Analysis of Electrochemical Experiments for Evaluation of Susceptibility to Embrittlement by Hydrogen Gas

R. E. Ricker, D. J. Pitchure, and M R Stoudt

Materials Science and Engineering Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899-8553

Introduction
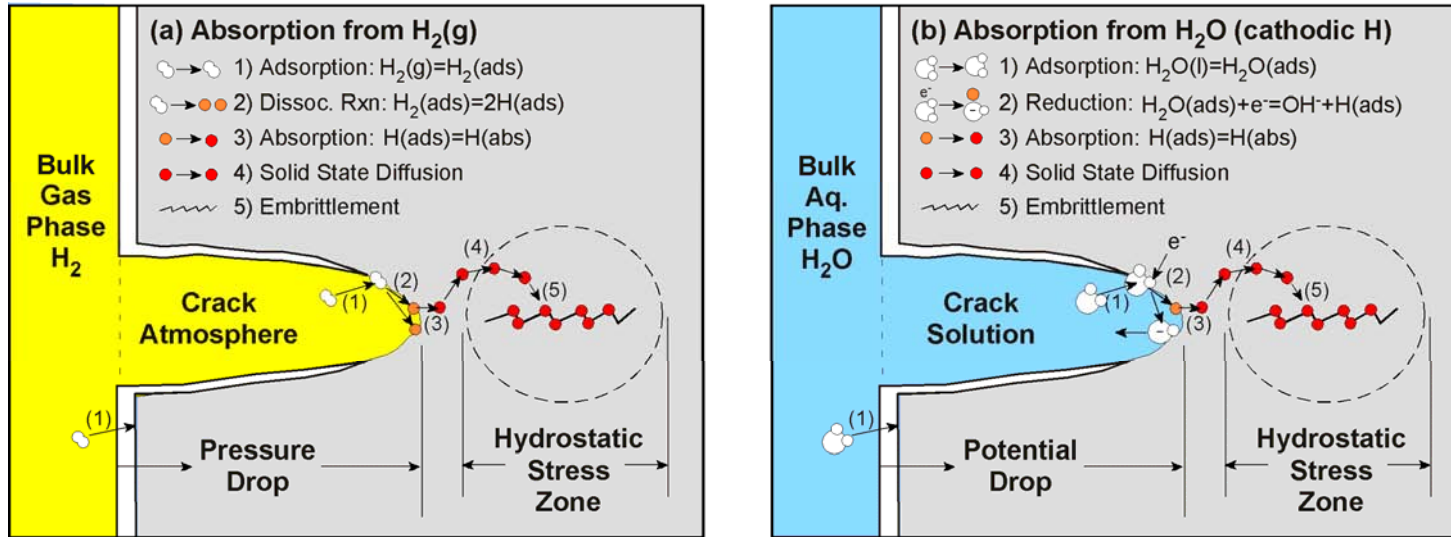## NIST Program Objectives

Innovation and growth in the emerging hydrogen economy will be facilitated by advances in two categories of testing methods:

- <u>Qualification methods</u> - to obtain design level data for codes and standards or to qualify existing materials and technologies for use with hydrogen

- <u>Research screening methods</u> - to enable innovation and guide the development of hydrogen resistant materials and technologies.

The NIST Materials Reliability and Metallurgy Divisions are collaborating on a program that is addressing both of these areas of need

Assumptions
Hydrogen Embrittlement

(a) Absorption from $H_2(g)$
1) Adsorption: $H_2(g)=H_2(ads)$
2) Dissoc. Rxn: $H_2(ads)=2H(ads)$
3) Absorption: $H(ads)=H(abs)$
4) Solid State Diffusion
5) Embrittlement

Bulk Gas Phase H_2 — Crack Atmosphere — (1) (2) (3) (4) (5) — Pressure Drop — Hydrostatic Stress Zone

(b) Absorption from H_2O (cathodic H)
1) Adsorption: $H_2O(l)=H_2O(ads)$
2) Reduction: $H_2O(ads)+e^-=OH^-+H(ads)$
3) Absorption: $H(ads)=H(abs)$
4) Solid State Diffusion
5) Embrittlement

Bulk Aq. Phase H_2O — Crack Solution — (1) (2) (3) (4) (5) e^- — Potential Drop — Hydrostatic Stress Zone

1. Hydrogen will cause embrittlement in fuel systems by a mechanism as illustrated at left above where embrittlement actually occurs in the hydrostatically stressed region of the plastic zone ahead of the crack tip.

2. The properties of the material and the concentration or activity of hydrogen in the hydrostatic zone determines the extent of embrittlement.

3. Therefore, the surface reactions can only influence embrittlement through hydrogen concentration or activity and equivalent concentrations will produce essentially identical behavior regardless of the hydrogen source.
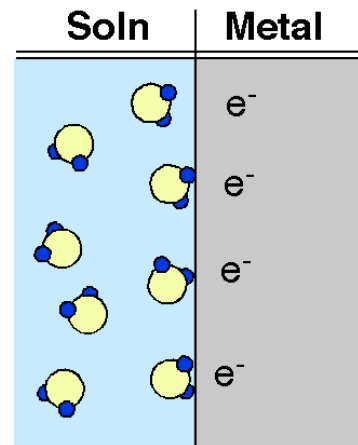
Electrochemical Hydrogen Charging Note
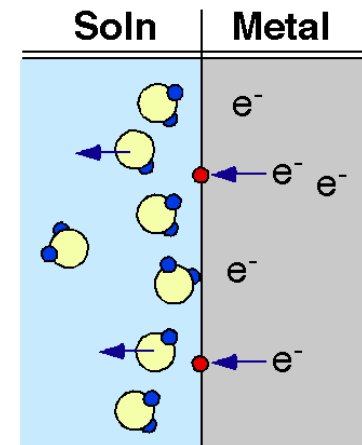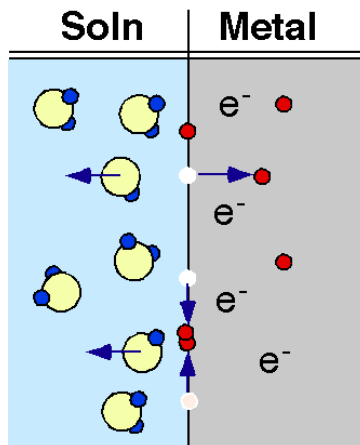## Cathodic Currents Produce H(ads) - The H(ads) Produces H$_2$(g)

a) E≈PZC
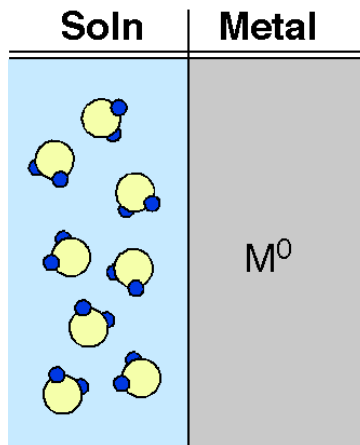
b) PZC>E

c) PZC>>E - H(ads)
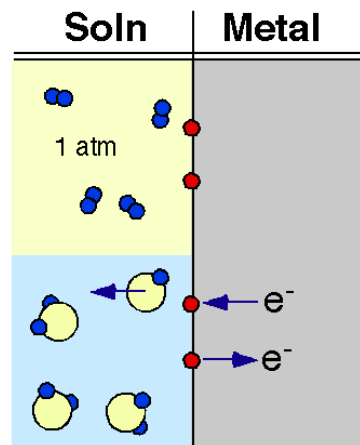
d) Recomb/Abs

e) E=E(H$^+$/H$_2$(1 atm))
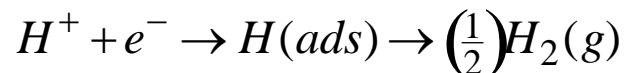
f) Bubble Nucleation

$\Delta G_{xs} = -nF\Delta E$
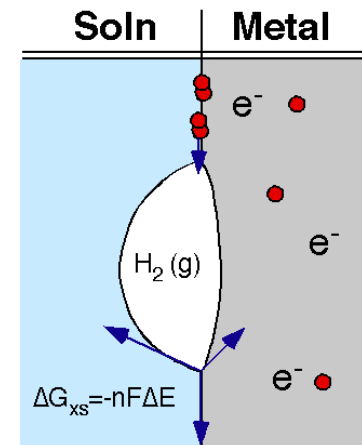
Therefore, the limiting partial pressure is not the pressure in the bubbles on the surface,
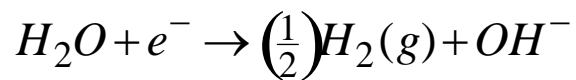*but the much greater pressure required to nucleate the bubbles.*

Electrochemistry
HER Basics and Electrochemical Equilibria for Fe in H₂O

- Reaction in acidic solutions

$$H^+ + e^- \rightarrow H(ads) \rightarrow \left(\tfrac{1}{2}\right)H_2(g)$$

- In neutral and basic solutions

$$H_2O + e^- \rightarrow \left(\tfrac{1}{2}\right)H_2(g) + OH^-$$

- Equilibrium Constant
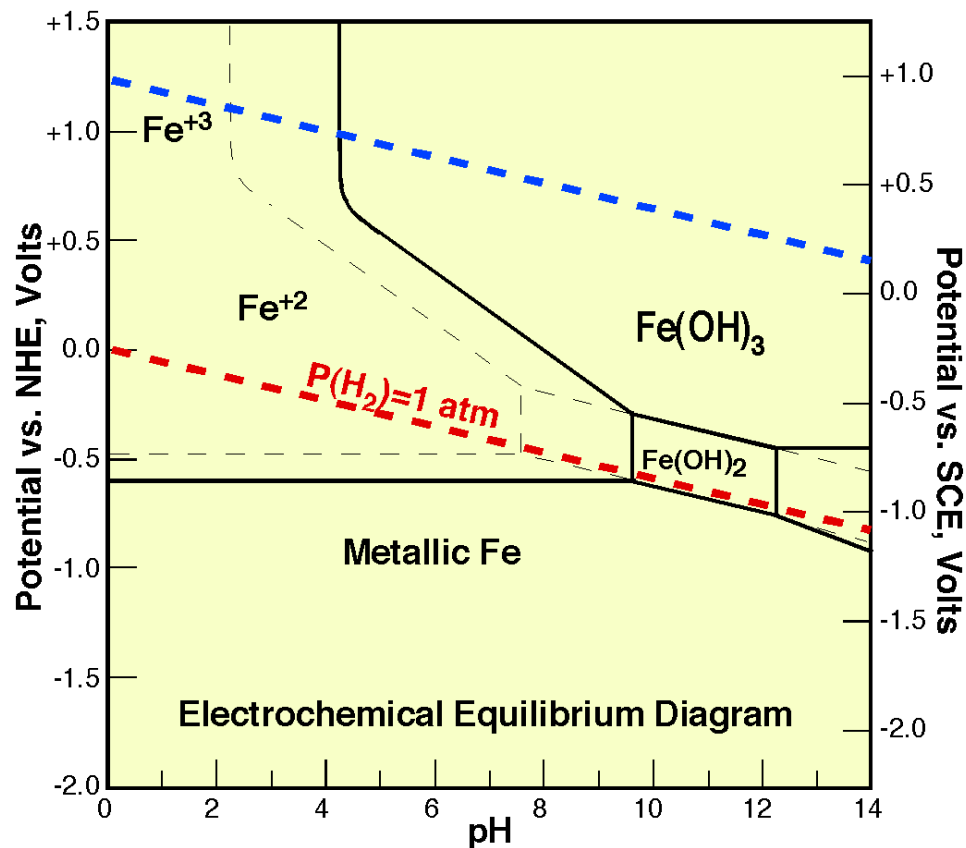
$$K_{eq} = \frac{[H_2]^{0.5}}{[H^+]}$$

- Potential and Free Energy

$$\Delta G = -nFE$$

- Nernst Equation

$$E_{eq} = E^0 - \left(\frac{RT}{nF}\right)\ln\left(K_{eq}\right)$$

$$E_{eq} = E^0 - (0.0296)\log[P(H_2)] - (0.059)pH$$



Electrochemical Equilibrium Diagram

Electrochemistry
Diffusion and Solubility Measurement Techniques

Electrochemical methods can be used to measure:

1) hydrogen diffusion rates
2) hydrogen solubility
3) hydrogen absorption from service environments
4) the influence of metallurgical variables on these factors

A. Electrochemical Permeation - Devanathan and Stachurski (1962) and ASTM G148
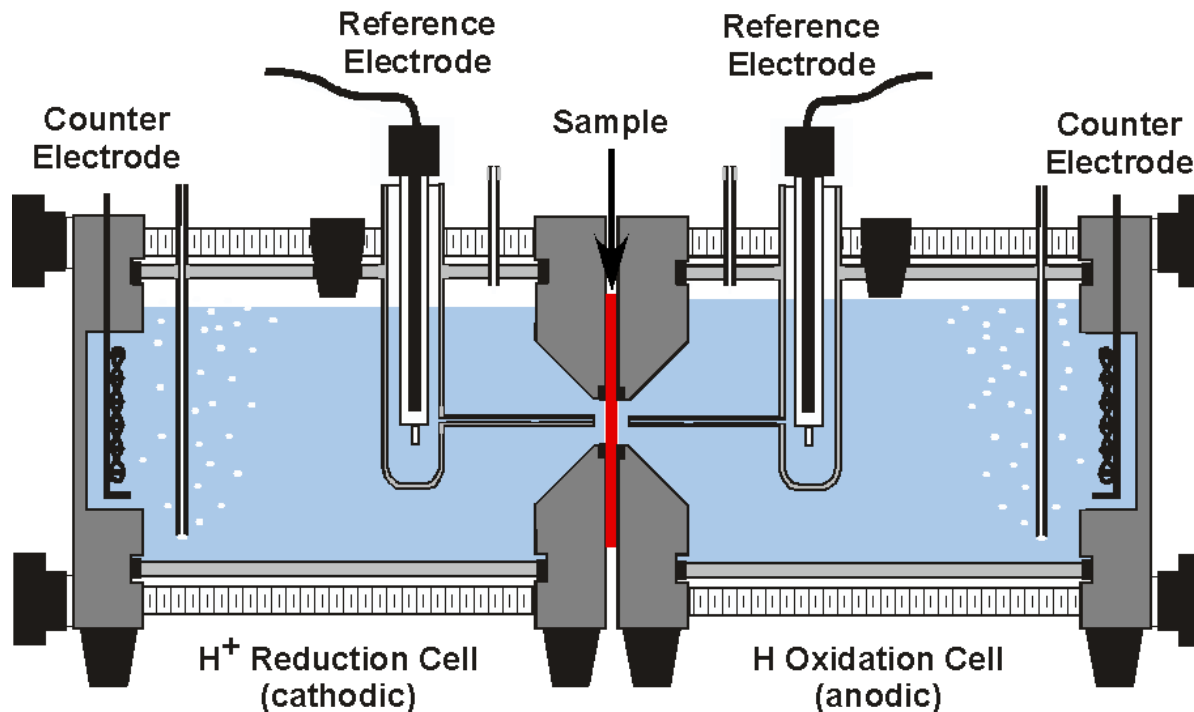
Electrochemical Permeation
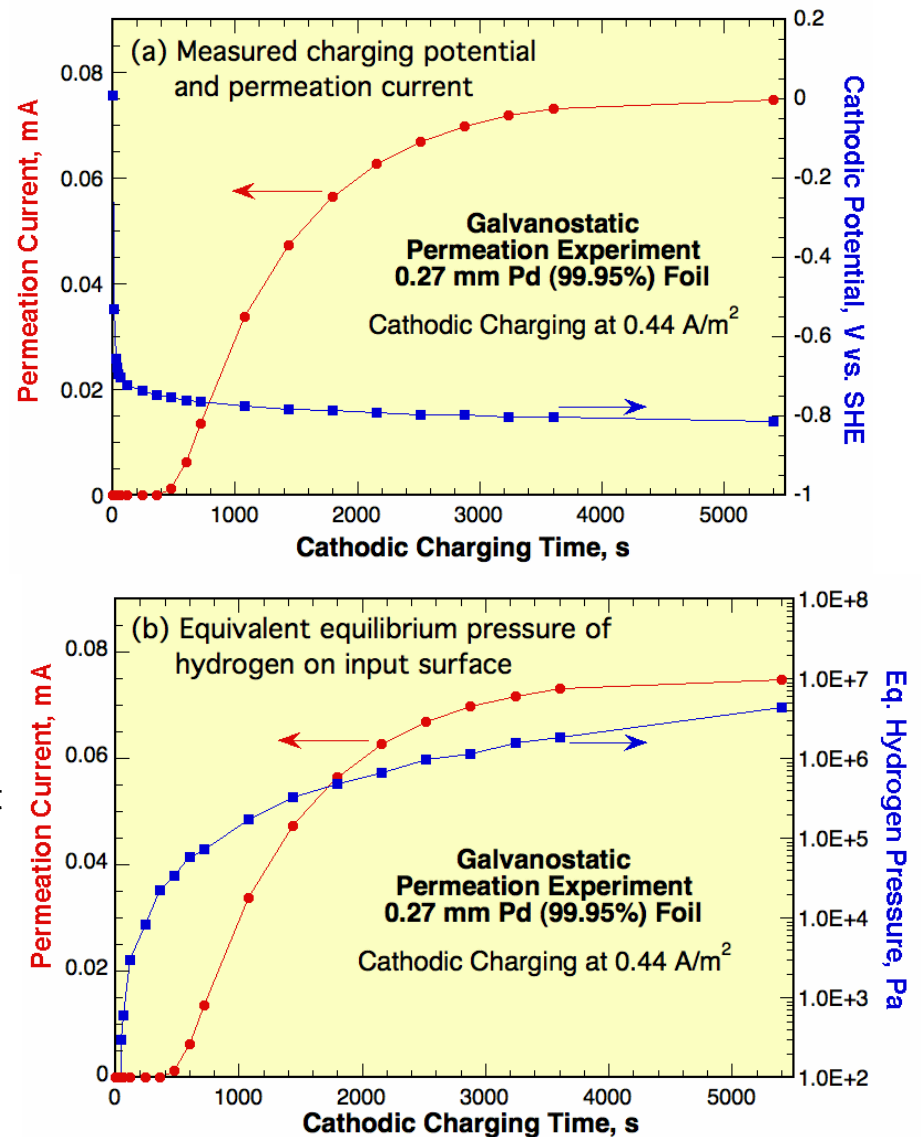## Evaluation of Constant Current Charging Conditions

The model used to estimate the diffusion coefficient from electrochemical permeation experiments assumes constant concentration at the input and output surfaces.

Devanathan and Stachurski (1962) and most investigators use constant cathodic current charging similar to that frequently used to charge mechanical property samples with hydrogen for testing.

By measuring the potential of the charging surface during a permeation experiment, Figure (a), and converting these measurements to the equivalent hydrogen pressure, Figure (b), it can be seen that the concentration on the input surface is not constant. In fact, it is constantly increasing over the duration of the test.

Therefore, constant current charging will delay the time required to reach steady state and lower the diffusion coefficient estimated from these experiments. Constant current charging should not be used for mechanical property samples because reproducible homogeneous distributions of hydrogen cannot be obtained.

Constant potential charging by closed loop control of sample potential with respect to a reference electrode reduces these errors.

(a) Measured charging potential and permeation current

Galvanostatic Permeation Experiment 0.27 mm Pd (99.95%) Foil

Cathodic Charging at 0.44 A/m^2

(b) Equivalent equilibrium pressure of hydrogen on input surface

Galvanostatic Permeation Experiment 0.27 mm Pd (99.95%) Foil

Cathodic Charging at 0.44 A/m^2

Electrochemistry
Diffusion and Solubility Measurement Techniques

B. Electrochemical Absorption-Desorption Experiments
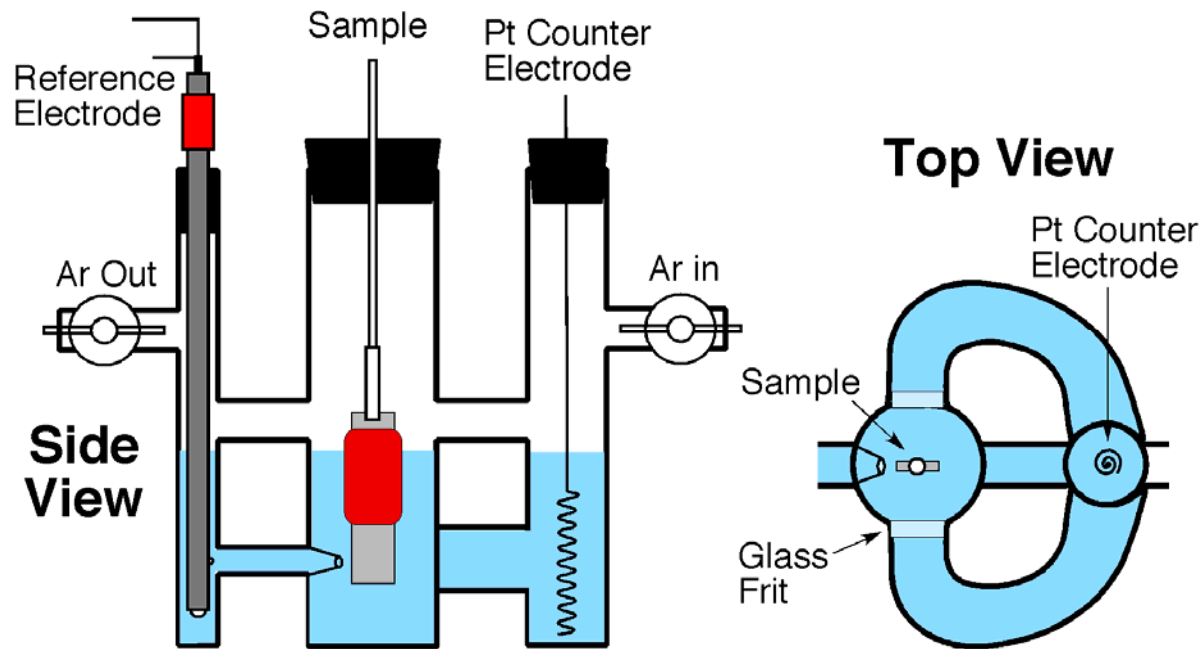
We started using this technique when we noted that the hydrogen charging current for flat tensile samples decreased with charging time indicating that the current was measuring hydrogen uptake and the samples were becoming saturated with hydrogen.

Electrochemical Absorption-Desorption
## Comparison of HY-100 and HSLA-100 Steels

Figure (a) shows a hydrogen desorption or extraction transient for 2 steels and figure (b) shows the total fluence from the sample as determined by integrating the measured current with respect to time.

By comparing these transients, it can be seen that (i) the diffusion rate in the samples is nearly equal, and (ii) the HY-100 steel held more hydrogen.

The diffusion coefficients determined from these transients by the time lag technique are

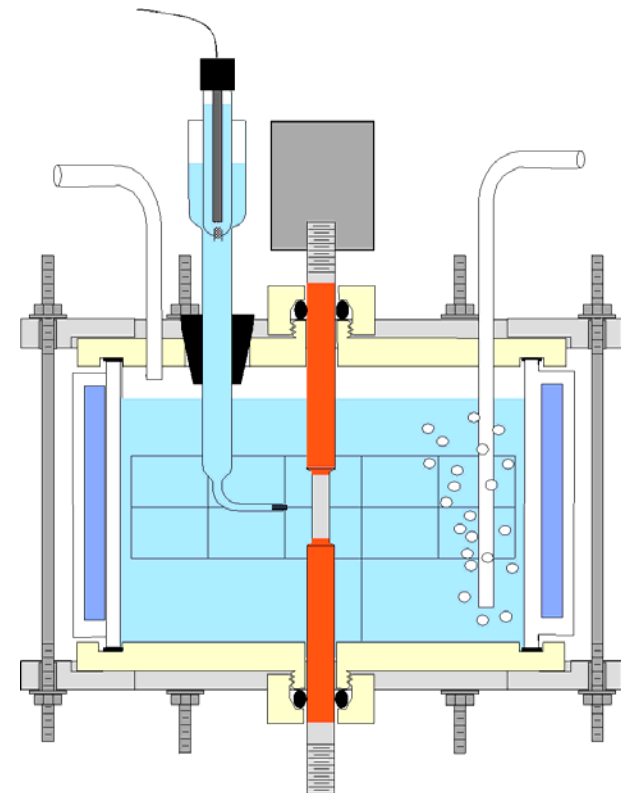And the hydrogen contents determined from these transients are

Comparing these numbers to
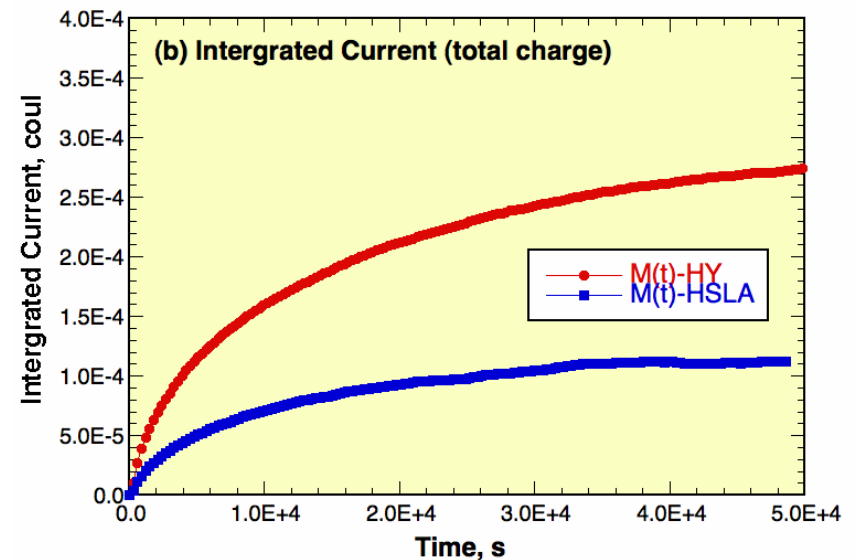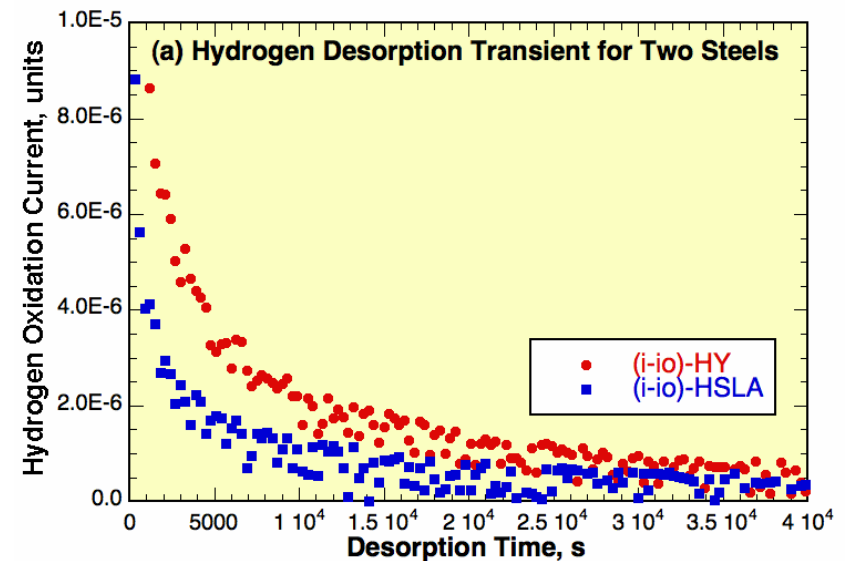
(a) Hydrogen Desorption Transient for Two Steels


(b) Intergrated Current (total charge)

Slow Strain Rate Tensile Testing Facilities for Testing in Aqueous Solutions Under Controlled Electrochemical Conditions and in Gasses at Constant Temperature and Pressure
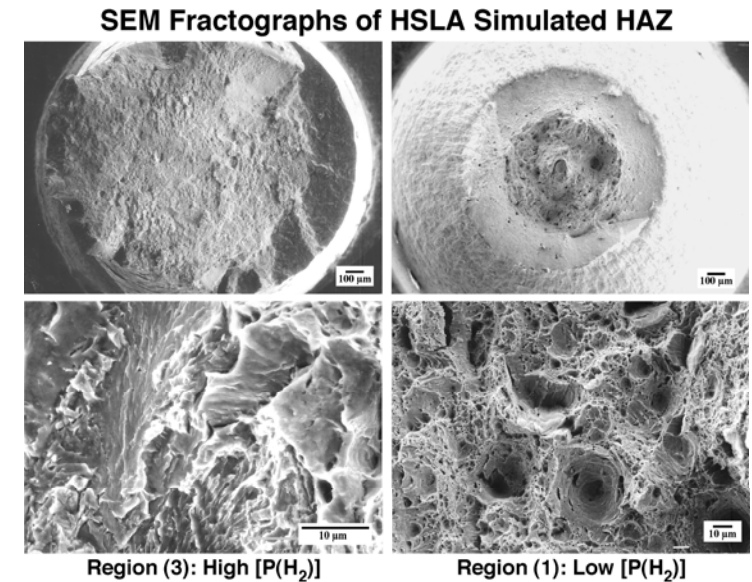
Mechanical Properties
Electrochemical Methods for Hydrogen Charging

Reduction in area results of slow strain rate tensile tests on two different types of steels (HY-100 and HSLA-100) and simulated weld heat affected zones (HAZ) as a function of the potentiostatically controlled potential of the sample with respect to a saturated calomel reference electrode (SCE)

Slow Strain Rate Tensile Tests
- HY-100 PM
- HY-100 HAZ
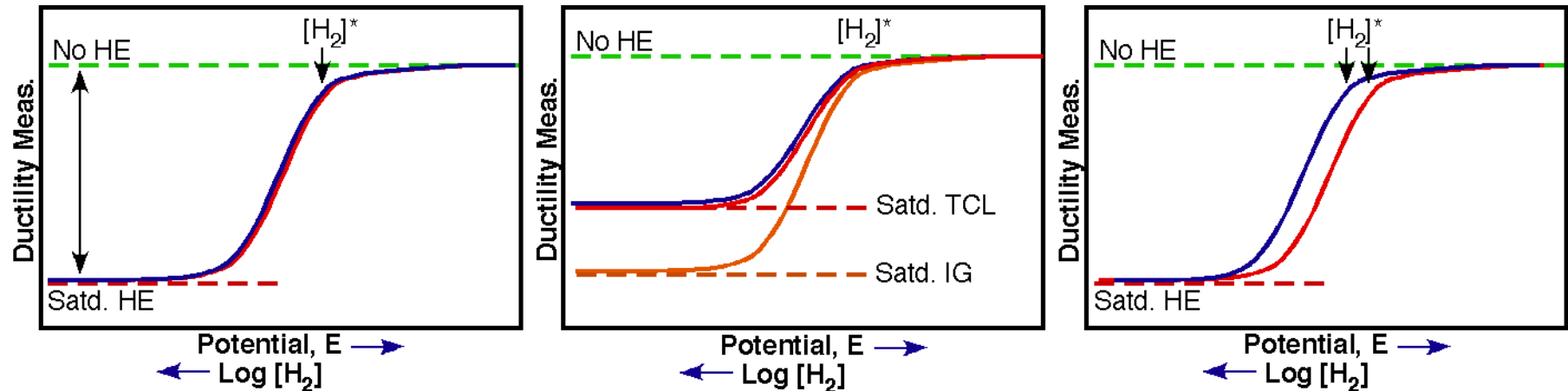- HSLA-100 PM
- HSLA-100 HAZ

Reduction in Area

Controlled Potential, Volts vs. SCE
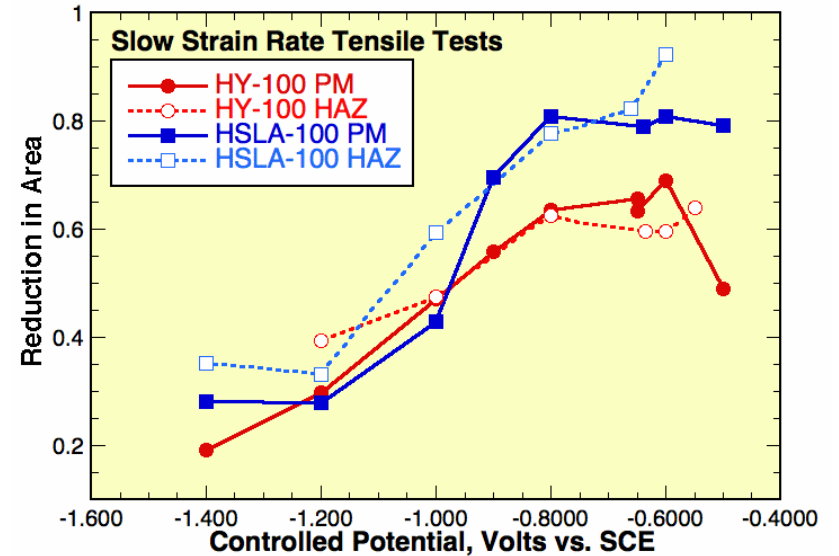
Influence of hydrogen partial pressure (fugacity) on the ductility and fracture mode of simulated weld HAZ samples.

SEM Fractographs of HSLA Simulated HAZ

Region (3): High [P(H$_2$)]   Region (1): Low [P(H$_2$)]

Mechanical Properties
Electrochemical Methods for Hydrogen Charging

It was assumed at the beginning of this paper that the extent of hydrogen embrittlement was determined by the properties of the materials and the hydrogen activity.

If this assumption is valid, then the results indicate that metrology research is needed to reduce the uncertainties in using electrochemical methods to charge samples with hydrogen.

This research needs to correlate electrochemical charging conditions with hydrogen contents to equivalent measurements on the same materials using gas phase techniques to identify the sources of experimental errors due to the assumption of equilibrium in the Nernst equation used to relate potential to hydrogen gas pressure.
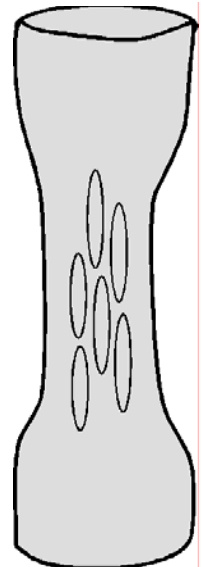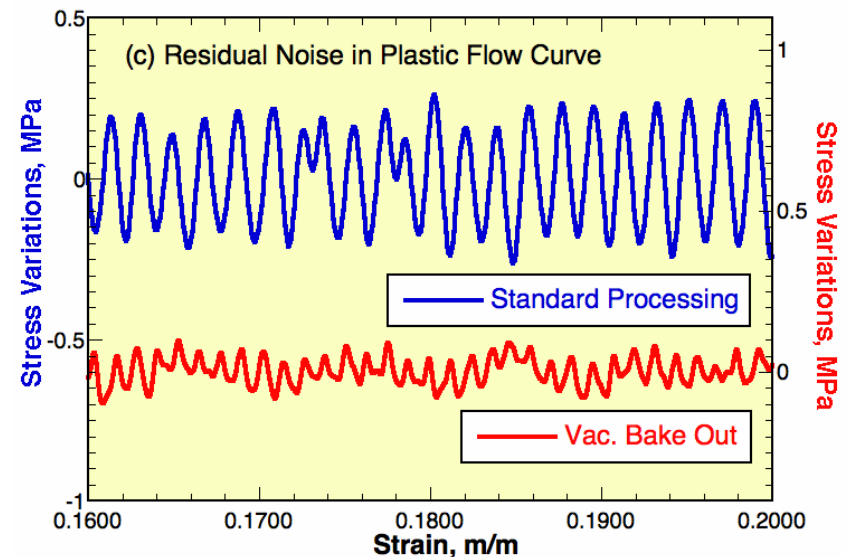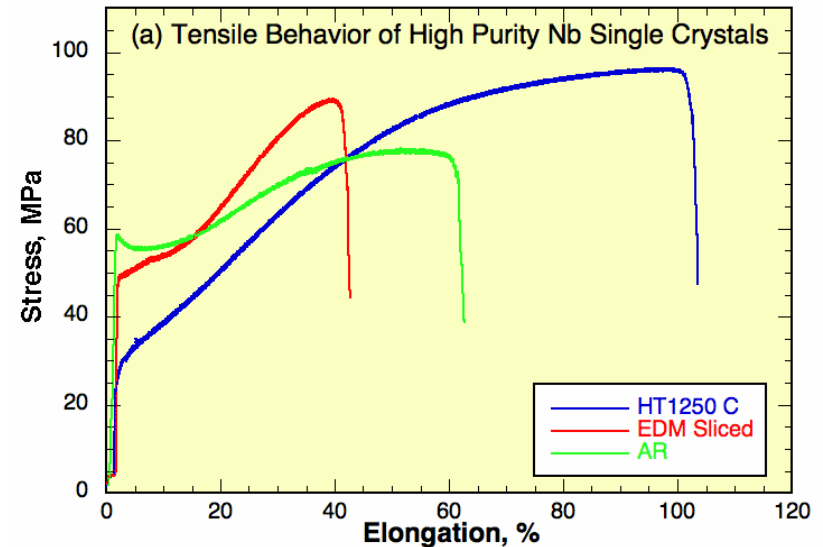
Analysis Methods
Time Series Analysis of Tensile Flow Curves

Tensile flow curves for high purity single crystal Nb samples following different processing paths.

The samples are of the same crystallographic orientation and only the processing is different.

Nb is sufficiently active to reduce hydrogen from aqueous solutions and the water vapor in air. Therefore, processing influence H uptake and vacuum annealing at 1250°C removes hydrogen.

Examination of the residual noise after subtraction of a curve fit to the tensile flow curve indicates that vacuum annealing reduces the serrated yielding attributed to interstitial interactions with dislocation motion.
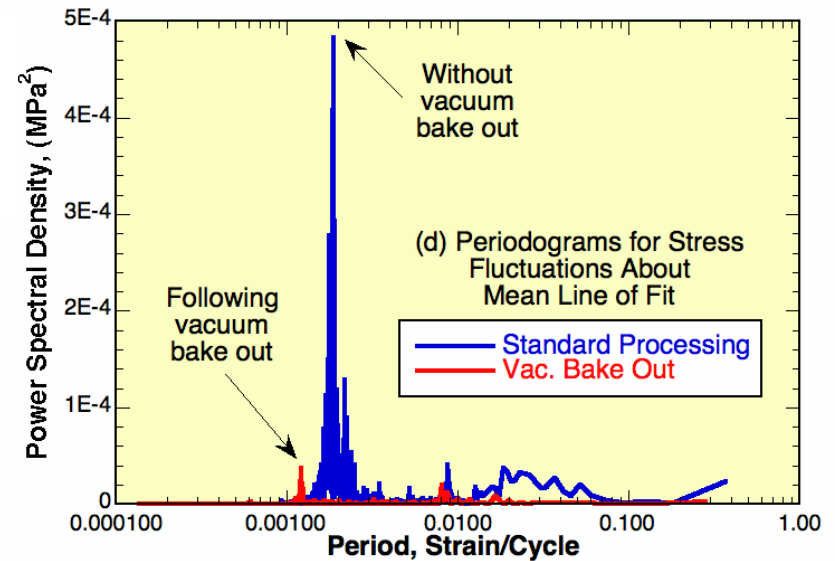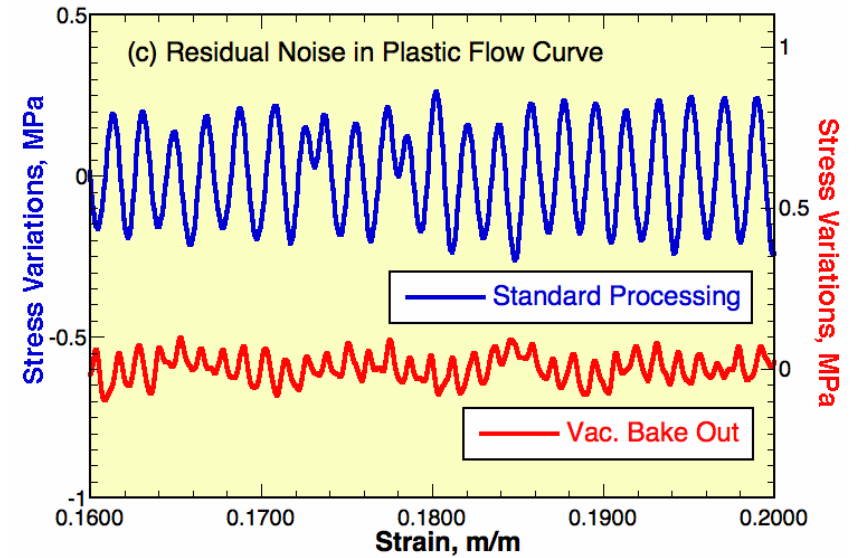

(a) Tensile Behavior of High Purity Nb Single Crystals

— HT1250 C
— EDM Sliced
— AR

(c) Residual Noise in Plastic Flow Curve

— Standard Processing
— Vac. Bake Out

Analysis Methods
Time Series Analysis of Tensile Flow Curves

Vacuum annealing reduces the serrated yielding attributed to interstitial interactions with dislocation motion.

Periodogram of the noise measured in the plastic flow curves of a sample following normal processing and after a vacuum anneal to bake-out hydrogen

(c) Residual Noise in Plastic Flow Curve

Standard Processing

Vac. Bake Out

Without vacuum bake out

Following vacuum bake out

(d) Periodograms for Stress Fluctuations About Mean Line of Fit
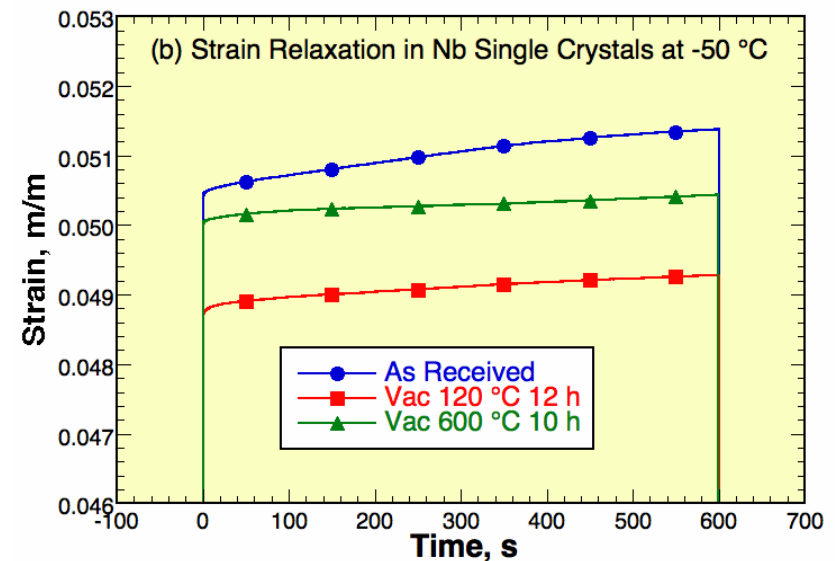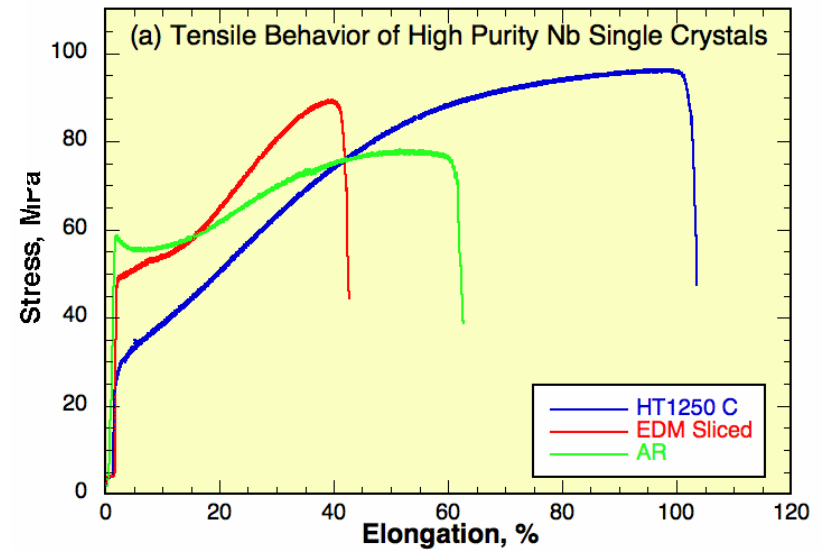
Standard Processing
Vac. Bake Out

Analysis Methods
Dynamic Modulus Analysis

Vacuum annealing reduces the serrated yielding attributed to interstitial interactions with dislocation motion.

Dynamic Modulus Analysis

Square wave loading can be used to evaluate the influence of absorbed hydrogen on the elastic and anelastic behavior of metals and alloys

Electrochemical Charging
Limitations and Sources of Error

1. <u>Equilibrium</u> - The Nernst equation that is used to relate electrode potential to hydrogen gas pressure assumes equilibrium. Therefore, it is not strictly correct anytime the system is not at equilibrium (e.g. anytime current is flowing).

2. <u>Current and pH</u> - Most investigators assume that the pH term in the Nernst equation is constant and equal to the bulk solution pH. However, this term is the pH seen by the surface of the sample which varies with the applied current density due to the reduction of hydrogen ions at the surface and the mass transport required to replinish these ions.

3. <u>Potential Drop</u> - When current is flowing, the resistivity of the electrolyte produces a potential gradient that is related to the current density distribution and the physical design of the measuring system. There are a number of experimental methods that can be used to minimize the errors due to these potential drops, but these assume that the samples has a uniform surface morphology (smooth and flat).

4. <u>Cracks</u> - Hydrogen is deposited electrochemically (plated) like any other metal and pH gradients, potential drops, and current distributions in a crack makes it difficult to control hydrogen absorption at a crack. Electrochemical charging of precracked samples should assume an inert crack tip and base cahrging time calculations on the time required for diffusion from the side faces of the samples.

5. <u>Passivity</u> - If under the charging conditions the sample is covered with a passive film, this film may block hydrogen entry. Increasing the hydrogen charging current can result in the pH at the surface of the sample increasing until passivity results and block hydrogen entry.

6. <u>Corrosion</u> - The thermodynamic driving force for corrosion of some alloys in some solutions is sufficient to reduce hydrogen and cause hydrogen uptake (e.g. Nb). Samples of these materials may absorb hydrogen from lab air or processing environments. These reactions may also make it difficult to control or measure hydrogen absorption.

Conclusions

1. Electrochemical reactions are a convenient method for introducing hydrogen into metals for studying hydrogen embrittlement, testing hypotheses, or guiding innovation.

2. Electrochemistry can be used to directly control or measure hydrogen activity (potential) or flux (current) in these studies for quantitative determination of properties or interactions