Standard Practice for
Conventions Applicable to Electrochemical Measurements in Corrosion Testing[1]

This standard is issued under the fixed designation G3; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers conventions for reporting and displaying electrochemical corrosion data. Conventions for potential, current density, electrochemical impedance and admittance, as well as conventions for graphical presentation of such data are included.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard. See also 7.4.

1.3 *This 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

IEEE/ASTM SI 10 Standard for Use of the International System of Units (SI) (the Modern Metric System)

3. Significance and Use

3.1 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 standard may be utilized when recording and reporting corrosion data obtained from electrochemical tests such as potentiostatic and potentiodynamic polarization, polarization resistance, electrochemical impedance and admittance measurements, galvanic corrosion, and open circuit potential measurements.

4. Sign Convention for Electrode Potential

4.1 The Stockholm sign invariant convention is recommended for use in reporting the results of specimen potential measurements in corrosion testing. In this convention, the positive direction of electrode potential implies an increasingly oxidizing condition at the electrode in question. The positive direction has also been denoted as the noble direction because the corrosion potentials of most noble metals, such as gold, are more positive than the nonpassive base metals. On the other hand, the negative direction, often called the active direction, is associated with reduction and consequently the corrosion potentials of active metals, such as magnesium. This convention was adopted unanimously by the 1953 International Union of Pure and Applied Chemistry as the standard for electrode potential **(1)**.[3]

4.2 In the context of a specimen electrode of unknown potential in an aqueous electrolyte, consider the circuit shown in Fig. 1 with a reference electrode connected to the ground terminal of an electrometer. If the electrometer reads on scale when the polarity switch is negative, the specimen electrode potential is negative (relative to the reference electrode). Conversely, if the electrometer reads on scale when polarity is positive, the specimen potential is positive. On the other hand, if the specimen electrode is connected to the ground terminal, the potential will be positive if the meter is on scale when the polarity switch is negative, and vice versa.

NOTE 1—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. Set the range switch to accommodate the dry cell voltage. The meter deflection will now show the direction of positive potential.

Also, the corrosion potential of magnesium or zinc should be negative in a 1 *N* NaCl solution if measured against a saturated standard calomel electrode (SCE).

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[1] This practice is under the jurisdiction of ASTM Committee G01 on Corrosion of Metals and is the direct responsibility of Subcommittee G01.11 on Electrochemical Measurements in Corrosion Testing.

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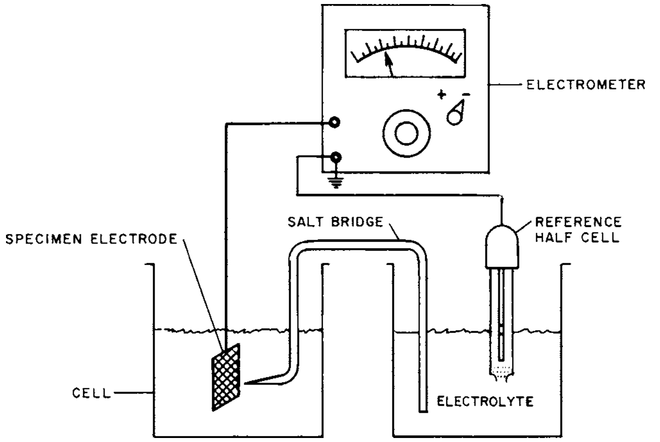
[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.



NOTE 1—The electrode potential of specimen is negative as shown.

FIG. 1 Schematic Diagram of an Apparatus to Measure Electrode Potential of a Specimen

5. Sign Convention for Electrode Potential Temperature Coefficients

5.1 There are two types of temperature coefficients of electrode potential: isothermal temperature coefficients and the thermal coefficients. The sign convention recommended for both types of temperature coefficients is that the temperature coefficient is positive when an increase in temperature produces an increase (that is, it becomes more positive) in the electrode potential. Likewise, the second temperature coefficient is positive when an increase in temperature produces an increase (that is, it becomes more positive) in the first temperature coefficient.

6. Sign Convention for Current and Current Density

6.1 The sign convention in which anodic currents and current densities are considered positive and cathodic currents and current densities are negative is recommended. When the potential is plotted against the logarithm of the current density, only the absolute values of the current density 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 axis and to the right of the origin on the abscissa 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 uniform convention is recommended for plotting current density-potential data, namely, plot current density along the abscissa and potential along the ordinate. In current density potential plots, the current density may be plotted on linear or logarithmic axes. In general, logarithmic plots are better suited to incorporation of wide ranges of current density data and for demonstrating Tafel relationships. Linear plots are recommended for studies in which the current density or potential range is small, or in cases where the region in which the current density changes from anodic to cathodic is important. Linear plots are also used for the determination of the polarization resistance R_p, which is defined as the slope of a potential-current density plot at the corrosion potential E_{corr}. The relationship between the polarization resistance R_p and the corrosion current density i_{corr} is as follows (**2, 3**):

$$\left[\frac{d(\Delta E)}{di}\right]_{\Delta E=0} = R_p = \frac{b_a b_c}{2.303(b_a+b_c)i_{corr}} \qquad (1)$$

where:

b_a = anodic Tafel slope,
b_c = cathodic Tafel slope, and
ΔE = the difference $E - E_{corr}$, where E is the specimen potential.

Fig. 2 is a plot of polarization, $E - E_{corr}$, versus current density i (solid line) from which the polarization resistance R_p has been determined as the slope of the curve at the corrosion potential E_{corr}.

7.3 *Potential Reference Points*—In plots where electrode potentials are displayed, some indication of the conversion of the values displayed to both the standard hydrogen electrode scale (SHE) and the saturated calomel electrode scale (SCE) is recommended if they are known. For example, when electrode potential is plotted as the ordinate, then the SCE scale could be shown at the extreme left of the plot and the SHE scale shown at the extreme right. An alternative, in cases where the reference electrode was not either SCE or SHE, would be to show on the potential axis the potentials of these electrodes against the reference used. In cases where these points are not shown on the plot, an algebraic conversion could be indicated. For example, in the case of a silver-silver chloride reference electrode (1 M KCl), the conversion could be shown in the title box as:

$$\text{SCE} = E - 0.006\ \text{V} \qquad (2)$$

$$\text{SHE} = E + 0.235\ \text{V}$$

where E represents electrode potential measured against the silver-silver chloride standard (1 M KCl).

NOTE 2—A table of potentials for various common reference electrodes is presented in Appendix X2.

7.4 *Units*—The recommended unit of potential is the volt. In cases where only small potential ranges are covered, millivolts or microvolts may be used. The SI units for current density are ampere per square metre or milliampere per square centimetre (IEEE/ASTM SI 10). Still in use are units expressed in amperes per square centimetre, and microamperes per square centimetre.

7.5 *Sample Polarization Curves*—Sample polarization plots employing these recommended practices are shown in Figs. 2-6. Fig. 3 and Fig. 4 are hypothetical curves showing active and active-passive anode behavior, respectively. Fig. 5 and Fig. 6 are actual polarization data for Type 430 stainless steel (UNS 43000) (**4**) and two aluminum samples (**5**). Fig. 3 and Fig. 4 are exhibited to illustrate graphically the location of various points used in discussion of electrochemical methods of corrosion testing. The purpose of Fig. 5 and Fig. 6 is to show how various

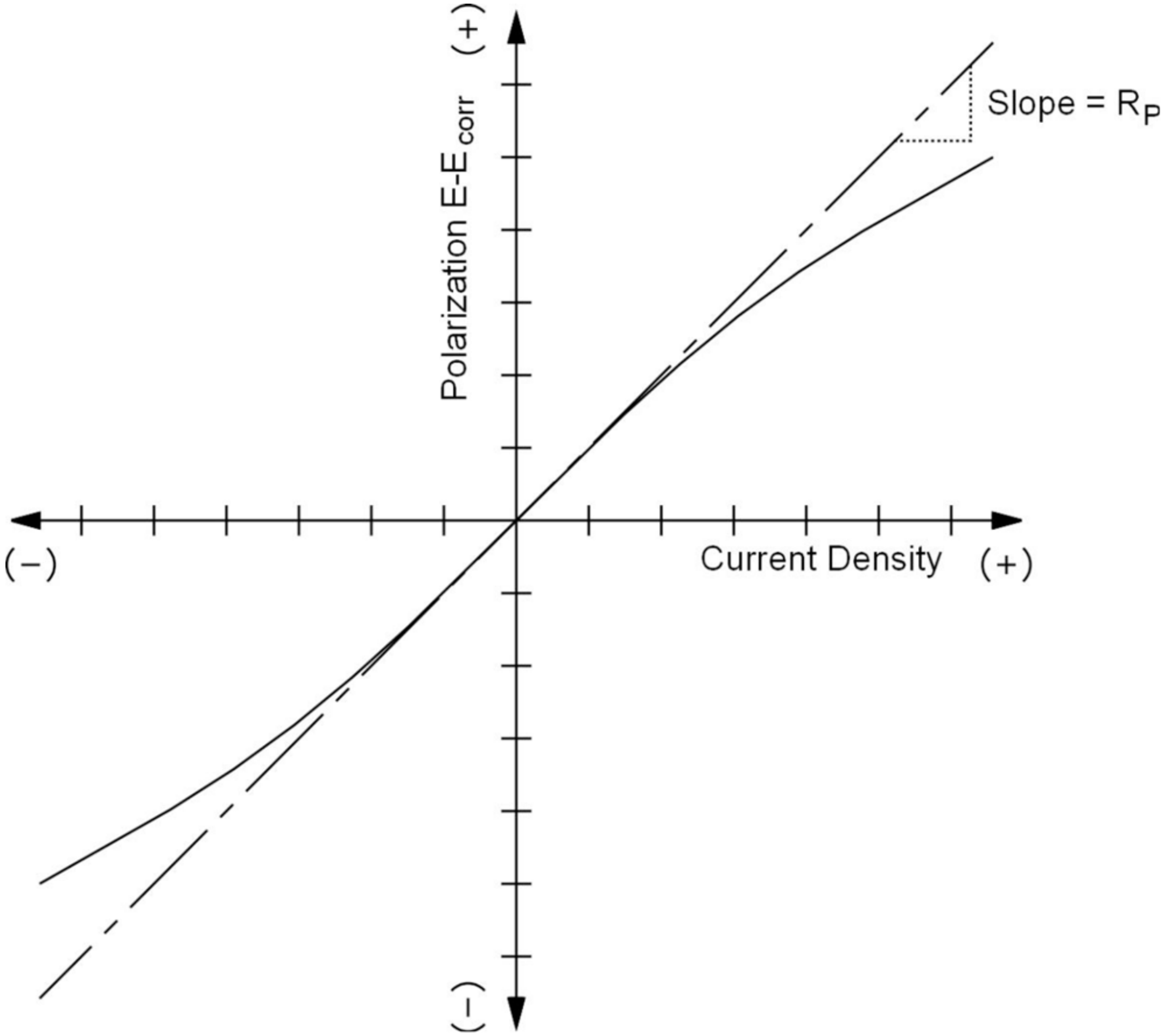


FIG. 2 Hypothetical Linear Polarization Plot

types of electrode behavior can be plotted in accordance with the proposed conventions.

8. Conventions for Displaying Electrochemical Impedance Data

8.1 Three graphical formats in common use for reporting electrochemical impedance data are the Nyquist, Bode, and Admittance formats. These formats are discussed for a simple electrode system modelled by an equivalent electrical circuit as shown in Fig. 7. In the convention utilized the impedance is defined as:

$$Z = Z' + j\,Z'' \tag{3}$$

where:

Z = real or in-phase component of impedance,
Z'' = the imaginary or out-of-phase component of impedance, and
j^2 = −1.

The impedance magnitude or modulus is defined as $|Z|^2 = (Z')^2 + (Z'')$. For the equivalent electrical circuit shown in Fig. 7, the imaginary component of impedance

$$Z'' = \frac{-1}{2\pi f C} \tag{4}$$

where:

f = frequency in cycles per second (or hertz, Hz, where one Hz is equal to 2π radians/s, and $w = 2\pi f$, where the units for w are radians/s), and
C = capacitance in farads.

The phase angle, θ is defined as:

$$\theta = \arctan(Z''/Z') \tag{5}$$

The admittance, Y, is defined as

$$1/Z = Y = Y' + jY'' \tag{6}$$

where:

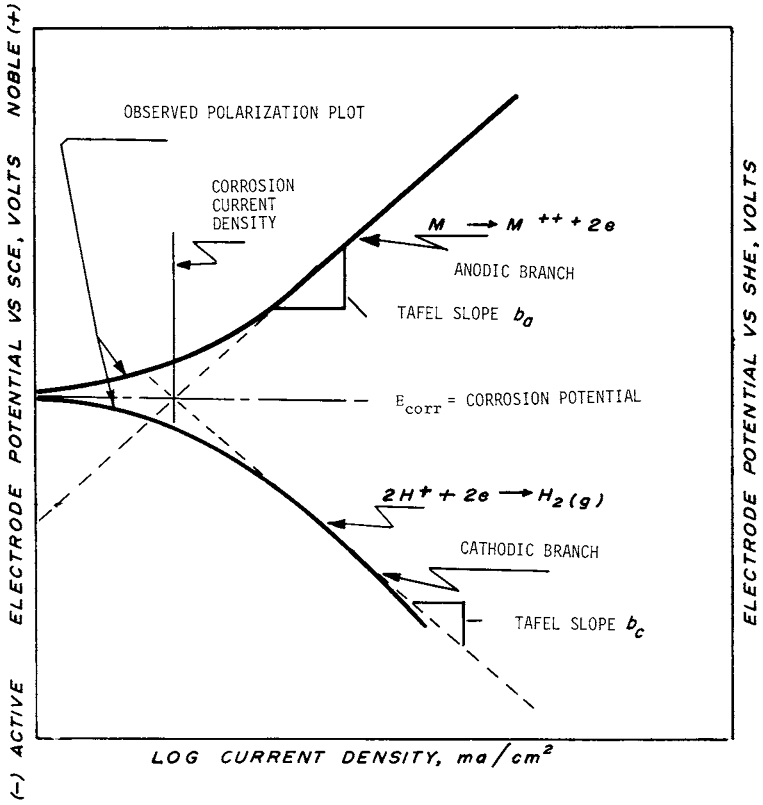


FIG. 3 Hypothetical Cathodic and Anodic Polarization Diagram

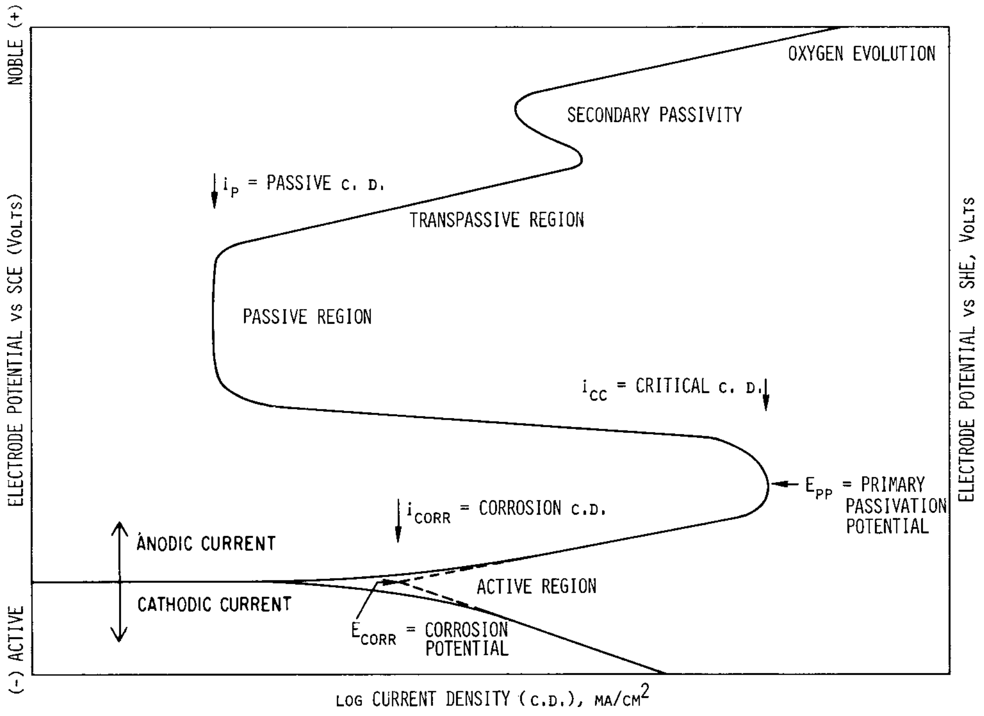


FIG. 4 Hypothetical Cathodic and Anodic Polarization Plots for a Passive Anode

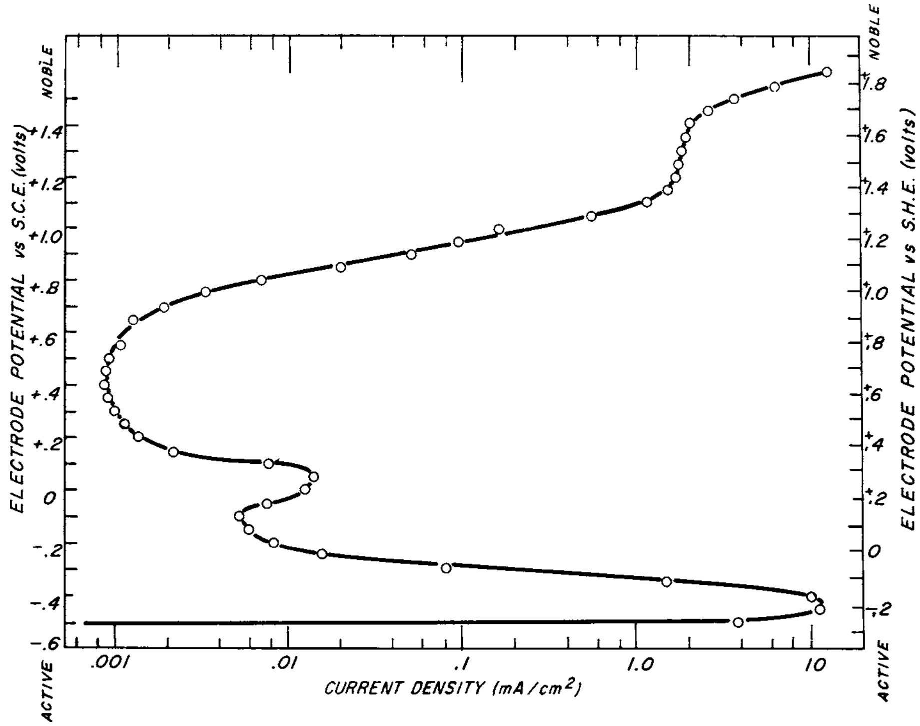


FIG. 5 Typical Potentiostatic Anodic Polarization Plot for Type 430 Stainless Steel in 1.0 *N* H_2SO_4

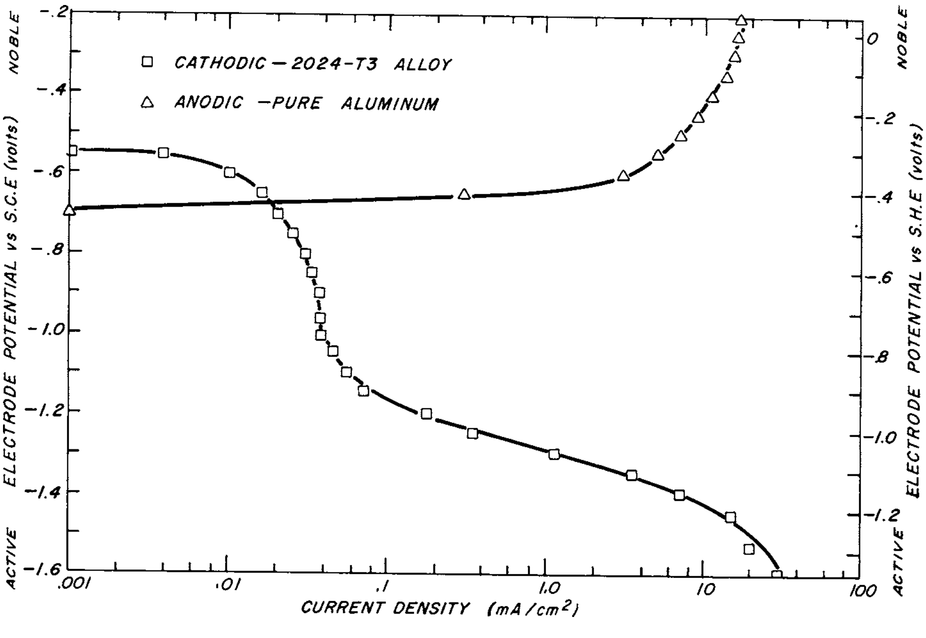


FIG. 6 Typical Polarization Plots for Aluminum Materials in 0.2 *N* NaCl Solution

Y' = real or in-phase component of admittance, and
Y'' = the imaginary of out-of-phase component of admittance.

8.2 *Nyquist Format (Complex Plane, or Cole-Cole):*

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 *x* axis (abscissa). Negative values of the imaginary component of impedance are plotted vertically from the origin parallel to the *y* axis (ordinate).

8.2.2 Fig. 8 shows a Nyquist plot for the equivalent circuit of Fig. 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 on the Nyquist plot. The magnitude of the appropriate impedance components increases when moving away from the origin of

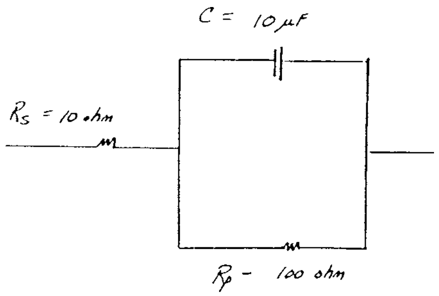


FIG. 7 Equivalent Electrical Circuit Model for a Simple Corroding Electrode

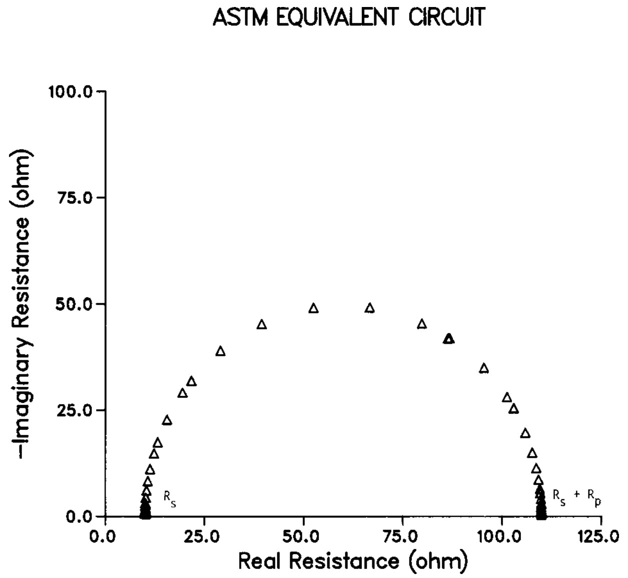


FIG. 8 Nyquist Plot for Equivalent Circuit of Fig. 7

the corresponding axes. Higher frequency data points are typically located towards the origin of the plot while lower frequency points correspond to the increasing magnitude of the impedance components.

8.2.3 Recommended units for both axes are ohm·cm^2. The units ohm·cm^2 are obtained by multiplying the measured resistance or impedance by the exposed specimen area. For a resistor and capacitor, or dummy cell equivalent circuit, the assumed area is 1 cm^2. Regarding the impedance data shown in Fig. 8 for the circuit of Fig. 7, the distance from the origin to the first (high frequency) intercept with the abscissa corresponds to R_s. The distance between the first intercept and the second (low frequency) intercept with the abscissa corresponds to R_p.

8.3 *Bode Format:*

8.3.1 Electrochemical impedance data may be reported as two types of Bode plots. In the first case, the base ten logarithm of the impedance magnitude or Modulus, |Z|, is plotted on the ordinate and the base ten logarithm of the frequency is plotted on the abscissa. In this practice increasing frequency values are plotted to the right of the origin parallel to the *x* axis (abscissa) and increasing values of impedance magnitude are plotted vertically from the origin parallel to the *y* axis (ordinate). The origin itself is chosen at appropriate nonzero values of impedance magnitude and frequency.

8.3.2 Fig. 9 shows a typical plot for the simple electrical circuit model of Fig. 7. The magnitude of the high frequency impedance where the impedance magnitude is independent of frequency corresponds to R_s. The difference in magnitude between the low frequency and the high frequency frequency-independent regions of impedance magnitude corresponds to R_p. These resistances are identical to those on the Nyquist format plot shown in Fig. 8.

8.3.3 In the second type of Bode plot, the negative of the phase angle, −θ, is plotted on the ordinate and the base ten logarithm of the frequency is plotted on the abscissa. In this practice, increasing values of the negative of the phase angle are plotted in the vertical direction from the origin along the *y* axis (ordinate). In this format, a pure capacitive behavior is plotted as a positive value of 90°. Fig. 10 shows a typical plot for the simple electrode model shown in Fig. 7.

8.3.4 The units for the frequency on both plots are either hertz (cycles per second) or radians per second (radians per second = 2π radians per cycle multiplied by the number of cycles per second). The units of the impedance magnitude are ohm·cm^2. The units ohm·cm^2 are obtained by multiplying the measured resistance or impedance by the exposed specimen area. The units of the phase angle are degrees.

8.4 *Admittance Format (Complex Plane)*—The real component of admittance is plotted on the abscissa and the imaginary component of admittance is plotted on the ordinate. In this practice positive values of the real component of admittance are plotted to the right of the origin parallel to the *x* axis (abscissa). Values of the imaginary component of impedance are plotted vertically from the origin parallel to the *y* axis (ordinate). Recommended units for both axes are ohm^{-1}· cm^{-2}. The units ohm^{-1}· cm^2 are obtained by dividing the measured

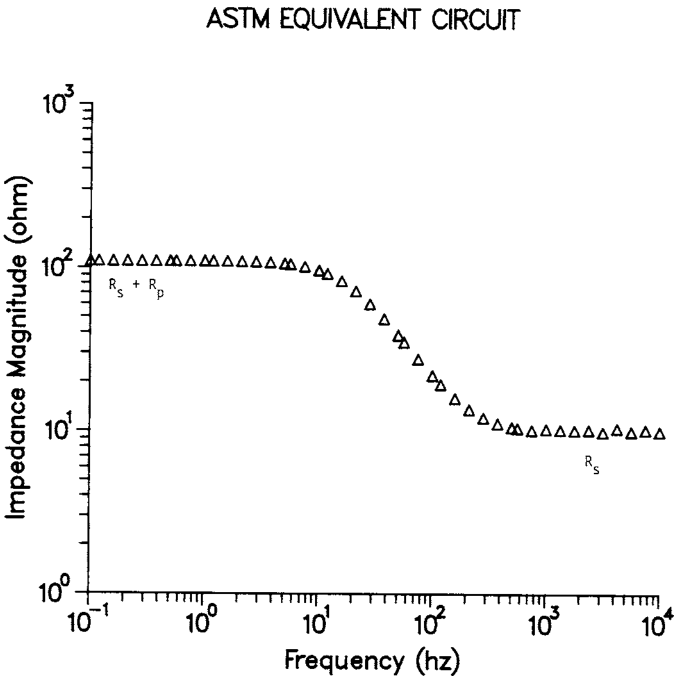


FIG. 9 Typical Plot for Simple Electrical Model of Fig. 7

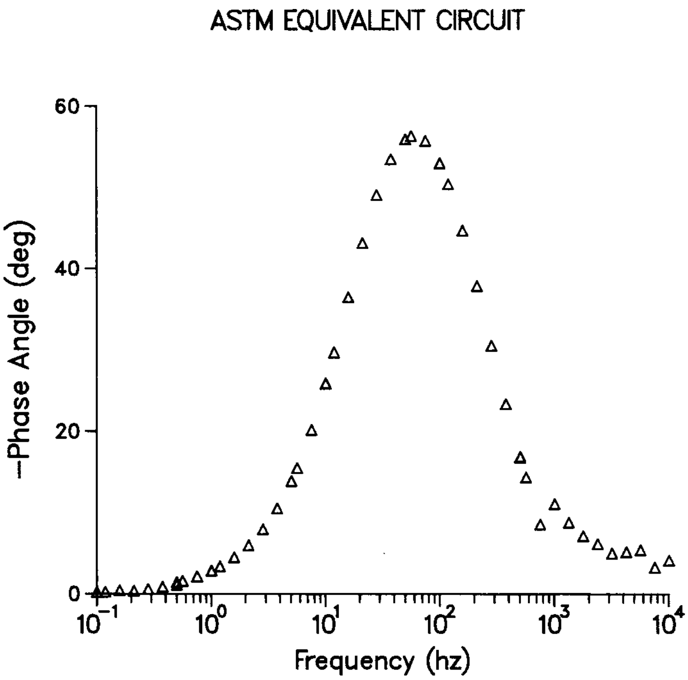


FIG. 10 Typical Plot for Simple Electrode Model Shown in Fig. 7

admittance (ohm^{-1}) by the exposed specimen area. The frequency dependence of the data is not shown explicitly on this type of plot. The magnitudes of the appropriate admittance components increase when moving away from the origin of the corresponding axes.

9. Keywords

9.1 ac impedance; Bode; convention; electrochemical impedance spectroscopy; electrochemical measurement; electrode potential; linear polarization; Nyquist; polarization resistance; potentiodynamic polarization; reference electrode

APPENDIXES

(Nonmandatory Information)

X1. INFORMATION ON OTHER CONVENTIONS

X1.1 Comparison of Gibbs-Ostwald Convention to Nernst-Latimer Convention

X1.1.1 Another sign convention, the Nernst-Latimer convention, has been used extensively by physical and analytical chemists in describing electrochemical reactions. This convention is based on the relationship:

$$\Delta G = -nFE^* \tag{X1.1}$$

where:

ΔG = change in Gibbs free energy,
n = number of charges per atom,
F = electrochemical equivalent in faradays, and
E^* = potential according to the Nernst-Latimer convention.

A consequence of this convention is that the sign of the potential depends upon the way that the reaction is written. For example, the anodic dissolution of copper can be expressed as:

$$\mathrm{Cu}^0 \rightarrow \mathrm{Cu}^{++}(\mathrm{aq}) + 2e \tag{X1.2}$$

where:

Cu^0 = metallic copper, crystalline, unit activity,
$\mathrm{Cu}^{++}(\mathrm{aq})$ = cupric ion in aqueous solution, and
e = one unit negative charge (an electron)

while the plating of copper can be written as:

$$\mathrm{Cu}^{++}(\mathrm{aq}) \rightarrow \mathrm{Cu}^0 - 2e \tag{X1.3}$$

In these two cases, the potential would have opposite signs even though both reactions occur simultaneously on a specimen. Tables of potentials for the oxidation of various metals relative to the standard state hydrogen potential have had wide circulation **(6)**. These values have been called "oxidation potentials" to denote the use of the Nernst-Latimer convention. Thus, the term "electrode potential" now implies the use of the Gibbs-Stockholm convention.

X1.2 Consequences of the Gibbs-Stockholm Convention

X1.2.1 To explore the consequences of the Gibbs-Stockholm convention, further consider a corroding metal surface:

$$\mathrm{M}^0 \rightarrow \mathrm{M}^{++}(\mathrm{aq}) + 2e \tag{X1.4}$$

The whole cell reaction with a hydrogen reference electrode would then be:

$$M^0 + 2H^+(aq) \rightarrow M^{++}(aq) + H_2(g) \tag{X1.5}$$

where:

$\mathrm{H}_2(\mathrm{g})$ = hydrogen in gaseous state.

The Gibbs free energy change would be given by the expression:

$$\Delta G = +nFE \tag{X1.6}$$

where:

E = measured electrode potential of Eq 4.

If this electrode potential were negative, then the metal surface would be active and the reaction would tend to occur spontaneously because the free energy is negative.

X1.2.2 Consider the effect of increasing the concentration of the metal ions in solution in Eq 4. The equilibrium electrode potential of the metal surface would become more noble according to the relationship:

$$\Delta E = +(RT/nF)\ln(a_2/a_1) \tag{X1.7}$$

where:

a_2 = metal ion activity of the more concentrated solution,
a_1 = metal ion activity of less concentrated solution,
R = appropriate gas law constant, and
ΔE = electrode potential in the concentrated solution minus electrode potential in the dilute solution.

Thus, increases in the activity of the oxidized species, for example, $M^{++}(aq)$, tend to increase the electrode potential. On the other hand, an increase in the activity of a reduced species will decrease the electrode potential. For example, consider the half-cell reaction:

$$2\ OH^-(aq) \rightarrow H_2O + 1/2\ O_2(g) + 2e \tag{X1.8}$$

Increasing the hydroxyl ion concentration reduces the electrode potential of this reaction.

X1.3 Electrode Potential Temperature Coefficients

X1.3.1 There are two types of temperature coefficients for electrochemical reactions. The isothermal temperature coefficient (7) is based on the definition that the half-cell reaction:

$$1/2\ H_2\ (g,\ 1\ atm) = H^+\ (aq,\ a = 1) + e \tag{X1.9}$$

where:

H_2 (g, 1 atm) = hydrogen gas at one atmosphere pressure and
H^+(aq, $a = 1$) = hydrogen ion in aqueous solution at unit activity

has a zero electrode potential *at any temperature.*

X1.3.1.1 Thus, this temperature coefficient is given by the change in potential of a cell composed of the specimen electrode and a standard hydrogen half cells. More formally, the first temperature coefficient is given by:

$$(dE/dT)_{iso} = \Delta S/nF \tag{X1.10}$$

where:

$(dE/dT)_{iso}$ = isothermal temperature coefficient of electrode potential,
T = absolute temperature, and
ΔS = entropy change for whole cell reaction.

X1.3.1.2 Therefore, an increase in the electrode potential with increasing temperature results in a positive temperature coefficient and signifies an increase in the entropy of the overall reaction including the reference half cell.

X1.3.2 The thermal temperature coefficient is defined by a metal-metal ion half cell at test temperature connected to an identical half cell at a reference temperature. These cells are complicated by the effect of thermal diffusion (Soret effect) and are not truly reversible. In general, if thermal diffusion is prevented, the thermal temperature coefficient is related to the isothermal temperature coefficient by a constant value which represents the entropy change in the reference electrode. Thus, for a standard hydrogen electrode:

$$(dE/dT)_{iso} = (dE/dT)_{th} - 0.871 \tag{X1.11}$$

where:

$(dE/dT)_{th}$ = thermal temperature coefficient of electrode potential,

when the temperature coefficients are expressed in mV/deg C (7).

X1.3.3 The second temperature coefficient is given by the second temperature derivative and is related to ΔCp, the sum of the heat capacities of the products minus the heat capacities of the reactants by the expression:

$$dE^2/dT^2 = \Delta Cp/nFT \tag{X1.12}$$

Thus, the second temperature coefficient is positive when the corresponding first temperature coefficient increases with increasing temperature. See Ref 7 for a more complete discussion.

X2. STANDARD REFERENCE POTENTIALS AND CONVERSION TABLE (7, 8)

X2.1 See Table X2.1 for reference potentials and conversion factors.

TABLE X2.1 Reference Potentials and Conversion Factors

Electrode	Potential (V) at 25°C		Thermal Temperature Coefficient,[A] mV/°C
	E^1[B]	E[C]	
(Pt)/H_2(**a** = 1) (SHE)	0.000	. . .	+0.87
Ag/AgCl/sat KCl	+0.196		
Ag/AgCl/1 M KCl	+0.235		+0.25
Ag/AgCl/0.6 M Cl^- (seawater)	+0.25		+0.22
Ag/AgCl/0.1 M Cl^-	+0.288	. . .	
Hg/Hg_2Cl_2/sat KCl (SCE)	+0.241	+0.244	+0.22
Hg/Hg_2Cl_2/1 M KCl	+0.280	+0.283	+0.59
Hg/Hg_2Cl_2/0.1 M KCl	+0.334	+0.336	+0.79
$Cu/CuSO_4$ sat	+0.30	. . .	+0.90
$Hg/HgSO_4/H_2SO_4$[D]	+0.616		

[A] To convert from thermal to isothermal temperature coefficiences subtract 0.87 mV/°C. Thus, the isothermal temperature coefficient for Ag/AgCl is -0.62 mV/°C.

[B] E^1 is the standard potential of the half cell corrected for the concentration of the ions.

[C] E also includes the liquid junction potentials for a saturated KCl salt bridge. To convert from one scale to another, add the value indicated.

[D] Potential given is for a range of H_2SO_4 Molalities as discussed in Ref **9**.

From (E^1)	To SHE	To SCE
H_2/H^+		-0.241
Ag/AgCl/sat KCl	+0.196	-0.045
Ag/AgCl/1 M KCl	+0.235	-0.006
Ag/AgCl/0.6 M Cl^- (seawater)	+0.25	+0.009
Ag/AgCl/0.1 M Cl^-	+0.288	+0.047
Hg/Hg_2Cl_2/ sat KCl (SCE)	+0.241	
Hg/Hg_2Cl_2/1 M KCl	+0.280	+0.039
Hg/Hg_2Cl_2/0.1 M KCl	+0.334	+0.093
$Cu/CuSO_4$sat	+0.30	+0.06
$Hg/HgSO_4/H_2SO_4$	+0.616	

Example:

An electrode potential of +1.000 V versus SCE would be (1.000 + 0.241 V) = +1.241 V versus SHE. An electrode potential of -1.000 V versus SCE would give (-1.000 + 0.241) = -0.759 V versus SHE.

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