Designation: G215 – 17

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:

$$Me = Me^{n+} + ne \tag{1}$$

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:

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

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:

$$2Hg = Hg_2^{++} + 2e \tag{3}$$

$$Hg_2^{++} + 2Cl^- = Hg_2Cl_2 \tag{4}$$

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:

$$Ag = Ag^+ + e \tag{5}$$

$$Ag^+ + Cl^- = AgCl \tag{6}$$

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

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[C] 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		+0.196	–	–	–
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.
[C] See Practice G3.

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 for information on the potentials of these electrodes. These electrodes are also second kind reference electrodes.[5] Because of the ban on mercury compounds, the KCl saturated silver/silver chloride electrode may supplant the SCE electrode for laboratory corrosion studies.

NOTE 4—Silver mesh electrodes for seawater usage are coated with a silver chloride layer and partially reduced to obtain a mixture of metallic silver and silver chloride. These electrodes are placed directly in the seawater without a liquid junction. They are rugged and have large surface areas. Because the composition of seawater varies both with location and time, there is significant variability with these electrodes. In addition, seawater polluted with hydrogen sulfide will change the potential significantly.

7.1.4 *Saturated Copper/Copper Sulfate Electrode*—This electrode has been used extensively in field corrosion studies and has been designated CSE. The electrode is based on Reaction (7) below:

$$Cu = Cu^{++} + 2e \quad (7)$$

The electrode consists of a pure copper specimen exposed to a saturated copper sulfate solution containing sulfuric acid of about 0.01 M (1 g/l). These electrodes have been used in contact with soils, concrete, and natural waters, but not seawater, because contamination with chloride affects their potential. However, they are not considered as accurate or reproducible as the SCE or silver/silver chloride electrodes. See Table 1 for information on the standard potential of this electrode.

NOTE 5—The addition of sulfuric acid to the copper sulfate solution is necessary to assure that the copper surface remains active. The pH of the solution must not exceed 2.9.[4]

7.1.5 *Mercury/Mercurous Sulfate Electrode*—This electrode is based on Reactions (8) and (9):

$$2Hg = Hg_2^{++} + 2e \quad (8)$$

$$Hg_2^{++} + SO_4^{-} = Hg_2SO_4 \quad (9)$$

This electrode has been used in corrosion studies in sulfuric acid to avoid the possibility of chloride contamination. It is also a second kind standard reference electrode. However, it has not been used widely enough to have established repeatability and reproducibility values. See Table 1 for information on the potential of this electrode.

7.2 *Temperature Variation in Standard Reference Electrodes*—The potential of standard reference electrodes varies with temperature. The standard state temperature is 25°C. The temperature coefficients of several of the standard reference electrodes are shown in Table 1. There are two temperature coefficients that are used for electrochemical reactions.[7]

7.2.1 The thermal temperature coefficient is defined as the potential difference that would be measured if identical standard reference electrodes were measured against each other with one at the standard state temperature and the other at the test temperature. The thermal temperature coefficient is calculated by dividing the potential difference by the difference in the temperatures. Thermal temperature coefficients are shown in Table 1.

7.2.2 The isothermal temperature coefficient is obtained by measuring the potential at the test temperature against the SHE at that temperature. The isothermal temperature coefficient is then the difference between that potential and the potential that would be measured at the standard state temperature divided by the temperature difference. The isothermal temperature coefficient may be calculated by subtracting 0.87 mV from the thermal temperature coefficient. Isothermal temperature coefficients can be used in predicting the thermodynamic stability of corrosion products at temperatures different from 25°C.

7.2.3 In many cases involving laboratory testing, a salt bridge is used to connect the standard reference electrode to the test environment. In these cases the standard reference electrode may be at a different temperature than the test temperature. In these cases, the temperature correction should be made based on the temperature of the standard reference electrode. See Appendix X1 for a sample calculation.

8. Standard Reference Electrodes—Errors, Issues, and Corrections

8.1 *Liquid Junction Potentials*—Because standard reference electrodes have a specific environment that is required to achieve their standard potential value, it is necessary to have a liquid junction between the standard reference electrode solution and the test environment solution.[4] This liquid junction can be created by means of a porous plug, a capillary leak path, a fritted joint wetted with the test liquid or some other type of controlled leak path. In any case, there will be a potential difference created across this leak path caused by the fact that anions and cations in the environments move at different rates as they pass through the liquid junction. In general, the magnitude of this potential difference can be minimized by selecting compounds for the reference that have cations and anions with similar mobilities. Potassium chloride and ammonium nitrate are often chosen for this reason. It should be noted that this error cannot be measured directly, but calculation approaches have been used to quantify its magnitude. In corrosion studies the magnitude of this error has been calculated to be in the range of a few millivolts and remains constant through the study. As a result, it is usually considered insignificant. See Practice G3 for some calculated liquid junction potentials.

8.2 *Loss of Leak Path*—It is necessary to maintain a leak path from the standard reference electrode to the test environment in order to permit the potential measurement to be made. The most common problem that occurs with capillary leak paths used in most SCE electrodes is dry out, which occurs when KCl crystals plug the capillary and create a very high resistance junction. A similar problem can occur when these electrodes are used in perchlorate containing solutions. The problem in this case is the formation of potassium perchlorate crystals in the capillary, because potassium perchlorate is sparingly soluble in aqueous systems. Visual examination of the electrode tip to check for crystal plugging is good practice, but it may not be sufficient to reveal the problem.

8.3 *Loss of Saturation*—When standard reference electrodes are used in dilute solutions, water can diffuse through the leak path into the reference electrode chamber, ultimately causing

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[7] De Bethune, A. J., *The Encyclopedia of Electrochemistry*, Hampel, C. A., Editor, Reinhold Publishing Co., 1964, pp. 432–434.

the solution concentration to become diluted. This will change the potential of the reference electrode and cause an error. In cases where a saturated KCl solution is used in the reference electrode chamber, it is good practice to examine the electrode regularly to assure that KCl crystals are present. In the case of the copper/copper sulfate reference electrodes, the solution should be examined for the presence of copper sulfate crystals. See NACE TM0211 for more details.

8.4 *Contamination*—Because the potential of the standard reference electrode is dependent upon the concentration of the metal ion in the solution surrounding the metal any extraneous compounds that change this concentration will affect the potential. In silver and mercury electrodes the presence of halides other than chloride will have serious effects on the potential of the electrode. Chlorides also affect the copper/copper sulfate electrode potential. Hydrogen sulfide and other sulfides are particularly damaging to all of these standard reference electrodes even at miniscule concentrations. Maintaining the purity of the fill solutions is essential to have good performance for all standard reference electrodes. Solutions used for maintaining leak path flow during storage should also be maintained free of contamination.

8.5 *High Resistivity Environments*—Although most environments where corrosion measurements are made have significant electrical conductivity, it is possible to encounter highly resistive environments. Examples include high purity water, glacial acetic acid and non-aqueous organic liquids such as methanol, ethanol, and acetone. In the case of organic solvents, sometimes it is possible to add an ionic material to increase the conductivity, but in other cases these systems may not permit conventional electrochemical methods. In general, liquids with resistivities greater than 10^6 ohm-cm may present problems.

9. Standard Reference Electrode Maintenance and Storage

9.1 *Dry Storage*—Because capillary leak systems can become plugged with KCl crystals it is important to keep the leak path open when the electrode is not in use. This may be accomplished by using an elastomeric cap that seals the electrode bottom thereby preventing evaporation and crystal formation. This approach may be effective for several months, but is not a long term solution to the problem.

9.2 *Water Immersion Storage*—Another approach that has been used for short term storage of standard reference electrodes is to keep the capillary tip immersed in purified water. This will assure that crystals do not form in the tip. The approach here is to keep the water level well below the solution level in the electrode so that the flow of electrolyte out of the electrode minimizes back diffusion of water into the electrode. This is usually effective for up to 30 days.

9.3 *Potassium Chloride Solutions Storage*—In the case of standard electrodes that use potassium chloride fill solutions, the tip of the electrode may be immersed in a potassium chloride solution of about the same concentration. This approach is successful for long term storage if the container that holds the electrode and solution is sealed sufficiently to avoid evaporation of the solution. Saturated potassium chloride solutions will show frosting and crystal growth above the liquid level if evaporation of water occurs. This can be unsightly and create issues of spilling the crystals when the electrode is removed.

NOTE 6—It is good practice to rinse electrodes with purified water or wipe them clean, or both, after usage to prevent contamination of solutions used to maintain the electrode leak path during storage.

10. Errors and Correction Approaches for Polarization Measurements

10.1 *Luggin-Haber Capillary Probe*—The measurement of electrode potentials in systems that have an impressed current on the test electrode surface have the problem that the current flowing through the solution also causes a potential change between the specimen surface and the reference electrode tip. One approach to minimizing this potential change is to have the electrode tip as close to the surface as possible. However, the presence of a relatively large item in the current path will shield the surface creating a different error. The traditional approach to dealing with this problem is to use a capillary probe made from a resistive material such as glass to provide an electrolyte path to the reference electrode that does not have any current flowing through it except for that necessary to make the measurement. These probes are known as Luggin or Luggin-Haber probes. They are usually drawn out to less than 1 mm diameter on one end and are connected to a vessel external to the test vessel and filled with the test solution. The reference electrode is placed in the external vessel. The probe tip is then placed close to the specimen surface so that it is not closer than its outer diameter from the surface. This will minimize the potential drop through the solution while also minimizing shielding errors. The actual placement of the tip will always depend upon the geometry of the cell and the items in it, but close proximity to the working electrode will minimize the resistivity error. See Test Methods G5 and G59 for examples of a Luggin-Haber probe.

NOTE 7—The terminology for this device is in recognition of Prof. Luggin's work to develop this approach. Unfortunately, Prof. Luggin died before his work was completed, and Fritz Haber completed the studies and published it. As a result, many investigators recognize both of these scientists.

10.2 *Current Interruption*—Another approach to eliminating the potential change caused by flowing current is to use a current interrupter on the current source. The potential change from current flow ceases instantly if the current ceases, but the electrode potential on the surface in question does not decay rapidly. The electrode potential can be measured briefly during the interruption. This approach has been used effectively in cathodic protection systems for underground piping systems where the reference electrode is not close to the test surface.

10.3 *High Frequency Superposition Signal*—Electrode surfaces have a capacitance associated with them that can be utilized to determine the resistance between the surface and the reference electrode. The approach is to use a high frequency signal superimposed on the polarization current. This signal will bypass the polarization resistance of the electrode and allow the resistance of the environment to be measured directly. This approach allows the polarization resistance to be corrected, and the specimen potential to be determined. See Practice G106 for an example of using high frequency signal to determine solution resistance.

10.4 *Finite Element Analysis*—Another approach is to calculate the potential change between the specimen electrode surface and the reference electrode using the solution resistivity and current flow. Because the system geometry may be difficult to model analytically, some investigators have used a finite element analysis to determine the potential error from current flow between the surface in question and the reference electrode tip. Commercially available programs have made this approach possible, but the details are beyond the scope of this guide.

11. Calibration and Verification of Standard Reference Electrodes

11.1 Calibration is not usually carried out with reference electrodes because for corrosion studies it is not necessary.

11.2 *Master Electrode*—Some laboratories maintain a master reference electrode and use it to check the potential of the reference electrodes used for testing. If the reference electrode that is to be used for testing shows a potential difference greater than repeatability for that type of electrode, it is rejected. A variation of this approach is to maintain two master electrodes and routinely check one against the other. As long as they agree, the master is considered acceptable and can be used to check electrodes for testing. It is good practice to check every reference electrode before and after the testing program is carried out. See also NACE TM0113–2013.

NOTE 8—In laboratories using many electrodes, storing them in a common vessel with a solution may be an approach to maintaining their functionality. However, it is important in this case to keep the master electrodes in a separate vessel or vessels to avoid possible contamination of the master electrodes.

11.3 *Group Electrode Systems*—Another variation used by some laboratories is to maintain a group of several commercial standard reference electrodes, and check all of them against each other before beginning a test program. Any electrode that show potential larger than the repeatability range for the type of electrode used is then rejected. In this case, the electrode must be consistently out of line with the other electrodes in the group. The use of a common storage vessel for all reference electrodes is not recommended because of the possibility of contamination of the storage solution that would affect all of the electrodes.

NOTE 9—Rejected electrodes may be discarded or refurbished by removing and replacing the fill solution. In the case where the electrode is refurbished, the electrode must be checked and found acceptable before being reused.

12. Report

12.1 The report required for any test method employing potential measurements should be provided. Using this guide does not exempt the user from required reporting requirements.

12.2 The potential values together with the identification of the reference electrode should be provided. When silver/silver chloride reference electrodes are used, the concentration of the KCl filling solution must be reported except in cases of direct immersion in seawater.

12.3 The verification technique used for standard reference electrodes should be provided with dates when the verification measurements were made.

12.4 For polarization measurements, the method on dealing with resistance losses should be explained in detail including the following if appropriate: If these losses are not significant, the basis for that determination should be stated.

12.4.1 Luggin Probe tip outer diameter and proximity to test surface if used.

12.4.2 Solution resistivity.

12.4.3 Current interruption time and frequency.

12.4.4 Details of error calculation approaches.

13. Keywords

13.1 calomel electrode; copper/copper sulfate electrode; current interruption; electrode potential; Luggin capillary probe; Luggin-Haber capillary probe; mercury/mercurous sulfate electrode polarization; nonstandard reference electrode; silver/silver chloride electrode; standard reference electrode

APPENDIXES

(Nonmandatory Information)

X1. SAMPLE CALCULATION OF TEMPERATURE CORRECTION

X1.1 Test Method G59 environment is 1.0 N sulfuric acid at 30°C. The measured specimen potential is -0.515 V versus SCE. Assume the reference electrode is at 25°C.

X1.2 Calculation of the specimen potential at 30°C:

X1.2.1 Thermal temperature coefficient of SCE = 0.22 mV/°C (Practice G3).

X1.2.2 $E_{SCE} = -0.515 + 0.22 \times 10^{-3} \times 5 = -0.515 + 0.0011 = -0.514$ V.

X1.3 Calculation of specimen potential versus SHE at 30°C:

X1.3.1 $E_{SHE} = -0.515 + 0.241 + (0.22 - 0.87) \times 10^{-3} \times 5 = -0.274 + (-0.65) \times 10^{-3} \times 5 = -.277$ V.

X2. PROCEDURE FOR MEASURING POTENTIAL OF GALVANIZED STEEL

X2.1 Cut specimen to size for testing.

X2.2 Attach electrical connection, screw or clamp.

X2.3 Mask all non-test areas with non-shrinking organic coating.

X2.3.1 Coating must be highly resistive.

X2.3.2 Coating must resist environment without losing adhesion.

X2.4 Prepare test solution.

X2.4.1 Example: 3.5 % sodium chloride.

X2.4.2 Adjust solution temperature if not ambient.

X2.5 Place specimen and reference electrode into solution.

X2.5.1 Support specimen and reference electrode so that they are not in contact, but the test area faces the reference electrode.

X2.6 Connect the specimen and reference electrode to the high impedance volt meter.

X2.7 Record the specimen potential after 5 min.

X2.8 Continue recording the specimen potential every 5 min until the change is less than 10 mV.

X2.9 Report the final potential.

X3. CALCULATION OF HYDROGEN OVERVOLTAGE

X3.1 Hydrogen overvoltage, HOV, is the negative potential difference between the specimen potential and the potential of the reaction:

$$H_2(g, 101.3\ kPa) + 2H_2O(1) = 2H_3O^+(Aq) + 2e \qquad (X3.1)$$

X3.2 For a specimen in a solution with a pH = X and an electrode potential of U Volts versus SCE the HOV is:

$$HOV = -(U + 0.241 + 0.0592\ X) \qquad (X3.2)$$

X3.3 Sample Calculation:

X3.3.1 U = -1.053 V vs. SCE, pH = 5.20, Temperature 25°C

X3.3.2 HOV* = -(-1.053 + 0.241 + 0.0592 × 5.20) = -(-1.053 + 0.241 + 0.307) = 0.504 V.

However, the actual HOV will be significantly lower because the polarization of the metal surface will cause the hydroxyl ion concentration to increase at the surface. The pH in equilibrium with an electrode at U = -1.053 V versus SCE is -(-1.053 + 0.241)/(0.0592 = 13.72. At that pH the HOV is zero. The actual HOV will depend upon the rate of generation of hydroxyl ions at the surface, and the rate of diffusion of hydroxyl ions away from the surface.