



Designation: G 5 – 94 (Reapproved 1999)^{e1}

Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements¹

This standard is issued under the fixed designation G 5; 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.

^{e1} NOTE—Footnote 4 was updated editorially August 2002.

1. Scope

1.1 This test method describes an experimental procedure for checking experimental technique and instrumentation. If followed, this test method will provide repeatable potentiostatic and potentiodynamic anodic polarization measurements that will reproduce data determined by others at other times and in other laboratories provided all laboratories are testing reference samples from the same lot of Type 430 stainless steel.

1.2 Values stated in SI units are to be regarded as the standard. Inch-pound units given in parentheses are for information only.

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:

E 1338 Guide for the Identification of Metals and Alloys in Computerized Material Property Databases²

G 3 Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing³

G 107 Guide for Formats for Collection and Compilation of Corrosion Data for Metals for Computerized Database Input³

3. Significance and Use

3.1 The availability of a standard procedure, standard material, and a standard plot should make it easy for an investigator to check his techniques. This should lead to polarization curves in the literature which can be compared with confidence.

3.2 Samples of a standard ferritic Type 430 stainless steel (UNS S43000) used in obtaining standard reference plot are available for those who wish to check their own test procedure and equipment.⁴

3.3 Standard potentiostatic and potentiodynamic polarization plots are supplied with the purchase of the reference material. These reference data are based on the results from different laboratories that followed the standard procedure, using that material in 1.0 N H₂SO₄. Maximum and minimum current values are shown at each potential to indicate the acceptable range of values.

3.4 This test method may not be appropriate for polarization testing of all materials or in all environments.

3.5 This test method is intended for use in evaluating the accuracy of a given electrochemical test apparatus, not for use in evaluating materials performance. Therefore, the use of the plots in Figs. 1 and 2 or Appendix X2 is not recommended to evaluate alloys other than Type 430, or lots of Type 430 other than those available through ASTM. The use of the data in this test method in this manner is beyond the scope and intended use of this test method. Users of this test method are advised to evaluate test results relative to the scatter bands corresponding to the particular lot of Type 430 stainless steel that was tested.

4. Apparatus

4.1 The test cell should be constructed to allow the following items to be inserted into the solution chamber: the test electrode, two auxiliary electrodes, a Luggin capillary with salt-bridge connection to the reference electrode, inlet and outlet for an inert gas, and a thermometer. The test cell shall be constructed of materials that will not corrode, deteriorate, or otherwise contaminate the test solution.

NOTE 1—Borosilicate glass and TFE-fluorocarbon have been found suitable.

¹ This test method is under the jurisdiction of ASTM Committee G-1 on Corrosion of Metals and is the direct responsibility of G01.11 on Electrochemical Measurements in Corrosion Testing.

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² *Annual Book of ASTM Standards*, Vol 14.01.

³ *Annual Book of ASTM Standards*, Vol 03.02.

⁴ These standard samples are available from Metal Samples, P.O. Box 8, Mumfords, AL 36268. 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.

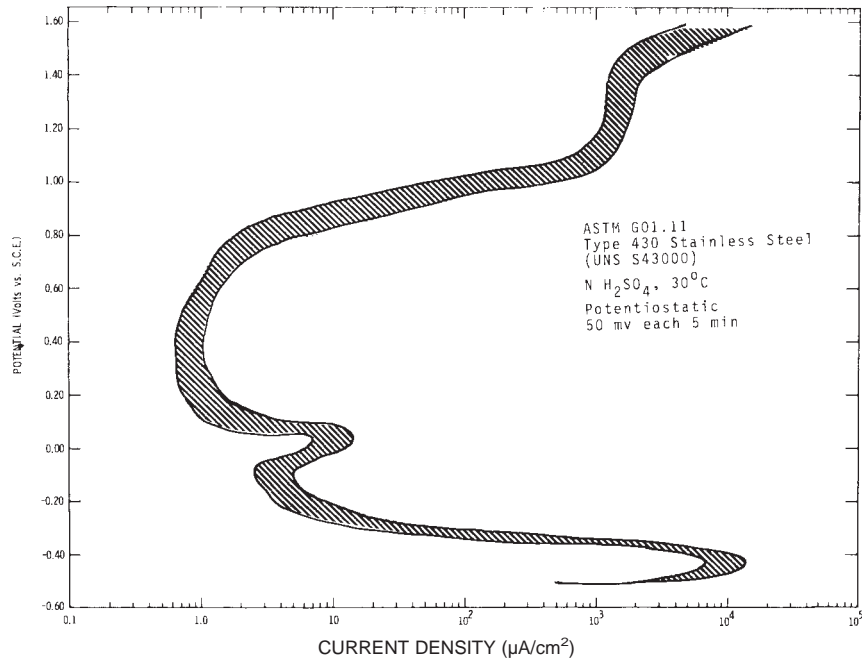


FIG. 1 Typical Standard Potentiostatic Anodic Polarization Plot

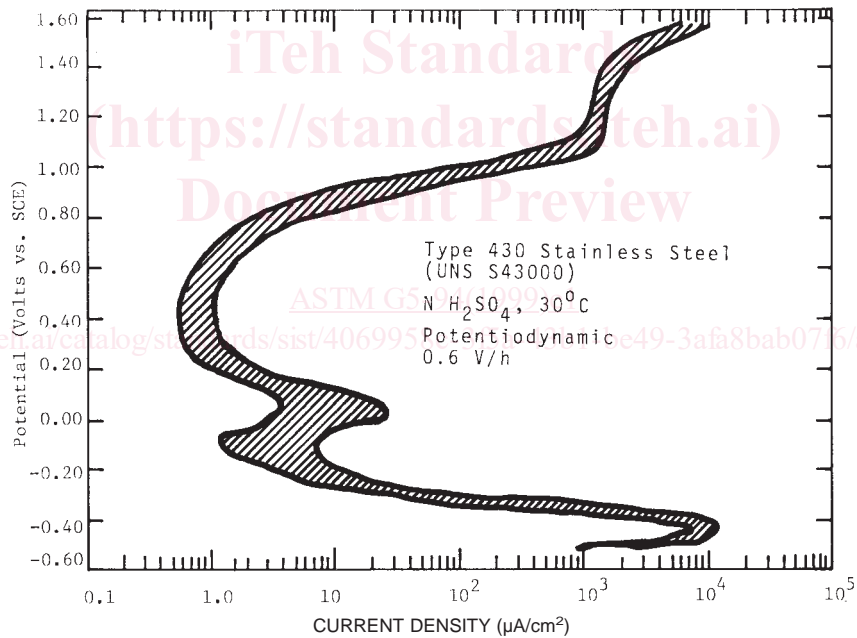


FIG. 2 Typical Standard Potentiodynamic Anodic Polarization Plot

4.1.1 A suitable cell is shown in Fig. 3 (1).⁵ A 1-L, roundbottom flask has been modified by the addition of various necks to permit the introduction of electrodes, gas inlet and outlet tubes, and a thermometer. The Luggin probe-salt bridge separates the bulk solution from the saturated calomel reference electrode, and the probe tip can be easily adjusted to bring it in close proximity with the working electrode.

⁵ The boldface numbers in parentheses refer to the list of references at the end of this test method.

4.2 Potentiostat (Note 2):

4.2.1 A potentiostat that will maintain an electrode potential within 1 mV of a preset value over a wide range of applied currents should be used. For the type and size of standard specimen supplied, the potentiostat should have a potential range from -0.6 to 1.6 V and an anodic current output range from 1.0 to 10⁵ µA.

4.3 Potential-Measuring Instruments (Note 2):

4.3.1 The potential-measuring circuit should have a high input impedance on the order of 10¹¹ to 10¹⁴ Ω to minimize

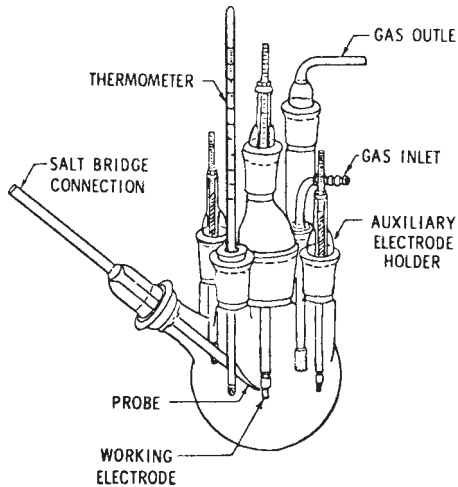


FIG. 3 Schematic Diagram of Polarization Cell (1)

current drawn from the system during measurements. Such circuits are provided with most potentiostats. Instruments should have sufficient sensitivity and accuracy to detect a change of 1.0 mV over a potential range between -0.6 and 1.6 V.

4.4 Current-Measuring Instruments (Note 2):

4.4.1 An instrument that is capable of measuring a current accurately to within 1 % of the absolute value over a current range between 1.0 and 10⁵ μA for a Type 430 stainless steel (UNS S43000) specimen with a surface area of approximately 5 cm².

4.5 Anodic Polarization Circuit:

4.5.1 A schematic potentiostatic anodic polarization wiring diagram (2) is illustrated in Fig. 4.

4.5.2 A scanning potentiostat is used for potentiodynamic measurements. For such measurements the potentiostat shall be capable of automatically varying the potential at a constant rate between two preset potentials. A record of the potential and current is plotted continuously using such instruments as an X-Y recorder and a logarithmic converter incorporated into the

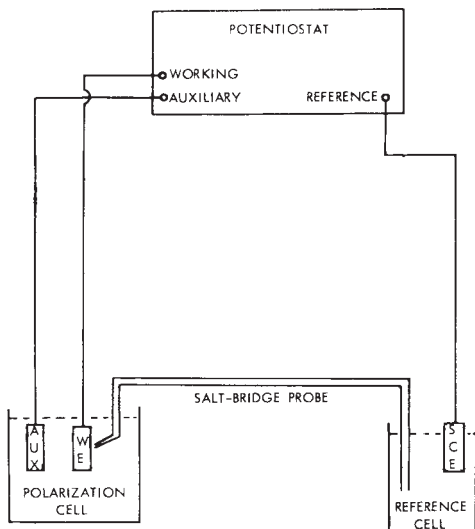


FIG. 4 Schematic Potentiostatic Anodic Polarization Wiring Diagram (2)

circuit shown in Fig. 4. Some potentiostats have an output of the logarithm of the current as a voltage, which allows direct plotting of the potential log current curve using an X-Y recorder.

NOTE 2—The instrumental requirements are based upon values typical of the instruments in 15 laboratories.

4.6 Electrode Holder (1):

4.6.1 The auxiliary and working electrodes are mounted in the type of holder shown in Fig. 5. A longer holder is required for the working electrode than for the auxiliary electrode. A leak-proof assembly is obtained by the proper compression fit between the electrode and a TFE-fluorocarbon gasket. (Too much pressure may cause shielding of the electrode or breakage of the glass holder, and too little pressure may cause leakage and subsequently crevice corrosion which may affect the test results.)

4.7 Electrodes:

4.7.1 Working Electrode, prepared from a 12.7-mm (1/2-in.) length of 9.5-mm (3/8-in.) diameter rod stock. Each electrode is drilled, tapped, and mounted in the manner discussed in 4.6.1.

NOTE 3—If specimen forms are used other than those called for by this test method, for example, flat sheet specimen, care should be taken since it was shown that crevices may be introduced which can lead to erroneous results (see Fig. X1.1).

4.7.1.1 The standard AISI Type 430 stainless steel (UNS S43000) should be used if one wishes to reproduce a standard reference plot. This material is prepared from a single heat of metal that is mill-annealed for 1/2 h at 815°C (1500°F) and air cooled. The chemical composition of the standard stainless steel is supplied with the purchase of reference material.

4.7.2 Auxiliary Electrodes:

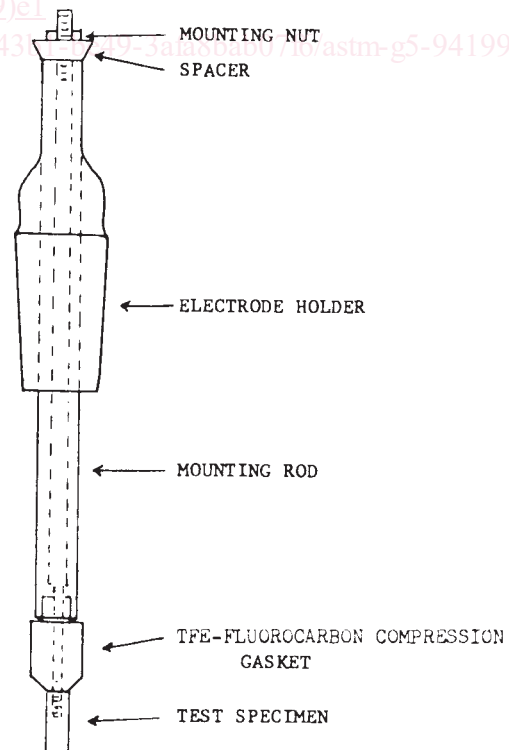


FIG. 5 Specimen Mounted on Electrode Holder

4.7.2.1 Two platinum auxiliary electrodes are prepared from high-purity rod stock. Each electrode is drilled, tapped, and mounted with a TFE-fluorocarbon gasket in the same manner as the working electrode. A large platinum sheet sealed into a glass holder is also acceptable.

4.7.2.2 A platinized surface may be utilized because of the increased surface area. This may be accomplished by cleaning the surface in hot aqua regia (3 parts concentrated HCl and 1 part concentrated HNO₃), washing, and then drying. Both electrodes are platinized by immersing them in a solution of 3 % platinum chloride and 0.02 % lead acetate and electrolyzing at a current density of 40 to 50 mA/cm² for 4 or 5 min (1, 3). The polarity is reversed every minute. Occluded chloride is removed by electrolyzing in a dilute (10 %) sulfuric acid solution for several minutes with a reversal in polarity every minute. Electrodes are rinsed thoroughly and stored in distilled water until ready for use. Since certain ions can poison these electrodes, periodic checks of platinized platinum potentials against a known reference electrode should be made.

4.7.2.3 Alternatively, graphite auxiliary electrodes can be used, but material retained by the graphite may contaminate subsequent experiments. This contamination can be minimized by using high-density graphite or avoided by routinely replacing the graphite electrode.

4.7.3 Reference Electrode (4):

4.7.3.1 A saturated calomel electrode with a controlled rate of leakage (about 3 μL/h) is recommended. This type of electrode is durable, reliable, and commercially available. Precautions shall be taken to ensure that it is maintained in the proper condition. The potential of the calomel electrode should be checked at periodic intervals to ensure the accuracy of the electrode. For other alloy-electrolyte combinations a different reference electrode may be preferred in order to avoid contamination of the reference electrode or the electrolyte.

4.7.3.2 Alternatively, a saturated calomel electrode utilizing a semi-permeable membrane or porous plug tip may be used. These may require special care.

5. Experimental Procedure

5.1 Prepare 1 L of 1.0 N H₂SO₄ from A.C.S. reagent grade acid and distilled water, for example, by using 27.8 mL of 98 % H₂SO₄/L of solution. Transfer 900 mL of solution to the clean polarization cell.

5.2 Place the platinized auxiliary electrodes, salt-bridge probe, and other components in the test cell and temporarily close the center opening with a glass stopper. Fill the salt bridge with test solution.

NOTE 4—When using a controlled leakage salt bridge, the levels of the solution in the reference and polarization cells should be the same to avoid siphoning. If this is impossible, a closed solution-wet (not greased) stopcock can be used in the salt bridge to eliminate siphoning, or a semi-permeable membrane or porous plug tip may be used on the salt bridge.

5.3 Bring the temperature of the solution to 30 ± 1°C by immersing the test cell in a controlled-temperature water bath or by other convenient means.

5.4 Reduce oxygen levels in solution prior to immersion of the test specimen. This may be accomplished by bubbling an

oxygen-free gas such as hydrogen, argon, or nitrogen at a rate of 150 cm³/min for a minimum of ½ h.

5.5 Prepare the working electrode surface within 1 h of the experiment. Wet grind with 240-grit SiC paper, wet polish with 600-grit SiC paper until previous coarse scratches are removed, rinse, and dry. (Drilled and tapped specimens can be threaded onto an electrode holder rod and secured in a lathe or electric drill for this operation.)

5.6 Determine the surface area by measuring all dimensions to the nearest 0.01 mm, subtracting the area under the gasket (usually 0.20 to 0.25 cm²).

5.7 Mount the specimen on the electrode holder as described in 4.6.1. Tighten the assembly by holding the upper end of the mounting rod in a vise or clamp while tightening the mounting nut until the gasket is properly compressed.

5.8 Degrease the specimen just prior to immersion and then rinse in distilled water.

5.9 Transfer the specimen to the test cell and adjust the salt-bridge probe tip so it is about 2 mm or 2 times the tip diameter, whichever is larger from the specimen electrode.

5.10 Record the open-circuit specimen potential, that is, the corrosion potential, after 55 min immersion. If platinum counter electrodes and hydrogen gas are used, record the platinum potential 50 min after immersion of the specimen.

5.11 Potential Scan:

5.11.1 Start the potential scan or step 1 h after specimen immersion, beginning at the corrosion potential (E_{corr}) for potentiodynamic measurements and the nearest 50-mV increment above E_{corr} for the potentiostatic measurements. Proceed through +1.60 V versus saturated calomel electrode (SCE) (active to noble).

5.11.2 In the potentiostatic method, use a potentiostatic potential step rate of 50 mV every 5 min, recording the current at the end of each 5-min period at potential. These steps are repeated until a potential of +1.6 V SCE is reached.

5.11.3 In the potentiodynamic method, use a potentiodynamic potential sweep rate of 0.6 V/h (±5 %) recording the current continuously with change in potential from the corrosion potential to +1.6 V SCE.

5.12 Plot anodic polarization data on semilogarithmic paper in accordance with Practice G 3, (potential-ordinate, current density-abscissa). If a potentiostat with a logarithmic converter is used, this plot can be produced directly during the measurement.

6. Standard Reference Plots

6.1 Standard polarization plots prepared from data obtained by following the standard procedure discussed in this test method are supplied with the purchase of reference material. Typical data are shown in Fig. 1 and Fig. 2 (5). The plots show a range of acceptable current density values at each potential. The average corrosion potential is –0.52 V, and the average platinized platinum potential is –0.26 V.

NOTE 5—The plots in Fig. 1 and Fig. 2 correspond to a lot of Type 430 stainless steel that is no longer available from ASTM (after July 1992). Figs. 1 and 2 are presented primarily for the discussion of precision and bias in Sections 6, 7, and Appendix X1. The scatter bands presented in Appendix X2 were developed from a round robin testing program on the lot of Type 430 stainless steel that is currently available from ASTM.

6.2 Typical deviations from the standard potentiostatic plot are shown and discussed in Appendix X1. Reference to this discussion may be helpful in determining the reasons for differences between an experimental curve and the standard plots.

6.3 The potentiodynamic standard curve shows good agreement with the potentiostatic standard curve determined at an equivalent overall polarization rate.

6.4 Differences in the size and placement of the scatter bands presented in Figs. 1 and 2 versus those in Appendix X2 are attributed to minor differences in the two heats of Type 430 stainless steel that were evaluated in separate round robins.

7. Precision and Bias

7.1 The repeatability of this test method is being developed. However, the repeatability on a previous interlaboratory test in which one material was run twice by one laboratory is shown in Fig. 6.

7.2 The reproducibility of this test method is being developed by interlaboratory testing.

7.3 There is no bias in this test method because the potentiodynamic curve is defined only in terms of this test method.

8. Keywords

8.1 anodic polarization; electrochemical testing; pitting; potentiodynamic; potentiostatic; sulfuric acid; Type 430 stainless steel

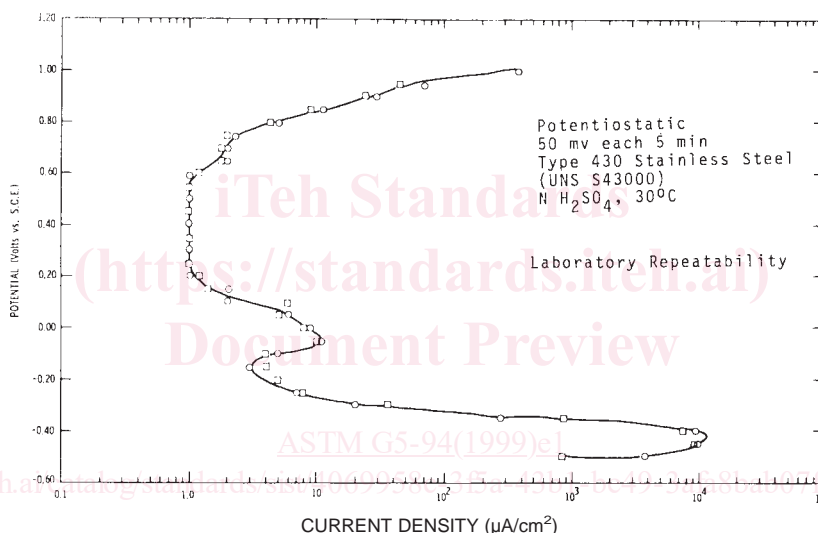


FIG. 6 Laboratory Repeatability of Potentiostatic Anodic Polarization Curve

APPENDIXES

(Nonmandatory Information)

X1. DEVIATIONS FROM STANDARD POLARIZATION PLOTS

X1.1 High Passive Current Densities (Crevice Effect)

X1.1.1 Examples of passive current densities which are greater than those for a standard potentiostatic plot are shown in Fig. X1.1. This effect is attributable to a crevice between the specimen and mounting material (6). The crevice may be the result of the mounting technique or the material used for mounting.

X1.1.2 The potential drop along the narrow path of the electrolyte within the crevice between the specimen and the mounting material prevents this area from passivating. Although the face of the specimen passivates, the high current density associated with the active crevice contributes to an increase in the measured current density. Specimen electrodes

for polarization measurements must be mounted without crevice sites to avoid such erroneous passive current densities.

X1.2 Low Passive Current Densities (Instrumental Effect)

X1.2.1 The low passive current densities shown in Fig. X1.2 are undoubtedly the result of instrumental problems. This effect can be eliminated by calibrating the current over the entire range of interest before conducting an experiment.

X1.3 Cathodic Currents During Anodic Polarization (Oxygen Effect)

X1.3.1 The “negative loop” at potentials between -0.350 V and -0.050 V, shown by dashed lines in Fig. X1.3, occurs when

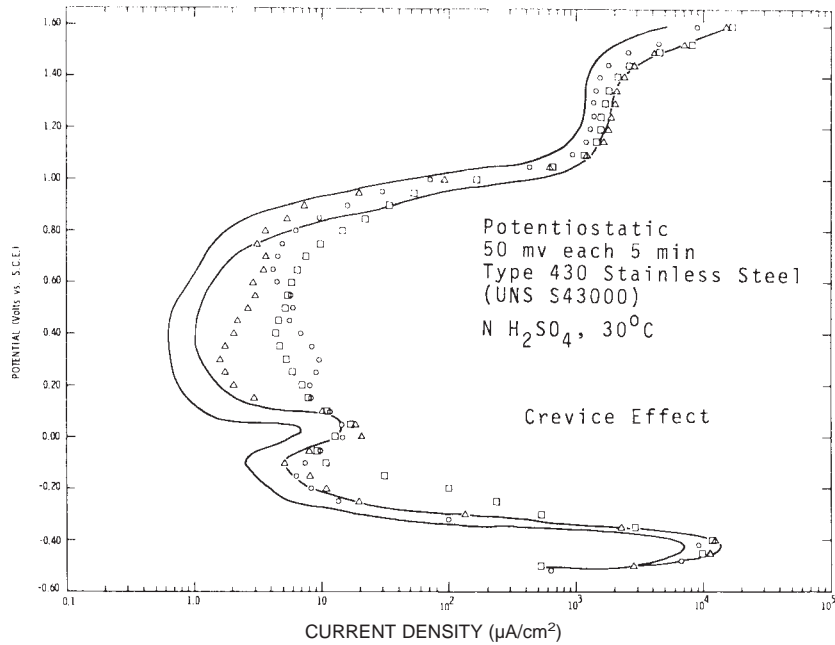


FIG. X1.1 Crevice Effect During Potentiostatic Anodic Polarization

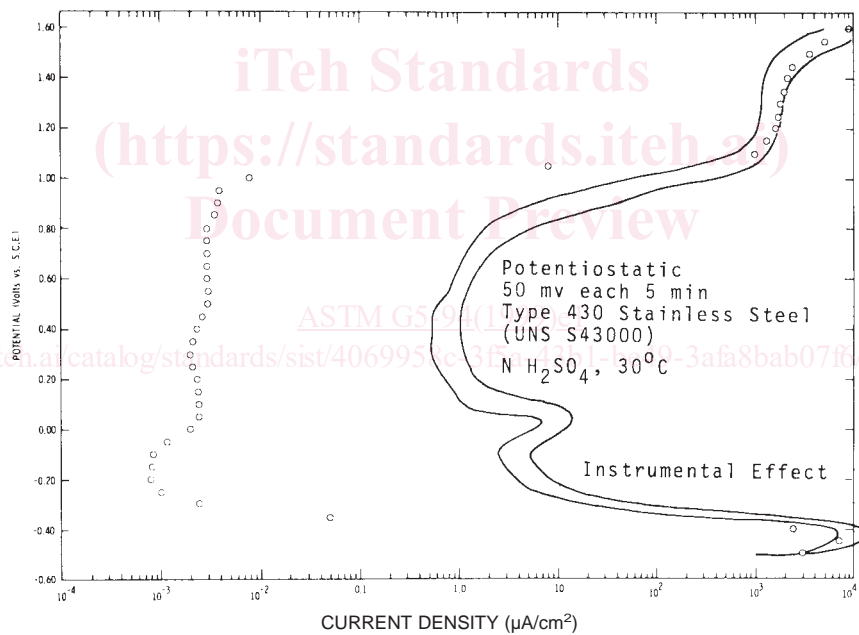


FIG. X1.2 Instrumental Effect During Potentiostatic Anodic Polarization

the total cathodic current exceeds the total anodic current. Such results are characteristic of oxygen being present in the solution (7). This effect can be anticipated if the recorded platinum potential is considerably more noble than -0.26 V. The gas purge should remove oxygen from the system, but

there may be an air leak or the purge gas may be contaminated with oxygen. It is necessary to take extreme care in the design of glassware equipment and to ensure a high order of purity in the gas that is used to avoid oxygen contamination.