Designation: G215 – 16

Standard Guide for Electrode Potential Measurement[1]

This standard is issued under the fixed designation G215; 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 guide provides guidance on the measurement of electrode potentials in laboratory and field studies both for corrosion potentials and polarized potentials.

1.2 The values stated in SI units are to be regarded as standard. Any other units of measurements included in this standard are present because of their wide usage and acceptance.

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]

C876 Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete

F746 Test Method for Pitting or Crevice Corrosion of Metallic Surgical Implant Materials

F2129 Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements to Determine the Corrosion Susceptibility of Small Implant Devices

F3044 Test Method for Test Method for Evaluating the Potential for Galvanic Corrosion for Medical Implants

G3 Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing

G5 Reference Test Method for Making Potentiodynamic Anodic Polarization Measurements

G59 Test Method for Conducting Potentiodynamic Polarization Resistance Measurements

G61 Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys

G69 Test Method for Measurement of Corrosion Potentials of Aluminum Alloys

G71 Guide for Conducting and Evaluating Galvanic Corrosion Tests in Electrolytes

G82 Guide for Development and Use of a Galvanic Series for Predicting Galvanic Corrosion Performance

G96 Guide for Online Monitoring of Corrosion in Plant Equipment (Electrical and Electrochemical Methods)

G97 Test Method for Laboratory Evaluation of Magnesium Sacrificial Anode Test Specimens for Underground Applications

G102 Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements

G106 Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Measurements

G150 Test Method for Electrochemical Critical Pitting Temperature Testing of Stainless Steels

G193 Terminology and Acronyms Relating to Corrosion

2.2 *NACE Standards:*[3]

TM0497–2012 Measurement Techniques Related to Criteria for Cathodic Protection on Underground or Submerged Metallic Piping Systems

TM0101–2012 Measurement Techniques Related to Criteria for Cathodic Protection of Underground Storage Tank Systems

TM0108–2012 Testing of Catalyzed Titanium Anodes for Use in Soils or Natural Waters

TM0109–2009 Aboveground Survey Techniques for the Evaluation of Underground Pipeline Coating Condition

TM0190–2012 Impressed Current Laboratory Testing of Aluminum Alloy Anodes

TM0211–2011 Durability Test for Copper/Copper Sulfate Permanent Reference Electrodes for Direct Burial Applications

TM0113–2013 Evaluating the Accuracy of Field Grade Reference Electrode

3. Terminology

3.1 *Definitions*—The terminology used herein shall be in accordance with Terminology G193.

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[1] This guide 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] Available from NACE International (NACE), 15835 Park Ten Pl., Houston, TX 77084, http://www.nace.org.

4. Summary of Practice

4.1 Electrode potential measurements are made by electrically connecting a high impedance voltmeter or electrometer between the specimen electrode and a suitable reference half-cell electrode. See Practice G3.

5. Significance and Use

5.1 Electrode potential is the reversible work that is required to transfer a unit of positive charge between the surface in question and a reference electrode through the electrolyte that is in contact with both electrodes. The sign of the electrode potential is determined by the Gibbs Stockholm Convention described in Practice G3.

5.2 The electrode potential of a surface is related to the Gibbs free energy of the oxidation/reduction reactions occurring at the surface in question compared to the Gibbs free energy of the reactions occurring on the reference electrode surface.[4]

5.3 Electrode potentials are used together with potential-pH (Pourbaix) diagrams to determine the corrosion products that would be in equilibrium with the environment and the electrode surface.[5]

5.4 Electrode potentials are used in the estimation of corrosion rates by several methods. One example is by means of Tafel line extrapolation, see Practices G3 and G102. Polarization resistance measurements are also determined using electrode potential measurements, see Test Method G59 and Guide G96.

5.5 Corrosion potential measurements are used to determine whether metal surfaces are passive in the environment in question, see Test Method C876.

5.6 Corrosion potential measurements are used in the evaluation of alloys to determine their resistance or susceptibility to various forms of localized corrosion, see Test Methods F746, F2129, G61, and G150.

5.7 Corrosion potentials are used to determine the metallurgical condition of some aluminum alloys, see Test Method G69. Similar measurements have been used with hot dipped galvanized steel to determine their ability to cathodically polarize steel. See Appendix X2.

5.8 Corrosion potentials are used to evaluate aluminum and magnesium alloys as sacrificial anodes for underground and immersion cathodic protection application, see Test Method G97 and NACE TM0190–2012.

5.9 Corrosion potentials are used to evaluate the galvanic performance of alloy pairs for use in seawater and other conductive electrolytes, see Test Method F3044, Guide G71, and Guide G82.

5.10 Electrode potential measurements are used to establish cathodic protection levels to troubleshoot cathodic protection systems and to confirm the performance of these systems in soils, concrete, and natural waters, see NACE TM0497, NACE TM0108, and NACE TM0109.

5.11 Electrode potential measurements are necessary for the determination of hydrogen overvoltage values in testing for hydrogen embrittlement and related issues with hydrogen cracking. See Appendix X3.

6. Potential Measurement

6.1 Electrode potentials are measured by placing a reference electrode in the corrosive electrolyte and electrically connecting a high impedance potential measuring instrument, such as an electrometer, potentiometer, or high impedance voltmeter, between the reference electrode and the object with the surface in question. The measuring instrument must be able to measure the potential difference without affecting either electrode to any significant degree. In general, devices with input impedances greater than 10^7 ohms have been found to be acceptable in most corrosion related measurements. In cases where the specimen is polarized by an external power source, it may be desirable to connect the potential measuring instrument directly to the specimen rather than using the conductor carrying the polarizing current to the specimen.

NOTE 1—When using a potential measuring instrument such as a high impedance voltmeter, the reference electrode should be connected to the negative or ground (black) terminal in order to have the instrument record the proper sign of the reading in accordance with Practice G3. However, for instruments that read only positive potentials, it may be necessary to reverse these connections to obtain the reading.

6.2 Two types of reference electrodes have been used in corrosion testing: standard reference electrodes and nonstandard reference electrodes.

6.2.1 Standard reference electrodes are widely used and they provide a known half-cell potential value versus the standard hydrogen electrode, SHE, half-cell. These electrodes are stable, and in most cases commercially available. It is possible also to construct them using known techniques.[6]

6.2.2 Nonstandard reference electrodes are used in cases where it is not necessary to know the actual value of the potential with reference to a chemical reaction, but it is important to know how the potential has changed as a surface is polarized or when environmental changes occur. These nonstandard reference electrodes should be stable with time, and they should not be significantly affected by the measuring process. Guide G96 provides information on nonstandard reference electrodes used in polarization resistance measurements. In some cases the nonstandard reference electrode is identical with the test electrode. In these cases a drift in the potential with time is acceptable as long as both the test and reference electrodes experience the same drift.

6.2.3 In some cases nonstandard reference electrodes are used because the environmental conditions are not suitable for standard reference electrodes. Pure zinc and zinc alloy (UNS Z12001, and Z12002, or Z14002) reference electrodes have been used in seawater and similar aqueous solutions although

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[4] Moore, Walter J. *Physical Chemistry*, 2nd Edition, Prentice Hall, Englewood Cliffs, NJ, 1955.

[5] Pourbaix, Marcel, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, NACE International, Houston, TX, 1974.

[6] Ives, David J. G. and Janz, George, J., *Reference Electrodes Theory and Practice*, Academic Press, New York, NY, 1961.

they have been observed to have significant potential drift with exposure. The potentials of these electrodes are determined by the corrosion potential of metal in the seawater. For pure zinc, the potential versus SHE is approximately -0.78 V, while for the zinc alloys, the potential is approximately -0.8 V. In some cases the corrosion potential of the zinc electrode has been measured against a standard electrode in a known environment before and after usage to obtain a measure of the drift that occurred.

7. Standard Reference Electrodes

7.1 Standard reference electrodes are based on having the primary electrochemical reaction occurring on the electrode surface at equilibrium. This implies that both the forward and reverse reactions are occurring at the same rate. In the general case, the electrochemical reaction can be expressed as shown in Eq 1:

$$\mathrm{Me} = \mathrm{Me}^{n+} + \mathrm{ne} \qquad (1)$$

Where Me represents a metal with a valence of n, and e represents an electron. The potential of this reaction is shown in Eq 2:

$$E = E^0 + 0.0592(T + 273.2)(n298.2)^{-1}\log[\mathrm{Me}^{n+}] \qquad (2)$$

where:

E = the electrode potential of the half-cell V,
E^0 = the electrode potential of the reaction at unit activity, V,
$[Me^{n+}]$ = activity of the Me ion,
n = the number of electrons transferred in the reaction, and
T = electrode temperature, °C.

NOTE 2—The activity of an ion is equal to the concentration of the ion multiplied by its activity coefficient.

7.1.1 *Standard Hydrogen Electrode*—The standard hydrogen electrode, SHE, is a first kind standard reference electrode.[5] This electrode is composed of a platinized platinum electrode immersed in an acid solution with a hydrogen ion activity of 1 (approximately 1 N) and in contact with hydrogen gas at a pressure of 101.3 kPa (1 atm) and 25°C. Although these electrodes have been used extensively in electrochemical studies to determine the thermodynamic properties of ions, they are almost never used in corrosion studies. However, this electrode is the reference point for all other standard reference electrodes.

7.1.2 *Saturated Calomel Electrode*—This electrode, designated SCE, has been the most widely used standard reference electrode for corrosion studies. The reason for its popularity is that it has been used in commercial electrometric pH meters, and consequently it has been easily available and is very reproducible. The SCE is based on the following reactions:

$$2\mathrm{Hg} = \mathrm{Hg_2}^{++} + 2\mathrm{e} \qquad (3)$$

$$\mathrm{Hg_2}^{++} + 2\mathrm{Cl}^- = \mathrm{Hg_2Cl_2} \qquad (4)$$

The compound, Hg_2Cl_2, mercurous chloride, is also known as calomel, and that is the reason for the electrode's designation. The mercury/mercurous chloride mixture is immersed in a saturated potassium chloride solution so that the mercurous ion concentration is determined by its solubility at that chloride level. This electrode has been designated a second kind electrode.[5] See Table 1 for information on the potential of this electrode. Although these standard reference electrodes have been widely used for many laboratory corrosion tests including Test Methods G5, G59, and others, their use may be restricted because of bans on mercury and its compounds.

NOTE 3—The term "saturated" when used to describe standard reference electrodes refers to the metal ion concentration, not the anion.

7.1.3 *Saturated Silver/Silver Chloride Electrode*—There are four silver/silver chloride electrodes, saturated with respect to the silver ion concentration, that have been used as standard reference electrodes. All of these electrodes are based on reactions (5) and (6) below:

$$\mathrm{Ag} = \mathrm{Ag}^+ + \mathrm{e} \qquad (5)$$

$$\mathrm{Ag}^+ + \mathrm{Cl}^- = \mathrm{AgCl} \qquad (6)$$

Because silver chloride is slightly soluble, the silver ion concentration is based on the chloride concentration. The silver/silver chloride combination is immersed in KCl solutions of various strengths. The solutions that have been used are 0.1 M, 1.0 M, saturated KCl, and seawater. Each of these solutions produces a different standard potential versus SHE. See

TABLE 1 Potentials of Standard Reference Electrodes and Related Information 25°C

NOTE 1—

s_r = repeatability standard deviation,
s_R = reproducibility standard deviation, and
– = indicates no standard values available.

Electrode	Designation	Potential V	s_r mV	s_R mV	Thermal Temperature Coefficient mV/°C
(Pt)H_2 (a = 1.0)	SHE	0.000			+0.87
Ag/AgCl/sat. KCl		+0.194	–	–	–
Ag/AgCl/1.0 m KCl		+0.235	–	–	+0.25
Ag/AgCl/0.1 M KCl		+0.288	–	–	+0.22
Ag/AgCl/Seawater		+0.25	–	–	–
Hg/Hg_2Cl_2/sat. KCl	SCE	+0.241	3[A]	7[A]	+0.22
Hg/Hg_2Cl_2/1.0 M KCl		+0.280	–	–	+0.59
Hg/Hg_2Cl_2/0.1 M KCl		+0.334	–	–	+0.79
Hg/Hg_2SO_4/H_2SO_4		+0.616	–	–	–
Cu/sat. $CuSO_4$	CSE	+0.30	10[B]	30[B]	+0.90

[A] See Test Method G69.
[B] See Test Method C876.