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**PEM Water Electrolysis, project MEGASTACK**

**D2.1 Coupling and up-scaling strategies for the development of multi-scale and multi-physic PEMWE performance models**

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## FOLLOW-UP OF THE REVISIONS

| Index | Date | Cause and description of the modification |
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## **Summary**

The main objective of the European MEGASTACK project is to develop a cost efficient stack design for MW sized PEM electrolysers, and to construct and demonstrate a prototype of this stack. In the approach proposed to reach this objective, one of the key tasks is the development and use of multi-scale and multi-physics models that will serve as an engineering tool to answer some design questions. In order to develop this tool, the idea is to combine different physical models at different scales. The objective of the present document is to identify early in the project the required input and output of the different partners' models and to propose possible coupling and up-scaling strategies to address different questions of the MW design.

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## 1. INTRODUCTION

Water electrolysis based on PEM technology has demonstrated its applicability to produce hydrogen and oxygen in a clean and safe way on site and on demand. However, PEM electrolyzers are still facing several challenges before full commercialization. The capital costs must be reduced while increasing the size of the system. In this context, the main objective of the MEGASTACK project is to develop a cost efficient stack design for MW sized PEM electrolyzers and to construct and demonstrate a prototype of this stack.

In the integrated approach proposed to reach this objective, one of the key tasks is the development and subsequent use of multi-scale and multi-phase models which will serve as engineering tools for the MW stack design. The development of these tools will allow a detailed understanding of heat and mass transport inside the cells and the stack, securing designs with minimal pressure drop, proper heat management and efficient water supply and gas removal.

Regarding PEMWE modeling, several performance models are reported in the literature [3] [2] [5] [1] [9]. These models are mainly based on thermodynamic principles, mass balance and Butler-Volmer kinetics and allow for simulating the electrochemical behavior of the electrolyser depending on the operating conditions (mainly temperature and pressure). Few models take into account mass transport limitation by diffusion [12] and almost no model is able to predict mass transport limitations in two-phase flow regimes. Furthermore, these models are usually 0D or 1D. They cannot capture the local current density distribution on the surface of the electrodes. For MW design, large area cells with surfaces between 600 cm<sup>2</sup> and 2000cm<sup>2</sup> has to be considered. For such large areas, heterogeneous local conditions are foreseen. For a proper understanding of pressure drop, heat management, water supply and gas removal in such large cells, the final model should be able to capture the local heterogeneous conditions.

In order to develop multi-physic and multi-scale models able to tackle the design questions of the MEGASTACK project, the idea is to combine different physical models at different scales (see Figure 1):

- At the cell scale, a two-phase flow model for gas bubble evolution, distribution and movement in the anode channels and possibly current collectors will be developed by SINTEF using the ANSYS FLUENT package.
- At the cell scale, a multi-physic model that considers electrochemical reaction kinetics, mass and momentum transport in the porous current collectors and heat management will be developed by Fraunhofer ISE using COMSOL Multiphysics.
- Finally, as the detailed models developed at the cell scale are expected to be computationally expensive, a stack model including the physics of the two previous models and based on appropriate averaged fields will be developed by CEA using MATLAB-SIMULINK. (see section 4.1 for a description of the averaged fields and corresponding averaging procedure)

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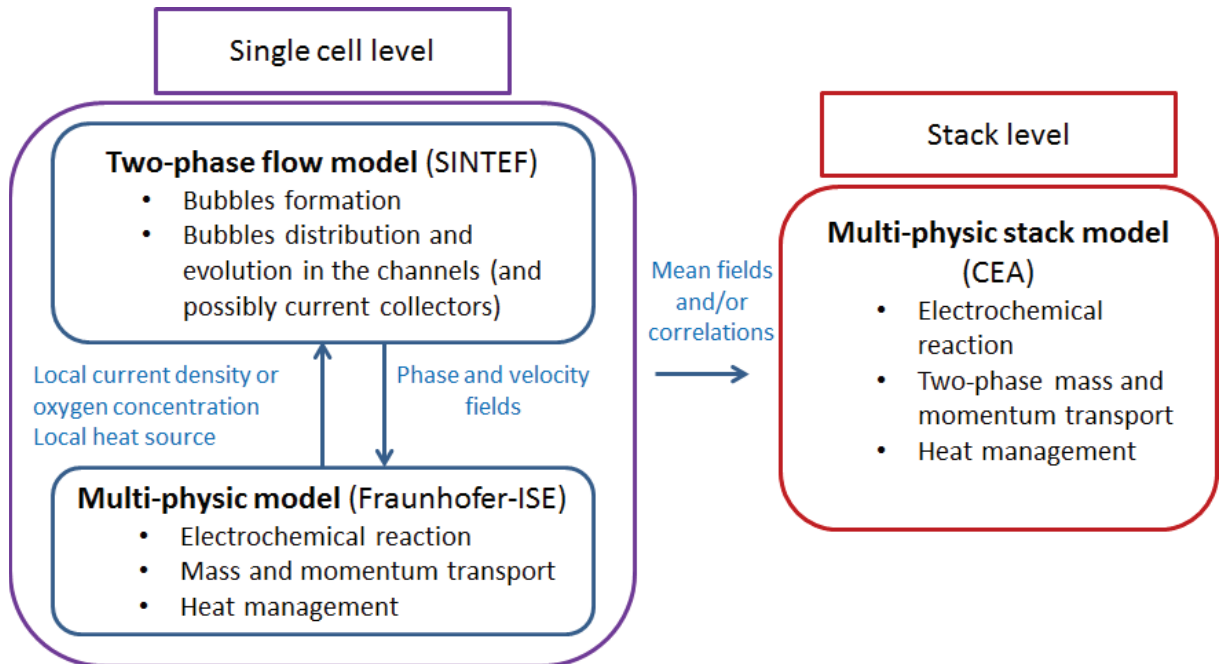


Figure 1: Multi-physic and multi-scale approach of the MEGASTACK project

The objective of the present document is:

- to identify early in the project the required input and output of the different models;
- to propose possible coupling and up-scaling strategies to address the different design questions of the MW electrolyser.

This report is organized as follows. Section 2 presents briefly the main design questions of the MW design that we would like to address in the MEGASTACK project. Section 3 details the three different models to better understand the needed input and possible output. Finally different coupling and up-scaling strategies are proposed in Section 4.



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## 2. MAIN DESIGN QUESTIONS

Before presenting the main design questions of the MEGASTACK project that need multi-physics models simulation, we present the main design characteristics of the MW ITM-power stack.

Figure 2 presents a cross-section view of the ITM cell design. The total height of one cell is around 8.4 mm and the frame height will be around 3 mm, based on mechanical design constraints. The thickness of the porous current collectors is not fixed at the moment. The necessity to use a flow field plate, instead of a spacer, at the anode side, should be confirmed.

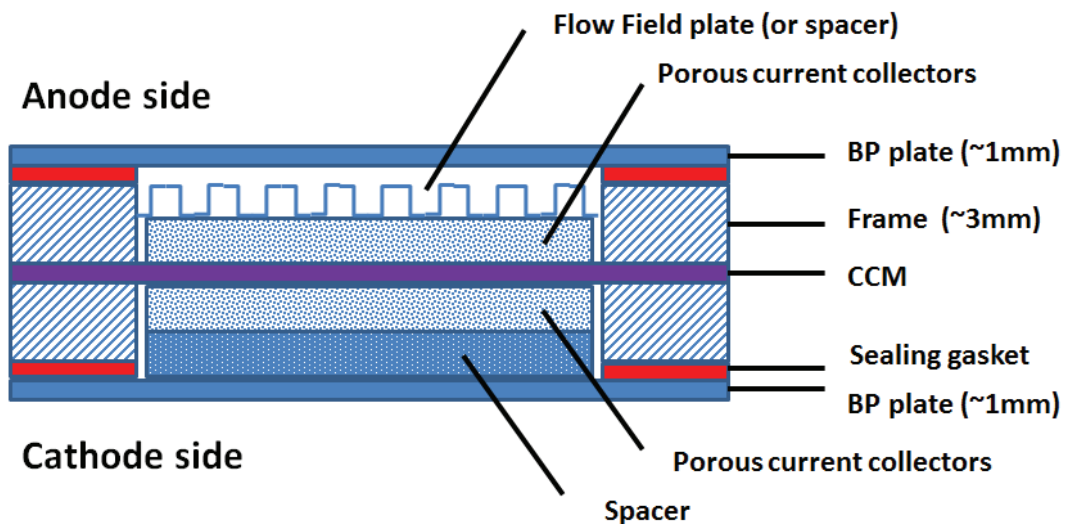


Figure 2: Cross-section view of cell components

Figure 3 presents a top view of a cell, with the location of the anode and cathode manifolds. The number and exact geometry of the manifolds is not fixed yet. Water is fed only on the anode side.

Figure 4 presents cross-section of the stack, focusing on the anode/cathode manifolds for water supply and water collection.

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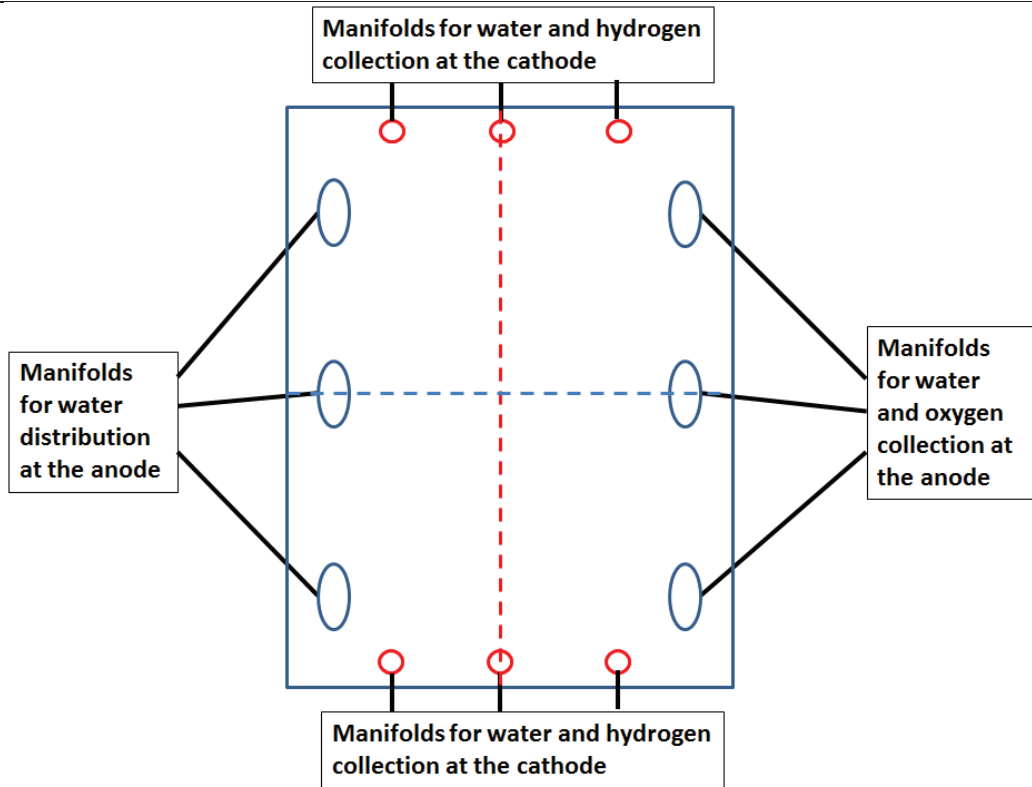
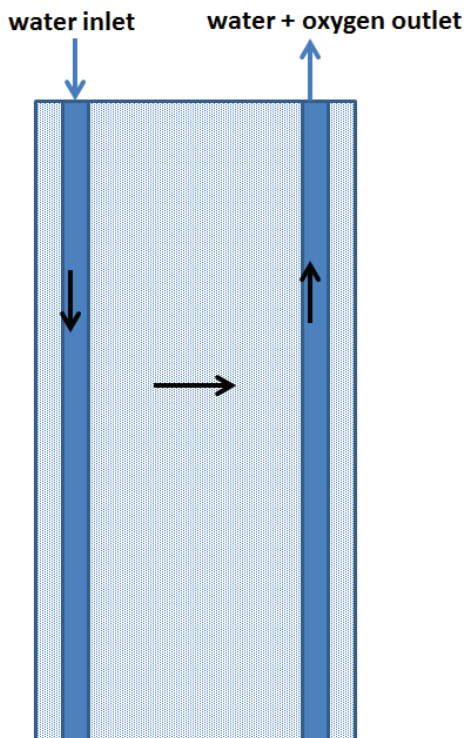


Figure 3: Top view of the cell

**Cross-section with anode manifolds**



**Cross-section with cathode manifolds**

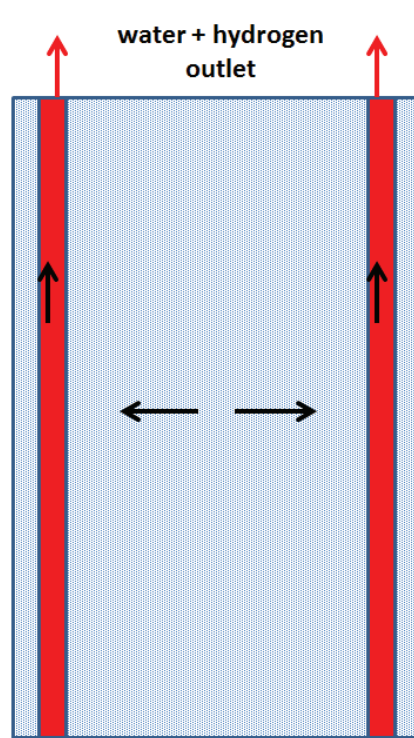


Figure 4: Cross-section views of the stack with anode/cathode manifolds

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Four design questions that need **multi-physics** models simulation have been identified at the moment:

- **Heat transfer limitation:**

*Operating constraint: Max  $\Delta T = 3$  K between inlet and outlet for standard operating conditions and also at high current density ( $3$  A/cm<sup>2</sup>).*

For large stack, heat removal implies large flow rates. Without the flow field plates, large flow rates implies important pressure drop:

- On the anode side, importance of the flow field plate (and characteristics) for proper heat removal while minimizing the pressure drop.

- **Mass transport limitation:**

*Operating specification: Operate the stack until  $3$  A/cm<sup>2</sup> without mass transfer limitation.*

- Optimize what can be optimized to try to reduce the mass transport limitation.

- **Current collector thickness:**

*Optimize its thickness to obtain the best performance while minimizing the cost*

- Impact of the current collector thickness on performance and heat and mass transport limitations. Give recommendations to WP4.

- **Homogeneous local conditions:**

*Design recommendations to operate the stack with local conditions as homogeneous as possible.*

Two other design questions have been identified, but they should require only **single-phase flow** simulations:

- **Design of the cell plate manifolds:**

*Optimize the geometry (number of manifold and detailed geometry) to have a flow as homogeneous as possible at the inlet of the cell.*

- **SINTEF proposes to perform these single-phase flow computations with FLUENT (no model development)**

- **Design of the stack manifolds:**

Is it possible to give recommendations for the design of:

- The inlet nozzle. Avoid too high velocity at the stack inlet that can lead to water starvation of the first cells.
- Varying section of the stack manifold. Optimize its section for homogeneous stack operating conditions.

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### 3. MODELS DESCRIPTION

#### 3.1 Two-phase flow model at channel and cell levels

##### 3.1.1 Main goal of the model

The main goal of the model is to study the two-phase flows in a PEM water electrolysis cell and to provide appropriate physical fields as input values either for the multi-physic model at cell level or for the more macroscopic model at stack level. A basic physical model is described in the following sections. Further developments of the model will be made during the project in order to consider all the aspects involved in the electrolysis process, such as two-phase flows in current collector (porous domain) and heat transfer.

##### 3.1.2 Geometry and scale

The current model mainly deals with the two-phase flows inside the **channels of the flow field plate**, at the **cell level**. It will be extended to study the two-phase flows also in the **current collectors**. Regarding the scale of description of the two-phase flow, the big bubbles are captured by the model, while the effect of the small one is modeled via *sub-grid treatment*. This means that the bubbles whose size is smallest than the size of the computing mesh are not explicitly described. However, their dynamic and effect are modeled using sub-grid models.

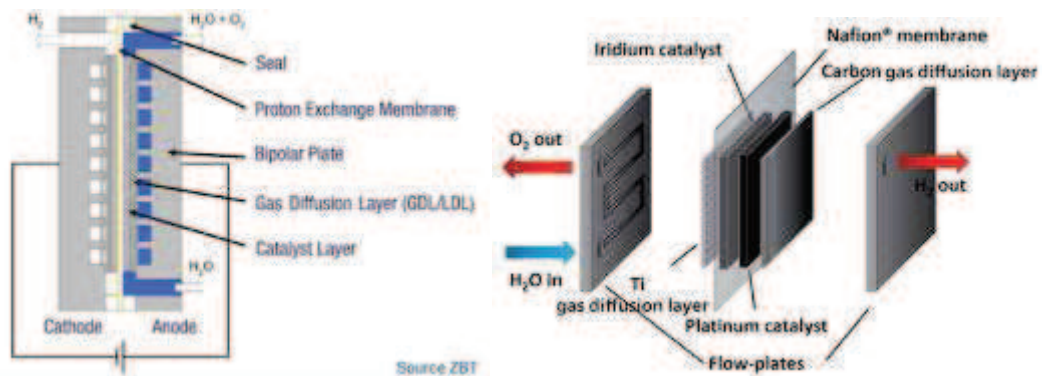


Figure 5: PEMWE assembly

##### 3.1.3 Physical model

###### Governing equations:

The evolution of macroscopic fluid-fields (velocity, density) is governed by the volume of fluid (VOF) model, where phase fractions  $\alpha_k$  are determined by a transport equation of the form:

$$\frac{\partial}{\partial t}(\alpha_k \rho_k) + \nabla \cdot (\alpha_k \rho_k \mathbf{u}) = S_k \quad (1)$$

where  $S_k$  is a source term for the  $k^{th}$  phase.

The following constraint applies to the phase fractions:

$$\sum \alpha_k = 1 \quad (2)$$

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A single momentum equation is solved for a mixture fluid, and the resulting velocity field is shared among the phases. Assuming that the mixed flow field is incompressible, the momentum equation is in the form:

$$\frac{\partial}{\partial t}(\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla p + \nabla \cdot (\mu(\nabla \mathbf{u} + \nabla \mathbf{u}^T)) + \rho \mathbf{g} + \mathbf{F} \quad (3)$$

The material properties, such as  $\rho$  and  $\mu$  are determined by the presence of the component phases in each control volume. In a gas-liquid two-phase system, for example, the density in each cell is given by:

$$\rho = \alpha_g \rho_g + (1 - \alpha_g) \rho_l \quad (4)$$

The transport and evolution of dissolved specie, i.e. dissolved  $O_2$  is solved by a generic advection-diffusion equation:

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla \cdot (\mathbf{u} \rho Y_i - \rho D_i^e \nabla Y_i) = S_i^p - S_i^c \quad (5)$$

where  $Y_i$  is mass fraction of the dissolved specie and  $D_i^e$  is effective diffusivity. The terms on the right-hand side of the equation,  $S_i^p$  and  $S_i^c$  describe source and sink terms due to production and consumption of the specie. For the dissolved  $O_2$  in water, the production is determined by Faraday's law according to local current density. The consumption consists of bubble nucleation and mass transfer to continuous gas phase.

#### Sub-grid treatment of bubbles:

The scales related to bubbly dynamics range from large scale bubbles to microscopic ones, which cannot be resolved in a practical calculation. A sub-grid population balance model (PBM) is used to treat the microscopic bubbles via a sub-grid phenomena as well as a transfer mechanism to resolved scales. The number density of bubbles is governed by an advection-diffusion equation:

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (f(\mathbf{u}) n_i - D_{n_i} \nabla n_i) = b_i - d_i \quad (6)$$

where  $f(\mathbf{u})$  is an advection function and  $D_{n_i}$  is a diffusion coefficient. The advection function serves as the principal model of coupling to fluid flow, simply by transport, while the diffusion coefficient will serve as a secondary source of bubble motion, preventing unphysical local accumulation of several bubbles. The birth and death terms  $b_i$  and  $d_i$  account for nucleation, nucleation, coalescence and mass transfer.

The bubble classes are described by an exponential discretization in volume:

$$V_{i+1} = q V_i \quad (7)$$

where  $q > 1$ , as shown in Figure 6.

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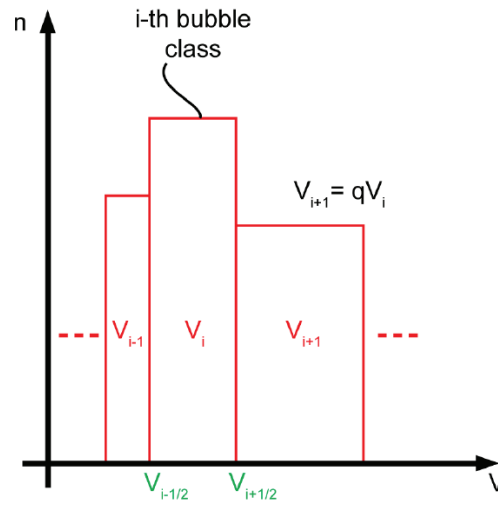


Figure 6: Sketch of discrete PBM distribution

- **Nucleation of gaseous bubbles**

In the model, nucleation of bubbles occurs when the local species molar fraction (or concentration) exceeds the (local) saturation molar fraction (solubility).

The rate of mass transfer of a bubble with surface area  $V = f_1 d^2$  is given by:

$$\dot{m} = f_1 d Sh D (c_b - c_s) \quad (8)$$

where  $Sh$  is the Sherwood number and  $D$  is diffusion coefficient.  $c_b$  and  $c_s$  are bulk concentration and saturation concentration respectively.

Considering an isobaric expansion of a bubble with volume  $V = f_2 d^3$ , the mass transfer rate can also be written as:

$$\dot{m} = \rho_g \frac{dV}{dt} = 3\rho_g f_2 d^2 \frac{dd}{dt} \quad (9)$$

Hence, the bubble diameter is determined as:

$$d(t) = \sqrt{K\Delta c t} + d(0) \quad (10)$$

where

$$K = \frac{2 Sh D f_1}{3 \rho_g f_2} \quad (11)$$

The time for a bubble reaching a detachment diameter is then calculated with the initial diameter  $d(0) = 0$ .

$$t_d = \frac{d_d^2}{K\Delta c} \quad (12)$$

Assuming the nucleation time is identical to the detachment time, the nucleation frequency with the number of active pores  $N_p$  is given as:

$$f = \frac{N_p K \Delta c}{d_d^2} \quad (13)$$



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- **Bubble birth and death due to coalescence**

For the case of sub-grid bubble treatment, bubble breakup is neglected. Considering binary interaction, the birth and death terms due to coalescence are given as:

$$b_i = \frac{1}{2} \int_0^{V_i} a(V_i - V', V') n(V_i - V') n(V') dV' \quad (14)$$

$$d_i = n(V_i) \int_0^{\infty} a(V_i, V') n(V') dV' \quad (15)$$

where the coalescence kernel  $a(V_i, V')$  is a measure of the frequency of collisions between bubbles of volume  $V_i$  and  $V'$  which successfully results in a bubble of volume  $V_i + V'$ .

Coalescence kernel

Bubble coalescence is considered as a three-step process. First, bubbles collide, trapping a small amount of liquid between them. The trapped liquid drains until the liquid film separating the bubbles reaches a critical thickness and ruptures, allowing for coalescence. Hence, the coalescence kernel is usually described as a product of the frequency of collisions  $\Omega_{ij}$  and the probability of coalescence  $P_{ij}^C$ .

$$a_{ij} = \Omega_{ij} P_{ij}^C \quad (16)$$

The collision frequency can be determined through a characteristic, relative velocity  $v_{ij}$  and a distance between two bubbles  $b_{ij}$ , i.e.

$$\Omega_{ij} = kv_{ij} b_{ij}^2 \quad (17)$$

Bubble coalescence is considered as the consequence of a successful collision event, the interaction time of two bubbles  $t_I$  exceeding the coalescence time required for liquid film to drain and rupture  $t_C$ . A simple expression of the coalescence probability is written as:

$$P_{ij}^C = \exp\left(-\frac{t_C}{t_I}\right) \quad (18)$$

- **Bubble birth and death due to mass transfer**

A growing population can be described as

$$\frac{dn_i}{dt} = \frac{G_V^{i-1} n_{i-1}}{V_i - V_{i-1}} - \frac{G_V^i n_i}{V_{i+1} - V_i} \quad (19)$$

where the first term on the right-hand side represents growth into the  $i^{\text{th}}$  bubble class while the second term represents growth out of the bubble class.  $G_V^i$  is the corresponding bubble growth rate.

$$G_V^i = \frac{dV_i}{dt} \quad (20)$$

- **Birth and death terms of bubble classes**

In the case of  $M + 1$  bubble classes, the birth and death terms of each bubble class are determined individually. For the smallest bubble class (i.e.,  $i = 1$ ), nucleation is considered as the birth term while the death term consists of bubble death due to coalescence and mass

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transfer. For other bubble classes ( $i = 2, \dots, M$ ), bubble birth and death are obtained from both coalescence and mass transfer. The bubble class ( $i = M + 1$ ) is treated as an additional class and the rate of change of the additional bubble class is determined by bubble birth due to coalescence and mass transfer.

### Coupling to macroscopic bubbles

In the present model, macroscopic (resolved) bubbles are treated directly by means of the VOF model. The PBM formalism is used to couple the two models involved. Considering a population of  $M$  bubble classes, the transition to the continuous phase is treated by extending the population with the aforementioned additional bubble class  $M + 1$ , which represents the smallest possible concentration of the gas phase. The additional bubble class is denoted as a ghost class with subscript  $G$ . The volume of a ghost bubble is defined as:

$$V_G = qV_M \quad (21)$$

The number density of the ghost bubbles is determined from the volume fraction of the gas phase, i.e.

$$n_G = \frac{\alpha_g}{V_G} \quad (22)$$

Considering coalescence of bubbles and mass transfer, its rate of change is analogous to that of the PBM and is given as:

$$\dot{n}_G = \frac{1}{2} \int_0^{V_G} a(V_G - V', V') n(V_G - V') n(V') dV' + \frac{G_M n_M}{V_G - V_M} \quad (23)$$

The rate of change for the ghost class serves as a mass source for the continuous gas phase, i.e. the source term of the gas phase in equation 1.

$$S_g = \rho_g V_G \dot{n}_G \quad (24)$$

Thus, once an entity of the population has evolved to the ghost class, it is transferred to the continuous phase from which the VOF model tracks further evolution.

### 3.1.4 Expected input/output

The model intends to study the gas-liquid two-phase flows and heat transfer in both current collector and channels of the flow field plate using VOF. Therefore, it will be necessary to extend the present formulation of the model to the porous media of the current collector and to consider heat transfer.

Expected input for the model would be the **local distribution of current density** on catalytic layer, which is directly related to gas bubble formation. If local distribution of current density is not available, another interesting input would be the **local distribution of dissolved oxygen** on the catalytic layer.

In addition, **local distribution of heat generation** due to the electrochemical reaction would be necessary for the model when studying heat transfer at cell level.



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The two-phase flow pattern predicted by the model should be an input for the multi-physics model at cell level in COMSOL. The averaged procedure applied to the phase and velocity fields obtained with the VOF model, should be coherent with the two-phase flow description used in the multi-physic model of COMSOL.

Furthermore, an average of the phase and velocity fields should be performed over time and over the section of the flow field channels to determine the mean void fraction and velocities at a scale coherent with the one used in the stack model and determine appropriate two-phase flow correlations.

### **3.2 Multi physics model at MEA and cell levels**

The model description covers the current status of a multi-physics model for high pressure PEM electrolysis cell operating at high current densities.

#### **3.2.1 Main goal of the model**

The main goal of the present model is to study the multi-physics relations in a PEM electrolysis cell and to predict the I-V-characteristics including all voltage losses at cell level. By means of sensitivity analysis the effect on the I-V-curve due to a variation of operating parameters, design parameters and material properties of the current collector can be studied. The main cell component of focus is the porous current collector. The effect of the current collector microstructure on the cell performance especially at high current densities ( $>2 \text{ A/cm}^2$ ) can be studied with the model. Therefore, the model can be used in design process with focus on upscaling issues on cell level.

In the MEGASTACK project the model will be extended by focusing on the following topics:

- Implementation of anisotropic material properties for current collector (such as in-plane and through-plane electrical conductivity, as well as gas and liquid permeability) to describe its electrical and hydraulic characteristics.
- Coupling with two-phase flow transport equation in porous domains to describe mass transport limitations in the current collector and in the catalyst layer at high current densities.
- Computation of the local current density distribution at the current collector/electrode interface.

#### **3.2.2 Geometry and mesh**

The current geometry is a 2D cross-section of a single cell (see Figure 7). The modeled components at macro scale are the current collectors, catalyst layer and the membrane. Separate flow channels are not included for the moment. For the different components, different quadrilateral meshes are used, that also include boundary layers.

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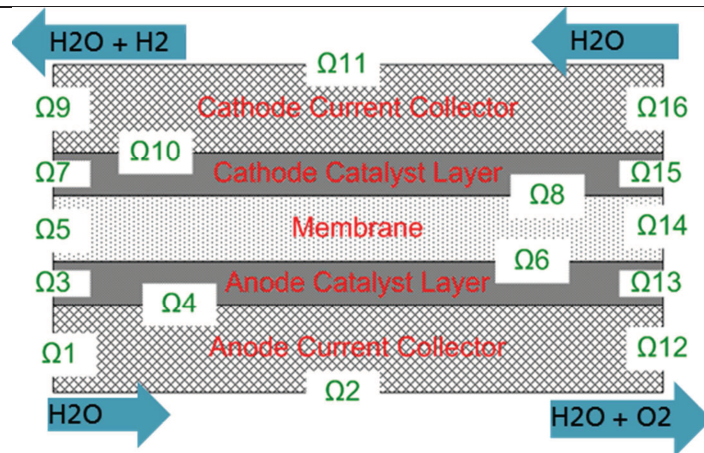


Figure 7: Cross-section of the cell considered in the multi-physic model at cell level.

To describe the different components with different physics the following domains are introduced:

| Component                 | Domain |
|---------------------------|--------|
| Anode current collector   | 1      |
| Anode catalyst layer      | 2      |
| Membrane                  | 3      |
| Cathode catalyst layer    | 4      |
| Cathode current collector | 5      |

### 3.2.3 Physical model

The multi-physics model uses codes of COMSOL Multiphysics and is solved by the finite element method containing different selectable solvers.

#### a. Electric currents

To handle stationary electric currents in conductive media the following governing equations are used in the domains 1, 2, 4, 5:

Governing equations:

Stationary equation of continuity:

$$\Delta \cdot J = Q_j \tag{25}$$

Ohms' law:

$$J = \sigma E + J_e \tag{26}$$

Gauss' law:

$$E = -\nabla V \tag{27}$$

Parameters:

- $J$  current density
- $J_e$  externally generated current
- $Q_j$  current source, sink

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$\sigma$  electric conductivity  
 $E$  electric field intensity

The electric conductivity is defined for the current collectors as well for the catalyst layers. For the domain 2 a constant electric current source and for domain 4 a constant current sink is defined.

The following boundary conditions are set.

| Boundary condition  | Equation        | Boundaries ( $\Omega$ )              |
|---------------------|-----------------|--------------------------------------|
| Electric potential  | $V = V_0$       | 11 ( $V_0=0$ ), 2 ( $V_0=V_{cell}$ ) |
| Electric insulation | $n \cdot J = 0$ | 1,3,6,7,8,9,12,13,15,16              |

### b. Ionic currents

To describe stationary ionic currents in conductive media the equations (25), (26), and (27) are used in the domains 2, 3, 4. The ionic conductivity is defined for the anode catalyst layer, the membrane and the cathode catalyst layer. For the domain 2 a constant ionic current sink and for domain 4 a constant current source is defined. The following boundary conditions are set.

| Boundary condition | Equation        | Boundaries ( $\Omega$ ) |
|--------------------|-----------------|-------------------------|
| Ionic insulation   | $n \cdot J = 0$ | 3,4,5,7,10,13,14,15     |

### c. Reacting flow in Porous Media

To describe mass and momentum transport in porous media, we currently use the following approach. Continuity equation and Brinkman model are used for the liquid water, while the different gases are supposed to be transported by the water in a solubilized form. Therefore the following equations are used in the domains 1, 2, 4, 5:

#### Governing equations:

Mass balance:

$$\nabla \cdot (-D_i \nabla c_i) + u \cdot \nabla c_i = R_i \quad (28)$$

Brinkman equation:

$$\frac{\rho}{\varepsilon_p} \left( (u \cdot \nabla) \frac{u}{\varepsilon_p} \right) = -\nabla p + \nabla \left[ \frac{1}{\varepsilon_p} \left\{ \mu (\nabla u + (\nabla u)^T) - \frac{2}{3} \mu (\nabla \cdot u) I \right\} \right] - \left( \frac{\mu}{k} + \frac{Q_{br}}{\varepsilon_p^2} \right) u \quad (29)$$

Continuity equation:

$$\nabla \rho \cdot u = Q_{br} \quad (30)$$

#### Parameters:

$c_i$  concentration of specie i (H<sub>2</sub> cathode, O<sub>2</sub> anode)  
 $D_i$  diffusion coefficient

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|                 |                                       |
|-----------------|---------------------------------------|
| $R_i$           | reaction rate expression for specie i |
| $\mu$           | dynamic viscosity of the fluid        |
| $u$             | Liquid velocity vector                |
| $\rho$          | density of the fluid                  |
| $p$             | pressure                              |
| $\varepsilon_p$ | porosity                              |
| $k$             | permeability of porous medium         |
| $Q_{br}$        | mass source, sink                     |

Density and dynamic viscosity of the fluid (water) are defined. For the anode domains (1, 2) the diffusion coefficient is defined for oxygen. For the cathode domains (4, 5) the diffusion coefficient is defined for hydrogen. For the domains 1, 2, 4, 5 the porosity and permeability is given. For the domain 2 a mass sink (water consumption, electroosmotic drag) and for domain 4 a mass source (water production, electroosmotic drag) is defined. For the domain 2 a reaction rate for oxygen (Faraday) and for domain 4 a reaction rate for hydrogen (Faraday) is defined.

The following boundary conditions are set for momentum transport.

| Boundary condition                               | Equation   | Boundaries ( $\Omega$ ) |
|--|--|-------------------------|
| Inlet fluid flow, (velocity)                     | $u = u_0$  | 1,3,15,16               |
| Outlet fluid flow, (pressure, no viscous stress) | $p = p_0,$<br>$[\mu(\nabla u + (\nabla u)^T)] \cdot n = 0$ | 12,13,7,9               |
| Wall, (no slip)                                  | $u = 0$  | 2,6,8,11                |

The following boundary conditions are set for mass transport.

| Boundary condition    | Equation                      | Boundaries ( $\Omega$ )           |
|-----------------------|-------------------------------|-----------------------------------|
| No flux               | $-n \cdot N_i = 0$            | 2,6,8,11                          |
| Species concentration | $c_i = c_{0,i}$               | 1,3 (oxygen),<br>15,16 (hydrogen) |
| Out flow              | $-n \cdot D_i \nabla c_i = 0$ | 7,9,12,13                         |

#### d. Heat transfer in porous media

To describe heat transfer in the fluid and the porous matrix the following equations are used in the domains 1, 2, 3, 4, 5:

Governing equations:

Heat equation (porous matrix):

$$\rho C_p u \cdot \nabla T = \nabla \cdot (k_{eq} \nabla T) + Q \quad (31)$$

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$$k_{eq} = \theta_p k_p + (1 - \theta_p)k \quad (32)$$

**Parameters:**

|            |   |
|------------|---|
| $\rho$     | density   |
| $C_p$      | heat capacity at constant pressure                      |
| $k$        | thermal conductivity of fluid                           |
| $k_{eq}$   | thermal conductivity (bulk)                             |
| $k_p$      | thermal conductivity of solid material in porous matrix |
| $\theta_p$ | volume fraction of solid material in porous matrix      |
| $u$        | liquid velocity field                                   |
| $Q$        | heat source, sink                                       |

Thermal conductivity, density and heat capacity of the fluid (water) are defined. For the domain 1 volume fraction, thermal conductivity, density and specific heat capacity is defined for the porous matrix. For the domains 1 and 5 volume fraction, thermal conductivity, density and specific heat capacity is defined for the porous matrix (current collector). For the domains 2, 3, 4 volume fraction, thermal conductivity, density and specific heat capacity is defined for the porous matrix (Membrane). For the domain 2 a hat source is defined as a function of cell current and total voltage loss.

The following boundary conditions are set for heat transfer:

| Boundary condition | Equation                   | Boundaries ( $\Omega$ ) |
|--------------------|----------------------------|-------------------------|
| Thermal insulation | $-n \cdot (k\nabla T) = 0$ | 2,5,11,14               |
| Wall, (no slip)    | $T = T_0$                  | 1,3,15,16               |

**e. Calculation of cell voltage**

To describe the I-V-characteristic the cell voltage is calculated by the following equation:

$$V_{cell} = E_0 + \sum \eta_{act} + \sum \eta_{ohm} + \sum \eta_{diff} + \eta_{bubble} \quad (33)$$

$E_0$  is the reversible cell voltage and it is evaluated by the empirical equation:

$$E_0 = 1.48 - 0.9 * 10^{-3}(T - 298) + \frac{RT}{4F} \ln \left( \frac{1}{P_o^{0.5}} \right) \quad (34)$$

$P_o$  is the operating pressure (assumed to be constant).

The **activation overpotential** is the sum of the anode and cathode activation overpotentials.

$$\sum \eta_{act} = \eta_{act,an} + \eta_{act,cat} \quad (35)$$

Assuming a homogenous current density distribution, the activation overpotentials are calculated from the Butler-Volmer equation:

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$$\eta_{act,an} = \frac{RT_{an}}{\alpha_{an}} \sinh^{-1} \left( \frac{i}{4 * i_{o,an}} \right) \quad (36)$$

$$\eta_{act,cat} = \frac{RT_{cat}}{\alpha_{cat}} \sinh^{-1} \left( \frac{i}{2 * i_{o,cat}} \right) \quad (37)$$

Where  $i_{0,i}$  is the exchange current density for the anode and cathode reaction respectively and is modeled by:

$$i_{0,i} = nSk_o \exp \left( \frac{-E_{act,i}}{RT} \right) \quad (38)$$

It is determined from rotating disk electrode (RDE) experiments.  $n$  is the number of electrons involved in the electrochemical reaction,  $S$  is the specific surface of the electro catalysts,  $k_o$  is the rate constant and  $E_{act,i}$  is the activation energy for the electrochemical reaction.

The **ohmic overpotential** is the sum of losses resulting from the resistance to the transport of protons through the membrane ( $\eta_{ohm,m}$ ) and resistance to the flow of electrons through the electrically conducting internal cell components. When the current collectors ( $\eta_{ohm,an}$ ,  $\eta_{ohm,cat}$ ) and bipolar plates are made from highly conductive metals like titanium, it is assumed that proton transport is the dominant cause for ohmic losses.

$$\sum \eta_{ohm} = \eta_{ohm,an} + \eta_{ohm,m} + \eta_{ohm,cat} \quad (39)$$

The ohmic loss over the membrane is calculated by the ohm's law:

$$\eta_{ohm,m} = \frac{d_{PEM}}{\sigma_{PEM}} i \quad (40)$$

where  $d_{PEM}$  is the thickness of the polymer electrolyte membrane and  $\sigma_{PEM}$  is its proton conductivity. The proton conductivity depends on the membrane hydration and is determined by means of the empirical equation:

$$\sigma_{PEM} = (0.005139\lambda - 0.00326) \exp \left( 1268 \left( \frac{1}{303} - \frac{1}{T} \right) \right) \quad (41)$$

$\lambda$  is the membrane hydration expressed as the ratio of mole water per mole of sulfone group. For Nafion membranes, the value of  $\lambda$  is usually between 14 and 21 depending on the level of hydration. In fuel cell where the hydration level can vary strongly, the exact determination of the  $\lambda$  value is critical. For water electrolysis though, where water is the main flow medium, it is assumed that the membrane is fully hydrated and a  $\lambda$  value of 25 is used.

The **diffusion overpotential** addresses the losses that arise from the poor transport of reactant water across the current collector to the active site due to the presence of dissolved gasses. It is the sum of the effect on the half cells:

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$$\sum \eta_{\text{diff}} = \eta_{\text{diff,an}} + \eta_{\text{diff,cath}} \quad (42)$$

The diffusion overpotential is estimated by the Nernst equation:

$$\eta_{\text{diff,an}} = \frac{RT_{\text{an}}}{nF} \ln \left( \frac{C_{\text{g,m}}}{C_{\text{g,ref}}} \right) \quad (43)$$

The diffusion overpotential for the cathode side is calculated respectively.  $C_{\text{g,m}}$  is the concentration of dissolved gas at the membrane/electrode interface. An averaged value at the membrane/electrode interface is considered.  $C_{\text{g,ref}}$  is the concentration of dissolved gas at a reference position. In PEM water electrolysis, oxygen is the gaseous species in the anode and hydrogen in the cathode. Gasses produced at the electrodes are transported away by the water flow, and momentum transport of the water flow is solved by the Brinkmann model (29) and species distribution by (28). Since the porous current collector is the cell component of focus, the  $C_{\text{g,ref}}$  value is taken as the concentration of dissolved species at the bipolar plate. Thus, the concentration overpotential takes into account the concentration gradient of the dissolved species across the current collector.

**Bubble overpotential** refers to losses at very high current densities due to low water stoichiometry and bubble coverage in the current collector. The water balance, bubble size and microstructure of the current collector are vital parameters for estimating the bubble overpotential. The “bubble overpotential” is estimated by using the following equation:

$$\eta_{\text{bubble}} = \frac{R * T_i}{2 * F} * \left( \frac{\alpha}{\beta} \right)^2 \quad (44)$$

Where  $\alpha$  is a factor that represents the ratio of produced gas (oxygen) to supplied water at the entrance of the cell:

$$\alpha = \frac{\dot{V}_{\text{gas}}(T, P, i)}{\dot{V}_{\text{h}_2\text{o}}} \quad (45)$$

and  $\beta$  is a factor describing the pore blockage as the ratio of pore and bubble diameter

$$\beta = \frac{d_p^2}{d_p^2 - (d_p - \delta_m)^2} \quad (46)$$

It is assumed that gas bubbles start to form only after the concentration of dissolved gasses in the surrounding water has reached full saturation. Gas bubbles are treated as ideal gasses and the mean bubble diameter is then calculated using the following relationship:

$$\delta_m = \frac{1}{n_{\text{nucleation sites}}} * \left( \frac{6 * \frac{R * T}{P} * \int_{\Omega_4} (C_{\text{gas}} - C_{\text{sat,gas}}) dx}{\pi} \right)^{1/3} \quad (47)$$

Where  $C_{\text{sat,gas}}$  is the supersaturation at the direct vicinity of the electrode interface and is estimated by means of Henry's law, while  $n_{\text{nucleation,sites}}$  is the theoretical number of

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bubbles. Thus far in literature, bubble size and bubbles effects have been considered mainly in the flow channels. The size of bubbles and the effect of coverage on the current collector/electrode interface have not been reported. In this model, although the approach of the tracking of nucleation, growth and detachment of discrete bubbles in a two-phase flow has not been followed, an aggregation method for estimating the critical bubble size at the current collector MEA interface and blockage of the current collector's pores has been developed. This together with the water stoichiometry is used to calculate the bubble overpotential as described in (44).

*Parameters:*

|                          |  |
|--------------------------|--|
| $V_{\text{cell}}$        | applied cell voltage   |
| $E_0$                    | open cell voltage, (as a function of operating temperature and pressure) |
| $\eta_{\text{act,an}}$   | anode activation over potential,   |
| $\eta_{\text{act,cat}}$  | cathode activation over potential  |
| $\eta_{\text{ohm,an}}$   | Voltage loss due to ohmic resistance in anode current collector          |
| $\eta_{\text{ohm,m}}$    | Voltage loss due to ohmic resistance in membrane                         |
| $\eta_{\text{ohm,cat}}$  | Voltage loss due to ohmic resistance in anode current collector          |
| $\eta_{\text{diff,an}}$  | diffusion over potential, anode  |
| $\eta_{\text{diff,cat}}$ | diffusion over potential, cathode  |
| $\eta_{\text{bubble}}$   | Voltage loss due to gas bubbles, anode                                   |

All voltage losses and over potentials are defined as variable expressions, that use the simulations results of the described physics in sections a to d.

### ***3.2.4 Expected input/output***

Expected Output ISE (current model):

The main goal of the present model is to study the multi-physics relations in a PEM electrolysis cell and to predict the I-V-characteristics including all voltage losses at cell level. The current model uses an aggregation method to calculate the “bubble overpotential”.

The **different voltage losses**, including their dependence to the operating conditions, can be used as an input for the electrochemical semi-empirical law of the stack model.

The current model can be used to calculate the **concentration profiles of dissolved oxygen**. These profiles can be used as input parameter for the two-phase model of SINTEF. The concentration profiles can be determined either at the electrode/current collector interface or at the current collector/channel interface depending on the domain considered by SINTEF (either current collector and channels; or only channels).

Expected Output ISE (extended model):



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The extended model will include a more detailed description (electrical and hydraulic characteristics) of the current collector by using **anisotropic material properties** and a consideration of the **layered structure** of the sinter/electrode assembly by ITM.

A further topic is the calculation of the **local current distribution** at the current collector/electrode interface. For this, the boundary condition for the current density (assumed constant in the present model) has to be redefined. This **local current distribution** and the associated **local distribution of heat generation** due to the electrochemical reaction will be provided as input parameter for the two-phase flow model of SINTEF.

This improvement will also give access to the **local overpotential**, which will thus be computed as a function of operating pressure and temperature and local conditions. This dependence of the overpotential on local conditions will be used as input parameter for the stack-model of CEA.

Further, the **mass transport limitation** due to **gas bubbles** in the porous domains and at the electrode interface will be considered to substitute/enhance the aggregation method.

#### Expected Input from ITM

Because the model is geometry based, cell design information and geometry data of a single cell and its single components are needed. To describe the electrical and hydraulic (single-phase) characteristics of the current collector the following data are expected from ITM (if possible for each single layer of the current collector)

- hydraulic permeability: gas and liquid, in-plane and through-plane.
- porosity, pore size distribution
- electrical conductivity (in-plane, through-plane), density

To describe the catalyst layer, the location of the catalyst is needed (coated current collector or membrane (MEA) as well as its thickness, porosity and pore size distribution. If available, other electrochemical parameters are also needed like the kinetic parameters (exchange current density from RDE measures) or alternatively the reaction rate constant, the electrochemical surface area and the activation energy.

To describe the membrane we need to know the kind of used membrane, the thickness, ionic conductivity and if known the gas permeability.

#### Expected Input from SINTEF:

The current model simplifies the fluid flow in the current collector by using the Brinkman equation for a single-phase flow. The oxygen and hydrogen are modeled as dissolved gases. Furthermore, the current model doesn't focus on the flow channel where free flow occurs.

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The expected input from SINTEF will depend on the two phase flow description that will be implemented in the extended multi-physics model. It could be time-averaged fields (void fraction, liquid and gas velocities) to be imposed in the current model. Or, if a time-averaged “macro-scale” two phase flow model is implemented at Fraunhofer, appropriate two-phase flow correlations in the anode channel and current collector.

Regarding the “macro-scale” two phase flow model, the Software COMSOL Multiphysics provides a “macroscopic” two-phase flow model that might be used to substitute equations (28) and (29). This model, available in the toolbox CFD: *Bubbly flow model*, tracks the averaged void fraction rather than in each bubble in detail. The model consists of two mass balances (one for liquid and one for gas), one momentum transport equation for the liquid and one algebraic equation between the liquid and gas velocity. If it is possible to implement our own algebraic equation of the form:

$$u_{slip} = \sqrt{\frac{4}{3} \delta_m g \frac{(\rho_L - \rho_G)}{C_d \rho_L}} \quad (48)$$

where  $C_d$  is the drag coefficient and  $\delta_m$  is the bubble diameter, one should be able to study the mass transport limitation of reactant in the current collector and the catalyst layer at high current densities.

### 3.3 Multi-physic model at stack level

The model description covers the current status of a multi-physics stack PEM Fuel cell model that is currently being adapted to PEM Water Electrolysers.

#### 3.3.1 Main goal of the model

The main goal of the **stack model** developed at CEA is to study the **main heterogeneities** between different cells of the stack, and the **main heterogeneities** along the cell (current density, temperature). The model is dynamic and is also used to study the **dynamic behavior** of the stack.

It can predict the I-V characteristic of the cell together with the main heterogeneities of different physical fields along the cell (species, current density, temperature...) to better analyze how the cell is working for different operating conditions.

It is thus used to study the **global performance** of the cell, together with the **main heterogeneities** along the cell and between the cells. It can be also used to study the dynamic response of the stack and its interaction with the system (not in the MEGASTACK project).

This stack model has been developed for PEM Fuel Cells [15] [10] [14] [7]. It will be extended to PEM Water Electrolyser in the MEGASTACK project.

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### 3.3.2 Geometry and mesh

At the cell level, it is a 1D+1D (or 2D+1D) model (Figure 8). The different components considered in the model are the bipolar plates, the channels of the flow field plates, the current collectors and the membrane. The two active layers (electrode) are modeled as interfaces between the current collectors and the membrane. One mesh is used in the thickness of each component. Thus the heterogeneities in the thickness of a component cannot be captured with this type of approach. On the surface of the cell (which corresponds to the top view of Figure 3), 10 meshes are typically used for each direction (10x10). This number is usually adapted to the main properties of the channel design.

At the stack level, it is a “3D” model, in the sense that several cell-models are connected together and the effect of the end plates of the stack are also considered (Figure 9).

Thus, with this approach, the MEA, the cell and the stack are modeled however with a **coarse description**. The main goal is to capture the main heterogeneities inside the cell/stack.

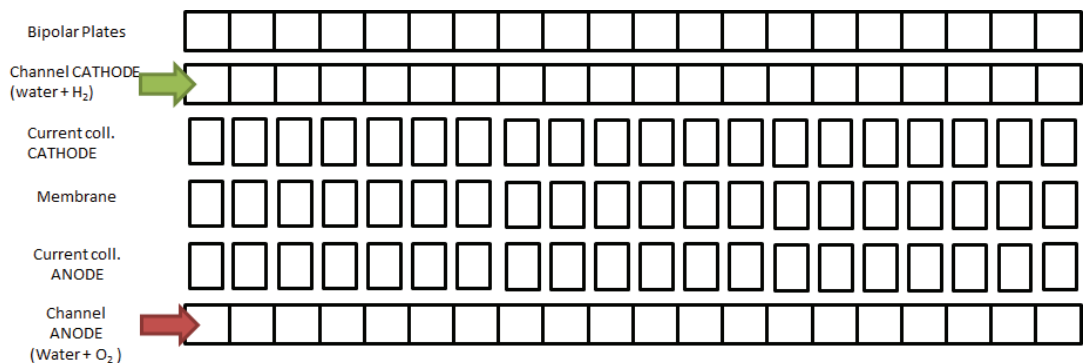


Figure 8: Geometry and meshing of a single cell for the “stack” model. The meshing is both on the surface (1D in the figure, or 2D) to capture the inlet/outlet heterogeneities and through the thickness of the cell (+1D)

### 3.3.3 Physical model

The stack model is developed under MATLAB/Simulink and is based on a bond graph approach (using similitude with *electrical RLC circuit*, [6]). It involves the combination of elementary blocks for **mass and energy balances** with others dedicated to **transport phenomena**, both for the in-plane (2D) and through-plane (1D) directions [4]. Each transport block is represented by a *resistive* element (called R) and each balance block is represented by a *capacitive* element (called C). The model can also be seen as a finite volume approach with the computation of mass and energy balance equations in each cell together with the computation of fluxes between the different cells (Figure 10).

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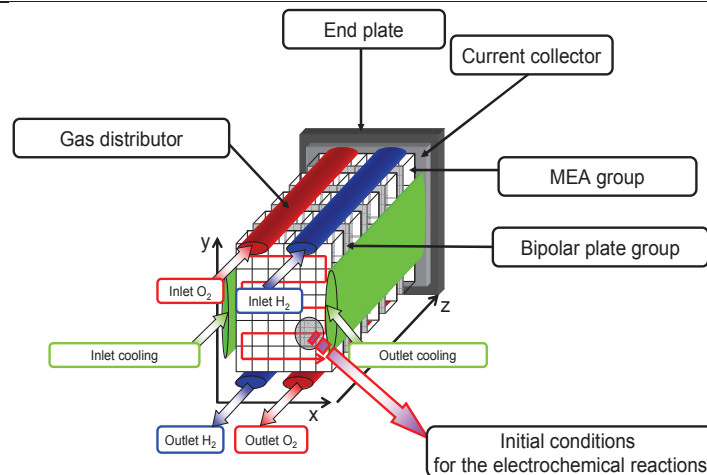


Figure 9: Geometry and meshing of a PEM Fuel Cell Stack

## Main hypothesis/approximations

- To describe the heat and mass transport of the water and of the gases, a **two-phase model** is considered. The different species considered are water (liquid, steam), oxygen and hydrogen.
- In the channel, liquid and gas phases are assumed to have the same pressure. But, in the current collectors, two pressures are considered to take capillarity effect into account.
- Gas phase properties are calculated using the perfect gas law even for steam.
- Liquid and gas are assumed to be at the same temperature. If steam is present, its partial pressure is at saturation.
- Calorific power is supposed to be constant and viscosity is temperature dependent.
- In liquid single-phase situations, to prevent numerical failure, the gaseous phase remains above a threshold with a minimum number of volumetric steam moles (set to a very low value). This is mandatory to calculate those of the liquid properties that come from the gas ones.

The equations used in the model are given in Table 1.

## Channels

**Two-phase flows** are considered with liquid water and either hydrogen or oxygen gas depending on the cell side:

- **Molar balance equations** are written for water (liquid + steam) and for non-condensable gas (equation 10 in Table 1). They involve all the fluxes of gas and water towards the adjacent meshes (in the channel) and towards the current collectors.
- **Velocities** of each phase are linked to **pressure drop** using flowrate coefficients linked to head loss coefficients (bond graph approach) (3, 3').
- **A balance for the total enthalpy** is written (water and gas). Heat exchange through the plate with adjacent cell channel is considered together with the heat flux associated with the mass flux toward the adjacent meshes (in the channel) and toward the current collectors (2). It gives access to the local temperature (4).

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Pressure of gas is then obtained from the perfect gas law using the molar concentration and the temperature (5). Pressure of liquid is assumed to be the same. Species mass fractions are calculated (9). The mole number of water is distributed into liquid and steam ones depending on the value of the water pressure compared to the saturation pressure (7).

### Current collectors, active layers

As in the channels, various balance equations are written:

- The **molar balance equations** are written for water (liquid + steam) and gas involving the molar fluxes toward the channel and the membranes (idem 10).
- **Velocities** of each phase are calculated using the Darcy law (11, 12).
- As in the channel, the **enthalpy balance equation** is written using heat fluxes towards channel and membrane (idem 2).

### Membrane

- A **water content balance** is written (16).
- **Water transport** is calculated thanks to electroosmotic drag (15) and to back diffusion (13). It results in the water content in the membrane from which **membrane conductivity** can be calculated.
- A **thermal balance** is written (17).

### Electrochemical answer at the catalyst interface

The local conditions in the anodic and cathodic current collectors/active layer domains are used to calculate the local electrochemical response of the cell, using a semi-empirical law that calculates the local electrochemical answer [13].

$$U = E_{rev} + \eta_{act} - RI \quad (49)$$

The over potential is calculated thanks to empirical coefficients fitted on experimental curves (20).

### Stack

Several cells working with different conditions can be calculated together. They are thermally coupled via their frontier plates using a classical Nusselt convection model (1).

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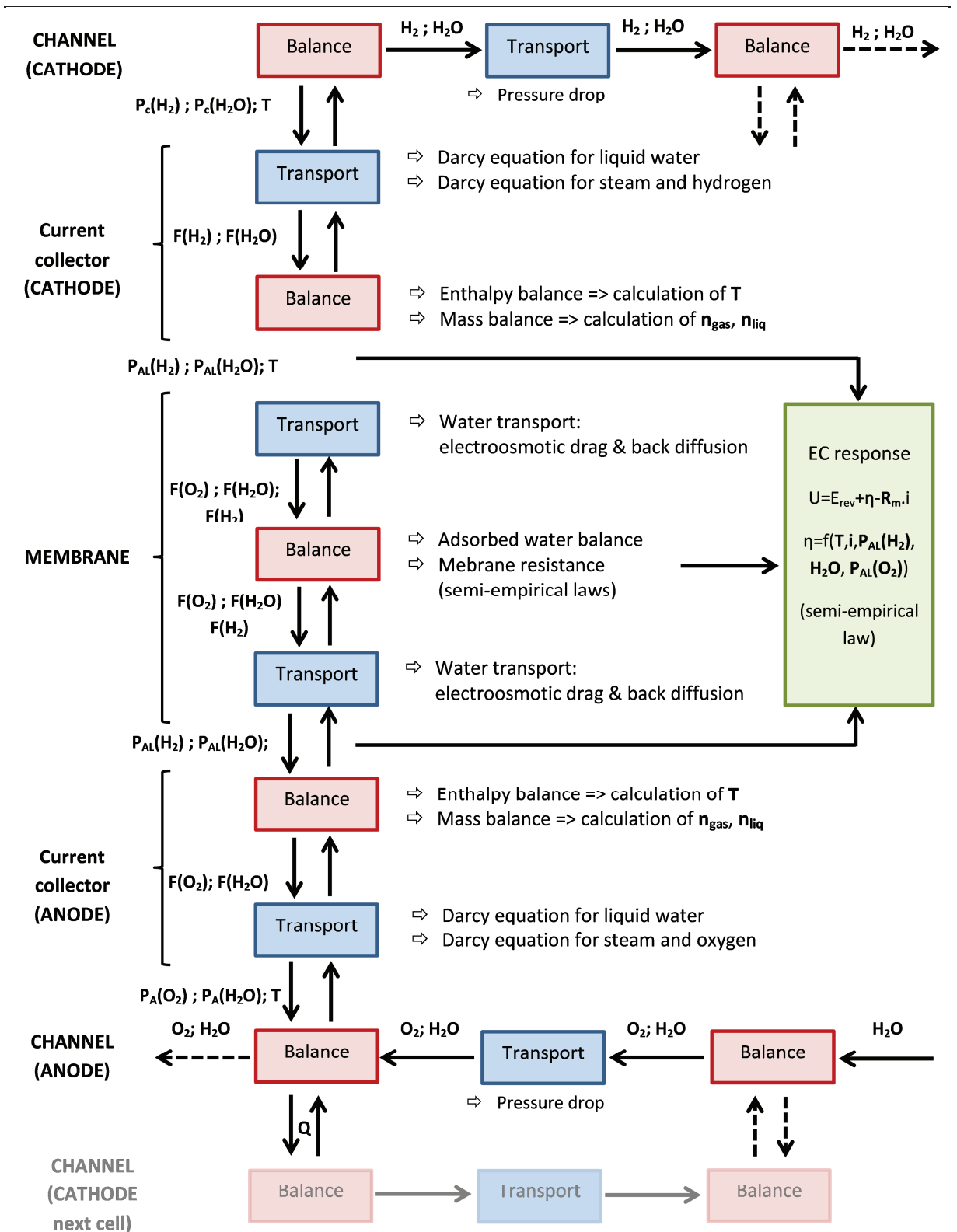


Figure 10: Overview of the physical models used for PEM Water Electrolyser

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| Name of the element | Function   | Equations solved  |  |
|---------------------|--|---|--|
| R_th                | Heat transfer flux   | $Q_j = h_j * S * (T_{in} - T_{out})$  | (1)  |
| C_th                | Thermal balance channel  | $\frac{dH}{dt} = \sum_j F_{H_i} + V \frac{dP}{dt} + \sum_j Q_i$   | (2)  |
| R_channel           | Transport of species along the channels  | $F_{gas} = (A/L) * (1-s) * C_{q\_gas} * \Delta P$<br>$F_{liq} = (A/L) * s * C_{q\_liq} * \Delta P$  | (3)<br>(3')                                    |
| C_channel           | Mass and energy balances, with thermal aspects and liquid water estimation   | $H = (n * C_p)_{H_2/O_2} * T + n_{liq} [C_{p_{sol}} T_{melt} + L_{melt}(T_{melt}) + C_{p_{liq}} (T - T_{melt})] + n_{vap} [C_{p_{sol}} (T_{melt} - T_0) + L_{melt}(T_{melt}) + C_{p_{liq}} (T_{vap} - T_{melt}) + L_{vap}(T_{vap}) + C_{p_{vap}} (T - T_{vap})]$ $P_{H_2O} = n_{H_2O} * R * T / V$ $n_{H_2O} = n_{liq} + n_{vap}$ $n_{vap} = P_{sat}(T) * V_{gas} / (R * T) \text{ if } P_{H_2O} > P_{sat}(T)$ $n_{vap} = n_{H_2O} \text{ if } P_{H_2O} < P_{sat}(T)$ $V_{gas} = V - n_{H_2O} * V_{liq} / (1 - x_{liq})$ $x_{liq} = n_{liq} / (n_{liq} + n_{vap})$ $\frac{dn_i}{dt} = \sum_{k=1}^i F_k$ | (4)<br>(5)<br>(6)<br>(7)<br>(8)<br>(9)<br>(10) |
| R_GDE               | Transport of species through the GDL and AL Darcy law  | $\frac{F_g}{S} = \frac{K K_{rg}(S)}{M_g \nu_g} \frac{\Delta P_g}{e} \text{ for gas}$ $\frac{F_l}{S} = \frac{K K_{rl}(S)}{M_l \nu_l} \frac{\Delta P_l}{e} \text{ for liquid}$ $K_{rg} = (1 - s)^3 \quad K_{rl} = s^3$  | (11)<br>(12)                                   |
| C_GDE               | Mass and energy balances   | <i>Same equations as in C_channel</i>   |  |
| R_membrane          | Transport of water through the membrane by diffusion and electro-osmosis, membrane protonic conductivity and resistance, water content of the membrane at the interface with the electrodes (anode and | $F_{diff} / S = (\rho_{sec} / EW) * D_\lambda * \Delta \lambda / e_m$ $D_\lambda (\lambda_i) = (6.707e^{-8} * \lambda_i + 6.387e^{-7}) * e^{(-2416 / T)}$ <p style="text-align: center;">Diffusion model [13]</p> $\lambda_i = \begin{cases} 0.043 + 17.81 * a_i - 39.85 * a_i^2 + 36.0 * a_i^3 & a_j \\ 14 + 1.4 * (a_i - 1) & \text{if } a_i > 1 \end{cases}$ $= \frac{P_{vap}}{P_{sat}(T)}$  | (13)<br>(14)<br>(15)                           |

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|                          |   |  |  |
|--------------------------|---|--|--|
|                          | cathode)  | <p>Adsorbption law [11]</p> $F_{eo} = a_{eo} * I / F$ <p>Electroosmosis flux [8]</p> $a_{eo} = 1 + 0.028 * \lambda_i + 0.0026 * \lambda_i^2$ $R_m = e_m / \sigma (\lambda, T)$ $\sigma (\lambda_i) = (33.75 * \lambda_i - 21.41) * \exp(- 1268 / T)$ <p>[16].</p>  |  |
| C_membrane               | Water content and temperature inside the membrane (thermal balance)         | $\frac{d\lambda_m}{dt} = \frac{EW}{\rho_{sec} * e_m * S} * \sum_i F_i$ $\frac{d}{dt} \left( (m_{liq} * C_{p_{liq}} + m_{Nafion} * C_{p_{Nafion}}) * T_m \right)$ $= \left( \sum_i Q_i + \frac{R_m}{S} * I^2 \right) +$ $C_{p_{liq}} * (F_{diff} + F_{eo}) * \sum_i (T_m - T_i)$  | (16)<br><br>(17)                         |
| Electrochemical response | Electrochemical response of the fuel cell and heat produced by the reaction | $U = E_{rev} - \eta - R_{cell} * I$ $E_{rev} = a_1 + a_2 * (T - T_0) + a_3 * T * \ln(a_{O_2}^{1/2} * a_{H_2} / a_{H_2O})$ $\eta = \beta_1 + \beta_2 * T + \beta_3 * T * \ln(i) + \beta_4 * T * \ln(P_{O_2}) + \beta_5 * T * \ln(P_{H_2})$ <p><math>\beta_6 * f(\text{liquid presence in catalyst layer})</math></p> $Q_{FC} = i * S * (U - E_{rev})$ | (18)<br><br>(19)<br><br>(20)<br><br>(21) |

Table 1: Equations of the stack model

**Nomenclature**

*Acronyms*

- AL: Active Layer
- CL: Catalyst Layer
- ECSA: Electrochemical Catalyst Specific Area
- GDE: Gas Diffusion Electrode
- GDL: Gas Diffusion Layer
- MEA: Membrane Electrode Assembly

*Symbols*

- A: channel section (m<sup>2</sup>)
- a: water activity (-)
- a<sub>eo</sub>: electro-osmotic drag coefficient (-)
- C<sub>p</sub>: calorific power (J)
- C<sub>q</sub>: pressure drop coefficient (m<sup>2</sup>.Pa<sup>-1</sup>.s<sup>-1</sup>)
- C<sub>g</sub>: gas concentration (mol.m<sup>-3</sup>)
- D: diffusion coefficient (m<sup>2</sup>.s<sup>-1</sup>)
- D<sub>λ</sub>: diffusion coefficient in the membrane (-)
- E<sub>rev</sub>: reversible potential (V)

- EW: membrane equivalent weight (kg)
- e: thickness (m)
- F: Faraday constant (C.mol<sup>-1</sup>)
- F<sub>j</sub>: volume flux for the species j (mol.s<sup>-1</sup>)
- F<sub>H</sub>: enthalpy flux from cell to next one
- H: enthalpy (J)
- h<sub>i</sub>: heat transfer coefficient for the fluid i (W.m<sup>-2</sup>.K<sup>-1</sup>)
- i: local current computed for each mesh (A.m<sup>-2</sup>)
- I: fuel cell current (A)
- K: relative permeability (-)
- L: channel length (m)
- L<sub>melt</sub>: melting heat (J)
- L<sub>vap</sub>: vaporization heat (J)
- M<sub>i</sub>: molar mass for the species i (kg.mol<sup>-1</sup>)
- m<sub>i</sub>: mass for the species i (kg)
- n<sub>j</sub>: moles for the species j (mol)
- P<sub>j</sub>: partial pressure for the j species (Pa)



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$q_{\text{gas}}$ : gas volume flow ( $\text{m}^3/\text{s}$ )  
 $Q$ : heat from thermal exchanges (W)  
 $Q_{\text{EC}}$ : heat produced by the electrochemical reactions (W)  
 $R$ : gas constant (-)  
 $R_i$ : resistance of the element  $i$  (ohm)  
 $R_p$ : pores radius (m)  
 $S$ : electrode surface ( $\text{m}^2$ )  
 $s$ : liquid water fraction (-)  
 $T$ : temperature (K)  
 $U$ : cell potential (V)  
 $V$ : volume ( $\text{m}^3$ )  
 $V_x, V_y$ : velocities for the coolant ( $\text{m}^2 \cdot \text{s}^{-1}$ )  
 $x_i$ : molar fraction for the species  $i$  (-)

#### Greek letters

$\beta$ : semi-empirical electrochemical reaction coefficients (-)  
 $\Delta P$ : pressure drop (Pa)  
 $\epsilon$ : porosity (-)

$\lambda_i$ : water content of the membrane at the interface with the electrode  $i$  (-)  
 $\lambda_m$ : water content inside the membrane (-)  
 $\nu$ : dynamic viscosity ( $\text{m}^2 \cdot \text{s}^{-1}$ )  
 $\eta$ : over potential (V)  
 $\rho_i$ : density for the species  $i$  ( $\text{kg} \cdot \text{m}^{-3}$ )  
 $\rho_{\text{sec}}$ : density of the membrane in a dry state ( $\text{kg} \cdot \text{m}^{-3}$ )  
 $\sigma$ : proton conductivity (S/m)  
 $\tau$ : tortuosity (-)  
 $\tau_{\text{degr}}$ : degradation rate of the Electrochemical Catalyst Specific Area ( $\text{m}^2/\text{s}$ )

#### Subscripts

$a$ : anode  
 $c$ : cathode  
 $m$ : membrane  
 $\text{melt}$ : melting point  
 $\text{sol}$ : solid state  
 $\text{vap}$ : vaporization point

### 3.3.4 Expected input/output

#### Expected input from ITM:

- Information about the design of the stack: number of cells, geometry of the cells and of its different components.
- Material properties of the different components when available (focus on current collector), membrane properties (Nafion? thickness?), catalyst layer properties (thickness? loading?).
- Operating conditions: nominal and “expected range”.

#### Expected input from SINTEF:

- In the CEA model, velocities or flowrates are obtained from pressure drop and flowrate coefficients (see equations 3 & 3'). These coefficients are linked to head loss coefficients. Until now these coefficients have been calibrated for single phase gaseous situations. In order to make them relevant to the two-phase flows encountered in PEMWE, **a validated model or semi-empirical correlation for the two-phase pressure drop coefficients in the channel** are expected from SINTEF.

- Since gaseous oxygen flows out from the active layer to the anodic current collector and channels, the liquid flowrate that effectively reaches the anodic active layer can be limited by this bubbles migration (see Figure 11). This is a mass transport limitation by “**blockage effect**”.

This flowrate limitation could be described by a local 2-phase CFD calculation but this approach is not compatible with the MatLab/Simulink tool. Therefore a macroscopic semi-empirical approach will be explored, based on a flooding model. This kind of model has been developed for counter-current two-phase flows, for example in vertical pipe flows with gas injection at the bottom and liquid injection at the top (see Figure 12). These models give the liquid flowrate  $Q_l$  capable to reach the bottom of

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the pipe (active layer in our case) as a function of the injected liquid flowrate  $Q_{inj}$  and of the gas flowrate  $Q_g$ . As expected, the higher the gas flowrate is; the lower the liquid flowrate capable to reach the bottom part of the pipe is. When the gas flowrate is sufficiently high, no water can flow down: this is the CCFL (Counter Current Flow Limitation). Of course these coarse models are deeply geometry dependent since they describe flows at very large scale, integrating local mechanisms such as interfacial friction without describing them.

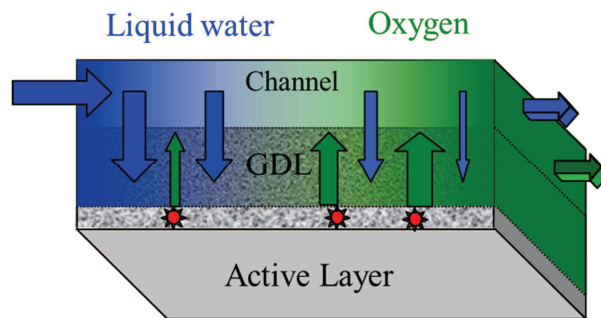


Figure 11: Spatial evolution of liquid and void fraction inside the GDL and channel on the anode side.

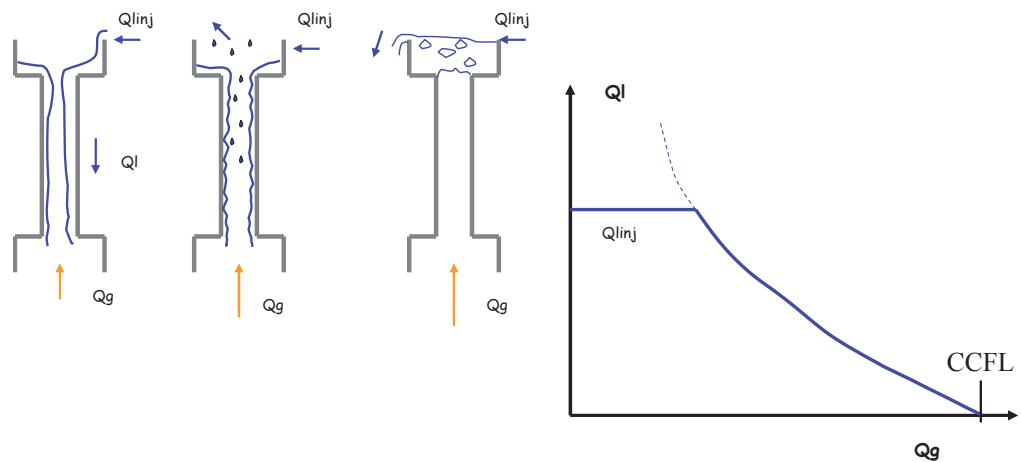


Figure 12: Flooding approach.

In the present situation, with oxygen bubbles that can limit the amount of liquid that reach the active layer, the flooding approach is relevant to the stack level of description. **We expect from SINTEF gas and liquid flowrates through the current collector either measured either obtained from the local two-phase model for the real conditions and geometry.**

Expected input from Fraunhofer:

- The electrochemical response of the CEA model (equations 18, 19, 20) is based on empirical coefficients  $\beta$  that need measurements to be fitted. At this stage, we don't know if the **mass transport limitation** at high current density is only due to the

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“**blockage effect**” in the current collector (fewer water reaches the active layer), or is also due to a “**bubble shielding effect**” (oxygen covers the active sites, which reduces the available active electrochemical area). To study the impact of these two effects on the mass transport limitations, **we expect from Fraunhofer data/model on the dependence of the over-voltage on the oxygen void fraction.**

- Since we are looking for the influence of the nominal operating pressure on the stack performances, **we also expect data/model about the pressure effect on the over-voltage.**

### Expected output of CEA model:

The main goal of the CEA modelling work in this project is to derive from the PEMFC model a **MatLab/Simulink stack model dedicated to PEMWE**. This model will be capable to **calculate the stack performance** as a function of current and operating conditions. Moreover it will be capable to calculate the coupling between the flowrates repartition, the electrochemical responses and the heterogeneities of heat release for different cells of the stack (see Figure 13). The model will then be used to analyze different design strategies for given operating conditions.

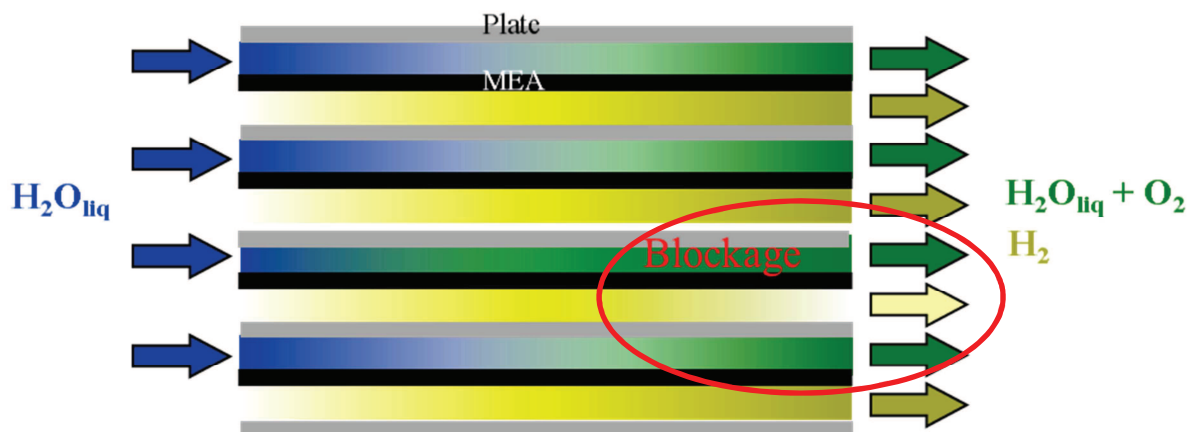


Figure 13: Stack heterogeneities.

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## 4. POSSIBLE COUPLING AND UP-SCALING STRATEGIES

The objective of this section is to identify early in the project the possible coupling and up-scaling strategies needed to answer the WP2 design questions in order to facilitate the exchange and/or post-processing between the different models and partners. These strategies could be of course up-dated during the course of the project.

Before presenting these strategies, we recall the different levels of description used in the different models, especially for the two-phase fluid description, in order to clarify the different *averaging procedures* that will need to be performed to exchange information between the models

### 4.1 Levels of description and averaging procedures

The different levels of description used in the different models are illustrated Figure 14 for the fields associated to the two-phase flow. The first picture shows the oxygen bubbles that came out of the current collector, to the flow field channel.

- At the first modeling scale (SINTEF model), a VOF model with sub-grid treatment is used. This means that the temporal evolution of the big bubbles is captured while the effect of the small ones is modeled.
- If the obtained results are **time-averaged**, one will obtain a 2D stationary void fraction field (and the corresponding “macroscopic” velocity fields). This second scale of description is coherent with the one used in the multi-physic model of Fraunhofer, in the sense that continuous stationary fields are considered and that those fields are discretized over the thickness of the component.
- If a **spatial average over the channel section** is applied to the previously obtained fields, one will obtain a 1D stationary void fraction profile. This third level of description corresponds to the one used in the stack model of CEA, where only one mesh is used in the thickness of the channel.

This means that different averages need to be considered when exchanging information between the different models. The chosen averages need to be coherent with the level of description of the models.

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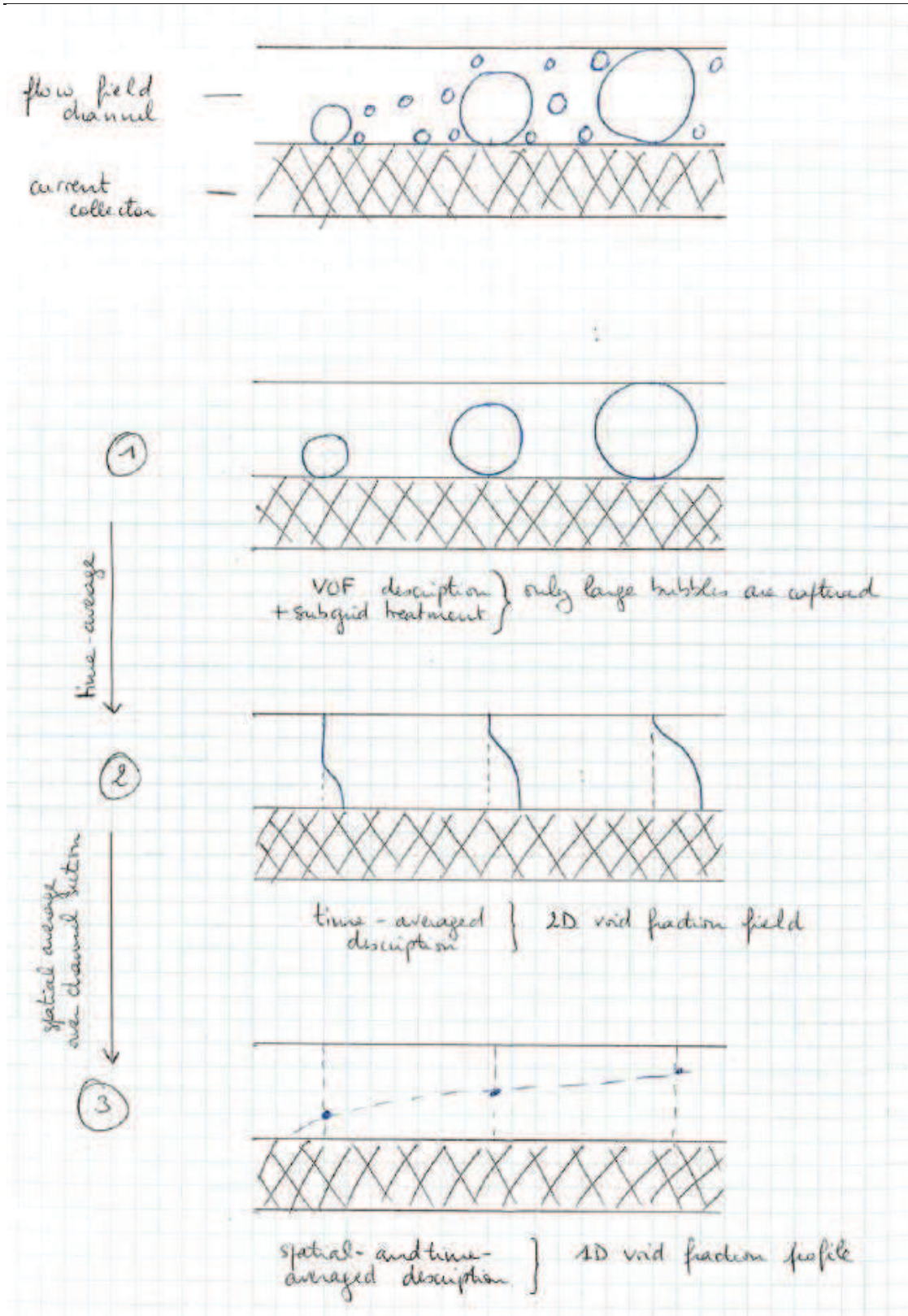


Figure 14: Different levels of description of the two-phase flow field and associated averages.



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## 4.2 Coupling strategy at the cell level

Regarding the **coupling** between the **two-phase flow model** and the **multi-physic model** at **cell level**, no direct coupling between the two codes (FLUENT and COMSOL) is planned at the moment. The coupling will be done mainly by exchanging fields from one model to the other. The possibility to easily exchange scalar and vector fields between FLUENT and COMSOL needs to be checked rapidly.

*From multi-physic to two-phase flow model:*

- For cell working at constant current density (current status of Fraunhofer code), **concentration profile of dissolved oxygen** at the current collector / catalyst layer interface will be provided to the two-phase flow model.
- Once the Fraunhofer model is able to tackle non-constant current density, the **local current density** at the current collector / catalyst layer interface will be provided to the two-phase flow model.
- If two-phase heat transfer is studied later in the project, the **local heat source** at the current collector / catalyst layer interface related to electrochemical reaction and the local heat source in the current collector related to Joule effect will be provided to the two-phase flow model.

*From two-phase flow model to multi-physics model:*

The interactions are not clarified at the moment. It will depend on the level of description of the two-phase flow of the extended model of Fraunhofer. For the moment, the Fraunhofer model is single-phase and considers the different gases as dissolved species.

- The **void fraction scalar field** in the current collector and at the current collector / catalyst layer interface will be provided to the multi-physics model to relate the bubble overpotential to local void fraction.
- The **time-averaged liquid and gas velocity fields** in the current collectors will be provided to the multi-physics model to study mass transport limitations.
- If a time-averaged “macro-scale” two-phase model is implemented at Fraunhofer, the exchange of information could be through appropriate two-phase flow correlations in the anode channel and current collector.

## 4.3 Up-scaling strategy between the cell and the stack models

Regarding the coupling between the cell level models of SINTEF and Fraunhofer and the stack model of CEA, no direct coupling is planned given the different scales of description. The objective is to determine correlations valid at the stack scale from the results obtained at the local/cell level scale using appropriate averaged/post-processing of the simulation results. Four different mechanisms have been identified at the moment:

- Determine **two-phase pressure drop correlations** in the **anode channels of the flow fields** from the two-phase flow simulation results. The two-phase variables need to be time- and spatially averaged to be coherent with the scale of description of the stack model.

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- Determine **mass transport limitation** by **blockage effect** in the **anode porous current collectors** at high current density from the two-phase flow simulations and / or experimental results.
  - Determine a correlation for the **bubble shielding effect** on the **anode electrode** at high current density. It should relate somehow a decrease of the active available surface depending on the local void fraction. This correlation could be derived either from the results of both the multi-physic model (bubble overpotential) and the two-phase flow model (local void fraction) or directly from electrochemical experimental results at high current density and low water flow rate.
  - Study two-phase heat transfer correlations in the channels, which is however, a lower priority.

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## **5. CONCLUSION**

The main objective of the European MEGASTACK project is to develop a cost efficient stack design for MW sized PEM electrolyzers, and to construct and demonstrate a prototype of this stack. In the approach proposed to reach this objective, one of the key tasks is the development and use of multi-scale and multi-physic models which will serve as an engineering tool to answer some design questions.

In this report, the main identified questions related to the MW design that need multi-physic simulations have been presented. Furthermore, the models of the different partners have been detailed in order to identify early in the project the needed input and possible output of the different models. Finally, possible coupling and up-scaling strategies between the different models have been proposed. These strategies could be of course up-dated during the course of the project.



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