

COMSOL physics builder file: An electro-chemo-mechanical framework for predicting hydrogen uptake in metals due to aqueous electrolytes

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Abstract

Documentation that accompanies the file *HydrogenDiffusion.mphphb*, a COMSOL physics builder module which implements stress- and concentration-based hydrogen diffusion within metals. In addition, it implements the Tafel, Heyrovsky, Volmer, and absorption reactions defining a metal-electrolyte interface, providing a convenient coupling to other COMSOL modules, or allowing a prescribed local pH and electrolyte potentials. Finally, it includes some simplified models for these metal-electrolyte interfaces, prescribing hydrogen influxes based on the environmental conditions. Example files detailing these use cases are also provided.

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1. Introduction

Hydrogen embrittlement is an important issue impacting metals exposed to environments such as ocean or rain water. Due to this contact with electrolytes, hydrogen is produced at the metal-electrolyte interface which in turn diffuses to within the metal where it can lead to changes in material strength. Since the surface reactions dictate the amount of available hydrogen, it is important to not just capture the hydrogen diffusion within the metal, but to also simulate or approximate the electrolyte-metal interface.

The model used in (Hageman and Martínez-Pañeda, 2022) and presented here allows for the simulation of hydrogen diffusion within metal, including relevant boundary conditions, within COMSOL Multiphysics. It is implemented as a physics-builder module, allowing it to be integrated and easily added to existing or new models without the need to manually alter equations. This document provides an explanation about the different domain and boundary features in Section 2, and gives several examples about the usage of this module in Section 3.

2. Module usage

2.1. Importing user modules in COMSOL

To use the included module, it first needs to be imported into COMSOL. Make sure the physics builder is enabled in the COMSOL settings *Preferences/Physics Builder/Enable Physics Builder*. Next, open the physics builder module file *HydrogenDiffusion.mphphb*. Here, the implementation of the module is visible,

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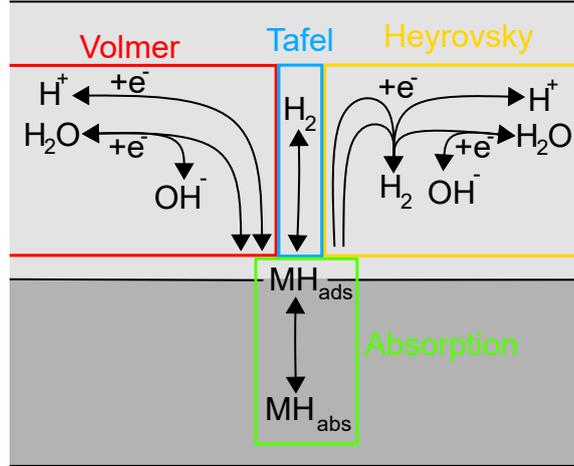


Figure 1: Overview of the reactions included within the module.

allowing for the domain and boundary features to be inspected, amended, and altered. To use the module inside simulations, click *Home/Physics Builder Manager* on the top toolbar to open the module manager. Right click *Development files* underneath *Archive Browser*, and select *Add Builder File*. This adds the module to the COMSOL module database, allows models using this module to be loaded, and allows new models to be created using this module in the same manner as any physics interface already included with COMSOL.

2.2. Domain model

Adding the *HydrogenDiffusion* physics to an existing model, or creating a new model using this interface initialises two domain features: A linear elastic material, and a diffusion model. The first is a standard COMSOL linear elastic material, and allows all other physics that are applicable to the linear elastic material to be added (such as damage, plasticity, etc.). This adds degrees of freedom for the displacements \mathbf{u} , and solves the static momentum balance:

$$\nabla \cdot \boldsymbol{\sigma}(\mathbf{u}) = \mathbf{0} \quad (1)$$

In order for this model to work, material properties have to be set for the domain in the materials tab for the Young's modulus, Poisson ratio, and density (not used in the model, but results in an error if unset).

The diffusion model adds degrees of freedom for the hydrogen concentration within lattice sites, C_L , and implements the hydrogen diffusion within a metal through:

$$\left(1 + \sum_i \frac{N_T^i/N_L e^{E_b^i/RT}}{\left(1 + C_L/N_L e^{E_b^i/RT} \right)^2} \right) \dot{C}_L + \nabla \cdot (-D_L \nabla C_L) + \nabla \cdot \left(\frac{D_L C_L \bar{V}_H}{RT} \nabla \sigma_H \right) = 0 \quad (2)$$

using the amount of lattice sites N_L , trap sites N_T with binding energy E_b , lattice diffusion coefficient D_L , partial molar volume of hydrogen \bar{V}_H , and reference temperature T_{ref} . All these properties can be directly set within the *Diffusion* domain feature. It also automatically ties into the linear elastic model to obtain the hydrostatic stress gradients, $\nabla \sigma_H$.

2.3. Boundary models

In addition to the above-described domain models, the module file also implements boundary conditions related to hydrogen diffusion. These boundary conditions can be added when the *Diffusion* domain feature is present.

35 *2.3.1. Concentration & NoFlux*

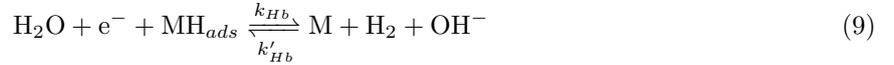
These two boundary features implement the standard prescribed concentration and no hydrogen flux boundary conditions. The no flux boundary condition solely requires the applicable boundaries to be selected (defaults to all boundaries that do not have other boundary conditions), whereas the prescribed concentration requires setting C_0 to the prescribed boundary lattice concentration.

40 *2.3.2. Electrolyte*

This boundary feature implements the mass conservation at the metal-electrolyte interface, adding a degree of freedom for the surface coverage θ . This degree of freedom is governed through the interfacial mass balance:

$$N_{ads}\dot{\theta}_{ads} - (\nu_{Va} - \nu'_{Va}) + (\nu_{Ha} - \nu'_{Ha}) + 2(\nu_T - \nu'_T) + (\nu_A - \nu'_A) - (\nu_{Vb} - \nu'_{Vb}) + (\nu_{Hb} - \nu'_{Hb}) = 0 \quad (3)$$

where N_{ads} is the concentration of surface absorption sites, and ν the surface reaction rates. The reactions that are included through this boundary model are:



with their forwards and backwards reaction rates given by:

$$\nu_{Va} = k_{Va}C_{H^+}(1 - \theta_{ads})e^{-\alpha_{Va}\frac{\eta_F}{RT}} \quad \nu'_{Va} = k'_{Va}\theta_{ads}e^{(1-\alpha_{Va})\frac{\eta_F}{RT}} \quad (10)$$

$$\nu_{Ha} = k_{Ha}C_{H^+}\theta_{ads}e^{-\alpha_{Ha}\frac{\eta_F}{RT}} \quad \nu'_{Ha} = k'_{Ha}(1 - \theta_{ads})p_{H_2}e^{(1-\alpha_{Ha})\frac{\eta_F}{RT}} \quad (11)$$

$$\nu_T = k_T\theta_{ads}^2 \quad \nu'_T = k'_T(1 - \theta_{ads})^2p_{H_2} \quad (12)$$

$$\nu_A = k_A(N_L - C_L)\theta_{ads} \quad \nu'_A = k'_AC_L(1 - \theta_{ads}) \quad (13)$$

$$\nu_{Vb} = k_{Vb}(1 - \theta_{ads})e^{-\alpha_{Vb}\frac{\eta_F}{RT}} \quad \nu'_{Vb} = k'_{Vb}C_{OH^-}\theta_{ads}e^{(1-\alpha_{Vb})\frac{\eta_F}{RT}} \quad (14)$$

$$\nu_{Hb} = k_{Hb}\theta_{ads}e^{-\alpha_{Hb}\frac{\eta_F}{RT}} \quad \nu'_{Hb} = k'_{Hb}(1 - \theta_{ads})p_{H_2}C_{OH^-}e^{(1-\alpha_{Hb})\frac{\eta_F}{RT}} \quad (15)$$

These reaction rates are accessible within COMSOL for post-processing through *hyd.Ra*, *hyd.Rar* for the forward and backward reaction rates for ν_{Va} , *hyd.Rb*, *hyd.Rbr* for reaction ν_{Ha} , etc. . For this boundary feature to work, reaction rate constants k and α have to be defined within the electrolyte feature. In addition, it requires setting the ion concentrations for the H^+ and OH^- concentrations, and prescribing the electric overpotential. These last three parameters can be set to the degrees of freedom of neighbouring domains to connect this model to the COMSOL-implemented *Tertiary Current Distribution*, *Nernst-Planck* module.

45 *2.3.3. ApproximateBoundary*

The *ApproximateBoundary* boundary feature approximates the hydrogen influx based on known environmental conditions. Given the metal potential E_m , electrolyte potential φ and the local pH, the hydrogen

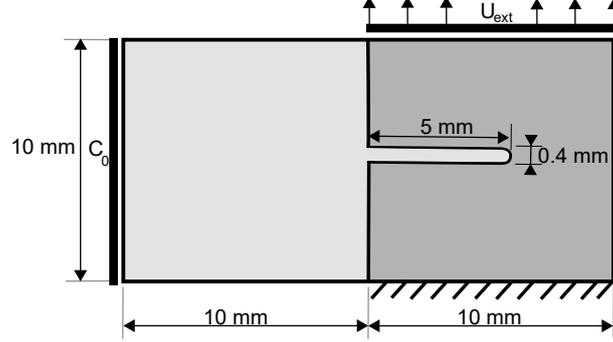


Figure 2: Domain used for example cases

influx is given as:

$$\begin{aligned} \tilde{J}_1 = & \left(1 - \frac{C_L}{\frac{k'_A}{k_A}(N_L - C_L) + C_L} \right) \left(k_{V_a} C_{H^+} e^{-\alpha_{V_a} \frac{(E_m - E_{eq} - \varphi)F}{RT}} + k_{V_b} e^{-\alpha_{V_b} \frac{(E_m - E_{eq} - \varphi)F}{RT}} \right) \\ & - \frac{C_L}{\frac{k'_A}{k_A}(N_L - C_L) + C_L} \left(k_{H_a} C_{H^+} e^{-\alpha_{H_a} \frac{(E_m - E_{eq} - \varphi)F}{RT}} + k_{H_b} e^{-\alpha_{H_b} \frac{(E_m - E_{eq} - \varphi)F}{RT}} + 2k_T \frac{k'_A}{k_A} (N_L - C_L) + C_L \right) \end{aligned} \quad (16)$$

This approximation assumes an equilibrium between the surface coverage and lattice hydrogen concentration, and thereby does not require the surface coverage to be treated as an independent degree of freedom.

50 2.3.4. EstimateBoundary

the final boundary feature present is the *EstimateBoundary*. This feature provides a rough estimate for the hydrogen influx based on environmental conditions. It assumes the surface coverage is small, and neglects all but the most dominant reactions. This gives the hydrogen influx as:

$$\tilde{J}_2 = (k_{V_a} 10^{-pH+3} + k_{V_b}) e^{-\alpha \frac{(E_m - \varphi)F}{RT}} \quad (17)$$

which requires the forward reaction constants k_{V_a} and k_{V_b} to be defined within the boundary feature, and requires the environmental pH and electrolyte potential to be known.

3. Included examples

Finally, we present three examples from (Hageman and Martínez-Pañeda, 2022). These cases simulate the domain shown in Figure 2, two 10×10 mm domains representing an electrolyte and metal, with a crack in the centre of the metal.

3.1. EstInflow.mph: Rough estimate hydrogen influx

The first example file implements the estimated hydrogen flux boundary condition. The *HydrogenDiffusion* feature is composed of *Linear Elastic Material 1* (with its properties for the Young's modulus and Poisson ratio taken from the material settings). and *Diffusion* (with its properties set within the feature itself). These two features together describe the interior of the domain. For the solid, we have the standard *Prescribed Displacement* and *Roller* boundary conditions.

The boundary condition for the hydrogen diffusion is set to no flux for the top, bottom, and right domain edges. For the left edge and on the crack edges, it is set to *EstimateBoundary*. Within this feature, we define the local pH and electrolyte potential, as obtained from the environmental conditions chart from

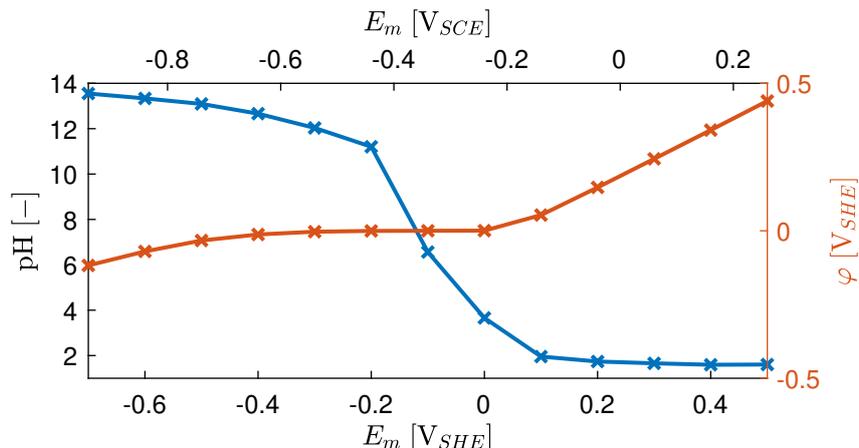


Figure 3: Environmental conditions after 10 minutes obtained from (Hageman and Martínez-Pañeda, 2022)

Figure 3. In addition, we set the electric potential of the metal, and define reaction constants for the acidic and non-acidic Volmer reactions. It should be noted that while the reference point for the electric potentials does not alter the results, the electrolyte and metal potentials should use the same reference, using V_{SHE} in this example case.

Finally, the mesh is set up using quadratic quadrilateral elements, and has a *Boundary Layer* set up for the metal-electrolyte interface. The solver has been set to use the *Automatic (Newton)* solver to use a Newton-Raphson method in which the tangential matrix is updated, has line-search limits of 10^{-6} and 0.5, and has been set to a maximum amount of 250 iterations. The time-dependent solver is set to manual to prevent COMSOL from deciding to reduce the time increment because of the boundary layers developed for the lattice concentration being too steep and quickly changing. In the manual time solver settings, we start of with an initial time increment of 10^{-5} s (not needed this small for this case, but used to be consistent across all cases) which is increased by 10% with every new time step taken. The results is set up to just produce a single figure, the lattice hydrogen concentration (defined as $C.L$ within COMSOL) after 10 minutes. This result is shown in Figure 4a.

3.2. *ApproxInflow.mph*: Approximated hydrogen influx

The second example case replaces the *EstimateBoundary* from the previous section with the *ApproximateBoundary* model. Within this model, the same environmental conditions are defined, but additional reaction constants for the forward Heyrovsky, and forward and backward absorption reaction are given. All other models and settings correspond to those explained in the previous section, and the resulting Lattice concentration is shown in Figure 4b.

3.3. *FullSimulation.mph*: Full simulation of electrolyte and metal domains

The final example case shows how to link hydrogen diffusion within the metal to a neighbouring electrolyte. Within the *HydrogenDiffusion* feature, we now use the *Electrolyte* boundary condition. Within this, we define all reaction constants for the hydrogen reactions and the amount of surface absorption sites. Instead of defining the H^+ , OH^- , and electric overpotential, we link these to the variables defined for the electrolyte cH for the H^+ concentration, cOH for the OH^- concentration, and $tcd2.eta_{er1}$ for the electric overpotential.

We define *Tertiary Current Distribution*, *Nernst-Planck* on the electrolyte domain, which solves the Nernst-Planck equations for advection and diffusion of charged particles under the assumption of local electro-neutrality. As dependent variables, we add 6 components for the H^+ , OH^- , Na^+ , Cl^- , Fe^{2+} , and $FeOH^+$ concentrations. We define the diffusion coefficients and charges of these species within the *Electrolyte 1* domain feature, and set the initial and boundary values in *Initial Values 1* and *Concentration 1* respectively.

To enforce the water auto-ionisation that enforces $\text{pH} + \text{pOH} = 14$ within the electrolyte, we add two reaction fluxes within the *Reactions 4* feature, defining the reactions using a penalty approach as:

$$R_{\text{H}^+} = R_{\text{OH}^-} = (10^{-8} - C_{\text{H}^+}C_{\text{OH}^-}) \cdot 10^5 \quad (18)$$

where 10^{-8} is the water auto-ionisation constant (in mol^2/m^6), and 10^5 is chosen sufficiently high to enforce this equilibrium, but low enough to not provide significant convergence issues.

On the electrolyte-metal boundary, we add a *Electrode Surface* boundary feature and set the electric potential of the metal to E_m (defined within the parameters). Within this feature, we have *Electrode Reaction 1* and *2* for the H^+ and OH^- inflows. Here, we provide the electrode kinetics as *User Defined* and provide the fluxes calculated within the *HydrogenDiffusion* module by setting them to $\text{hyd.JHplus} * F_const$ for the H^+ influx (with Stoichiometric coefficient -1), and $-\text{hyd.JOHminus} * F_const$ for the OH^- influx (with Stoichiometric coefficient 1). We also set the equilibrium coefficients of these reactions to 0 , which is used by the *HydrogenDiffusion* model to calculate these fluxes. Finally, we add the corrosion surface reaction in a standard manner by defining the exchange current density and transfer coefficient. For the reactions of Fe^{2+} within the electrolyte, we add two final reactions. Reaction 2, defining the reaction fluxes as:

$$R_{\text{H}^+} = k_{fe}C_{\text{Fe}^{2+}} - k'_{fe}C_{\text{FeOH}^+}C_{\text{H}^+} \quad (19)$$

$$R_{\text{Fe}^{2+}} = -k_{fe}C_{\text{Fe}^{2+}} + k'_{fe}C_{\text{FeOH}^+}C_{\text{H}^+} \quad (20)$$

$$R_{\text{FeOH}^+} = k_{fe}C_{\text{Fe}^{2+}} - k'_{fe}C_{\text{FeOH}^+}C_{\text{H}^+} \quad (21)$$

and reaction 3 with reaction fluxes

$$R_{\text{H}^+} = k_{feoh}C_{\text{FeOH}^+} \quad (22)$$

$$R_{\text{FeOH}^+} = -k_{feoh}C_{\text{FeOH}^+} \quad (23)$$

In the results, we can now provide the pH within the electrolyte (defined through $-\log_{10}(c_{\text{H}^+}/1000)$) as well as the lattice hydrogen concentration within the metal, as shown in Figure 4c. We can also plot other ion concentrations such as the iron ions using c^{Fe} , or surface reaction rates using $\text{hyd.Ra} - \text{hyd.Rar}$.

4. Concluding remarks

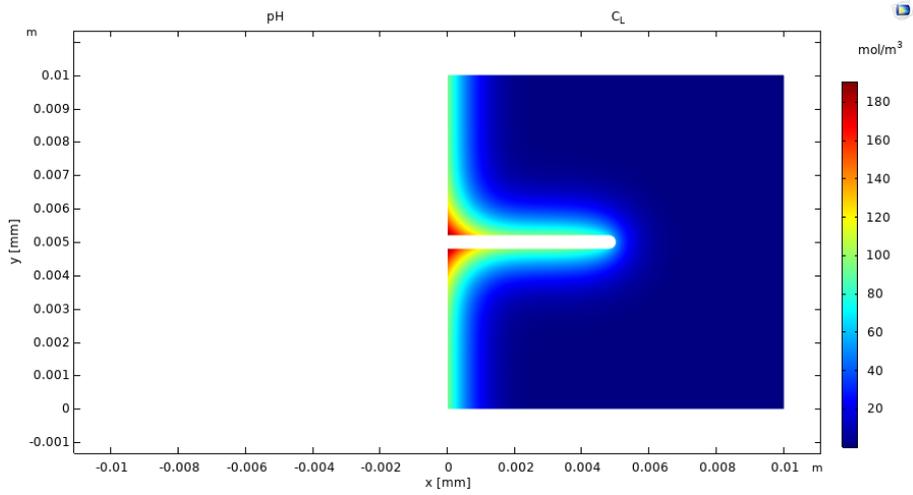
We have provided a COMSOL physics builder module which allows hydrogen diffusion within metals to be simulated as easily as any other physics build into COMSOL. This module implements:

- Stress and diffusion driven hydrogen transport within metals
- No flux and prescribed hydrogen concentration boundary conditions
- Boundary conditions to obtain a rough estimate and a reasonable approximation of the hydrogen entering the metal
- An implementation of the Volmer, Tafel, Hydrovsky, and absorption reactions, taking into account surface concentration changes over time

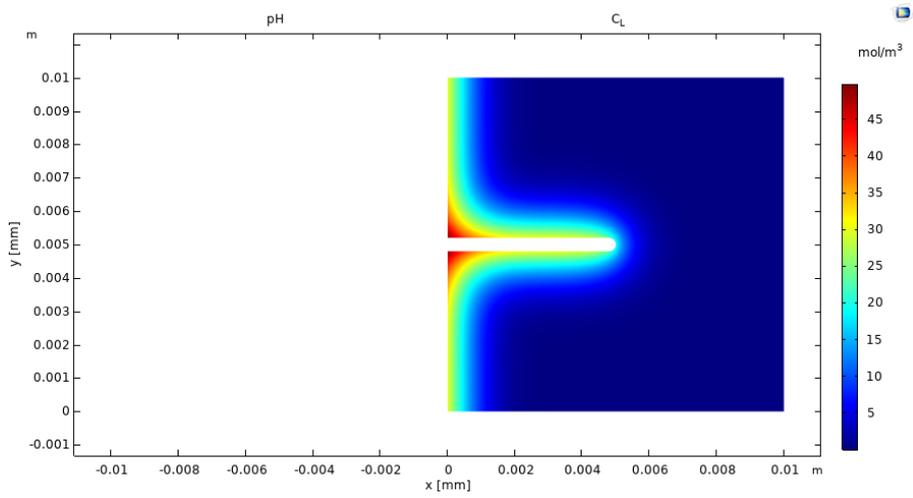
We have also provided some examples for how these models can be used, and how they can be coupled to other modules within COMSOL. These models allow for obtaining accurate predictions for the hydrogen uptake within metals by simulating both the electrolyte and the metal, or obtaining quick estimates of the hydrogen distribution within the metal.

Acknowledgments

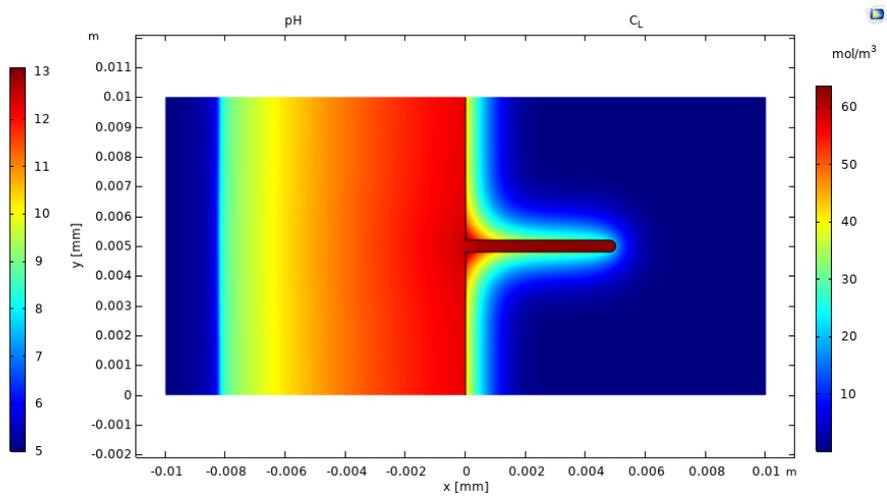
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(a) Estimated hydrogen flux case



(b) Approximate hydrogen flux case



(c) Full simulation case

Figure 4: Resulting lattice hydrogen concentration for the example cases.