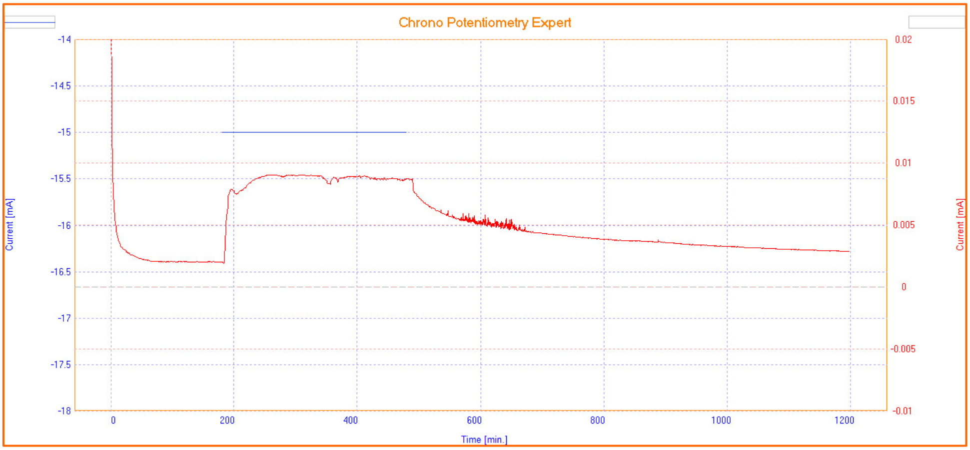
Application Note

General Electrochemistry
AP-GE17

Investigation of Hydrogen Permeation Through Steel



The purpose of this application note concerns the development of a test to study the diffusion of hydrogen through metallic materials. This phenomenon is known as hydrogen permeation (HPF). Hydrogen is an element that weakens steels therefore understanding and controlling of its diffusion into metal will influence economically on different aspect of industry.

Origalys ElectroChem

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INTRODUCTION

Hydrogen is the smallest element that exists. It can diffuse very easily in metal structures, at temperatures close to ambient. Between the metal and the hydrogen, there may be interactions in the volume (diffusion, trapping) and at the surface (adsorption, absorption).

The interaction mechanisms and the consequences on the mechanical strength of the parts are information necessary for the marketing of steels and the optimization of their behavior to fight against embrittlement. One of the important option is diffusion of hydrogen through metal structure.

This application note aims to find optimize parameters based on electrochemical hydrogen permeation technique.

Mechanism of Hydrogen Absorption

The hydrogen loading of the metal can be done in contact with different types of sources of hydrogen like as: gaseous hydrogen (H2), or a proton (H^+) from a hydrogenating species (H_2O, H_3O^+, H_2S,HS, etc.) Basic solution consisted OH^-.

a) Acid medium

In an acid medium, the dissolution reaction of the metallic species takes place in association with the reduction of the proton.

$$H^+ + e^- \rightarrow H_{ads}$$

INTRODUCTION

There are two recombination mechanisms to reform H_2 in acidic area:

1. $H_{ads} + H_{ads} \rightarrow H_2$
2. $H_{ads} + H^+ + e\ metal \rightarrow H_2$

Globally it could be considered as the reaction

$2\ (H^+ + e^-) \rightarrow 2\ H_{ads} \rightarrow (1-\varepsilon)\ H_2$ or $2\varepsilon\ H_{ads}$

b) Basic medium

In an adsorbed basic medium:

$2\ H_2O + 2\ e^- \rightarrow 2\ H_{ads} + 2\ OH^-$

$H_{ads} \rightarrow (1-\varepsilon)\ H_2$ or $2\varepsilon\ H$

The surface is then covered with H absorption in the metal with respect to an acid medium.

In this text all performances were run in basic solution consisting NaOH 0.1M. Evidently the reaction of Hydrogen permeation will follow as "Basic medium".

Figure 1 shows the schema of two mechanism which could be exist for diffusion of hydrogen: Interstitial and substitutional mechanism [1].

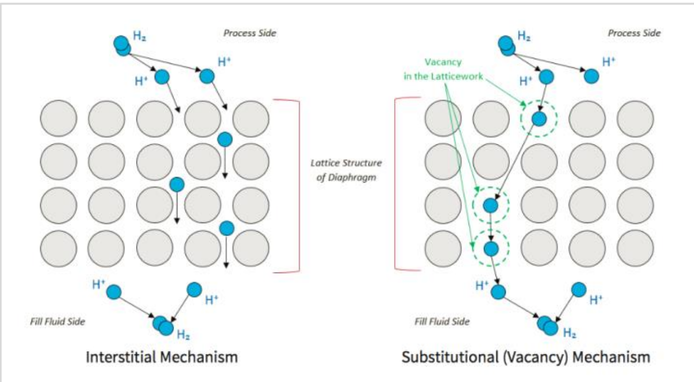


Figure 1: Schematic mechanism of hydrogen diffusion towards metal

Experimental assembly

Figure 2 shows schema of experimental assembly of a reaction in which permeation of hydrogen is supposed to be studied.

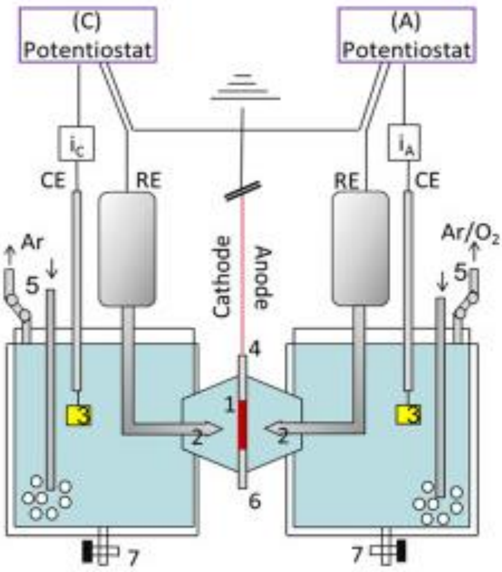


Figure 2: Schema of experimental assembly of hydrogen permeation

Basically, you need two potentiostats, and two cells. One of them will act as hydrogen producer (source of hydrogen) which is called "charging cell". By the other cell, the permeation of hydrogen will be detected which is called "detection cell".

For each cell, one reference electrode and one auxiliary electrode is needed. The working electrode is the metal plate that is common between two cells [2,3,4].

Experimental assembly

Note: In standard texts and articles there are recommended to pay attention to below items:

- **Purge neutral gas for deoxygenating the solutions**
- **Paladising the metal surface to block the protons of metal and prevents the formation of oxide layer**
- **Agitating the cells**
- **Using graphite as auxiliary electrode and not platinum, to avoid adsorption of hydrogen by platinum [3,4].**

In this application note, none of the mentioned above points were used, and a remarkable result was obtained.

Hardware Setup

Two potentiostats were used for this manipulation controlled by OrigaViewer software. The cells and electrodes were connected to potentiostats as figure 3. Configuration of each cell was 3 electrode inverted (found in « Start » box of flow chart.

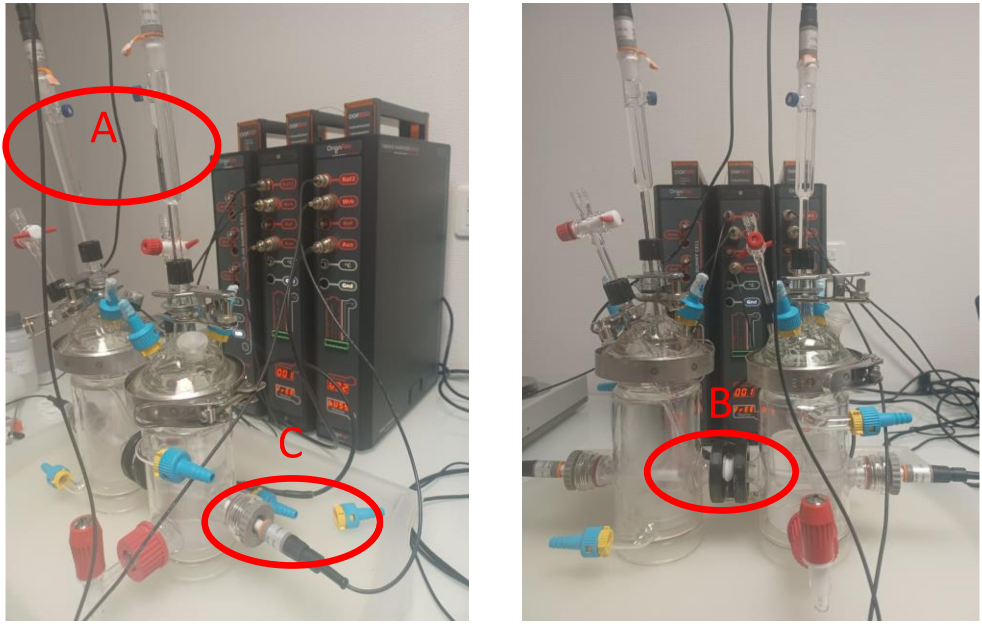


Figure 3: experimental setup; A) Reference electrodes, B) Work electrode (steel disc), C) Auxiliary electrode

The sample (working electrode) must be clean and has a polished and mirror surface without any corrosion on its surface.

PARAMETERS

The methods are carried out by the OrigaViewer software. Flow charts for each cell are identified in Figures 4 and 5.

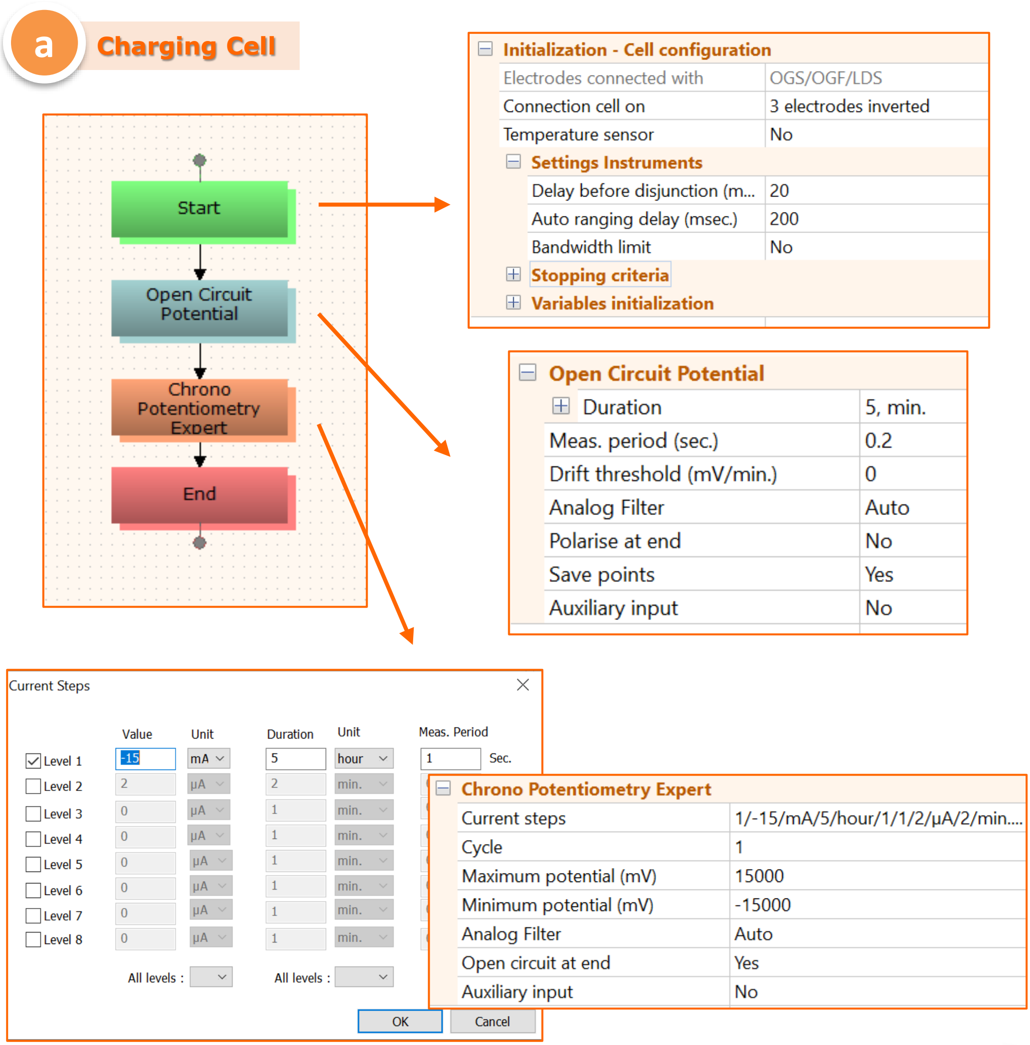
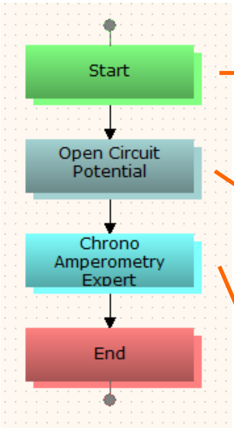


Figure 4: Parameters of flow chart related to charging cell

PARAMETERS

b Detection Cell



Initialization - Cell configuration	
Electrodes connected with	OGS/OGF/LDS
Connection cell on	3 electrodes inverted
Temperature sensor	No
Settings Instruments	
Delay before disjunction (m...	20
Auto ranging delay (msec.)	200
Bandwidth limit	No
Stopping criteria	
Variables initialization	

Open Circuit Potential	
Duration	5, min.
Meas. period (sec.)	0.2
Drift threshold (mV/min.)	0
Analog Filter	Auto
Polarise at end	No
Save points	Yes
Auxiliary input	No

Potential Steps

	Value	Versus		Duration	Unit	Meas. Period	
☑ Level 1	540	REF	mV	20	hour	1	Sec.
☐ Level 2	200	REF	mV	2	min.	0.1	Sec.
☐ Level 3	0	REF	mV	1	min.	0.1	
☐ Level 4	0	REF	mV	1	min.	0.1	
☐ Level 5	0	REF	mV	1	min.	0.1	
☐ Level 6	0	REF	mV	1	min.	0.1	
☐ Level 7	0	REF	mV	1	min.	0.1	
☐ Level 8	0	REF	mV	1	min.	0.1	

All levels : All levels :

OK

Chrono Amperometry Expert	
Mode	Normal
Potential steps	1/540/REF/20/hour/1/1/200/REF/2...
Cycle	1
Ohmic Drop Comp.	No
Maximum range	Auto
Minimum range	Auto
Analog Filter	Auto
Maximum current (mA)	100
Minimum current (mA)	-100
Open circuit at end	Yes
Auxiliary input	No

Figure 5: Parameters of flow chart related to detection cell

Result & Discussion

For this test, initially only the detection cell was filled with NaOH 0.1M, after 3 hours of imposing the potential of 540 mV on the detection cell (to have a good stabilization), the charging cell was filled with NaOH 0.1M by beginning to impose the current of -15 mA for 5 hours on this cell while continuing to impose potential on the detection cell. The two related curves are overlayed together in figure 6.

In order to have a better detection of hydrogen permeation current, a smoothing of 10 is applied.

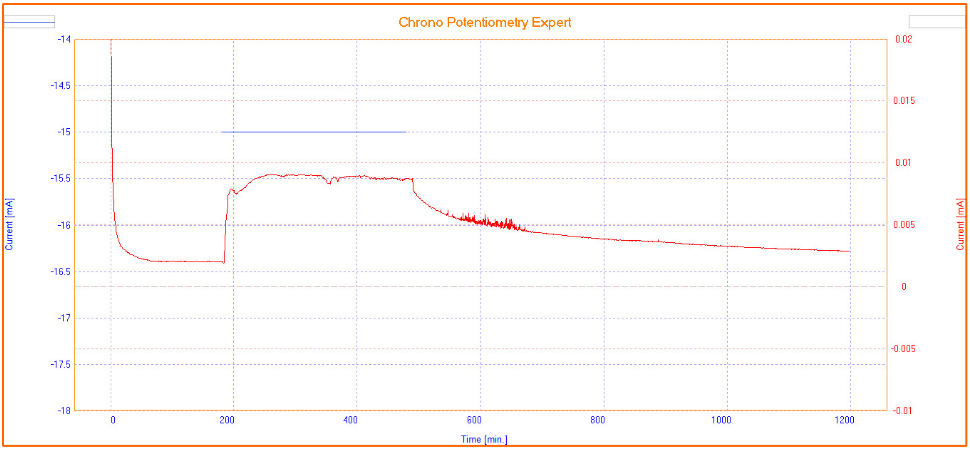


Figure 6: Curve results of hydrogen permeation in two cells:

- *Chrono potentiometry on charging cell* (blue)
- *Chrono Amperometry on detection cell* (red)

Calculation

Time-lag Method

By carrying out permeation tests, a curve will be obtained at the output expressing the current Ip detected as a function of time. From the curve obtained, the diffusion coefficient can be calculated simply with the time-lag method:

$$D_{eff} = \frac{e^2}{6t_{lag}}$$

Where:

t-lag: time of permeation which is obtained at 61.7% of J_{ss} of steady-state

J_{ss}: permeation current

e: thickness of the membrane steel disc (cm) [in this test it is 0.02 cm]

D_{eff}: diffusion coefficient ($cm^2 . s^{-1}$)

	Test hydrogen permeation
J_{ss}	**7.1 µA**
t-lag	**6.3 minutes (378 Seconds)**
D_{eff}	**1.76 E-7 $cm^2.s^{-1}$**

Table 1

Table 1 shows gained results from the electrochemical curves through t-lag calculation method.

INSTRUMENT AND ELECTRODES

Figure 7: 2 OrigaFlex OGF500

Electrode setup	
Sample	Steel plate by 200 µm of thickness
Instrument	2 OrigaFlex OGF500
Software	OrigaViewer
Auxiliary electrode	Platine disk electrode Ø10 103mm
Reference electrode	Reference electrode Ag/AgCl 120mm
Solution	NaOH 0.1M

Figure 8: Hydrogen permeation cell assembly

Reference:

[1] Yokogawa Electric Corporation, Page 9-32, AN-P-20220616-02

[2] Electrochimica Acta Volume 189, 2016, Pages 111-117

[3] Corrosion Science, Volume 80, 2014, Pages 517-522

[4] ISO-17081, Method of mesurement permeation and determination of hydrogen uptake and transport in metals by an electrochemical technique, edition: 2014-06-01

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