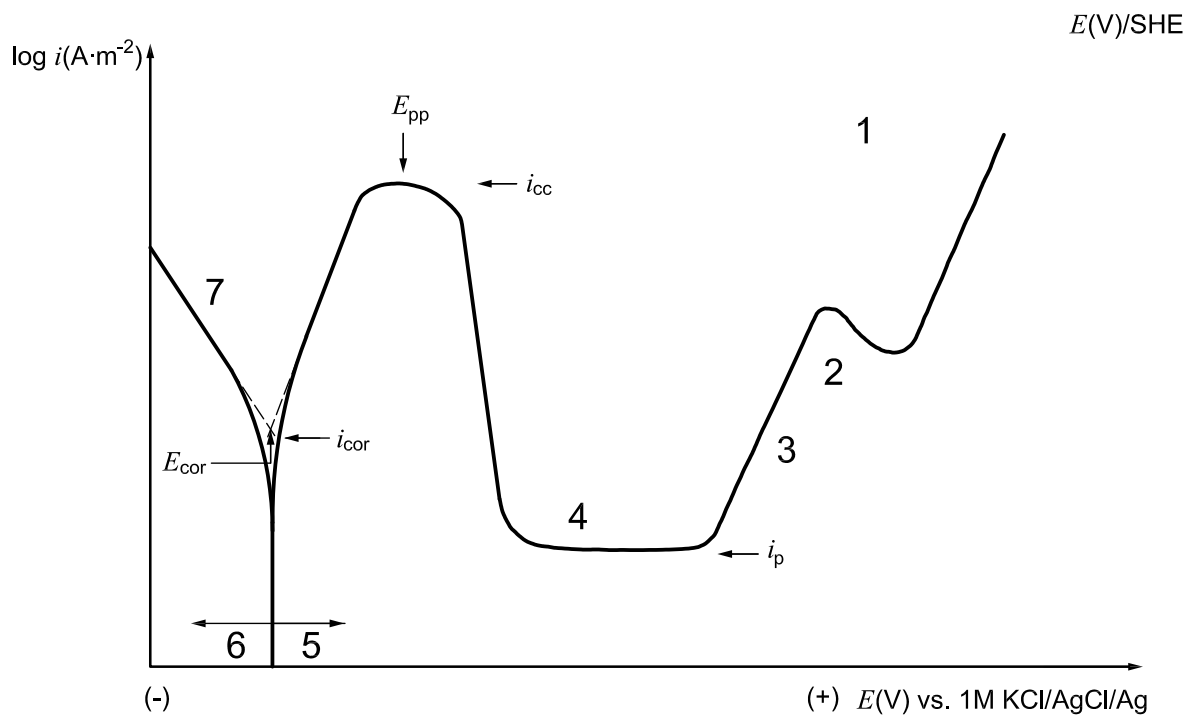
Sample polarization plots employing these recommended practices are shown in Figures 2 to 6. Figures 3 and 4 are hypothetical curves showing active and active-passive anode behaviours, respectively. Figures 5 and 6 are actual anodic polarization data for Type 430 stainless steel (UNS 43000)^[4] and cathodic polarization data of Type 2024-T3 aluminium alloy^[5]. The purpose of Figures 3 and 4 is to illustrate the location of various points used in discussion of electrochemical methods for corrosion testing. The purpose of Figures 5 and 6 is to show how various types of electrode behaviours are plotted in accordance with this convention.



Key

- 1 cathodic branch
- 2 anodic branch
- 3 observed polarization plot
- b_a anodic Tafel slope
- b_c cathodic Tafel slope
- E electrode potential
- E_{cor} corrosion potential
- i current density
- i_{cor} corrosion current density

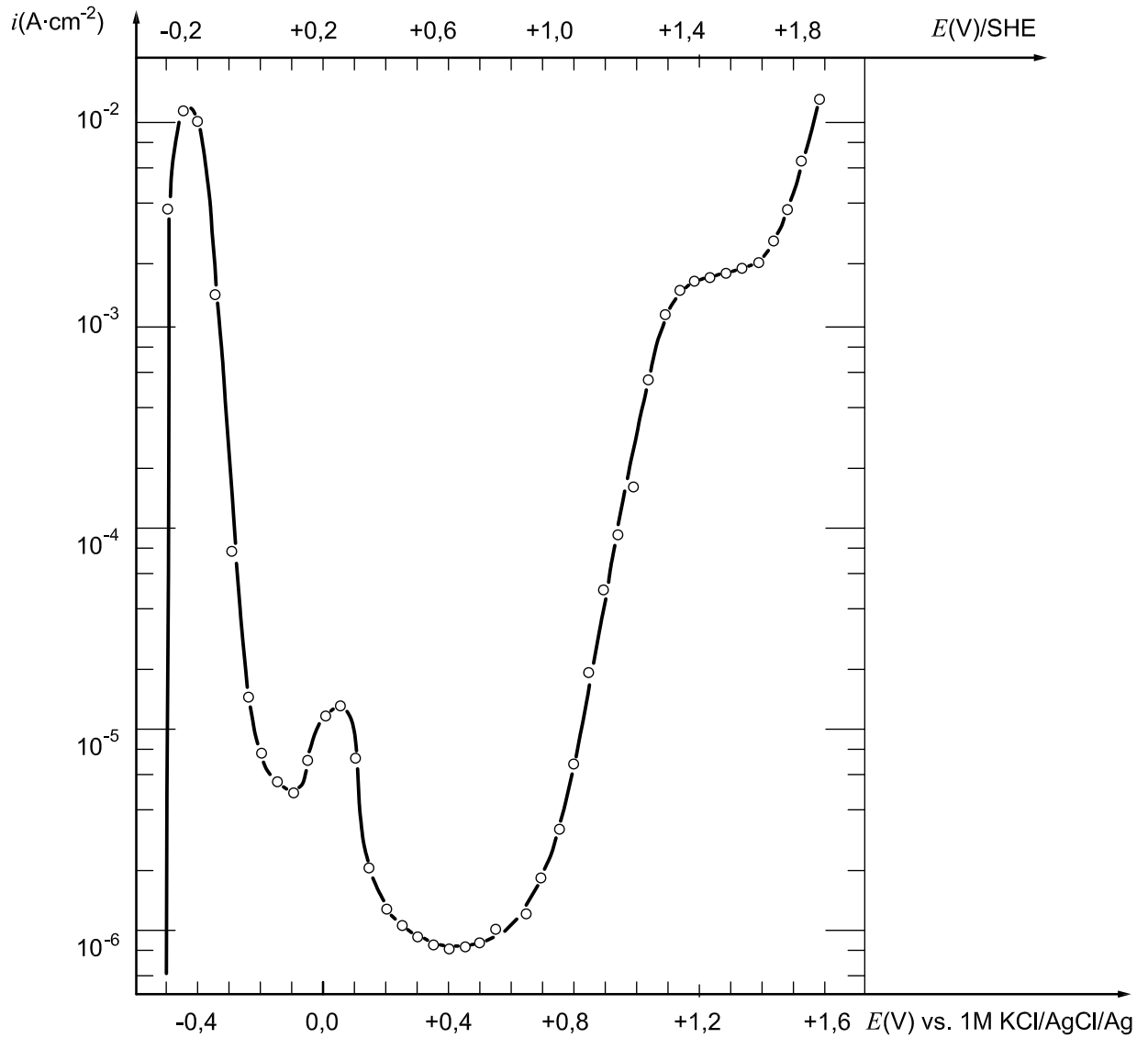
Figure 3 — Hypothetical cathodic and anodic polarization diagram



Key

- 1 oxygen evolution
- 2 secondary passivity
- 3 transpassive region
- 4 passive region
- 5 anodic current
- 6 cathodic current
- 7 active region
- E electrode potential
- E_{pp} primary passivation potential
- E_{cor} corrosion potential
- i current density
- i_{cor} corrosion current density
- i_{cc} critical current density
- i_p passive current density

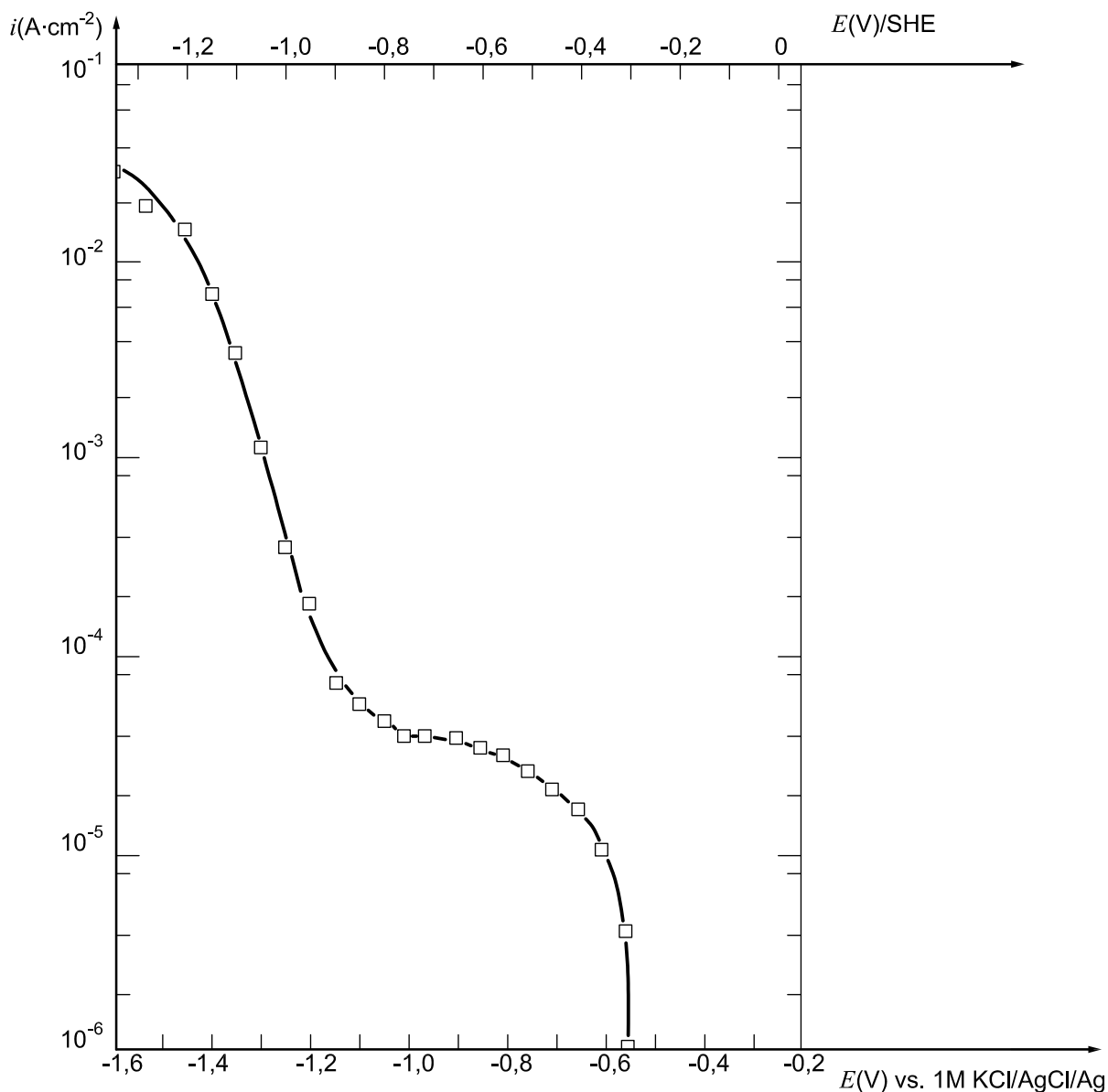
Figure 4 — Hypothetical cathodic and anodic polarization curves for a passivating metal



Key

- E electrode potential
- i current density

Figure 5 — Typical anodic polarization plot for type 430 stainless steel in 0,5M H₂SO₄



Key

- E electrode potential
- i current density

Figure 6 — Typical cathodic polarization plots for aluminium alloys of type 2024-T3 in 0,2M NaCl solution

8 Conventions for displaying electrochemical impedance data

8.1 General

Two graphical formats in common use for reporting electrochemical impedance data are the Nyquist and the Bode formats. A simple electrode system modelled by the equivalent electrical circuit as shown in Figure 7 is discussed. By convention, the impedance Z is defined as:

$$Z = \text{Re } Z + j \times \text{Im } Z \quad (3)$$

where

$\text{Re } Z$ is the real or in-phase component of impedance;

$\text{Im } Z$ is the imaginary or out-of-phase component of impedance;

j is $\sqrt{-1}$.

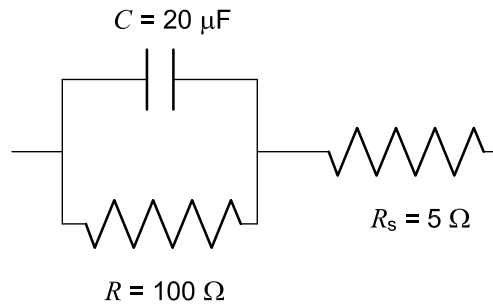


Figure 7 — Equivalent electrical circuit model for a simple corroding electrode

The impedance magnitude or modulus is defined as $|Z| = \sqrt{(\text{Re } Z)^2 + (\text{Im } Z)^2}$. For the equivalent electrical circuit shown in Figure 7, the imaginary component of impedance is designated as:

$$\text{Im } Z = \frac{1}{2\pi f C} (-j) \quad (4)$$

where

f is the frequency, in hertz (Hz), where the angular frequency $\omega = 2\pi f$, in radians per second;

C is the capacitance, in farads (F).

The phase angle θ is defined as:

$$\theta = \arctan(-\text{Im } Z / \text{Re } Z) \quad (5)$$

8.2 The Nyquist format (complex plane)

8.2.1 The real component of impedance is plotted on the abscissa and the negative of the imaginary component is plotted on the ordinate. In this practice, positive values of the real component of impedance are plotted to the right of the origin parallel to the abscissa. Negative values of the imaginary component for impedance are plotted to the upper side of the origin parallel to the ordinate.

8.2.2 Figure 8 shows the Nyquist diagram for the equivalent circuit shown in Figure 7. The frequency dependence of the data is not shown explicitly on this type of plot. However, the frequency corresponding to selected data points may be directly annotated as shown in Figure 8. The magnitude of the impedance is shown as a distance between a datum and the origin. Higher-frequency data points are typically located near the origin, while lower-frequency points with increasing magnitude are far from the origin.

8.2.3 Recommended units for both axes are ohms per square centimetre ($\Omega \cdot \text{cm}^2$). The impedance values in unit $\Omega \cdot \text{cm}^2$ are obtainable by multiplying the measured impedance by the exposed specimen area. For a resistor, a capacitor, or a dummy cell equivalent circuit, the assumed area is 1 cm^2 . Regarding the impedance

data shown in Figure 8 for the equivalent circuit of Figure 7, the distance from the origin to the first (high-frequency) intercept with the abscissa corresponds to R_s . The distance between the first and the second (low-frequency) intercepts with the abscissa corresponds to R_p .

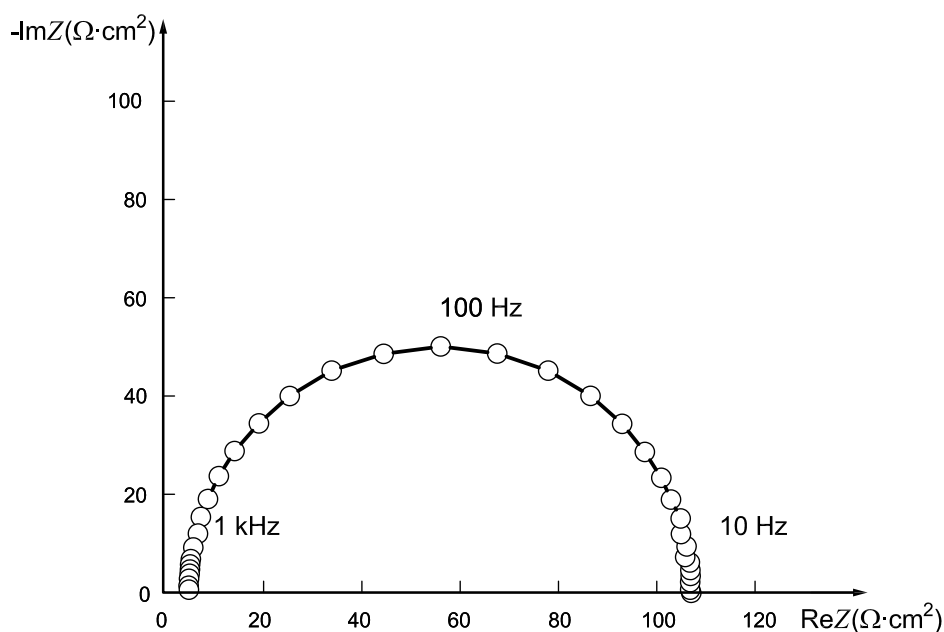


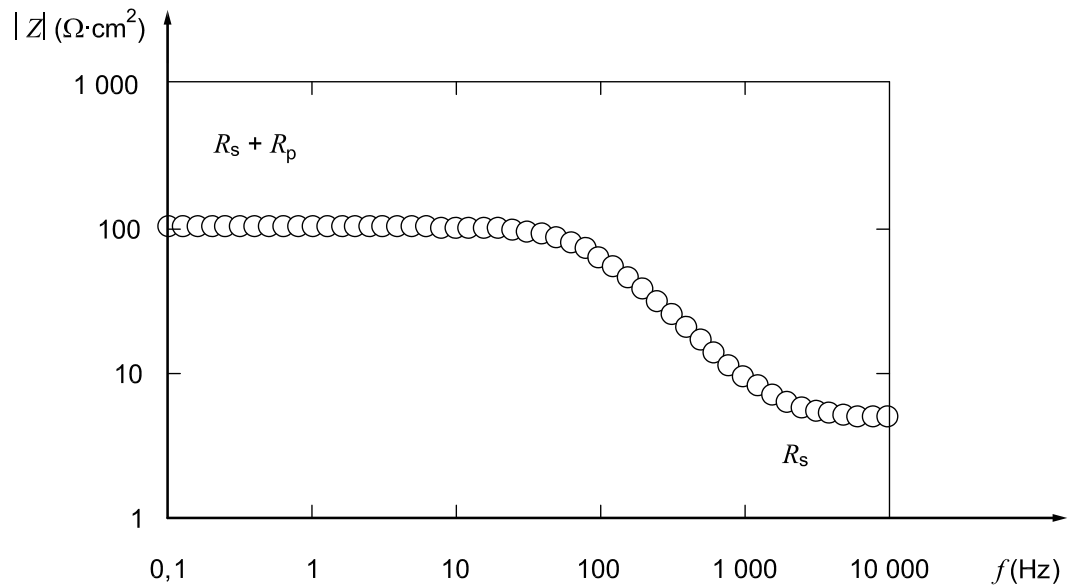
Figure 8 — Nyquist diagram for equivalent circuit of Figure 7 with area assumed of 1 cm²

8.3 The Bode format

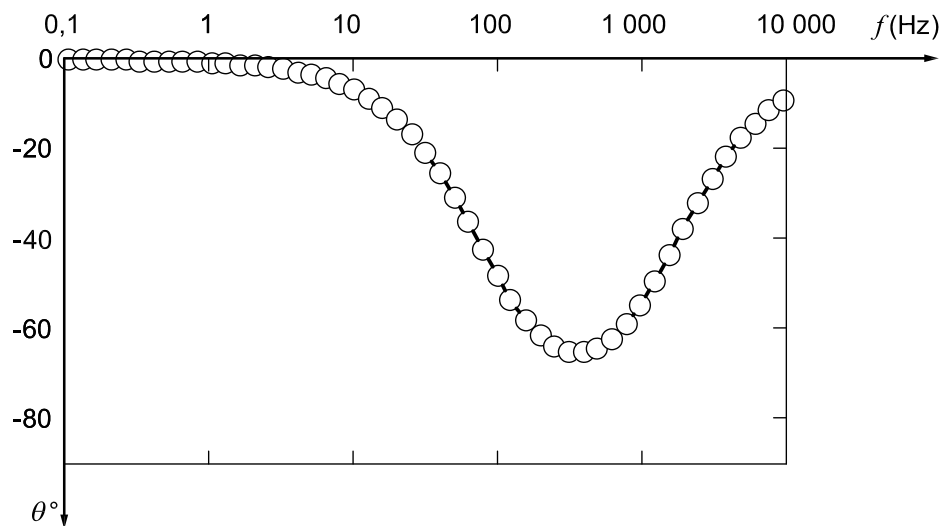
8.3.1 Electrochemical impedance data may be reported as the Bode diagram which consists of a set of two types of plots: i.e. the base-ten logarithm of the frequency is plotted on the abscissa and the base-ten logarithm of the impedance magnitude or modulus $|Z|$ on the ordinate. In this practice, increasing frequency values are plotted to the right of the origin parallel to the abscissa and increasing values of impedance magnitude are plotted vertically from the origin parallel to the ordinate. The origin may be chosen at appropriate non-zero values of impedance magnitude and of frequency.

8.3.2 Together with the set mentioned in 8.3.1, the phase angle or phase shift θ is recommended to be plotted on the ordinate in the linear scale against the base-ten logarithm of the frequency on the abscissa. In this practice, increasing negative values of the phase angle are plotted in the lower direction along the ordinate. In this format, a purely capacitive behaviour is plotted at -90° .

8.3.3 Figures 9 a) and 9 b) show a set of typical formats for the model as shown in Figure 7. The high-frequency impedance magnitude independent of frequency corresponds to R_s . The low-frequency impedance magnitude independent of frequency corresponds to $R_s + R_p$. The difference between the low-frequency and the high-frequency resistive impedances corresponds to R_p . These resistances are identical to those shown on the Nyquist diagram in Figure 8.



a)



b)

Key

- f frequency
- Z impedance
- θ phase shift
- R_s, R_p see 8.3.3

Figure 9 — Bode diagram for the simple electrical model of Figure 7 with an assumed area of 1 cm²

8.3.4 The unit for the frequency on both plots is either hertz (Hz) or cycles per second or radians per second (rad/s). The unit of the impedance magnitude is ohms per square centimetre ($\Omega \cdot \text{cm}^2$). The unit $\Omega \cdot \text{cm}^2$ is obtained by multiplying the measured impedance by the exposed specimen area. The unit of the phase angle is degree or radian; the former is more conventional.

Annex A (informative)

References electrodes and their temperature dependence

A.1 Reference electrodes

Table A.1 shows a series of widely used reference electrodes and their potential without consideration of the liquid junction potential for various solutions.

Table A.1 — Reference electrodes and conversion factors

Electrode	Potential at 25 °C <i>E</i> (V) vs. SHE
$H^+(a = 1) H_2(p_{H_2} = 1 \text{ atm}) Pt$ (SHE)	0,000
KCl(1M) AgCl Ag (1M SSCE)	0,235
KCl(3,5M) AgCl Ag (3,5M SSCE)	0,202
KCl(sat.) AgCl Ag (sat. SSCE)	0,197
KCl(sat.) Hg ₂ Cl ₂ Hg (SCE)	0,241
H ₂ SO ₄ (0,5M) Hg ₂ SO ₄ Hg	0,682
NaOH(0,1M) HgO Hg	0,165

EXAMPLE An electrode potential of +1,000 V versus SCE = (1,000 V + 0,241 V) = +1,241 V versus SHE.
An electrode potential of -1,000 V versus SCE = (-1,000 V + 0,241 V) = -0,759 V versus SHE.

A.2 Temperature dependence of typical reference electrodes

A.2.1 By definition, potential of a standard hydrogen half-cell is zero at any temperature.

A.2.2 Usual reference electrodes have the temperature dependences of their half-cell potentials. Standard electrode potentials of KCl/AgCl/Ag and KCl/Hg₂Cl₂/Hg reference electrodes, coupled with the standard hydrogen half-cell at different temperatures are tabulated in Table A.2, where liquid-junction potentials are included.

Table A.2 — Standard potentials and temperature coefficients of reference electrodes

		Potential <i>E</i> (V) vs. SHE at the temperature <i>T</i> (°C)							<i>dE/dT</i> (mV/deg at 25 °C)
		10	15	20	25	30	35	40	
KCl (at 25 °C)	3,5M	0,215	0,212	0,208	0,205	0,201	0,197	0,193	-0,73
	saturated	0,214	0,209	0,204	0,199	0,194	0,189	0,184	-1,01
Hg ₂ Cl ₂ /Hg	saturated	0,254	0,251	0,248	0,244	0,241	0,238	0,234	-0,67

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