



Standard Practice for Evaluation of Hydrogen Uptake, Permeation, and Transport in Metals by an Electrochemical Technique¹

This standard is issued under the fixed designation G148; 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 gives a procedure for the evaluation of hydrogen uptake, permeation, and transport in metals using an electrochemical technique which was developed by Devanathan and Stachurski.² While this practice is primarily intended for laboratory use, such measurements have been conducted in field or plant applications. Therefore, with proper adaptations, this practice can also be applied to such situations.

1.2 This practice describes calculation of an effective diffusivity of hydrogen atoms in a metal and for distinguishing reversible and irreversible trapping.

1.3 This practice specifies the method for evaluating hydrogen uptake in metals based on the steady-state hydrogen flux.

1.4 This practice gives guidance on preparation of specimens, control and monitoring of the environmental variables, test procedures, and possible analyses of results.

1.5 This practice can be applied in principle to all metals and alloys which have a high solubility for hydrogen, and for which the hydrogen permeation is measurable. This method can be used to rank the relative aggressivity of different environments in terms of the hydrogen uptake of the exposed metal.

1.6 *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:³

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 Devanathan, M.A.V., and Stachurski, Z., *Proceedings of Royal Society*, A270, 90–102, 1962.

³ 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.

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

3. Terminology

3.1 Definitions:

3.1.1 *charging, n*—method of introducing atomic hydrogen into the metal by galvanostatic charging (constant charging current), potentiostatic charging (constant electrode potential), free corrosion, or gaseous exposure.

3.1.2 *charging cell, n*—compartment in which hydrogen atoms are generated on the specimen surface. This includes both aqueous and gaseous charging.

3.1.3 *decay current, n*—decay of the hydrogen atom oxidation current due to a decrease in charging current.

3.1.4 *Fick's second law, n*—second order differential equation describing the concentration of diffusing specie as a function of position and time. The equation is of the form $\partial C(x,t)/\partial t = \partial/\partial x D_1 \partial/\partial x [C(x,t)]$ for lattice diffusion in one dimension where diffusivity is independent of concentration. See 3.2 for symbols.

3.1.5 *hydrogen flux, n*—the amount of hydrogen passing through the metal specimen per unit area as a function of time. The units are typically concentration per unit area per unit time.

3.1.6 *hydrogen uptake, n*—the concentration of hydrogen absorbed into the metal (for example, g/cm³ or mol/cm³).

3.1.7 *irreversible trap, n*—microstructural site at which a hydrogen atom has a infinite or extremely long residence time compared to the time-scale for permeation testing at the relevant temperature, as a result of a binding energy which is large relative to the migration energy for diffusion.

3.1.8 *mobile hydrogen atoms, n*—hydrogen atoms that are associated with sites within the lattice.

3.1.9 *oxidation cell, n*—compartment in which hydrogen atoms exiting from the metal specimen are oxidized.

3.1.10 *permeation current, n*—current measured in oxidation cell associated with oxidation of hydrogen atoms.

3.1.11 *permeation transient, n*—the increase of the permeation current with time from commencement of charging to the attainment of steady state, or modification of charging conditions (that is, rise transient). The decrease of the permeation

current with time resulting from a decrease in charging current (that is, decay transient).

3.1.12 *recombination poison*, n —chemical specie present within the test environment in the charging cell which enhances hydrogen absorption by retarding the recombination of hydrogen atoms adsorbed onto the metal surface into hydrogen gas.

3.1.13 *reversible trap*, n —microstructural site at which a hydrogen atom has a residence time which is greater than that for the lattice site but is small in relation to the time to attain steady-state permeation, as a result of low binding energy.

3.2 Symbols:

3.2.1 For the purposes of this practice the following symbols apply:

A	= exposed area of specimen in the oxidation cell (cm^2)
$C(x,t)$	= lattice concentration of hydrogen as a function of position and time (mol/cm^3)
C_o	= sub-surface concentration of atomic hydrogen at the charging side of the specimen (mol/cm^3)
D_{eff}	= effective diffusivity of atomic hydrogen, taking into account the presence of reversible and irreversible trapping (cm^2/s)
D_l	= lattice diffusion coefficient of atomic hydrogen (cm^2/s)
F	= faraday's constant (9.6485×10^4 coulombs/mol)
$I(t)$	= time dependent atomic hydrogen permeation current (μA)
I_{ss}	= steady-state atomic hydrogen permeation current (μA)
$J(t)$	= time-dependent atomic hydrogen permeation flux as measured on the oxidation side of the specimen ($\text{mol}/\text{s}/\text{cm}^2$)
J_{ss}	= atomic hydrogen permeation flux at steady-state ($\text{mol}/\text{s}/\text{cm}^2$)
$J(t)/J_{\text{ss}}$	= normalized flux of atomic hydrogen
L	= specimen thickness (cm)
t	= time elapsed from commencement of hydrogen charging (s)
t_b	= elapsed time measured extrapolating the linear portion of the rising permeation current transient to $J(t) = 0$ (s)
t_{lag}	= time to achieve a value of $J(t)/J_{\text{ss}} = 0.63$ (s)
x	= distance into specimen from the charging surface measured in the thickness direction (cm^2).
τ	= normalized time ($D_l t/L^2$)
τ_{lag}	= Normalized time to achieve a value of $j(t)/J_{\text{ss}} = 0.63$ (s)

4. Summary of Practice

4.1 The technique involves locating the metal membrane (that is, specimen) of interest between the hydrogen charging and oxidation cells. In the laboratory, the charging cell contains the environment of interest. Hydrogen atoms are generated on the membrane surface exposed to this environment. In field or plant measurements, the wall of the pipe or vessel can be used as the membrane through which measurement of hydrogen flux are made. The actual process environment is on the charging

side of the membrane which eliminates the need for a charging cell. See 7.1 for guidance on various specimen configurations.

4.2 In gaseous environments, the hydrogen atoms are generated by adsorption and dissociation of the gaseous species. In aqueous environments, hydrogen atoms are produced by electrochemical reactions. In both cases, some of the hydrogen atoms diffuse through the membrane and are then oxidized on exiting from the other side of the metal in the oxidation cell.

4.3 The conditions (for example, environment and the electrode potential) on the oxidation side of the membrane are controlled so that the metal surface is either passive or immune to corrosion. The background current established under these conditions prior to hydrogen transport should be relatively constant and small compared to that of the hydrogen atom oxidation current.

4.4 The electrode potential of the specimen in the oxidation cell is controlled at a value sufficiently positive to ensure that the kinetics of oxidation of hydrogen atoms are limited by the flux of hydrogen atoms, that is, the oxidation current density is diffusion limited.

4.5 The total oxidation current is monitored as a function of time. The total oxidation current comprises the background current and the current resulting from oxidation of hydrogen atoms. The latter is the permeation current.

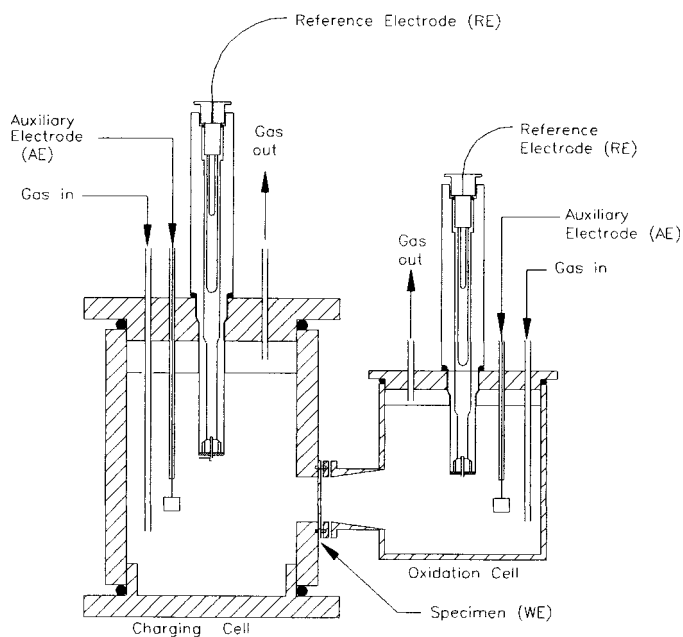
4.6 The thickness of the specimen is selected usually to ensure that the measured flux reflects volume (bulk) controlled hydrogen atom transport. Thin specimens may be used for evaluation of the effect of surface processes on hydrogen entry or exit (absorption kinetics or transport in oxide films).

4.7 In reasonably pure, defect-free metals (for example, single crystals) with a sufficiently low density of microstructural trap sites, atomic hydrogen transport through the material is controlled by lattice diffusion.

4.8 Alloying and microstructural features such as dislocations, grain boundaries, inclusions, and precipitate particles may act as trap sites for hydrogen thus delaying hydrogen transport. These traps may be reversible or irreversible depending on the binding energy associated with the particular trap sites compared to the energy associated with migration for hydrogen in the metal lattice.

4.9 The rate of hydrogen atom transport through the metal during the first permeation may be affected by both irreversible and reversible trapping as well as by the reduction of any oxides present on the charging surface. At steady state all of the irreversible traps are occupied. If the mobile hydrogen atoms are then removed and a subsequent permeation test conducted on the specimen the difference between the first and second permeation transients can be used to evaluate the influence of irreversible trapping on transport, assuming a negligible role of oxide reduction.

4.10 For some environments, the conditions on the charging side of the specimen may be suitably altered to induce a decay of the oxidation current after attainment of steady state. The rate of decay will be determined by diffusion and reversible trapping only and, hence, can also be used to evaluate the effect of irreversible trapping on transport during the first transient.



NOTE—A Luggin capillary should be used for more accurate measurement of potential when the current is large.

FIG. 1 PTFE Hydrogen Permeation Cell (with double junction reference electrodes, used for electrochemical charging)

4.11 Comparison of repeated permeation transients with those obtained for the pure metal can be used in principle to evaluate the effect of reversible trapping on atomic hydrogen transport.

4.12 This practice is suitable for systems in which hydrogen atoms are generated uniformly over the charging surface of the membrane. It is not usually applicable for evaluation of corroding systems in which pitting attack occurs unless the charging cell environment is designed to simulate the localized pit environment and the entire metal charging surface is active.

4.13 This practice can be used for stressed and unstressed specimens but testing of stressed specimens requires consideration of loading procedures.

5. Significance and Use

5.1 The procedures described, herein, can be used to evaluate the severity of hydrogen charging of a material produced by exposure to corrosive environments or by cathodic polarization. It can also be used to determine fundamental properties of materials in terms of hydrogen diffusion (for example, diffusivity of hydrogen) and the effects of metallurgical, processing, and environmental variables on diffusion of hydrogen in metals.

5.2 The data obtained from hydrogen permeation tests can be combined with other tests related to hydrogen embrittlement or hydrogen induced cracking to ascertain critical levels of hydrogen flux or hydrogen content in the material for cracking to occur.

6. Apparatus

6.1 The experimental set-up shall consist of a separate charging and oxidation cell of a form similar to Fig. 1. Sealed oxidation cells, in which an additional material (usually palla-

dium), either plated or sputter deposited onto or clamped against the specimen and the flux exiting this additional material is measured may be used provided that it is demonstrated that the introduction of this additional interface has no effect on the calculated diffusivity. The clamping of this additional material may provide inaccurate permeation currents in some systems due to the barrier effect at the interface (that is, oxides, air gaps and so forth will act as a diffusion barrier).

6.2 Non-metallic materials which are inert to the test environment should be used for cell construction.

6.2.1 At temperatures above 50°C, leaching from the cell material (for example, silica dissolution from glass in some environments) can modify the solution chemistry and may influence hydrogen permeation.

6.2.2 Polytetrafluoroethylene (PTFE) is an example of a material suitable for elevated temperatures up to about 90°C.

6.2.3 Where metallic chambers are necessary (for containment of high pressure environments), the materials chosen shall have a very low passive current to ensure minimal effect on the solution composition and shall be electrically isolated from the membrane.

6.3 The O-ring seal material should be selected to minimize possible degradation products from the seals and contamination of the solution. This problem is particularly of concern with highly aggressive environments and at high test temperatures.

6.4 Double junction reference electrodes may be used where necessary to avoid contamination of test solutions. At elevated temperatures, the use of a solution conductivity bridge arrangement with suitable inert materials is recommended.

6.5 The location of the reference electrode in each compartment shall ensure minimal potential drop between the specimen and the reference electrode. A Luggin capillary may be useful in cases where the solution resistivity is high, small cell volumes are used and long tests are conducted. See Guide G96 for further guidance.

6.6 Recording of oxidation (and, as appropriate, charging) current shall be made using a standard resistor and a high internal impedance digital voltmeter or by direct measurement using a current monitoring device.

6.7 The measurement devices should be traceable to national standards and calibrated prior to testing.

6.8 In some cases, stirring of the solution in the charging cell may be required. This should be performed using suitable stirring motor and apparatus.

7. Specimen

7.1 *Design*—Specimens may be in the form of plate or pipe. The dimensions shall enable analysis of the permeation transient based on one-dimensional diffusion. For example, for plates with a circular exposed area, the radius exposed to the solution should be sufficiently large relative to thickness. A ratio of radius to thickness of 10:1, or greater, is recommended. This condition may be made less stringent if the exposed area in the oxidation side is smaller than that on the charging side. A ratio of radius to thickness of 5:1 is acceptable if the radius of the exposed area on the oxidation side is reduced to 90 % of the area of the charging side. For pipes, the ratio of the outer radius to the inner radius should be less than 1:1 if the

experimental results are to be analyzed based on the equations for planar diffusion. Other specimen configurations may be used if limited by material form or equipment configuration. However, it should be realized that such conditions may limit the rigorous analysis of the data thus resulting in only qualitative information. However, in some cases, this may be sufficient to rank the influence of various environmental or material variables on hydrogen charging severity.

7.2 Preparation:

7.2.1 Hydrogen atom permeation may be influenced by microstructural orientation. The form of the original material should be indicated (for example, bar or plate) and the location and orientation of the specimen relative to that of the original material should be defined.

7.2.2 The manufacture of sheet specimens should be considered carefully. Various methods of machining may be used including electrochemical discharge machining (EDM) and mechanical cutting.

7.2.3 EDM is particularly useful for preparing slices of material but may introduce hydrogen into the metal. Although hydrogen dissolved in lattice sites or reversible trap sites may be lost subsequent to EDM, hydrogen atoms may be retained in irreversible trap sites. The amount of hydrogen generated and the extent of ingress into the metal will depend on the details of the EDM process and the material characteristics, but sufficient material should be removed by subsequent machining to ensure that all residual hydrogen atoms are removed.

7.2.4 Slices of material can be prepared by fine mechanical cutting and this method is preferred.

7.2.5 Sheet specimens shall be machined to the required thickness. Care should be taken in machining to minimize surface damage.

7.2.6 The thickness of the specimen in the region of interest shall be as uniform as possible with a maximum variation not greater than $\pm 5\%$.

7.2.7 The oxidation side of the specimen shall be mechanically polished to a repeatable finish. A 600 grit surface finish is recommended. The charging side may be similarly treated or used in condition similar to the service condition being modeled. Electropolishing of specimens may also be employed in appropriate cases where surface machining is difficult and may produce excessive cold working damage. However, electropolishing may induce hydrogen into the metal and may require the use of a low temperature heat treatment to reduce the amount of hydrogen in the metal prior to testing.

7.2.8 After polishing, the specimen shall be cleaned in non-chlorinated solvents to remove traces of polishing chemicals and degreased.

7.2.9 The final thickness shall be measured in at least five locations in the exposed region of the membrane. The specimen shall then be degreased in a suitable non-chlorinated solvent and stored in a dry environment or a dessicator.

7.2.10 Coating of the exit surface of the specimen with palladium or some other suitable material (for example nickel) to reduce the background current shall be undertaken at this stage, if required.

7.2.10.1 A thin palladium coating which does not resist through put of hydrogen is sometimes applied to one or both

sides of the membrane following initial removal of oxide films for the protection of the membrane.

7.2.10.2 A palladium coating on the charging face of the membrane will affect the sub-surface hydrogen concentration in the substrate and the measured permeation current. It is important to verify that the calculated diffusivity is not influenced by the coating. Electrochemical methods of forming the coating can introduce hydrogen atoms into the material and may influence the subsequent permeation measurements. Argon etching of the surface followed by sputter coating with palladium can avoid this problem. Palladium coating is particularly useful for gaseous charging.

7.2.10.3 Palladium coating of the oxidation side of the specimen can enhance the rate of oxidation and, thereby, enable attainment of transport limited oxidation of hydrogen atoms at less positive potentials than for the uncoated specimen.

7.2.11 A suitable electrical connection shall be made to the specimen remote from the active areas.

7.2.12 The specimen shall be uniquely identified. Stamping or scribing on the specimen remote from the active areas is recommended.

8. Test Environment

8.1 The test environment shall be relevant to the intended application, where applicable, or otherwise the environment should be chosen to facilitate ease and reliability of making hydrogen permeation measurements. Suggestions for suitable systems for the latter case are given in [Appendix X1](#).

8.2 The environments in the charging cell should be of purity for the intended purpose.

8.3 The environment in the oxidation cell shall be prepared using recognized analytical grade chemicals and distilled or deionized water of purity sufficient to avoid unintentional contamination.

8.4 If the environment in the charging cell is aqueous, the solution shall be either that directly used in service or a laboratory environment prepared with the purity as indicated in [8.3](#). Gaseous environments should simulate those for the intended application.

8.5 In some cases for which higher purity of the charging solution is desirable, the solution may be prepared using appropriate high purity analytical grade chemicals or pre-electrolysis may be employed. Pre-electrolysis can be used to remove certain cationic contaminants by cathodic deposition and usually involves applying a voltage difference between two platinum electrodes in the solution of interest. The area of the cathode should be as large as reasonable to enhance the rate of removal of contaminants.

8.6 A volume of solution to metal area ratio greater than 20 ml/cm² is usually adequate. The volume of solution in the oxidation chamber need not be particularly large since the extent of reaction is usually relatively small.

8.7 The volume of solution in the charging cell depends on the particular choice of environment and the extent of reaction on the specimen. Poisons added to enhance hydrogen entry may be consumed with time. The volume of solution shall be sufficient to minimize changes in solution composition during the course of the experiment, or periodic replenishment shall

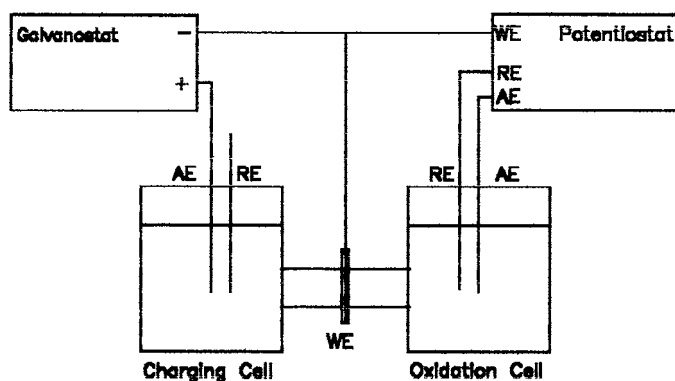


FIG. 2 Electrochemical Hydrogen Permeation Cell Assembly and the Measuring Apparatus

be used, as needed, to maintain the consumable species within suitable levels within the charging cell.

8.8 Flow of solution in the charging cell can affect the local environment at the surface in some cases. Where solution flow is relevant to a service condition, the flow conditions shall be simulated or testing should be conducted to enable repeatable conditions, whether using stirrers or vigorous purging or slow bubbling where the gas purge tube has been positioned close to the specimen.

8.9 Variations in the pH of the charging solution during a permeation transient may influence the form of the transient, even under constant charging current, because of its influence on surface films.

8.10 The temperature of the solution typically has a significant effect on hydrogen permeation. The temperature of the solutions in charging and oxidation cells should be nominally the same and maintained constant to $\pm 0.5^\circ\text{C}$ for the period of the experiment. Any variation should be recorded. This may be achieved using a temperature-controlled room or, in the case of small cells, by heating or cooling the outside of the cell with a thermostatically controlled fluid. In the latter case, when the charging compartment is refreshed continuously from a reservoir using a recirculation system, the temperature of the solution in the reservoir should be controlled carefully to minimize temperature gradients across the specimen.

9. Test Procedure

9.1 The specimen shall be prepared to desired surface finish and the thickness measured.

9.2 The solutions shall be prepared and pre-electrolysis carried out where desirable.

9.3 The pH of the solutions should be measured, if appropriate (see 10.1).

9.4 The reference electrodes shall be checked against at least one, and preferably two, other reference electrodes and shall be accurate to ± 5 mV. The choice of reference electrode is optional.

9.5 The two-compartment cell shall be put together with seals as appropriate. The cell assembly shall be connected to the electronic measuring apparatus as shown in Fig. 2.

9.6 The solution for the oxidation cell shall be added to the relevant chamber and vigorous purging with a suitable inert gas should be commenced to deaerate the solution quickly, even if

deaerated previously to minimize aeration during solution transfer. The potential shall be set to the control value ($+300$ mV SCE is typical for several metals exposed to 0.1M NaOH (see 9.12). The magnitude of the background oxidation (passive) current will depend on the system but values lower than $0.1 \mu\text{A}/\text{cm}^2$ are usually readily attainable.

9.7 The time at which the environment is added to the charging cell depends on the characteristics of the system but, ideally, addition of the environment should be made after the oxidation current has achieved a steady, low value. In some cases, aqueous solution may be added to the charging cell prior to the establishment of the steady-state oxidation current provided that exposure does not generate significant hydrogen, for example, a passivating system with a very low passive current.

9.8 In testing at elevated temperature, care should be taken to minimize thermal shock when adding the solution to the charging side as this can sometimes result in significant perturbation of the passive current in the oxidation cell.

9.9 If the solution is to be deaerated, this shall be done prior to addition to the charging cell or deaeration should commence by vigorous purging on addition of the solution to the charging cell to remove oxygen quickly depending on the sensitivity of the environment or material to oxygen contamination. Deaeration shall be continued during the test as required.

9.10 The stirring motor should be switched on, where used. For non-passivating systems galvanostatic charging or potentiostatic charging shall commence on exposure of the specimen.

9.11 For measurement of hydrogen permeation, the total oxidation current (comprising background passive current and atomic hydrogen oxidation or permeation current) shall be monitored versus time until steady-state is achieved.

9.12 The electrode potential of the specimen exposed to the oxidation compartment shall be chosen to ensure bulk transport-limited kinetics for oxidation of hydrogen atoms. In a preliminary test, and ideally for the test conditions for which the oxidation current is largest, the control potential on the oxidation side should be increased and the incremental current monitored. An initial increase in current will be obtained but for transport-limited kinetics this should subsequently decrease to a steady-state value equivalent to that obtained prior to the change in potential. If the steady current at the new potential is significantly higher, the electrode potential should be increased progressively until the steady current at each potential becomes independent of potential. This condition will define the control potential for the system.

9.13 In aqueous solutions, the exposure conditions on the charging side of the membrane may be chosen to represent a particular service situation involving corroding conditions or the conditions may be selected to maintain constancy of the sub-surface hydrogen concentration.

9.13.1 For characterization of hydrogen transport in the bulk of the material, galvanostatic charging is preferred. For reliable measurement, only minor changes in potential during testing should occur. Significant variation in potential indicates

changing surface state and unsteady boundary conditions which render uncertain the interpretation of the permeation transients.

9.13.2 Potentiostatic charging may also be used provided there are no significant variations in the current.

9.13.3 Variations immediately following exposure do not necessarily have an important influence on the permeation transient provided that the duration is short compared to the overall time of the transient.

9.14 In many cases, the measurements of permeation current versus time are useful in characterizing the severity of hydrogen charging. The parameters that should be noted are $J_{\max}$ and J_{ss} for the conditions being examined. In cases where J_{ss} is much less than $J_{\max}$, the indications are (a) formation of protective films on the charging surface of the membrane which impede hydrogen permeation, (b) formation of internal voids, blisters, or internal hydrogen induced cracking or (c) depletion of species in the charging solution such as recombination poisons.

9.15 To distinguish the effects of irreversible and reversible trapping on hydrogen transport, the charging current should be reduced to zero and sufficient time allowed for hydrogen atoms in interstitial lattice sites and reversible trap sites to exit. Monitoring of the permeation current will indicate when all the mobile hydrogen has been removed. If the charging current is not reduced to zero and, consequently, a permeation current remains, a residual concentration gradient exists and this will complete interpretation of subsequent increasing permeation transients. This consideration applies also to tests in which step increases in charging current are made (see 9.16). Irreversible trapping will not be detected using this procedure if the traps are already full (for example, from material processing) prior to the first permeation study.

9.16 The charging current may be reduced by reducing the applied current or potential or by changing the environment. If it is intended to analyze the decay current, the requirement for a defined boundary condition in analyzing the transient, means that the conditions on the charging side should be such as to oxidize or recombine the hydrogen at its transport limited rate.

9.17 Repetitive permeation transients may also be generated for some systems by withdrawing the specimen after attainment of steady-state permeation and allowing the hydrogen atoms to diffuse out. Elevated temperature baking may also be used to accelerate removal, provided this produces no microstructural changes. The specimen surface may then be repolished, cleaned, and the permeation procedure repeated.

9.18 The final pH of the solutions should be measured if appropriate 10.1).

9.19 The final thickness of the specimen shall be measured if significant corrosion has occurred.

9.20 Replicate tests should be conducted to determine repeatability of the measurements for the particular test conditions used.

9.21 Unless the thickness of the specimen represents a particular service application or required test condition, tests should be performed on at least three different specimen thicknesses. With increasing thickness of specimen, the significance of surface processes on the rate of transport will be

diminished with respect to transport through the bulk of the material. These tests will indicate the relative extent to which the transport of hydrogen is controlled by transport through the bulk of the material, or by surface processes, for example, absorption kinetics or transport through an oxide film.

10. Environmental Control and Monitoring

10.1 For galvanostatic/potentiostatic tests in very acid or alkaline solutions (0.1 M or greater), environmental variations during a test are often negligible, assuming that significant corrosion is not allowed to occur. In near-neutral solutions, pH changes may occur and the pH should be measured before and after a test.

10.2 For reliable interpretation of hydrogen permeation measurements, the surface condition in the charging cell should remain constant during a test. However, in some cases, changing corrosion conditions (for example, due to film formation) make it impossible to obtain constant charging conditions. For this reason, monitoring of the electrode potential is useful in galvanostatic tests because it gives an indication of changing surface state. Similarly, monitoring of the current is important in potentiostatic tests.

10.3 For tests in which H_2S gas is bubbled through the solution, monitoring of dissolved H_2S content of the solution by sampling and measurement should be conducted. Unless the purpose of the test is to define transient behavior, sufficient time shall be allowed for equilibrium to be obtained prior to exposure of the test specimen.

10.4 For tests with other recombination poisons, it is recommended that sampling of the charging solution be performed before and after permeation tests are made, at least once, for the particular experimental conditions being evaluated, to determine the extent of depletion of the poison that occurred during the test.

11. Procedures For Analysis of Results

11.1 The background current associated usually with the passive current of the oxidation cell shall be subtracted from the measured oxidation current prior to analysis of both steady-state and transient permeation currents.

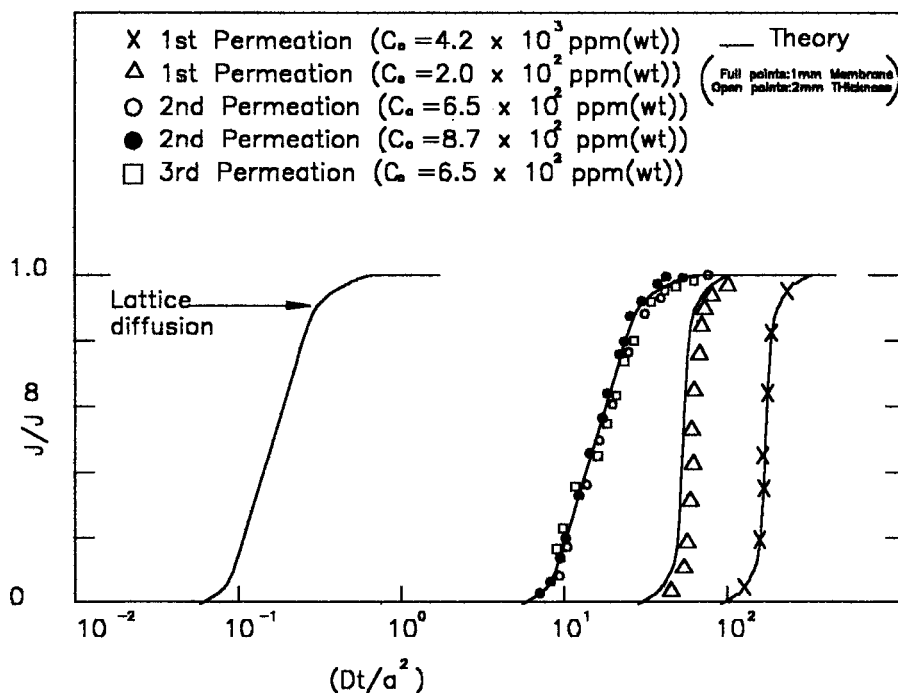
11.2 Analysis of the Steady-State Permeation Current:

11.2.1 The steady state permeation current (J_{ss}) gives information on the subsurface concentration of hydrogen atoms at the charging surface as follows:

$$J_{ss} = \frac{J_{ss}/A}{F} = \frac{D_1 C_0}{L} \quad (1)$$

For highly alloyed metals and for multiphase metals, Eq 1 may be inadequate. In highly alloyed metals, the lattice diffusion coefficient (D_1) may vary greatly from that of the primary element (for example, iron in corrosion resistant steels). In multiple materials (for example, in duplex stainless steels) diffusion path tortuosity and alternative diffusion paths through the material may need to be considered or an appropriate value of D_1 utilized.

11.2.2 A plot of J_{ss} against reciprocal thickness should be linear for volume controlled transport although this requires that the C_0 value in the separate experiments be identical.



NOTE—Rising permeation transients for BS 970 410S21 stainless steel in acidified NaCl at 77°C. Results show irreversible trapping (1st transient) and dependency on charging conditions (C_0 value). Note the time of delay and steepening of the curves relative to lattice diffusion (Fick's law), the similarity of second and third transients and the independence of thickness.

FIG. 3 Permeation Transients

11.2.3 When reversible trapping *only* is important *and* when the permeation transient for this case can be represented by Fick's first law, then:

$$J_{ss} = \frac{D_{eff} C_0}{L} \quad (2)$$

11.2.4 For some systems a peak in the transient may be observed and a steady current may not be attained. This can be due to the development of voids in the material or changes, or both, in surface film (for example, build up of corrosion product) on the charging side of the specimen.

11.3 Analysis of Permeation Transient:

11.3.1 The effective diffusion coefficient can be calculated based on the elapsed time (t_{lag}) at $J(t)/J_{ss} = 0.63$, the breakthrough time (t_b) or the slope method.⁴ For the calculation based on the elapsed time the following equation should be used:

$$D_{eff} = \frac{L^2}{6t_{lag}} = \frac{D_1}{6\tau_{lag}} \quad (3)$$

The effective diffusivity based on breakthrough time is given by the following equation:

$$D_{eff} = \frac{L^2}{15.3t_b} = \frac{D_1}{15.3\tau_b} \quad (4)$$

In the slope method, the effective diffusivity can be calculated from the slope of a plot of $\log(J_{ss} - J(t))$ versus $1/t$ which is linear with a slope of $L^2 \log(e)/4D$.

11.3.2 The values for D_{eff} calculated by the two methods or by curve fitting to the permeation transient shall be in agreement, if Fick's second law is applicable.

11.3.3 To verify applicability of Fick's second law to the permeation transient, plot the permeation transient in the form of normalized flux ($J(t)/J_{ss}$) against the logarithm of normalized time, τ , where $J(t)$ is calculated from

$$J(t) = \frac{I(t) / A}{F} \quad (5)$$

11.3.4 Compare the normalized transient with that derived from Fick's second law which for rising transients is given by:

$$\frac{J(t)}{J_{ss}} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 \pi^2 \tau) \quad (6)$$

where:

$$\tau = D_{eff} t / L^2$$

A summation from $n = 1$ to 6 is sufficiently accurate and in many cases $n = 3$ is acceptable.

11.3.5 If the permeation transient is steeper than predicted from Fick's second law, this indicates that trap occupancy is significant. A permeation transient which is less steep than predicted from Fick's second law is often an indication of unsteady surface conditions. If volume-controlled transport is of primary interest, this test should be repeated with increased specimen thickness to confirm the results.

11.3.6 If the first permeation transient takes longer than the second permeation transient, that is the normalized permeation curves are displaced to longer times (see Fig. 3 in Appendix X1), it can be deduced that irreversible traps exist and affect permeation.

⁴ McBreen, J., Nanis, L., and Beck, W., *Journal of Electrochemical Soc.*, Vol 113, 1966, pp. 1218–1222.

11.3.7 In the absence of void or blister formation or hydrogen induced cracking, the second and subsequent transients should show the same permeation behavior provided the C_0 values are similar.

11.3.8 An effective diffusion coefficient may be calculated for transients steeper than that associated with Fick's second law using Eq 3 but it has no theoretical basis since the steepness of the permeation transient indicates a changing effective diffusivity with time. Hence, values based on t_{lag} and t_b will differ. For comparative purposes, it is recommended that the calculation based on t_{lag} should be quoted.

11.3.9 Analysis of second and subsequent transients, which are steeper than predicted by Fick's second law, may be carried out to quantify the binding energy and the density of reversible trap sites. However, the analysis is non-trivial and involves numerical solution of mass conservation equations incorporating diffusion and reversible trapping with the trap occupancy term incorporated.

11.3.10 Analysis of *first* permeation transients which are steeper than Fick's second law should account for both reversible and irreversible traps and this, also, necessitates numerical analysis.

11.3.11 When peaks in the transients are observed (see 11.2.4), this implies the value of the effective diffusivity is also varying with time and analysis is uncertain, but Eq 3 may be used as an empirical estimate at $J(t)/J_{ss} = 0.63$.

11.3.12 In analyzing the results from step charging experiments, initial hydrogen flux shall be accounted for. A simple subtraction may not be valid. An initial atomic hydrogen concentration gradient exists in the metal and this renders conventional analysis invalid unless the initial steady permeation current is less than 5 % of the final steady current. More extensive analysis may be required.

12. Reporting

12.1 Report the following information:

12.1.1 Test material characterization in terms of specification, product form, chemical composition, and heat treatment.

12.1.2 The orientation and location of the specimen relative to parent product.

12.1.3 Method of specimen preparation.

12.1.4 Average thickness of specimen and exposed area in charging and oxidation cells. Average thickness of specimen

after test, if changed. If the distribution of the thickness (see 7.2.6 and 7.2.9) is outside the recommended range, the individual measured values should be reported.

12.1.5 Description of the environment chamber and the volume of solution in the charging and oxidation cells. For gaseous charging, the pressure of the gas in the charging compartment should be specified.

12.1.6 Initial solution composition and purity of solvent and chemicals in both compartments. Where appropriate, pH, degree of aeration, flow conditions, and temperature and final values of these variables should be recorded. For tests in aqueous solutions containing H_2S , the initial and final concentrations should be recorded.

12.1.7 For gaseous charging, the composition and purity of the gas should be stated.

12.1.8 The test procedure should be described with reference to the recommendations in Section 9.

12.1.9 The controlling electrode potential in the oxidation cell in terms of the standard hydrogen electrode or a saturated calomel electrode at 25°C. A Ag/AgCl electrode may also be used provided the electrode solution is defined.

12.1.10 The electrochemical conditions in the charging cell and any variation during the test, for example, significant variation in electrode potential during galvanostatic charging.

12.1.11 The method of obtaining repeat transients.

12.1.12 The appearance of the surfaces of the specimen after testing if changed significantly from the initial condition.

12.1.13 The form of the data output is optional but shall include at least the background passive current density and the steady-state permeation current density or the C_0 value. The lattice diffusivity used in Eq 1 to calculate C_0 shall be reported. The effective diffusion coefficient may also be reported but its method of determination should be quoted. The variability of the parameters should be indicated. A representative example of $J(t)/J_{ss}$ or $I(t)/L_{ss}$ versus t or τ should be included.

12.1.14 The shape of the transient relative to the prediction from Fick's law should be noted and observation of any peak in the transient should be reported.

13. Keywords

13.1 charging; decay current; diffusivity; electrochemistry; flux; hydrogen; permeation; transient



APPENDIX

(Nonmandatory Information)

X1. SUGGESTED TEST CONDITIONS FOR SPECIFIC ALLOY TYPES

X1.1 *General*—This appendix gives examples of test conditions suitable for measurement of hydrogen diffusivity and trapping within the volume of the material for alloy systems for which a reliable range of data and testing experience are available.

X1.2 Stainless Steels*X1.2.1 Martensitic Stainless Steel:*

X1.2.1.1 The environment in both cells should be 0.1M NaOH. The potential in the oxidation cell should be set at about +300 mV (SCE). Cathodic polarization with charging currents of about 1 mA/cm² can be used to generate hydrogen. On attainment of steady-state, the potential of the charging surface can be set to +300 mV (SCE). The permeation current will then decay to the passive current and the cathodic charging current can then be reapplied to generate a second permeation transient.

X1.2.1.2 An alternative approach to the cathodic polarization which generates much higher C_0 values and permeation currents involves using acidified 0.5 M NaCl in the charging cell. At a pH value of about 2.6, the oxide film is rapidly dissolved and charging is induced by the corrosion current. Subsequent transients can be obtained by removal of the specimen and baking out the hydrogen overnight at about 80°C before retesting.

X1.2.1.3 Since the steel is ferritic, diffusivities are relatively high and specimen thicknesses of about 250 μm or greater at 20°C and about 1 mm at 80°C are recommended.

X1.2.2 Duplex Stainless Steel:

X1.2.2.1 The environment in both cells should be 0.1M NaOH and the potential of the specimen in the oxidation cell should be +300 mV (SCE). Cathodic polarization with charging currents of about 1 mA/cm² can be used to generate hydrogen atoms. Subsequent transients can be determined by polarizing the charging surface to +300 mV (SCE) before reapplying cathodic charging.

X1.2.2.2 Specimens of 100 μm thickness are typically used at 20°C. At temperatures greater than 80°C, typical specimen thickness used is 200 μm.

X1.2.3 Austenitic Stainless Steel:

X1.2.3.1 The test conditions should be those for duplex stainless steel. Since the diffusivity of hydrogen in austenitic stainless steel is very low, testing at a temperature of about 80°C is recommended. The acceptable specimen thickness depends on the temperature and specific recommendations for

this alloy type are not possible because of lack of data. Nevertheless, the values of thickness recommended for the duplex stainless steel would probably be more than adequate for austenitic stainless steels and could be adopted initially.

X1.3 Nickel Alloys

X1.3.1 The test conditions should be those for duplex stainless steels.

X1.3.2 The diffusivity of these face centered cubic alloys will be small compared to body centered cubic systems. Accordingly, testing at elevated temperatures (for example, 80°C) may be preferred. Specimen thicknesses of 200 μm or greater are recommended for pure nickel and 100 μm or greater for Alloys 600 (NJS N06600), X-750 (UNS N07750), and 718 (UNS N07718) at 80°C.

X1.4 Carbon, Carbon-Manganese and Other Low Alloy Steels

X1.4.1 0.1 M to 1 M NaOH is recommended for the environment in the oxidation cell with the electrode potential set to +300 mV (SCE). No specific recommendation can be given for the environment in the charging cell. For example, cathodic charging in 0.1M NaOH leads to a transient surface state with permeation transients which are usually shallower than Fick's law and not very repeatable. The transients can be very prolonged with a slow drift to steady-state. Testing in acid solution can lead to the development of voids and a peak in the current transient which makes analysis difficult.

X1.4.2 Palladium coating of the charging surface prior to cathodic charging in 0.1M NaOH can minimize variations in surface conditions during the permeation transient and yield repeatable transients provided the specimen thickness is adequate.

X1.4.3 The effective diffusivity of low alloy steels can vary by orders of magnitude depending on the material composition and microstructure and general recommendations for the thickness of the specimen cannot be made. For tests at 20°C, the specimen thickness can range from 1.0 mm to the order of centimeters.

X1.4.4 Aqueous charging of low alloy steels in H₂S environments may give rise to high values of the hydrogen permeation current. Depending on the thickness of specimen, palladium coating of the oxidation surface may provide more repeatable data because of the increased efficiency of the hydrogen atom oxidation reaction.

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