CFD simulations of electrolyte flow uniformity and recirculation in alkaline water electrolysis cells

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Introduction

In the coming years, considerable efforts will have to be made to reduce greenhouse gas emissions to as close to zero as possible in order to limit the increase in global average temperature to 1.5°C, as stated in the Paris Agreement [1]. One way to decarbonize a wide range of sectors – including transport, iron and steel production and chemicals manufacture – is to use green hydrogen as an energy carrier to store and deliver usable and clean energy. Currently, the most mature technology used to produce hydrogen is Alkaline Water Electrolysis (AWE). It uses an alkaline solution, typically KOH between 1 and 6 M, at a temperature in the range 30-80°C, a diaphragm and Ni-based electrodes. This process can be further enhanced in terms of sustainability through the utilization of renewable electricity for conducting electrolysis. The primary hurdle associated with this technology revolves around improving the efficiency and diminishing capital expenditure (CAPEX) of the electrolyzer [2].

Recent experimental studies in our group have shown that it is possible to significantly improve the performance of such alkaline electrolyzers by shifting from traditional gap cells to zero-gap cells, wherein the anodic and cathodic chambers are filled with 3D porous electrodes such as foams and 3D-printed structures [2,3]. The advantage of using such 3D structures is that the available surface area for hydrogen production is much higher. At the same time, increased hydrogen production may lead to stagnant gases trapped in the complex porous channels of the foam. This is the reason why optimised electrolysis cells with forced electrolyte flow have been developed at the lab scale to favor bubble removal. A double elbow configuration was also used in order to guide the flow and enhance its spread throughout the cell, to take advantage of the whole area provided by the 3D electrodes [2].

Efforts have then been made in order to apply the same methodology – i.e. using 3D porous electrodes and forced electrolyte flow – to an industrial scale electrolyzer. Unfortunately, it was impossible to get such low cell voltages as with the lab-scale setup. This is mainly due to the fact that the pilot cells are not optimized for forced electrolyte flow, leading to a non-optimal distribution of the electrolyte and therefore to a poorer performance of the electrolyzer. The aim of this work is to perform Computational Fluid Dynamics (CFD) simulations to assess the behavior of the electrolyte within a pilot cell in order to find some optimal configuration that homogenizes the flow, reduces recirculation of the electrolyte and favors bubble removal.

The main objective of this research is to define parameters – based on a Residence Time Distribution (RTD) analysis – that will allow to compare the performance of different cell configurations. The first parameter will be used to evaluate the level of flow uniformity inside the electrolysis cell while the second one will give an estimation of flow recirculation. Modification of the injection channels as well as the addition of porous media will be considered as options to improve the performance of the electrolyzer.

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Methodology

The geometry of the pilot-scale cathodic chamber considered as a reference configuration for this work is depicted in Figure 1. It consists in a flat cylinder of diameter 20 cm and of thickness 6 mm. The inlet is located at the bottom of the cell and has a diameter of 2 mm while the outlet, at the top, presents a diameter of 3 mm. The electrolyte is a 30 wt% KOH solution at 70°C and its flow is forced at the entrance of the chamber by imposing an inlet flow rate Q_{in} corresponding to an inlet velocity v_{in}. The considered inlet velocities are in the range of 0.3 to 1.9 m/s. The latter is fixed by the applicable maximal power of the pilot pumps.

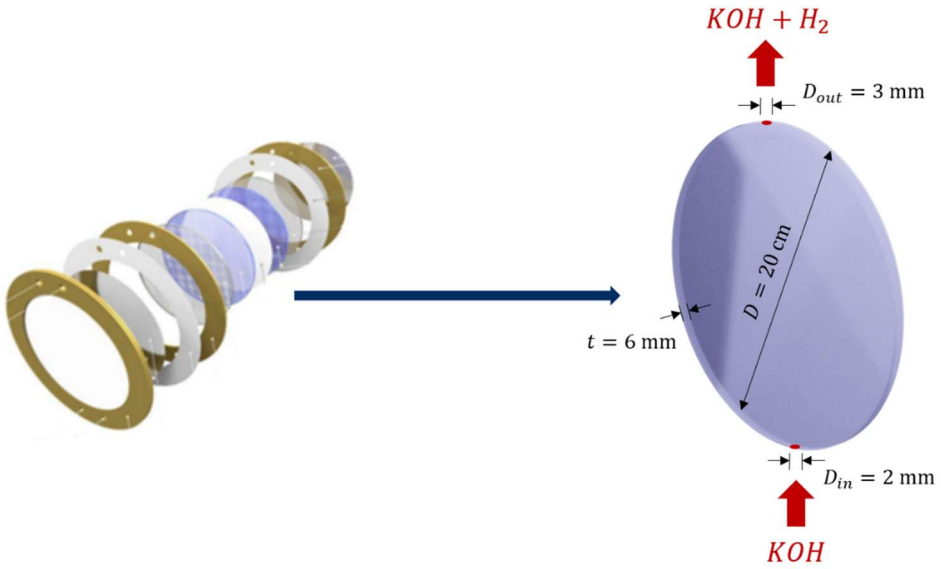

Figure 1: Reference configuration of the cathodic chamber of one single water electrolysis cell

To simulate the electrolyte flow within the cell, the incompressible Navier-Stokes equations for a single-phase flow were solved using the finite volume method implemented in OpenFOAM. The assumption of 2D flow is made since the thickness of the chamber is small compared to its diameter and the k-ω turbulent model is used to account for turbulence. Concerning the addition of porous electrodes within the cell, it is possible to describe explicitly the exact foam geometry based on high-resolution micro-CT (computed tomography) scanned data. Unfortunately, this is highly demanding from a computational point of view. To counter this problem, spatially averaged equations are used to account for porosity, based on the Darcy-Forchheimer law and on the intrinsic and inertial permeabilities of the porous structure [4]. In what follows, two foams will be considered with different characteristic pore sizes $a = 450$ µm and $a = 3000$ µm, respectively.

In order to assess flow uniformity and recirculation of the flow within the electrolysis cell, two parameters will be defined based on a Residence Time Distribution (RTD) analysis. This method consists in the injection of a tracer at the inlet of a reactor at time $t = 0$ s and in measuring the concentration of tracer at the outlet as a function of time, $C(t)$. This concentration can be determined numerically by solving the convection-diffusion equation [5]. Based on this concentration, it is possible to calculate the RTD function $E(t)$ that gives an indication of the number of fluid elements leaving the reactor after having spent a given time inside it.

The first parameter, aimed at determining flow uniformity and the presence of dead/stagnant zones within the cell, is called the dimensionless time [5] and is defined as the ratio between the mean residence time of the fluid inside the cell of volume V, and the space time, i.e. the time that would be required to fill the whole space available at fixed inlet flow rate:

$$\theta = \frac{t_m}{\tau} = \frac{\int_0^\infty t\, E(t)\, dt}{V/Q_{in}} \; [-]$$

This parameter gives an image of the effective volume used inside the cell. Two cases must be identified here: $\theta < 1$ and $\theta \geq 1$. On the one hand, $t_m < \tau$ and so the mean time spent by the fluid inside the cell is lower than the time required to fill it. In other words, there will be some dead/stagnant zones of low velocity in the cell where no hydrogen will be produced. On the other hand, $t_m \geq \tau$ which means that fluid elements remain in the cell for a time higher or equal to the space time. In this specific case, the electrolyte will have time to homogenize over the whole volume and to fill all the space. In other words, no dead zones are to be expected and the electrolyte will be uniformly distributed over the area provided by the electrodes, enhancing hydrogen production.

Another phenomenon which may occur during hydrogen production inside the porous electrode is the entrapment of hydrogen bubbles inside the domain. For this reason, it is interesting to determine whether the electrolyte goes directly from the inlet to the outlet of the chamber or if it recirculates, leading to poor evacuation of the bubbles. A second parameter is therefore defined to characterize this recirculation phenomenon [6]. It is called the dimensionless variance and it is defined as the ratio between the variance of the RTD function and the square of the mean residence time:

$$\sigma_\theta^2 = \frac{\sigma^2}{t_m^2} = \frac{\int_0^\infty (t - t_m)^2\, E(t)\, dt}{\left(\int_0^\infty t\, E(t)\, dt\right)^2} \; [-]$$

This parameter gives an image of the level of mixing inside the electrolysis cell. When $\sigma_\theta^2 = 0$, it means that there is no mixing of the flow since the RTD function presents no dispersion around the mean residence time. This case corresponds to an ideal plug flow. Next to this, when $\sigma_\theta^2 \geq 0$, some mixing of the flow occurs, which could lead to entrapment of hydrogen bubbles in the cell.

Discussion

The approach described in the previous section has been applied to the reference cell presented in Figure 1. Figure 2.a shows the velocity profile inside the domain for an inlet velocity of 1.5 m/s. As observed, the electrolyte forms a jet stream flow at the entrance of the chamber due to the small inlet diameter compared to the much larger diameter of the cell chamber. This leads to an inhomogeneous distribution of the flow, with some zones that are not flushed by the electrolyte. Computation of the dimensionless time allows to quantify the degree of homogeneity. Its profile as a function of the inlet velocity has been plotted in Figure 2.b. It clearly shows that flow uniformity increases as the inlet flow rate increases (i.e. as θ increases). However, for the range of velocities considered in our pilot, the dimensionless time remains quite low (lower than 0.3) meaning that distribution of the electrolyte is poor. In order to quantify the occurrence of recirculation of the flow, the dimensionless variance has been calculated as shown in Figure 2.c. It appears that σ_θ^2 also increases as v_{in} increases, which

means that a higher flow rate leads to a higher mixing of the flow. This also explains why there are fewer dead zones as the inlet flow rate is increased. Contradictory conclusions arise from these two parameters, since a higher flow rate is desired from a uniformity point of view while lower velocities will generate less recirculation of the flow. For this reason, an optimum needs to be found. Since the dimensionless time remains so low and the dimensionless variance so high (far above 1), new configurations have to be considered in order to improve the performance of the electrolyzer.

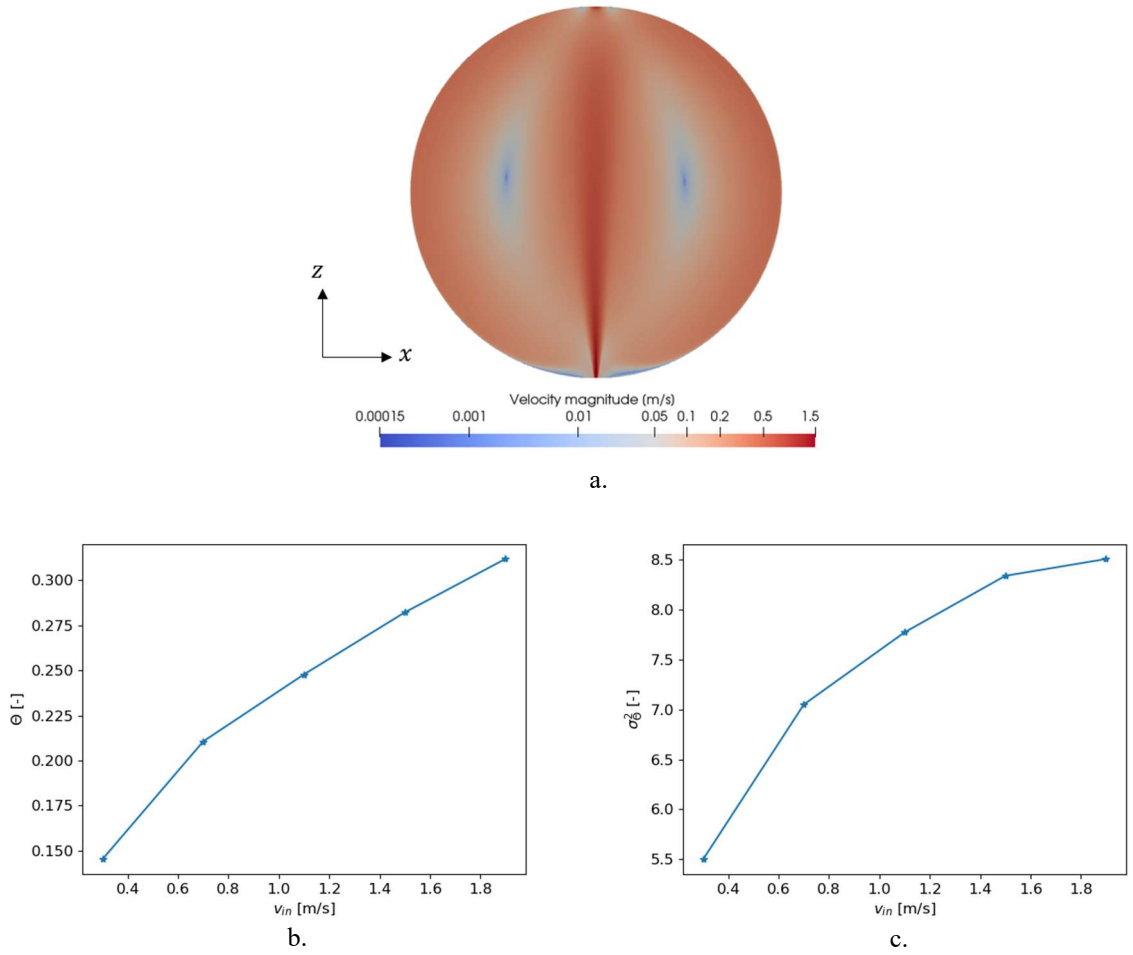

Figure 2: (a) Velocity profile for the reference configuration with $v_{in} = 1.5$ m/s. (b) Dimensionless time and (c) dimensionless variance as a function of inlet velocity.

At first, since the inlet opening seems to be the critical point in terms of distribution of the flow, different inlet configurations have been studied, such as a bigger inlet diameter (4 mm instead of 2 mm), an inclined inlet (at 45° to the right) and three inlets. The dimensionless times and variances of these three new configurations have been compared to the reference case in Figure 3. Concerning flow uniformity, it appears that increasing the size of the inlet or inclining the inlet channel leads to a lower value of θ. However, increasing the number of inlets clearly lowers the risk of dead zones in the cell. Next to this, the reference configuration and the case with a larger inlet present high dimensionless variances over the velocity range considered, which means that these configurations generate a lot of recirculation. The cells with three inlets or with an inclined inlet are more suited to avoid recirculation of the electrolyte. From these observations, the case with three inlets might be the most suited to improve distribution of the flow while lowering the level of mixing. However, this configuration presents some

disadvantages. The major drawback from a design point of view is that it requires a modification of the cell geometry. Moreover, as observed in Figure 3.a, this solution is not durable. For example, if the number of cells in the electrolyzer increases, the inlet flow rate in one cell will be lower, meaning that the value of θ will decrease significantly. Finally, it is clearly possible to lower recirculation even more to approach the ideal value of $\sigma_\theta^2 = 0$.

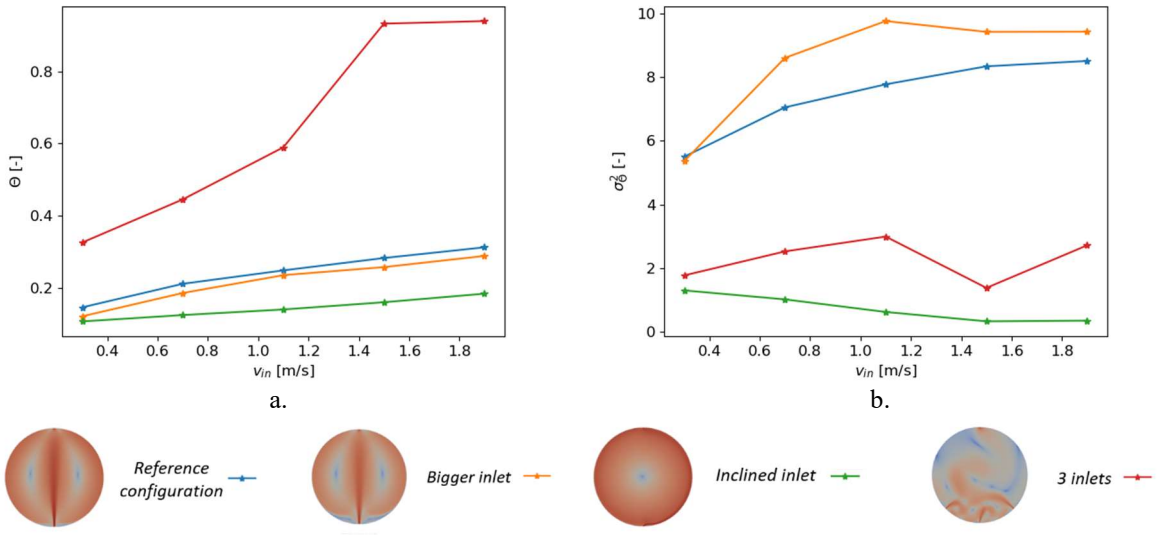

Figure 3: (a) Dimensionless time and (b) dimensionless variance as a function of inlet velocity for different inlet configurations.

To tackle these hurdles, the possibility to add porous structures within the electrolysis cell has been considered in order to better distribute the flow. Figure 4 compares the values of θ and σ_θ^2 for the reference configuration, the case with three inlets and for electrolysis cells filled with foams presenting pore sizes of 450 and 3000 µm.

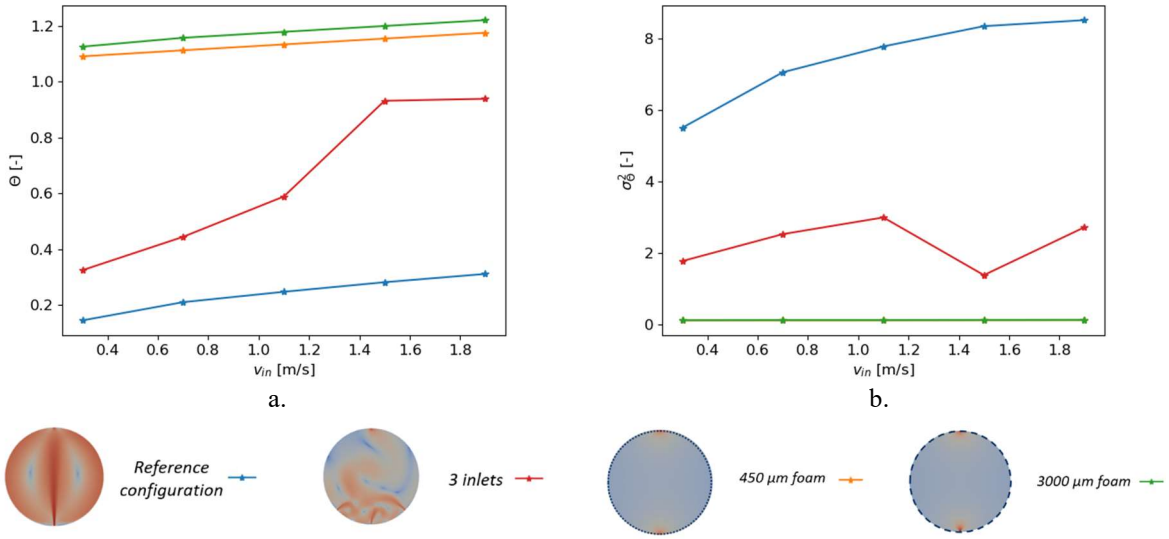

Figure 4: (a) Dimensionless time and (b) dimensionless variance as a function of inlet velocity after the addition of foams in the domain.

Figure 4.a highlights the fact that adding 3D porous structures in the cathodic chamber allows to homogenize the electrolyte distribution over the whole volume of the cell, resulting in a dimensionless time higher than 1. In other words, no dead zones are to be expected, on the contrary to the reference case and the case with 3 inlets. The fact that the 3000 µm foam presents a higher dimensionless time is simply due to the fact that the electrolyte takes more time to go out of the cell since it is more likely to be stuck somewhere within the larger pores. In terms of flow recirculation, the addition of foams helps to lower the value of σ_θ^2 significantly (i.e. close to 0) as observed in Figure 4.b. In this case, both foams present nearly similar results and the curves overlap on the graph. However, the 450 µm foam presents a slightly lower dimensionless variance which confirms the fact that the flow will present a lower risk to recirculate when the porous structure is finer.

Conclusions

In this work, CFD simulations have been used to extract two parameters that allow to quantify flow uniformity and flow recirculation in alkaline water electrolysis cells. The main objective is to find a cell configuration that homogenizes the flow ($\theta \geq 1$) without generating mixing of the electrolyte in the cell ($\sigma_\theta^2 \to 0$). Therefore, an optimum has to be found between these two parameters such that we take advantage of the whole surface area of the electrodes but without getting hydrogen bubbles trapped into the cathodic chamber. As a first step, modifying the inlet channels of the cell seemed to be an interesting solution to improve the performance of the cell. However, significantly better results are obtained by adding porous media inside the cell since it increases the effective volume covered by the electrolyte and it lowers risks of flow recirculation within the chamber. This quantitative analysis is a first step to assess the performance of AWE electrolyzers and it allows to compare different geometries on the same ground. Multiphase modeling will be a further step in the validation of the results that were obtained here.

Acknowledgements

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