Study of an Alkaline Electrolyzer Powered by Renewable Energy

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Abstract: Modeling of water electrolyzers can be considered a fundamental optimization tool for production of hydrogen by renewable energy. This work reports the model developed in COMSOL of an alkaline water electrolysis cell powered by a PV-module. The geometry model was created taking as reference a commercial electrolysis cell. The model involves transport equations for both liquid and gas phases, charge conservation and forces balances for the study of coalescence phenomena. Results showed changes on gas profiles with the evolution of solar irradiation during the day, as well as changes on void fraction and potential distribution.

Keywords: Water electrolysis, renewable energy, hydrogen, void fraction, coalescence

1. Introduction

The production of H_2 from renewable energy surplus is seen as a key strategy for energy storage. *Centro Nacional del Hidrógeno* (CNH2) works actively in this direction, which is considered a strategic line in order to achieve a sustainable future energy.

Alkaline electrolysis is a highly developed technology in the industry and the main way to obtain sustainable hydrogen. Nowadays, commercial alkaline electrolyzers are designed for a constant power supply. However, renewable energies are non-dispatchable because of their strong dependence on weather conditions. The fluctuations in power supplies to the electrolyzer could cause problems such as generation of explosive mixtures, corrosion of materials, lower efficiency, pressure drops, changes of temperature, etc. The design of alkaline electrolyzers powered by renewable energy is a critical issue to avoid these problems. For these reasons, the CFD simulation is an important design tool.
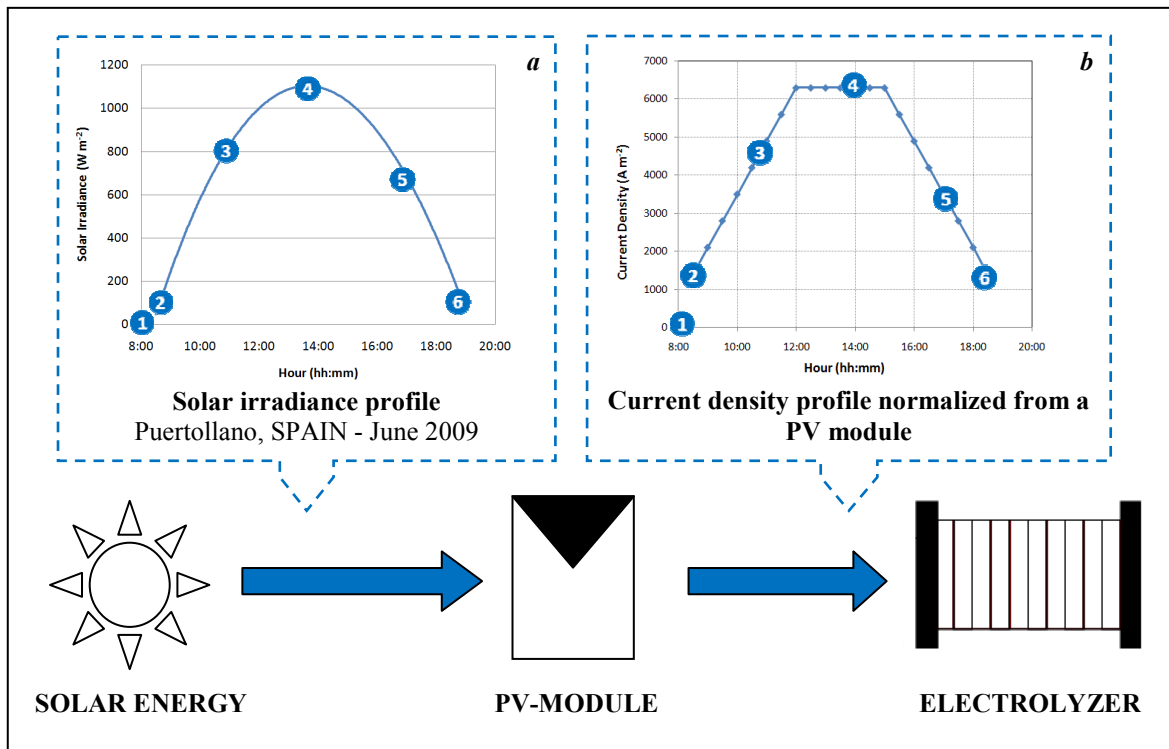

Figure 1: Electrolyzer powered by a PV-module: a) irradiation profile; b) current density profile.

This work reports the model of an alkaline electrolysis cell powered by a PV-module (Fig 1). Fig 1a is a typical solar irradiance profile for a sunny day in Southern Spain. Fig. 1b shows a current density profile implemented in COMSOL® from a PV-module that powered the electrolyzer. To this aim, *Interpolation Function* tool was used. Maximum value of solar radiation occurs at 14:00.

2. Model Set-Up

2.1. Alkaline electrolysis water

During alkaline water electrolysis the following reactions take place:

- On *cathode*, the evolution of H_2 gas take place:

$$4H_2O + 4e^- \rightarrow 2H_2(gas) + 4OH^-$$
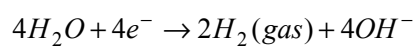
- On *anode*, O_2 gas is generated according with:

$$4OH^- \rightarrow O_2(gas) + 2H_2O + 4e^-$$

In a typical operation, electrolyte (KOH) enters in the anodic and cathodic compartments by the bottom inlets. Over the active surface of electrodes, water splits following the electrochemical reactions described above, evolving oxygen and hydrogen, respectively for anode and cathode. The mixture of generated gases and electrolyte leaves the compartment through the upper outlets (Fig 2).

2.2. Model Geometry

Taking as reference a modified commercial electrolysis cell (Fig 2a), the geometry of the model was built following fluid dynamic requirements. In this way, simplifications were made in order to reduce the model complexity (Fig 2c). As result, a good approximation can be made just by 2D geometry, which allows an optimal study of the main involved variables (Fig 2e).

3. Formulation of the problem in COMSOL Multiphysics®

Depending of studied phenomena, the model can be divided into:

- Water electrolysis by renewable energies, with *Electric Currents* and *Two phase-flow bubbly flow* modules.
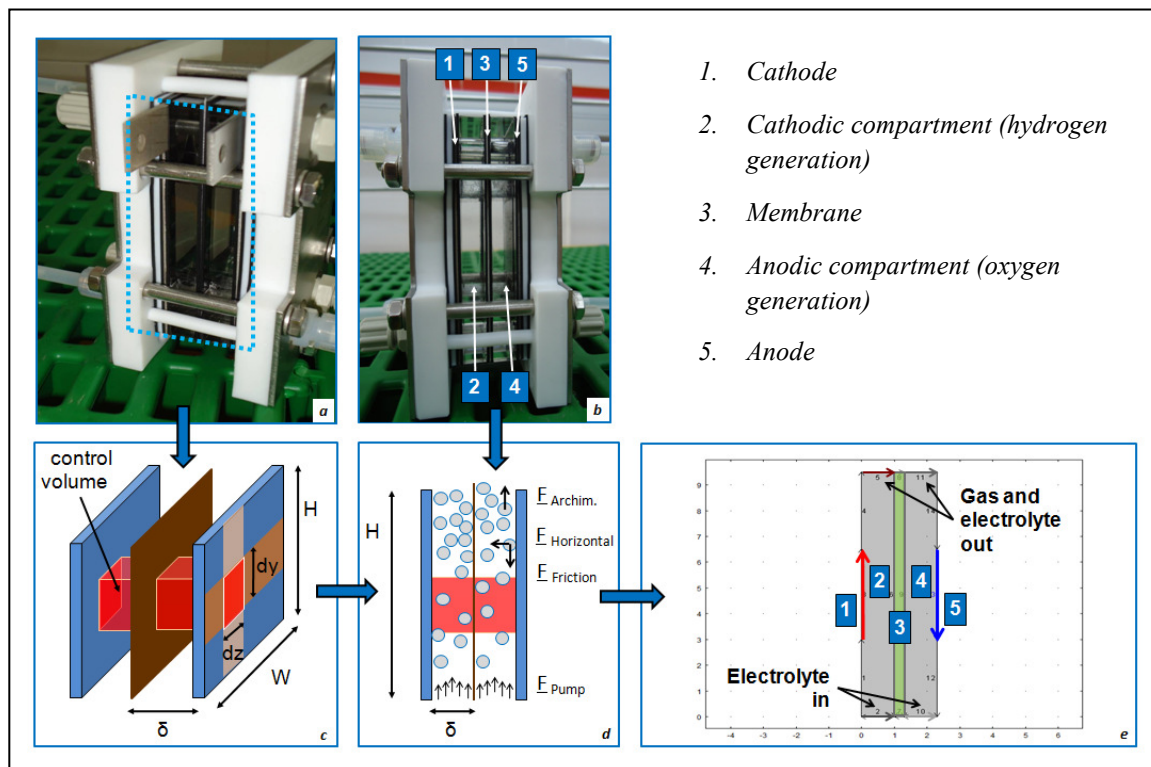

1. *Cathode*
2. *Cathodic compartment (hydrogen generation)*
3. *Membrane*
4. *Anodic compartment (oxygen generation)*
5. *Anode*

Figure 2: Geometry of a commercial electrolysis cell implemented on COMSOL Multiphysics®.

- Motion of bubbles next to electrode surface with *Two phase-flow phase field* module of COMSOL®.

Table 1 shows the boundary settings and initial conditions used in the model (see Appendix).

3.1 H_2 generation by Renewable Energy

Charge transport was studied using *Electric Currents* module of COMSOL®, which solves a current conservation problem for the scalar electric potential V [1]. For time dependent studies, the continuity equation takes the form (1):

$$\nabla \cdot \vec{J} = -\nabla \cdot d \frac{\partial}{\partial t}((\varepsilon_o \varepsilon_r \nabla V)$$
$$-\nabla \cdot (\sigma \nabla V - \vec{J}_e) = dQ_j \qquad (1)$$

In this case, electric transport charges on electrodes is not considered, and only ionic transport is studied inside the electrolysis cell.

On the other hand, movement of gases and liquid was modeled applying *Laminar Bubbly Flow* module of COMSOL®. This application mode describes the two-phase flow using a Euler-Euler model. The module solves for the volume fraction occupied by each of two phases, without defining each bubble in detail. It is a macroscopic model for two-phase fluid flow. It treats the two phases as interpenetrating media, tracking the averaged concentration of the phases. One velocity field is associated with each phase, and the dynamics of each of the phases are described by a momentum balance equation and a continuity equation. Following simplifications are considered when this module is used [2]:

- The gas density is negligible compared to the liquid density.

- The motion of the gas bubbles relative to the liquid is determined by a balance between viscous drag and pressure forces.

- The two phases share the same pressure field.

For this simulation, high level of bubble definition was not required, and this approach allows reducing the computational cost doing a good approximation to our system.

For *Laminar Bubbly Flow*, sum of the momentum equations for the two phases gives: a momentum equation for liquid (2):

$$\phi_l \cdot \rho_l \cdot \frac{\partial \vec{u}_l}{\partial t} + \phi_l \cdot \rho_l \cdot \vec{u}_l \cdot \nabla \vec{u}_l = -\nabla p +$$
$$\nabla \cdot \left[\phi_l \cdot (\eta_l + \eta_T) \cdot \left(\nabla \vec{u}_l + \nabla \vec{u}_l^T - \frac{2}{3} \cdot (\nabla \vec{u}_l) \cdot \vec{I} \right) \right]$$
$$+ \phi_l \cdot \rho_l \cdot \vec{g} + \vec{F} \qquad (2)$$

A continuity equation (3),

$$\frac{\partial}{\partial t}(\phi_l \cdot \rho_l + \phi_g \cdot \rho_g) +$$
$$\nabla \cdot (\phi_l \cdot \rho_l \cdot \vec{u}_l + \phi_g \cdot \rho_g \cdot \vec{u}_g) = 0 \qquad (3)$$

And a transport equation (4) for the volume fraction of gas,

$$\frac{\partial \phi_g \cdot \rho_g}{\partial t} + \nabla(\phi_g \cdot \rho_g \cdot \vec{u}_g) = -m_{gl} \qquad (4)$$

Where (m_{gl}) is the mass transfer rate from gas to liquid.

In order to complete the system, auxiliary equations were used:

- Activation overpotentials (η) were defined for cathode and anode by Butler-Volmer equations form (Tafel equation):

$$\eta = 2.3 \cdot \frac{R \cdot T}{\alpha \cdot F} \cdot \log\left(\frac{i}{i_o}\right) \qquad (5)$$

- Bruggeman equation (6) relates the variation of conductivity of electrolyte (σ) with the volume fraction of gases (f), for each section.

$$\sigma = \sigma_o \cdot (1 - f)^{1.5} \qquad (6)$$

- Gases generated fluxes on active surfaces of electrodes are defined by Faraday equation, for H_2 (7) and O_2 (8):

$$\dot{m}_{H2} = \frac{i \cdot M_{H2}}{2 \cdot F} \qquad (7)$$

$$\dot{m}_{O2} = \frac{i \cdot M_{O2}}{4 \cdot F} \qquad (8)$$

3.2. Motion of bubbles

During the rise of gas inside the electrolyzer the coalescence of bubbles happens frequently. To determine the motion of a bubble it is necessary to determine the forces acting on it and put a balance on the amount of movement as in Fig 2d [3, 4]:

- Archimedes' principle to determine the buoyancy. In commercial electrolyzers, the residence time of bubbles is small due to the forces of Archimedes and the void fraction is small.

- Friction force according to the drag coefficient

- Horizontal force of the bubble-electrode and bubble-bubble interactions

- Pump force.

These phenomena can be modeled in COMSOL® by *laminar two-phase flow, phase field*. This application mode describes the two-phase flow dynamics using a Cahn-Hilliard equation. The equation describes the process of phase separation, by which the two components of a binary fluid spontaneously separate and form domains pure in each component.

COMSOL Multiphysics® solves the Cahn-Hilliard equation by two equations (9), (10):

$$\frac{\partial \phi}{\partial t} + \vec{u} \cdot \nabla \phi = \nabla \cdot \frac{\gamma \lambda}{\varepsilon^2} \nabla \psi \qquad (9)$$

$$\psi = -\nabla \cdot \varepsilon^2 \nabla \phi + (\phi^2 - 1)\phi + \left(\frac{\varepsilon^2}{\lambda}\right)\frac{\partial f_{ext}}{\partial \phi} \qquad (10)$$

Where (u) is the fluid velocity, (γ) is the mobility, (λ) is the mixing energy density, and (ε) is the interface thickness parameter. The (ψ) variable is referred to as the phase field help variable [5].

The transport of mass (3) and momentum (11) is governed by the incompressible Navier-Stokes equations including surface tension (st):

$$\rho \frac{\partial \vec{u}}{\partial t} + \rho(\vec{u} \cdot \nabla)\vec{u} = \nabla \cdot \left[-p\vec{I} + \mu\left(\nabla \vec{u} + \nabla \vec{u}^T\right)\right] + \vec{F}_g + \vec{F}_{st} + \vec{F}_{ext} + \vec{F} \qquad (11)$$

4. Mesh

For electrolysis cell model, a triangular mesh was generated (Fig 3a). Mesh elements were coarse predefined on the electrolyte domain, but normal on the membrane and electrodes boundaries.

In the case of motion of bubbles, a physics-controlled mesh was used (Fig 3b). The mesh is finer on the bubble domain.
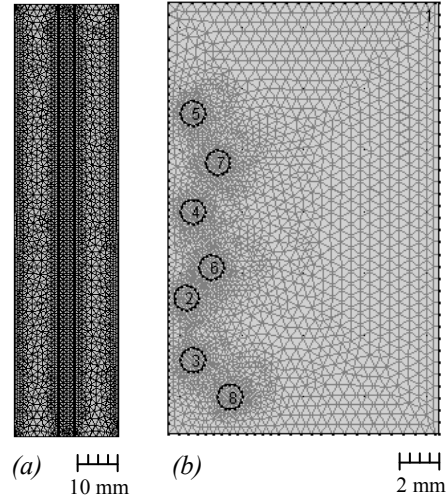

(a) 10 mm *(b)* 2 mm

Figure 3: Mesh generation for the used geometry: a) mesh for hydrogen generation model; b) mesh for bubbles motion model.

5. Results

5.1. Polarization Curve

In Fig 4, a typical polarization curve is shown [6, 7]. According with other authors [8], oxygen and hydrogen overpotentials are the main source of reaction resistances, and at high current densities, it is very significant the effect of Ohmic losses.
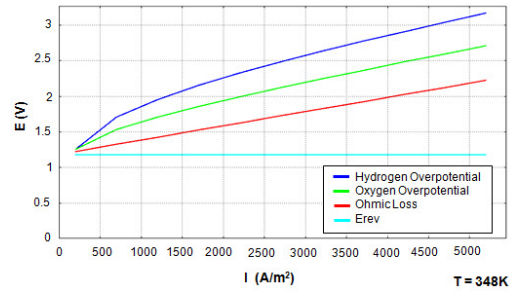

Figure 4: Polarization curve, including over-potentials and ohmic losses contributions.

5.2. I-V Distributions

On Fig 5 it is possible to follow the dynamic evolution of potential distribution over the electrolysis cell during operation. Applied potential increases with increasing of current density. Attending current vector arrows, it can be seen higher values of current next to electrodes extremes, which is in agreement with observed for electrochemical models by other authors [9].
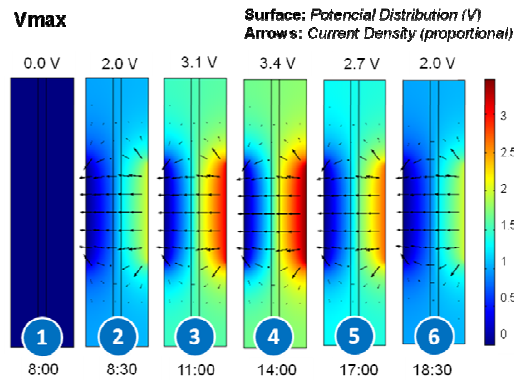

Figure 5: Potential distribution of electrolysis cell when it is powered by a PV-module.

5.3. Gas generation profile

Evolution of hydrogen profile can be evaluated from picture on Fig 6. Hydrogen void fraction (occupied space by hydrogen bubbles) draws a typical profile next to electrode surface [10, 11]: void fraction progressively increases on vertical direction of electrode.
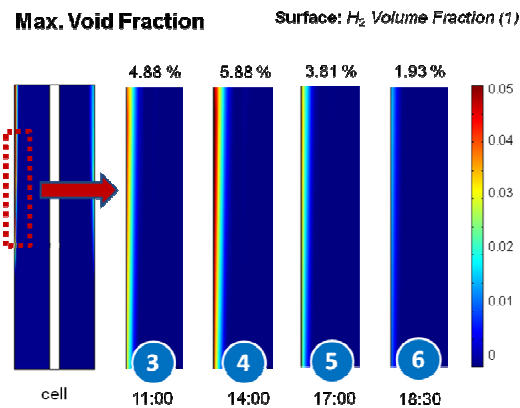

Figure 6: Hydrogen volume fraction evolution for electrolysis cell during a day operation.

The predicted void fraction of hydrogen at 4 different points along the electrode surface is reported on Fig 7. H is the height of the electrode and point x=0 corresponds with the surface of electrode. As can be seen, next to the electrode surface volume fraction reaches the highest value, and decreases towards the membrane. Void fraction also increases from bottom to top of electrode due to accumulated generation of gas, and effect of forced convection [12], as observed in Fig 6.
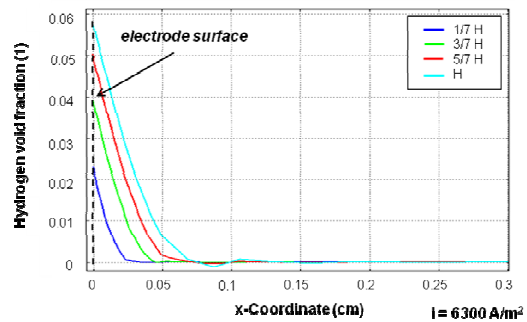

Figure 7: Void fraction distribution at four locations.

Influence of current density on generated gas is reported on Fig 8. As expected, hydrogen void fraction increases at higher current density values. From this plot it can be also deduced that higher the current density, higher the gas penetration at lateral direction, because of increasing of lateral velocity of gas [13].
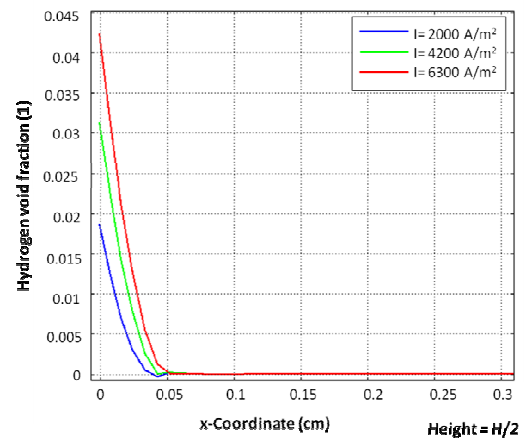

Figure 8: Void fraction of gas for different values of current density.
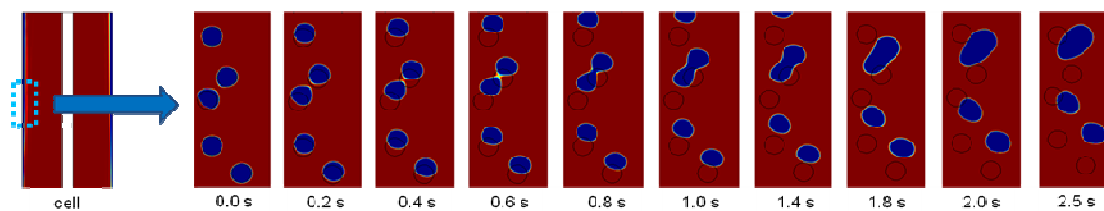
Figure 9: Detail of coalescence phenomena between hydrogen bubbles

5.4. Coalescence phenomena

Fig 9 shows a model of coalescence between two bubbles of hydrogen using COMSOL Multiphysics®.

During electrolysis of water, the bubbles rise by buoyancy and join in the upper regions of the cell. The study of coalescence lets us know the dynamic of the gas: generation, distribution, evolution, etc.

6. Conclusions

- COMSOL® was used to model the behavior of an electrolysis cell for hydrogen production.

- The distribution of oxygen and hydrogen gas when the cell is powered by a PV module was obtained.

- Using the model developed in COMSOL®, we determined the current and potential distribution along the electrolysis cell.

- COMSOL® can model phenomena of localized coalescence.

7. References

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9. Acknowledgements

10. Appendix

Table 1: Constants**,** Sub-domain and Boundary Settings

Symbol	Value	Description
p	1 bar	Pressure operation
T	348 K	Temperature operation
$i_{o,c}$	0.02 A/m^2	Exchange current density (cathode)
$i_{o,a}$	0.016 A/m^2	Exchange current density (anode)
σ_0	130 S/m	Electrolyte (30% KOH) conductivity
σ	67 S/m	Membrane (PTFE) conductivity
v0	0.1 m/s	Inlet velocity
R	8.31 J K^{-1} mol^{-1}	Ideal gas constant
F	96485 C	Faraday constant
α	0.5	Charge transfer coefficient