

Application Note AN-EC-032

Hydrogen permeation with a single instrument according to ASTM G148

Dedicated µStat-i MultiX software tools help researchers streamline hydrogen permeation studies

The Devanathan-Stachurski cell (or «H cell») is successfully used to evaluate the permeation of hydrogen through sheets or membranes. An H cell consists of two electrochemical compartments separated by a sheet which acts as a working electrode (WE) in both cells.

This setup allows the generation of hydrogen (H_2) in the charging cell by applying a controlled potential or constant current. Hydrogen diffuses through the sample (i.e., sheet or membrane) and is electrochemically detected in the oxidation compartment where the H_2 is oxidized by applying a constant potential [1]. The anodic current is directly proportional to the amount of hydrogen penetrating through the sample with time.

As small amounts of hydrogen pass through the sheet or membrane, a very sensitive potentiostat is required for its detection. In addition, since the two electrochemical cells share the same WE, two independent channels in floating mode with galvanostatic isolation are used. A study of the hydrogen permeation properties of different iron sheets is discussed in this Application Note while taking the instrumental requirements into account.

FUNDAMENTAL CONCEPTS

The steady-state permeation current (*Jss*) of hydrogen transient curves gives information about the subsurface concentration of hydrogen atoms at the charging surface (*C0*).
Where J_{ss} is the atomic hydrogen permeation flux at steady-state, A is the exposed area of the sample in the oxidation cell, *F* is the Faraday constant, D_1 is the lattice diffusion coefficient of atomic hydrogen, C_0 is the subsurface concentration of hydrogen as measured at the charging side of the sample, and *L* is the thickness of the sample.

$$J_{ss} = \frac{J_{ss}/A}{F} = \frac{D_1/C_0}{L}$$

When only reversible trapping is important and the permeation transient can be represented by Fick's first law of diffusion. Where D_{eff} is the effective diffusivity of atomic hydrogen. This characteristic parameter can be calculated based on three different methods.

$$J_{ss} = \frac{D_{eff}\, C_0}{L}$$

1. The elapse time (*tlag*) method considers the following equation when the normalized flux of atomic hydrogen (*J(t)/Jss*) is equal to 0.63:

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

2. The breakthrough time (*tb*) method is based on the following equation:
3. With the slope method, *Deff* can be calculated from the slope of a plot of log(|*Jss*–*J*(*t*)|) vs. 1 / *t*.

$$D_{eff} = \frac{L^2}{15.3t_b}$$

INSTRUMENTATION AND SOFTWARE

Electrochemical experiments are performed using µStat-i Multi16 (STAT-I-MULTI16, Figure 1), a multichannel bipotentiostat, galvanostat, and impedance analyzer (MultiplEIS® technology). Galvanic isolation is required for hydrogen permeation experiments when working in floating mode. A galvanic isolation option is available in groups of four channels in µStat-i Multi16.

The H cell (H-CELL, Figure 1) consists of two electrochemical compartments (250 mL) and PTFE caps with holes of different diameters suitable for a variety of electrodes. This cell provides an exposed area of 1.77 cm^2 (1.5 cm diameter).

In the charging cell where the hydrogen generation takes place, a platinum counter electrode (CE, PT.SHEET) and Ag/AgCl reference electrode (RE, 6.0733.100) are used. A steel CE (6.0343.110) and Ag/AgCl RE (6.0728.120) are used in the detection cell. Both compartments of the H cell use the same WE—in this case, iron sheets 2 mm thick.

DropView 8400M software controls the µStat-i Multi16 instrument and includes dedicated tools for the analysis of hydrogen permeation experiments.



Figure 1. µStat-i Multi16 instrument with H-CELL

PROCEDURE

In order to remove the hydrogen already present in the iron samples, metallic sheets are pretreated at 80 ºC overnight before the experiments are performed.

The charging cell is filled with 0.1 mol/L HCl and 0.2 g/L As_2O_3 as hydrogen precursor, while 0.1 mol/L NaOH is used in the detection cell. Hydrogen permeation studies involve the following procedure:

1. Initially, amperometric detection is performed in the detection cell by applying +0.30 V. The charging cell is not activated.
2. Decay of the current must be observed in the detection cell. The decay time depends on the sample that is being tested.
3. Once the current acquired in the detection cell is close to 0 µA, a cathodic polarization is carried out in the charging cell. According to ASTM G148 [1], charging transient is performed considering currents of -1 mA/cm2. Potentiometric detection at -1.8 mA is applied in the experiments shown in this Application Note.
4. Detection of hydrogen flux through the WE requires different times depending on the properties of the sheet (e.g., composition, structure, porosity, etc.). In order to carry out a decay transient, the electrochemical generation of hydrogen in the charging cell is stopped while the detection cell continues the amperometric measurement.

Steps 3 and 4 can be repeated to produce consecutive charging and decay transients, respectively.

RESULTS

Two iron sheets of 2 mm thickness are evaluated using the procedure explained in the previous section. Figure 2 shows the charging and decay transients obtained with these samples.

Different electrochemical profiles are obtained depending on the properties of each sample. For example, iron sheet 1 (Figure 2, in orange) exhibits the highest hydrogen diffusivity due to the higher current recorded. On the other hand, sample 2 (Figure 2, in blue) not only shows a lower current, but also a delay in the hydrogen transport due to its lower permeability.

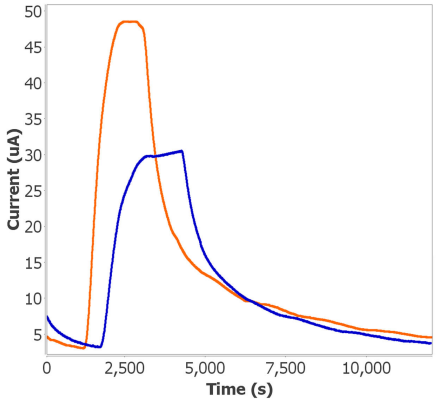


Figure 2. Charging and decay transients of two iron sheets

DATA ANALYSIS

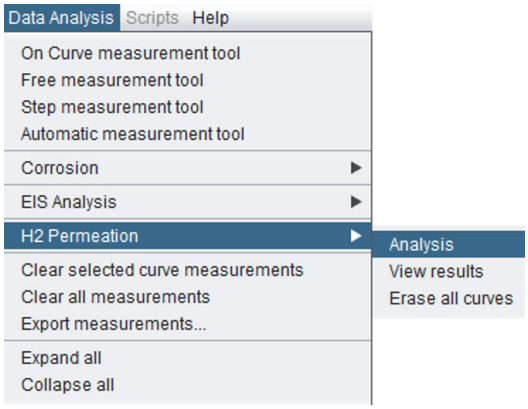


Figure 3. Select the «Analysis» option for «H2 Permeation» in the Data Analysis drop-down menu.

Experimental results are analyzed using the H2 permeation module implemented in DropView 8400M. To facilitate the understanding of this tool, only the permeation through sample sheet 2 is explained.

1. Select the electrochemical curve and click on «H2 Permeation» in the Data Analysis drop-down menu (Figure 3). Then, select the «Analysis» option.

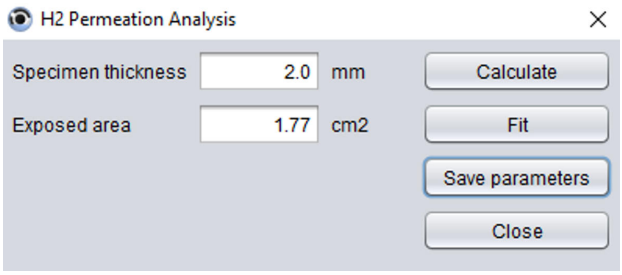


Figure 4. Type in the specimen thickness and the exposed area

2. In the empty fields, type the thickness and the exposed area of the sample used in the experiment (Figure 4). Click the «Calculate» button to obtain the characteristic parameters associated with the evaluated sample.

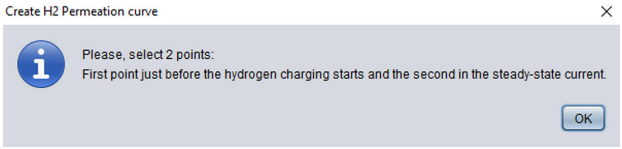


Figure 5. Select two points in the charging transient to apply the fitting analysis

3. Two points must be selected: the first one before the charging transient starts, and the second one when the system achieves a steady state (Figure 5).

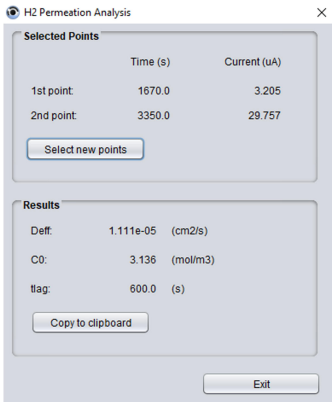


Figure 6. Characteristic parameters are automatically calculated in the software

4. Different parameters such as the effective diffusivity of atomic hydrogen (*Deff*), the subsurface concentration of atomic hydrogen at the charging side (*C0*), and the time to achieve a value of normalized flux of atomic hydrogen ($J(t)/Jss$) = 0.63 (*tlag*) are then automatically calculated (Figure 6).

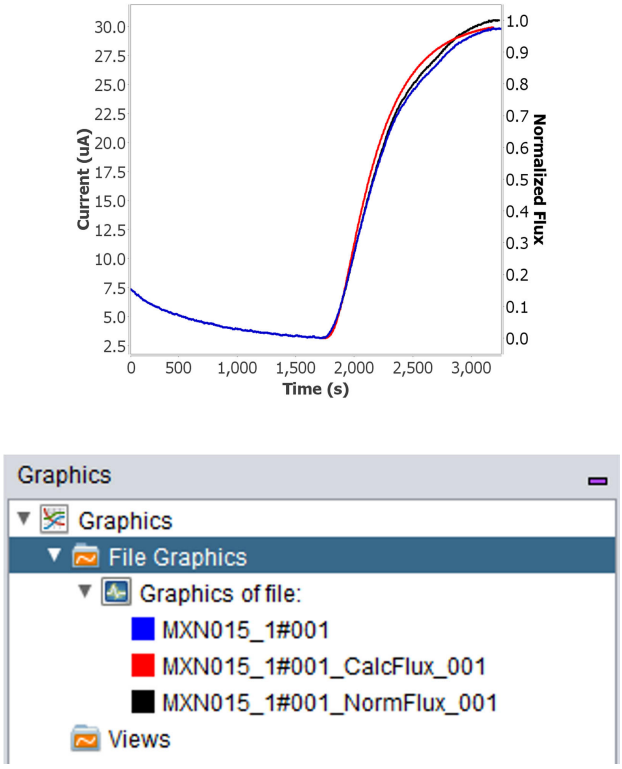


Figure 7. CalcFlux» (red line) and «NormFlux» (black line)

5. In Figure 7, two additional curves are plotted in the graphical representation apart from the raw curve (in blue): «CalcFlux» (red line) corresponds to the applied algorithm and «NormFlux» (black line) is associated with the normalized hydrogen flux (secondary axis). The obtained results are always available just by selecting the «CalcFlux» curve (Figure 7, in red) and the «View results» option included in the H2 permeation module (Figure 3).

Following the described steps, D_{eff}, C_0, and t_{lag} for the two iron samples are obtained (Table 1).

Table 1. Characteristic parameters obtained from the hydrogen charging transient.

Sample	D_{eff} (cm^2/s)	C_0 (mol/m^3)	t_{lag} (s)
1	1.35×10^{-5}	4.231	500
2	1.11×10^{-5}	3.136	600

CONCLUSION

This Application Note illustrates the use of the Metrohm DropSens µStat-i Multi16 instrument to perform hydrogen permeation experiments according to ASTM G148. This instrument allows users to work with two channels in floating mode and offers the required sensitivity for these studies.

µStat-i Multi16 allows users to perform multi-hydrogen permeation experiments with up to eight H cells in only one instrument.

The H cell used in this study consists of two compartments: the charging cell to generate hydrogen and the detection (or oxidation) cell to detect the hydrogen permeated through the working electrode.

DropView 8400M software includes dedicated tools for the analysis of these experiments. The H_2 permeation module allows easy and quick fitting of the hydrogen transients and the automatic calculation of experimental parameters such as the effective diffusivity and the concentration of hydrogen.

REFERENCES

1. ASTM International. *Standard Practice for Evaluation of Hydrogen Uptake, Permeation, and Transport in Metals by an Electrochemical Technique*; ASTM G148-97(2018); ASTM International, 2018. DOI:10.1520/G0148-97R18

CONTACT

Metrohm RUS
ул. Корабельная 9А,
помещ. 5/1
115142 Москва
info@metrohm.ru

CONFIGURATION



Platinum sheet electrode

This electrode consists of a thin sheet of platinum embedded into a glass shaft. This electrode can be used as a counter electrode for most electrochemical measurements. The surface area is approximatively 1 cm2.



Ag/AgCl reference electrode

Silver / silver chloride reference electrode with c(KCl) = 3 mol/L as reference electrolyte.
This reference electrode is suitable for aqueous applications and the SGJ 14/15 enables easy assembly.



Separate steel electrode

Steel auxiliary electrode for CVS



Ag/AgCl reference electrode

Inner reference system with electrolyte c(KCl) = 3 mol/L. For use with electrolyte vessel made of plastic 6.1245.010.