ASTM INTERNATIONAL

Designation: G 106 – 89 (Reapproved 1999)

Standard Practice for
Verification of Algorithm and Equipment for Electrochemical Impedance Measurements[1]

This standard is issued under the fixed designation G 106; 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 describes an experimental procedure which can be used to check one's instrumentation and technique for collecting and presenting electrochemical impedance data. If followed, this practice provides a standard material, electrolyte, and procedure for collecting electrochemical impedance data at the open circuit or corrosion potential that should reproduce data determined by others at different times and in different laboratories. This practice may not be appropriate for collecting impedance information for all materials or in all environments.

1.2 *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:*
D 1193 Specification for Reagent Water[2]
G 3 Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing[3]
G 5 Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements[3]
G 15 Terminology Relating to Corrosion and Corrosion Testing[3]
G 59 Practice for Conducting Potentiodynamic Polarization Resistance Measurements[3]

3. Terminology

3.1 *Definitions*—For definitions of corrosion related terms, see Terminology G 15.
3.2 *Symbols:*

C = capacitance (farad-cm^{-2})

E' = real component of voltage (volts)
E'' = imaginary component of voltage (volts)
E = complex voltage (volts)
f = frequency (s^{-1})
I' = real component of current (amp-cm^{-2})
I'' = imaginary component of current (amp-cm^{-2})
I = complex current (amp-cm^{-2})
j = $\sqrt{-1}$
L = inductance (henry – cm^2)
R_s = solution resistance (ohm-cm^2)
R_p = polarization resistance (ohm-cm^2)
R_t = charge transfer resistance (ohm-cm^2)
Z' = real component of impedance (ohm-cm^2)
Z'' = imaginary component of impedance (ohm-cm^2)
Z = complex impedance (ohm-cm^2)
α = phenomenological coefficients caused by depression of the Nyquist plot below the real axis, α is the exponent and τ is the time constant(s).
θ = phase angle (deg)
ω = frequency (radians-s^{-1})

Subscripts:
x = in-phase component
y = out-of-phase component

4. Summary of Practice

4.1 Reference impedance plots in both Nyquist and Bode format are included. These reference plots are derived from the results from nine different laboratories that used a standard dummy cell and followed the standard procedure using a specific ferritic type alloy UNS-S43000[4] in 0.005 M H$_2$SO$_4$ and 0.495 M Na$_2$SO$_4$. The plots for the reference material are presented as an envelope that surrounds all of the data with and without inclusion of the uncompensated resistance. Plots for one data set from one laboratory are presented as well. Since the results from the dummy cell are independent of laboratory, only one set of results is presented.

4.2 A discussion of the electrochemical impedance technique, the physics that underlies it, and some methods of interpreting the data are given in the Appendix X1-Appendix

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[1] This practice is under the jurisdiction of ASTM Committee G-1 on Corrosion of Metals and is the direct responsibility of Subcommittee G01.11 on Electrochemical Measurements in Corrosion Testing.
Current edition approved Sept. 29, 1989. Published November 1989. Originally published as G 106-89. Last previous edition G 106 - 89 (1994)$^{\epsilon 1}$.
[2] *Annual Book of ASTM Standards*, Vol 11.01.
[3] *Annual Book of ASTM Standards*, Vol 03.02.

[4] These standard samples are available from ASTM Headquarters. Generally, one sample can be repolished and reused for many runs. This procedure is suggested to conserve the available material. Order PCN 12–700050–00.

X6. These sections are included to aid the individual in understanding the electrochemical impedance technique and some of its capabilities. The information is not intended to be all inclusive.

5. Significance and Use

5.1 The availability of a standard procedure, standard material, and standard plots should allow the investigator to check his laboratory technique. This practice should lead to electrochemical impedance curves in the literature which can be compared easily and with confidence.

5.2 Samples of a standard ferritic type 430 stainless steel (UNS 430000) used to obtain the reference plots are available for those who wish to check their equipment. Suitable resistors and capacitors can be obtained from electronics supply houses.

5.3 This test method may not be appropriate for electrochemical impedance measurements of all materials or in all environments.

6. Apparatus

6.1 *Dummy Cell*—The dummy cell used to check the equipment and method for generating electrochemical impedance data is composed of a 10 Ω precision resistor placed in series with a circuit element composed of a 100 Ω precision resistor in parallel with a 100 μF capacitor. The resistors should have a stated precision of ±0.1 %. The capacitor can have a precision of ±20 %. The cell can be constructed from readily available circuit elements by following the circuit diagram shown in Fig. 1.

6.2 *Test Cell*—The test cell should be constructed to allow the following items to be inserted into the solution chamber: the test electrode, two counter electrodes or a symmetrically arranged counter electrode around the working electrode, a Luggin-Haber capillary with salt bridge connection to the reference electrode, an inlet and an outlet for an inert gas, and a thermometer or thermocouple holder. The test cell must be constructed of materials that will not corrode, deteriorate, or otherwise contaminate the solution.

6.2.1 One type of suitable cell is described in Reference Test Method G 5. Cells are not limited to that design. For example, a 1-L round-bottom flask can be modified for the addition of various necks to permit the introduction of electrodes, gas inlet and outlet tubes, and the thermometer holder. A Luggin-Haber capillary probe could be used to separate the bulk solution from the saturated calomel electrode. The capillary tip can be easily adjusted to bring it into close proximity to the working

electrode. The minimum distance should be no less than two capillary diameters from the working electrode.

6.3 *Electrode Holder*—The auxillary and working electrodes can be mounted in the manner shown in Reference Test Method G 5. Precautions described in Reference Test Method G 5 about assembly should be followed.

6.4 *Potentiostat*—The potentiostat must be of the kind that allows for the application of a potential sweep as described in Reference Test Method G 5 and Reference Practice G 59. The potentiostat must have outputs in the form of voltage versus ground for both potential and current. The potentiostat must have sufficient bandwidth for minimal phase shift up to at least 1000 Hz and preferably to 10 000 Hz. The potentiostat must be capable of accepting an external excitation signal. Many commercial potentiostats meet the specification requirements for these types of measurements.

6.5 *Collection and Analysis of Current-Voltage Response*— The potential and current measuring circuits must have the characteristics described in Reference Test Method G 5 along with sufficient band-width as described above. The impedance can be calculated in several ways, for example, by means of a transfer function analyzer, Lissajous figures on an oscilloscope, or transient analysis of a white noise input using a Fast Fourier Transform algorithm. Other methods of analysis exist.

6.6 *Electrodes*:

6.6.1 Working electrode preparation should follow Reference Test Method G 5, which involves drilling and tapping the specimen and mounting it on the electrode holder.

6.6.2 Auxillary electrode preparation should follow Reference Test Method G 5. The auxillary electrode arrangement should be symmetrical around the working electrode.

6.6.3 Reference electrode type and usage should follow Reference Test Method G 5. The reference electrode is to be a saturated calomel electrode.

7. Experimental Procedure

7.1 *Test of Algorithm and Electronic Equipment (Dummy Cell)*:

7.1.1 Measure the impedance of a dummy cell consisting of a 10 Ω resistor in series with a parallel combination of a 100 Ω resistor and a 100 μF capacitor. The circuit diagram is shown in Fig. 1.

7.1.2 Typical connections from the potentiostat are shown in Fig. 1. Connect the auxillary electrode and reference electrode leads to the series resistor side of the circuit. Connect the
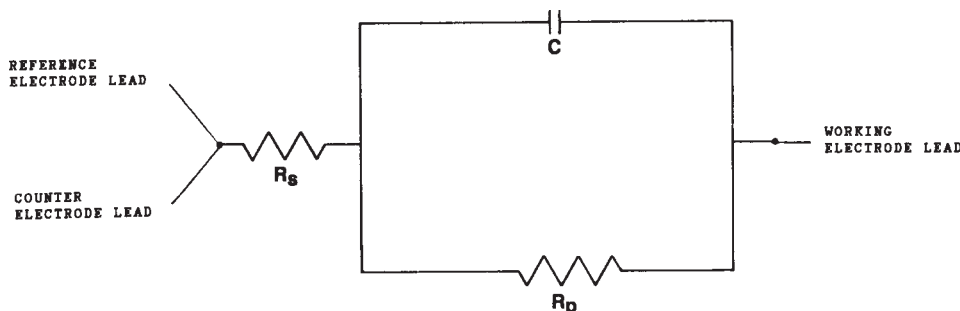

FIG. 1 Circuit Diagram for Dummy Cell Showing Positions for Hook-Up to Potentiostat

working electrode lead to the opposite side of the circuit beyond the resistor-capacitor parallel combination.

7.1.3 Set the potential at 0.0V. Collect the electrochemical impedance data between 10 000 Hz (10 kHz) and 0.1 Hz (100 mHz) at 8 to 10 steps per frequency decade. The amplitude must be the same as that used to check the electrochemical cell, 10 mv. The resulting frequency response when plotted in Nyquist format (the negative of the imaginary impedance versus the real impedance) must agree with that shown in Figs. 2-4. Testing with the electrochemical cell should not be attempted until that agreement is established. Results using the dummy circuit were found to be independent of laboratory.

7.2 *Test of Electrochemical Cell*:

7.2.1 Test specimens of the reference material should be prepared following the procedure described in Reference Test Method G 5. This procedure involves polishing the specimen with wet SiC paper with a final wet polish using 600 grit SiC paper prior to the experiment. There should be a maximum delay of 1 h between final polishing and immersion in the test solution.

7.2.2 Prepare a 0.495 M Na_2SO_4 solution containing 0.005 M H_2SO_4 from reagent grade sulfuric acid and sodium sulfate and Type IV reagent water described in Specification D 1193. The test is to be carried out at 30 ± 1°C.

7.2.3 At least 1 h before specimen immersion, start purging the solution with oxygen-free argon, hydrogen, or nitrogen gas at a flow rate of about 100 to 150 cm^3/min. Continue the purge throughout the test.

7.2.4 Transfer the specimen to the test cell. Adjust the Luggin-Haber probe tip so that it is no less than two capillary diameters from the sample. However, since this distance will affect the uncompensated solution resistance, the greater the distance, the larger the resistance. Therefore, close placement is important.
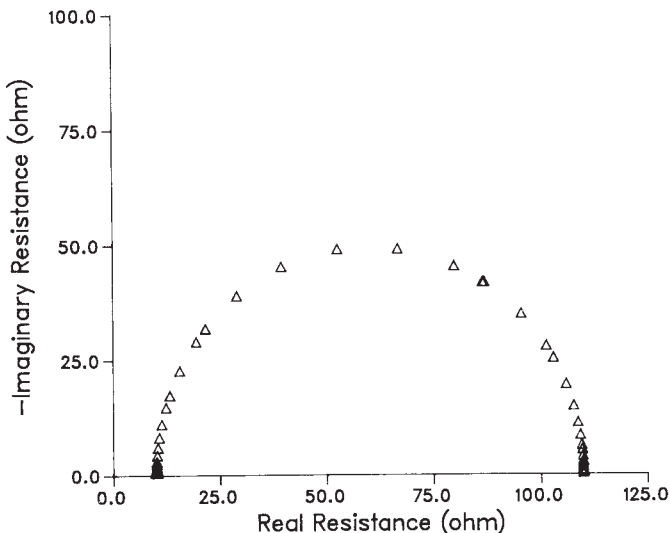
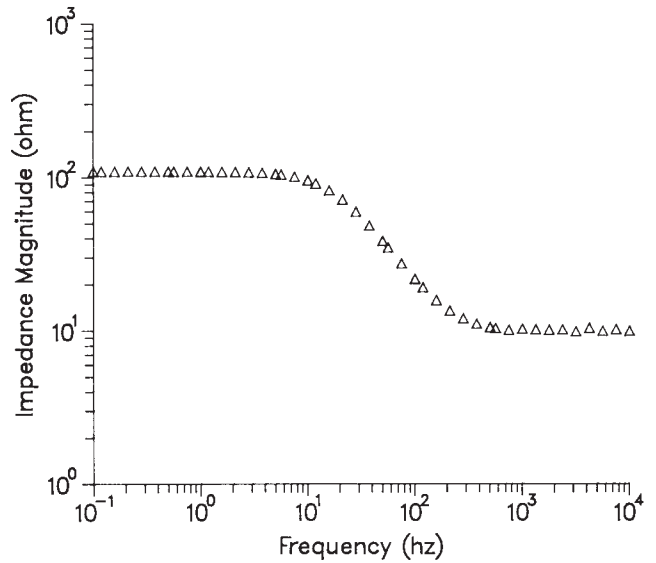

FIG. 3 Bode Plot, Impedance Magnitude Versus Frequency, of Electrochemical Impedance Response for Dummy Cell
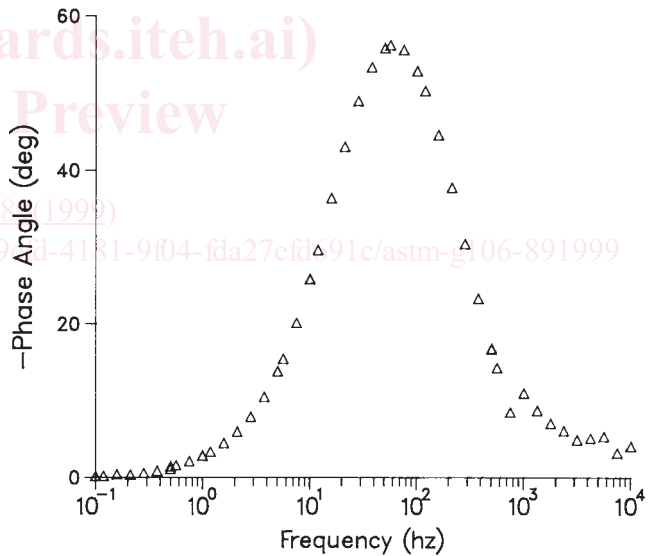

FIG. 4 Bode Plot, Phase Angle Versus Frequency, of Electrochemical Impedance Response for Dummy Cell

7.2.5 Connect the potentiostat leads to the appropriate electrodes, for example, working electrode lead to working electrode, counter electrode lead to counter electrode, and reference electrode lead to reference electrode. Hook-up instructions provided with the potentiostat must be followed.

7.2.6 Record the open circuit potential, that is, the corrosion potential, for 1 h. The potential should be about −645 mv ±10 mv relative to the saturated calomel electrode. If the potential is more positive than −600 mv (SCE) then the specimen may have passivated. If so, remove the specimen and repolish with 600 grit wet silicon carbide paper. Then reimmerse the sample

FIG. 2 Nyquist Plot of Electrochemical Impedance Response for Dummy Cell

and monitor the corrosion potential for 1 h. If the potential again becomes more positive than −600 mv (SCE) check for oxygen contamination of the solution.

7.2.7 Record the frequency response between 10 000 Hz (10 kHz) and 0.1 Hz (100 mHz) at the corrosion potential recorded after 1 h of exposure using 8 to 10 steps per frequency decade. The amplitude must be the same as that used in 6.1.3, 10 mv.

7.2.8 Plot the frequency response in both Nyquist format (real response versus the negative of the imaginary response) and Bode format (impedance modulus and phase angle versus frequency). Frequency can be reported in units of radians/second or hertz (cycles/s).

7.2.9 There was no attempt to estimate circuit analogues for the electrochemical impedance curves since there is no universally recognized, standard method for making such estimates.

8. Standard Reference Results and Plots

8.1 *Dummy Cell*:

8.1.1 The results from nine different laboratories were virtually identical and overlayed each other almost perfectly. Typical plots of the raw data are shown in Figs. 2-4. No attempt has been made to estimate the variance and standard deviation of the results from the nine laboratories. The measured values of R_s, R_p, and the frequency at which the phase angle is a maximum must agree with these curves within the specifications of the instrumentation, resistors, and capacitors before testing of the electrochemical cell commences. See 9.1.1.

8.2 *Electrochemical Cell*:

8.2.1 Standard electrochemical impedance plots in both Nyquist format and Bode format are shown in Figs. 5-7. These are actual results from one laboratory. Figs. 8-10 show plots in both Nyquist and Bode formats which envelop all of the results from the nine laboratories. The solution resistance from each laboratory was not subtracted out prior to making this plot.

8.2.2 The average solution resistance from the nine laboratories in 3.3 Ω-cm² ± 1.8 Ω-cm²(one standard deviation). The solution resistance of the user's test cell as measured by the
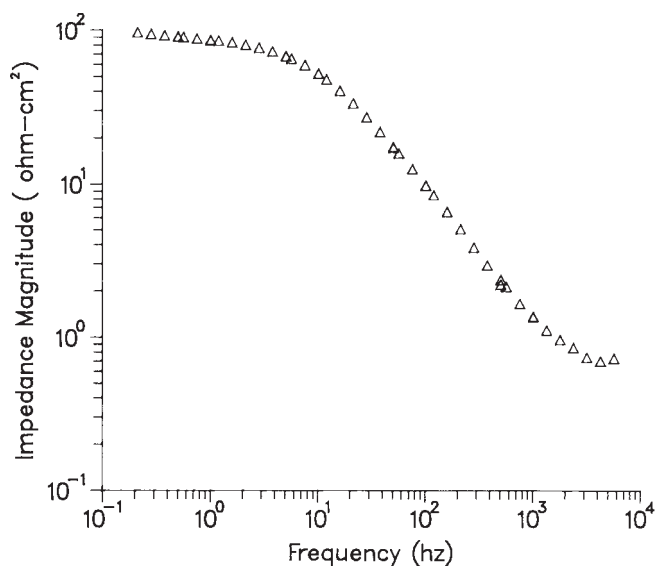

FIG. 6 Bode Plot, Impedance Magnitude Versus Frequency, for UNS-S43000 From One Laboratory
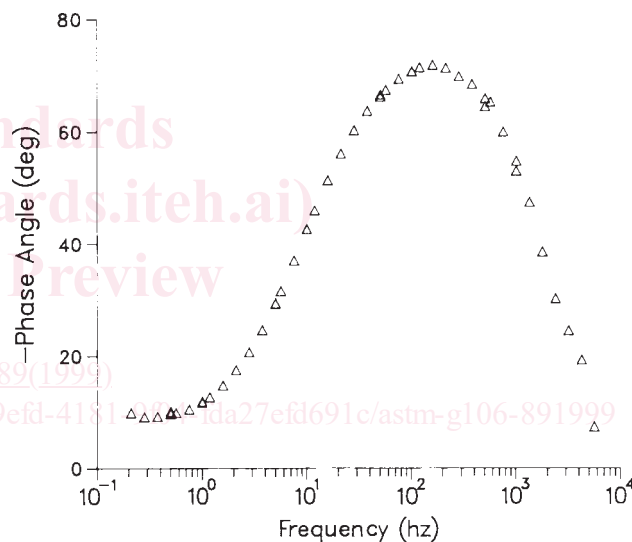

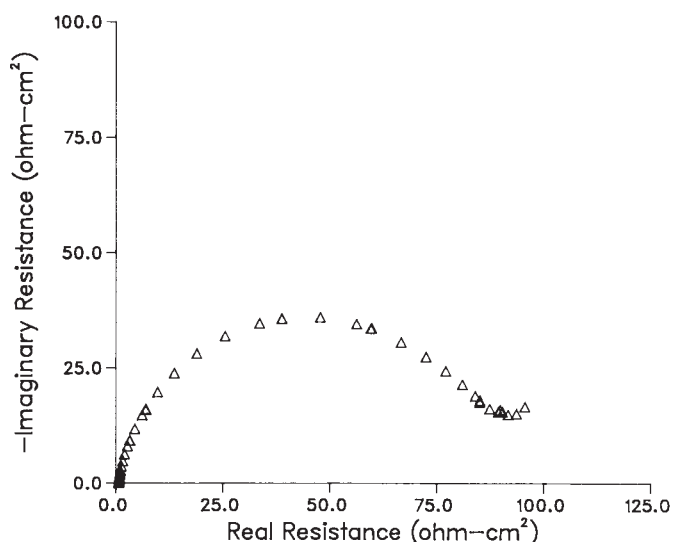FIG. 7 Bode Plot, Phase Angle Versus Frequency, for UNS-S43000 From One Laboratory

high frequency intercept on the Nyquist plot must lie in this range to use agreement with Figs. 8-10 for verification of the electrochemical test cell. If the uncompensated resistance lies outside of this range, it should be subtracted from the results (see 7.2.4). Then, results from the electrochemical test cell can be compared with the results in Figs. 11-13 to verify the test cell. Figs. 11-13 envelop all of the results from the nine laboratories with the uncompensated resistance subtracted out.

9. Precision and Bias

9.1 *Dummy Cell*:

9.1.1 Reproducibility of the results for the dummy cell is dependent on the precision of the resistors and capacitor used to construct the dummy cell. Precision resistors (±0.1 %) should be used to construct the dummy cell. Most capacitors have a precision of ±20 %. A change in the value of the

FIG. 5 Nyquist Plot of Typical Frequency Response for UNS-S43000 From One Laboratory
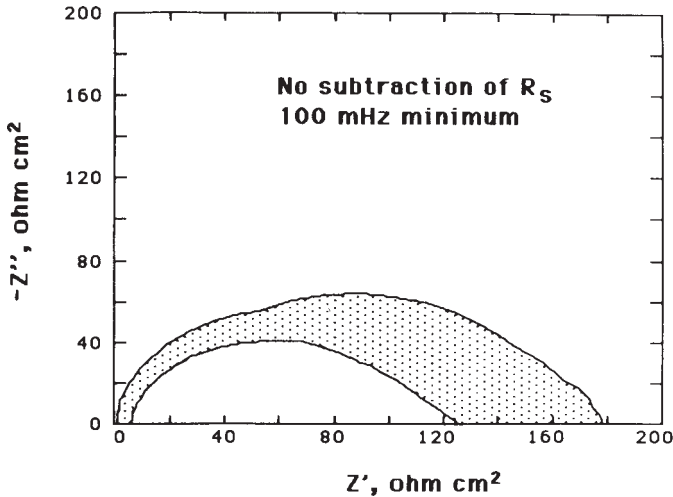
FIG. 8 Envelope of Data From All Laboratories, Nyquist Plot, Solution Resistance Included
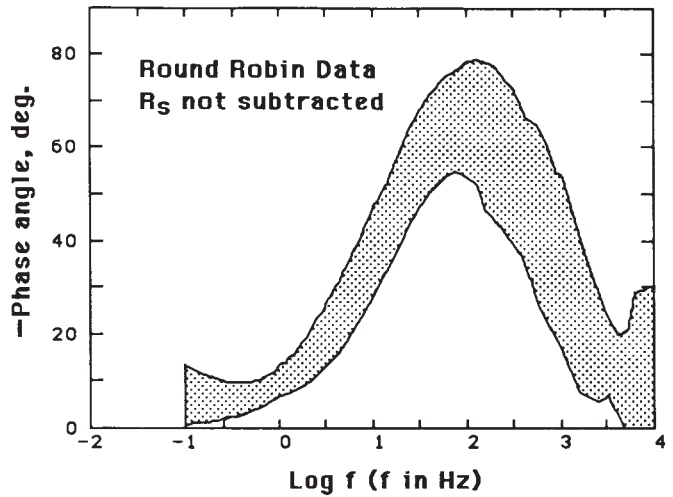

FIG. 10 Envelope Of Data From All Laboratories, Bode Plot (Phase Angle Versus Frequency), Solution Resistance Included
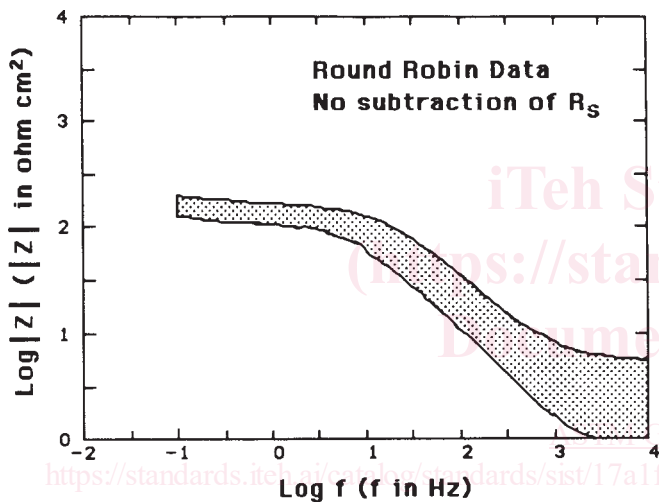

FIG. 9 Envelope of Data From All Laboratories, Bode Plot (Impedance Magnitude Versus Frequency), Solution Resistance Included
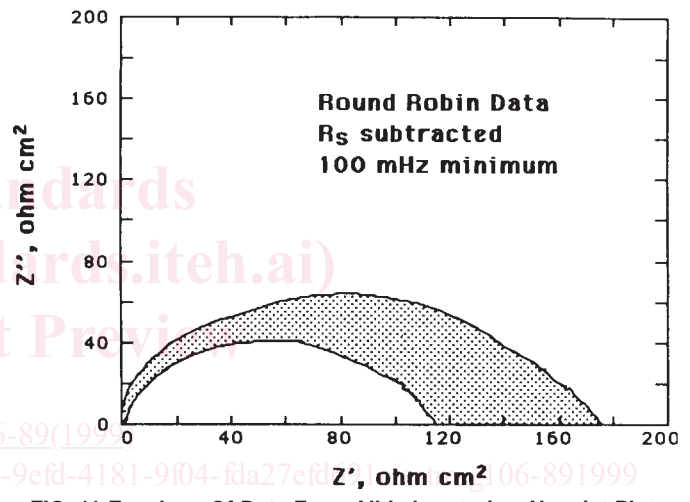

FIG. 11 Envelope Of Data From All Laboratories, Nyquist Plot, Solution Resistance Removed

capacitor will change the frequency at which the maximum phase angle occurs in Fig. 4. In Nyquist format the intercepts with the real axis should agree with the resistor values (R_s and R_p) shown in Fig. 2.

9.2 *Electrochemical Cell*:

9.2.1 The reported corrosion potential was −645 mV ± 9 mV (one standard deviation). The corrosion potential varied between −627 mV and −662 mV with most of the results lying between −640 mV and −650 mV.

9.2.2 The increasing scatter with decreasing frequency seen in the plots is most likely caused by a competing (mass transfer) contribution becoming important at low frequency. This mechanism results in a second time constant arising at frequencies lower than 50 to 100 mHz. The magnitude of this time constant is dependent on the cell geometry and its effect on convection. Thus, reproducibility of the second time constant between laboratories would be expected to be poor. Since this effect will have a greater effect on the frequency response

at the lower frequencies in the test, the scatter in the results increases with decreasing frequency.

9.2.3 The increasing scatter in the high frequency portion of Figs. 8-10 is caused by the variation in uncompensated resistance among laboratories. A large contributor to the uncompensated resistance is the solution resistance. This resistance is a function of cell geometry, position of the reference electrode sensing point relative to the working electrode, etc. Further information can be found in Refs (1–2).[5]

10. Keywords

10.1 ac impedance; algorithm verification; Bode; dummy cell; equipment verification; electrochemical impedance; electrochemical impedence spectroscopy; electrochemical measurement; Nyquist; polarization resistance; steel

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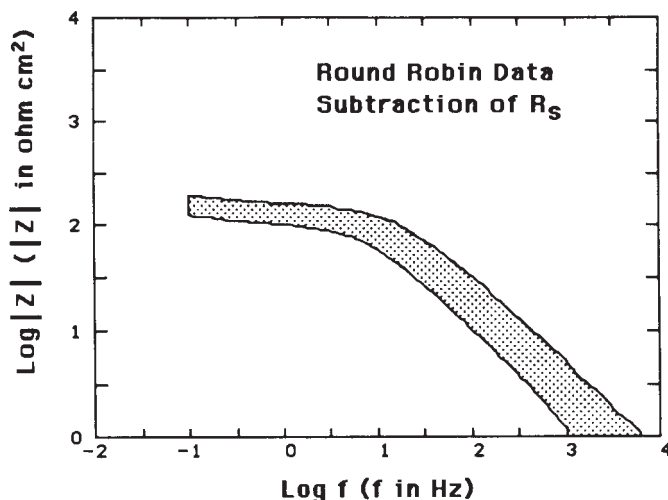[5] The boldface numbers in parentheses refer to the list of references at the end of this standard.

FIG. 12 Envelope Of Data From All Laboratories, Bode Plot
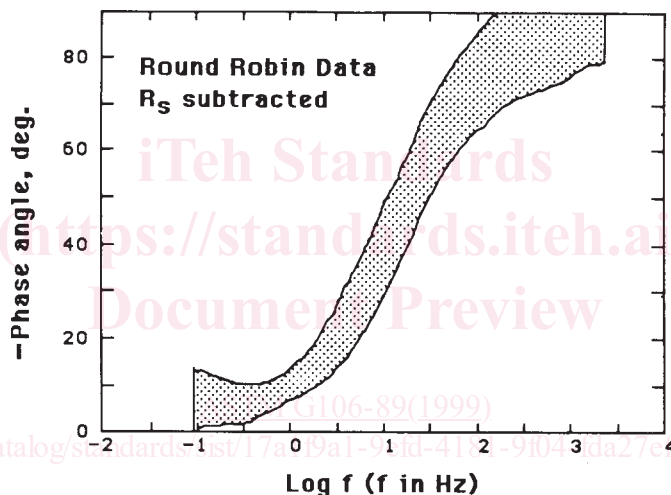(Impedance Magnitude Versus Frequency), Solution Resistance
Removed

FIG. 13 Envelope Of Data From All Laboratories, Bode Plot
(Phase Angle Versus Frequency), Solution Resistance Removed

APPENDIXES

(Nonmandatory Information)

X1. TECHNIQUE BACKGROUND

X1.1 An electrochemical process may often be modeled by linear circuit elements such as resistors, capacitors, and inductors. For example, the corrosion reaction itself can often be modeled by one or more resistors. The ability to model a corrosion process in this manner gives rise to one practical attribute of the electrochemical impedance technique. Simple AC circuit theory in terms of circuit analogues can be used to model the electrochemical corrosion process. Such modeling can facilitate understanding and lead to better prediction of corrosion rates and overall corrosion behavior. A number of reviews exist on the electrochemical impedance technique (3-7)[5] that illustrate the utility of this type of modeling.

X1.2 Direct current can be viewed as current generated in the limit of zero frequency. Under conditions of direct current, for example zero frequency, Ohm's law can be written as:

$$E = I \times R \qquad (X1.1)$$

X1.3 All symbols are defined in 3.2. In this case, the proportionality factor relating current to voltage is composed only of one or more actual resistors. When the frequency is not zero, as would occur from an imposition of a frequency dependent voltage or current, Ohm's law becomes:

$$E = I \times Z \qquad (X1.2)$$