Experimental Study of the Gravity-Fed Laminar Electrolyser

Towards Increased Flexibility and Product Purity

Vincent Botond Polet







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Cover: Render of the Gravity-Fed Laminar Electrolyser by Vincent Botond Polet



Preface

Dear reader,

With this short preface, I would like to take the opportunity to thank all those who contributed towards this thesis project, which is my final assignment as a master's student at the Delft University of Technology.

Firstly, I would like to express my gratitude to Nico, my daily supervisor, who helped me through the good and the tough times. I must not always have been easy to manage, especially when my cell was leaking (often). Thank you for the encouraging words and guidance throughout the project. Your expertise and patience were essential in completing this thesis. I would also like to extend my thanks to Willem, whose insights and feedback helped me refine my work and also for creating a warm atmosphere within the research group.

Additionally, I must express my appreciation to my fellow students and friends at the university, who created a supportive and motivational environment. Special thanks to Bart, Marnix, Alex, Kevin, Jelmer, Sohan, and Gilles for providing help and/or companionship during the long and often solitary lab sessions.

I would also like to express my gratitude to running and music, which kept me grounded during days and weeks when it felt like the struggle piled up and progress seemed out of reach.

Lastly, I want to thank my family for their support during my studies. Their belief in me kept me motivated throughout this journey.

Thank you for reading, and I hope you find this work both insightful and inspiring.

Vincent Botond Polet Delft, November 2024

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Nomenclature

Symbols

| Symbol | Definition | Unit |
|---------------|---|---------------------------|
| Roman large | | |
| A | Area | [m ²] |
| $C_{O,eq}$ | Concentration of oxidized species in bulk electrolyte | [mol/m ³] |
| C_O | Concentration of oxidized species close to electrode | [mol/m ³] |
| $C_{R,eq}$ | Concentration of reductive species in bulk elec- trolyte | [mol/m ³] |
| C_R | Concentration of reductive species close to elec- | [mol/m ³] |
| D | Diffusion coefficient | [m ² /s] |
| E | Voltage/Potential | ĪV1 |
| F | Faraday constant | [C/mol] |
| G | Gibbs Free Energy | [J] |
| H | Height | [m] |
| H | Enthalpy | [J/mol] |
| Ι | Current | [A] |
| J | Current density | [A/cm ²] |
| K | Separator permeability | [m ²] |
| N | Molar flux | [mol/m ² /s] |
| P | Power | [W] |
| P | Pressure | [Pa] |
| R | Gas constant | [J/mol/K] |
| R | Resistance | [Ω] |
| S | Entropy | [J/K] |
| S | Solubility | [mol/m ³ /bar] |
| T | Temperature | [K]/[C] |
| X_e | Dimensionless Hydraulic Entrance Length | [-] |
| <u> </u> | Volumetric flow rate | [m ³ /s] |
| Roman small | | |
| С | Concentration | [mol/m ³] |
| d | Thickness | [m] |
| f_g | Gas evolution efficiency | [-] |
| <i>g</i> | Gravitational acceleration constant | [m/s ²] |
| k | Mass transfer coefficient | [m/s] |
| p | Pressure | [bar] |
| t | lime | [S] |
| v | Velocity | [m/s] |
| 2 | Charge number | [-] |
| Greek symbols | | |
| α | Charge transfer coefficient | |
| α_B | Bunsen Coefficient | |
| β | Aspect Ratio | [-] |
| δ | Boundary layer thickness | [m] |
| ϵ | Porosity | |
| η | Dynamic viscosity | [Pas] |

| Symbol | Definition | Unit |
|-------------|--------------|----------------------|
| Roman large | | |
| κ | Conductivity | [S/m] |
| ρ | Density | [kg/m ³] |
| au | Tortuosity | [-] |

Acronyms

| Acronym | Definition |
|---------|--|
| AEM | Anion-exchange membrane electrolysis |
| AWE | Alkaline water electrolysis |
| BESS | Battery Energy Storage System |
| BoP | Balance of Plant |
| CAPEX | Capital Expense |
| CCS | Carbon Capture & Storage |
| CFE | Capillary Fed Electrolyser |
| EIS | Electrochemical Impedance Spectroscopy |
| ESS | Energy Storage System |
| EU | European Union |
| GC | Gas Chromatograph |
| GDE | Gas Diffusion Electrode |
| HER | Hydrogen Evolution Reaction |
| HP | Hot Pressed |
| HTO | Volume fraction of hydrogen in oxygen |
| LEL | Lower Explosion Limit |
| MEA | Membrane Electrode Assembly |
| OER | Oxygen Evolution Reaction |
| OPEX | Operating Expense |
| ORR | Oxygen Reduction Reaction |
| OTH | Volume fraction of oxygen in hydrogen |
| PEM | Proton Exchange Membrane Electrolysis |
| PMMA | Polymethylmethacrylate |
| PTFE | Polytetrafluoroethylene or Teflon |
| RES | Renewable Energy Source |
| RPM | Revolutions Per Minute |
| SMR | Steam Methane Reforming |
| SOEC | Solid Oxide Electrolysis |
| SS | Stainless Steel |
| ZGE | Zero-gap Electrolyser |

Abbreviations

| Abbreviation | Definition |
|-------------------------|-----------------------|
| act | Activation |
| ano | Anode |
| cat | Cathode |
| cell | Electrolysis Cell |
| conc | Concentration |
| diff | Diffusive |
| eff | Effective |
| el | Electrolyser |
| elyte | Electrolyte |
| eq | Equilibrium |
| g | Gas |
| l | Liquid |
| min | Minimal |
| nom | Nominal |
| perm | Permeation |
| pore | Separator Pore |
| prod | Production |
| sep | Separator or Membrane |
| sol | Solvent |
| Compounds and Materials | |
| 220 | Zirfon UTP 220 |
| 500 | Zirfon UTP 500 |
| CO_2 | Carbon Dioxide |
| H ₂ | Hydrogen |
| H_2O | Water |
| КОН | Potassium Hydroxide |
| O ₂ | Oxygen |

Dimensionless Numbers

| Dimensionless Number | Definition |
|----------------------|-----------------------|
| Reynolds number (Re) | $rac{ ho v d}{\eta}$ |
| Schmidt number (Sc) | $\frac{\eta}{ ho D}$ |
| Sherwood number (Sh) | $\frac{kd}{D}$ |

Abstract

Alkaline water electrolysis is praised as one of the most promising technologies for sustainable hydrogen production. Still, gas crossovers at low current densities limit its operating range, especially when paired with intermittent renewable energy sources. This study investigates the Gravity-Fed Laminar Electrolyser concept, designed to separate gas products and electrolyte flow at the production site and reduce gas crossovers below the industrial safety limit of 2% at low current densities, addressing the limitations of traditional zero-gap electrolysers.

In-situ experiments were conducted using a custom-built prototype, focusing on performance and crossover concentration at low current densities ($0.13 \, A/cm^2$, $0.09 \, A/cm^2$, $0.06 \, A/cm^2$ and $0.03 \, A/cm^2$). The study tested various electrode-membrane combinations, including nickel meshes and felts paired with Zirfon 220, Zirfon 500 and ePTFE, and three channel widths (1 mm, 0.7 mm, and 0.5 mm). Hydrogen in oxygen (HTO) concentrations were measured using a gas chromatograph. The volumetric flow rate of the electrolyte (30 w% KOH) was measured using a flow metre at the cell outlet. The electrolyte influx temperature was simultaneously controlled using a magnetic hot plate stirrer and a thermocouple.

The experiments revealed that low Reynolds numbers (< 1300) that arise from decreasing the channel widths create a laminar flow regime that reduces hydrogen advection to the electrolyte bulk. However, stagnant flow regions may develop in the vicinity of the inert channel boundaries, where diffusion dominates and leads to the increase of cross-over rates at low current densities. In terms of anodic hydrogen concentration (HTO), Zirfon assemblies exhibited similar trends: an increasing anodic hydrogen concentration with declining current densities results in a peculiar drop at the ultimate measurement point of 0.03 A/cm^2 . Concerning ePTFE configurations, the crossover rate showed an unmistakable correlation with the current density.

During the iterative process of optimising performance, numerous findings were reported. Among the tested electrode setups, nickel mesh exhibited superior performance compared to nickel felt, attributed to its open structure and ability to conform to the Zirfon layer, thereby enhancing contact and facilitating hydrogen release. Substituting the anode with a stainless steel mesh improved performance in the ePTFE configuration, while, for their Zirfon counterpart, an adverse effect was observable. Furthermore, hot pressing showed a positive impact, allowing effective integration of meshes with Zirfon 500 and ePTFE materials. Increasing the circulated electrolyte temperature improved catalytic activity, reduced ohmic resistances, and increased the current density starting at a lower onset voltage.

Based on the insights gained in this study, the Gravity-Fed Laminar Electrolyser has a vast potential to improve its performance further and proves to be a viable concept for operating within safety limits at low current densities.

\sum

Introduction

Human-driven climate change has reached a point where its critical threat to global society cannot be ignored. The Paris Agreement states that the involved governments have pledged to keep the maximum increase in global temperature below the notorious 1.5° C compared to preindustrial levels by 2050 [53]. To achieve this goal, imperative measures must be taken, the most pressing being the substitution of fossil fuels with sustainable alternatives. The most promising and widely adopted renewable sources in current times are wind and solar energy.

Unfortunately, this shift towards intermittent power sources from baseload supplying coal and gas power plants entrails the necessity for immediate capacity increase of Energy Storage System (ESS). Although battery energy storage systems (BESS) can mitigate daily supply and demand fluctuations, due to their cyclic and steep calendar aging [11][28], other long-term and seasonal storage forms must be implemented. Green hydrogen produced by water electrolysis with renewable electricity is deemed to answer this difficult challenge while staying on the path toward a sustainable future. Moreover, hydrogen is also believed to contribute to the electrification of other parts of the energy sector, namely high-temperature industrial processes, long-haul maritime transport, truck cargo shipping, and air freight [50].

Currently, only 4 % of the hydrogen produced comes from electrolysis, of which only a fraction is considered green hydrogen, depending on the mix of electricity supplied [14], the majority comes from carbon-intensive processes, mainly through SMR, also known as grey hydrogen [18][6]. Due to its low cost and proven technology, grey hydrogen producers are attempting to cover up their emissions by adding CCS to their procedure, which is then rebranded as blue hydrogen. As a result of the 3.5 % fugitive methane emissions that are supposed to power the SMR and CCS process, having a GWP20 86 times higher than CO2, the total equivalent carbon dioxide emissions for blue hydrogen are only 9 - 12 % lower compared to that of grey hydrogen [19]. For green hydrogen to become widely available, it has to become economically viable and eliminate the cost gap between its competitors. To achieve this feat, strides are necessary in the energy sector, as well as in policymaking; these include carbon taxes, a further decline in renewable electricity costs, and predominantly the cut in both OPEX and CAPEX of electrolyser stacks [6].

With regard to electrolysis technologies, several promising alternatives are capable of contributing to the global landscape of hydrogen production. These include Solid Oxide Electrolysis (SOEC), Proton Exchange Membrane Electrolysis (PEM), Anion-Exchange Membrane Electrolysis (AEM), and Alkaline Water Electrolysis. AWE and PEM are reported to have reached a high level of technological maturity, while SOEC and AEM are still in the development and experimental phase. Another aspect to consider is the use of scarce and precious metals, for which PEM is renowned because it requires iridium and platinum as catalysts for the OER and ORR, respectively. In contrast, AWE operates with widely available materials, such as nickel and steel; additionally, its high maturity and proven industrial application make it one of the main possible contributors to the decrease in the cost of green hydrogen and the acceleration of the energy transition [43].

2.1. Alkaline Water Electrolysis

Going back to the beginnings of electrolysers, the basic configuration was as simple as two electrodes submerged in an ion-conducting electrolyte (figure 2.1). The gases produced would simply rise because of their buoyancy in the electrolyte until collected in reservoirs situated above each electrode. The initial designs faced numerous issues, including rapid degradation in alkaline conditions, poor thermal regulation, and substantial ohmic losses [41]. Achieving an optimal balance of efficiency and product purity was crucial, and it was heavily dependent on the interelectrode distance. Increasing this parameter raises the ohmic resistance of the electrolyte and, on the other hand, has the benefit of lower crossover concentration levels.

A typical modern AWE stack consists of several adjacent cells separated by bipolar plates, which serve as current collectors and help distribute the current from one cell to the next. The cathode of a cell is connected to the anode of the following cell, connecting them in series adds up the voltage of every cell, yielding a higher total output voltage of the stack. The cells are compressed together with endplates and gaskets to ensure sealing and water tightness. The alkaline electrolyte is typically a potassium hydroxide (KOH) solution in which the anode and cathode are submerged and, after connecting through an external electrical circuit, produce oxygen and hydrogen, respectively. Between the two electrodes, a separator is responsible for maintaining the purity of hydrogen and oxygen and preventing cross-contamination while allowing the transport of ions. The OER and HER occur at the electrodes according to the following equations:

| Cathode : | $2\mathrm{H}_2\mathrm{O} + 2e^-$ | \rightarrow | $H_2 + 2OH^-$ | $E_{cat}^{0} = -0.828 V$ | (2.1) |
|-----------|----------------------------------|---------------|------------------------|---------------------------------|-------|
| Anode : | $2\mathrm{OH}^-$ | \rightarrow | $0.5O_2 + H_2O + 2e^-$ | $E^0_{ano} = +0.401 \mathrm{V}$ | (2.2) |
| Total: | H_2O | \rightarrow | $H_2 + 0.5O_2$ | $E_{cell}^{0} = -1.229 V$ | (2.3) |



Figure 2.1: The basic structure and principle of operation of an alkaline electrolysis cell [43].

Several concepts emerged throughout the evolution of AWE. The conventional arrangement has a defined gap between the electrodes, although the ohmic resistance of the electrolyte along this gap causes a decrease in efficiency. For this reason, the zero gap configuration, in which the electrodes are placed directly on each side of the diaphragm, offers the potential to reach higher performance by reducing these losses [33]. The ionic conductivity of the diaphragm is a crucial parameter; its hydrophilic characteristic will allow a higher degree of pore saturation of the material, improving the conductivity, and enhancing the separation of gaseous products. However, the dissolved gaseous products of the reactions can still permeate through the layer. Currently, the most widely implemented diaphragm materials in zero-gap electrolysers (ZGEs) are produced by AGFA under the product name Zirfon. These are available with different specifications, namely UTP 220, UTP 500 and UTP 500+ [46][47][45]. The polysulfone core of the 500 series membranes shows excellent mechanical stability even at elevated temperatures and harsh alkaline environments [22]. It also incorporates polyphenylene sulphide fabric and is coated with zirconium oxide, which due to its hydrophilic essence improves the wettability of the membrane and therefore its ionic conductivity [60][51].

From a process management perspective, AWE stacks have several criteria to abide by. They must be operated at constant pressure to achieve efficient hydrogen and oxygen production, avoiding fluctuations and repeated pressure cycles, which affect electrochemical reactions and can ultimately also have an undesirable effect on the integrity of components [48]. Consequently, to achieve equal pressures on the catholyte and anolyte sides of the cell, the two cycles are often mixed before entering the cell. Furthermore, pressure control valves are responsible for decreasing the liquid height differences, as in the presence of large pressure differences, the pressure-driven convection increases drastically and leads to a higher crossover contamination flux. Another critical aspect to take into account is the management of thermal gradients, which prevents the formation of localised hotspots, influencing the performance and durability of cells [20].

The current performance of AWE electrolysers is constrained by a relatively low nominal current density and a limited load range. The nominal current density is a result of the balance of the CAPEX and OPEX of the stacks. Although operating at higher current densities increases hydrogen production per unit of investment, it also reduces energy efficiency and thus increases the OPEX. The minimum load refers to the lowest current density at which an electrolyser can operate safely. Operating below this threshold can cause significant gas cross-contamination, creating hazardous explosive mixtures [8]. Minimisation of this flux is of critical importance since a hydrogen-in-oxygen mixture has a Lower Explosive Limit (LEL) of 3.8 mol% [59], due to the diffusivity and solubility of hydrogen in KOH exceeding that of oxygen, the volume fraction of hydrogen in oxygen(HTO) is the defining metric for safety measures. [40][13]. For this reason, the International Organisation for Standardisation has established the maximum HTO for water electrolysis at 2% [23]. Thus, for an electrolyser to work safely in industrial circumstances, these safety measures must be met at all times. This issue is especially critical when electrolysers are connected to the fluctuating electricity supply of renewable energy sources, forcing electrolyser shutdowns below the minimum load, leading to reduced operating hours and increased material degradation.

2.2. The Flexibility of AWE stacks

The main shortcoming of currently available industrial AWE stacks is their limited operating range, which becomes prevalent at low current densities, where the diffusion crossover mechanism dominates. This lower current restriction makes the technology less flexible and compliant with sudden surges and declines in supplied power. Therefore, integrating them with RESs is challenging, considering their intermittency and volatility in power output.

In conventional alkaline electrolysers, simulations using dynamic power supply profiles revealed concerning levels of HTO at current densities below 20 % of the nominal load [37]. This inaccessible load range forces a high level of cooperation in terms of load repartition within the same plant, which means operating often at part load. Production at these levels results in lower efficiency [1], leading to higher energy consumption per unit of hydrogen produced, directly affecting the production costs of each kilogramme of hydrogen at the plant outlet [55]. Running these systems below their optimal performance range can result in further inefficiencies and increased wear [6]. Consequently, frequent shutdowns and operating at part load can affect peripheral systems such as pumps, compressors, and cooling systems that are typically optimised for full-load operation.

To illustrate the importance of operating range, Figure 2.2 shows a strategy for load repartition among several stacks with increasing wind power load [52]. Initially, when the wind power P_{Wind} is less than the minimum operational power $P_{ele,min}$ of the first electrolyser to be initiated (EL1) electrolyser, all four electrolysers are in the off state, as illustrated in 2.2 (a). Once the wind power P_{Wind} exceeds the minimum operational power $P_{ele,min}$, EL1 is activated, as shown in 2.2 (b). As P_{Wind} continues to increase, the power output of EL1, denoted as P_{ele1} also increases. In 2.2 (c), when the power of EL1 P_{ele1} reaches its rated capacity P_{ele} the power is reduced to $P_{ele,m}$ and second electrolyser in line (EL2) is started with its power set to P_{ele2} = P_{ele} - $P_{ele,m}$ as depicted in 2.2(d). This process continues sequentially for the remaining electrolysers until the peak power load is reached. In case of a decrease in load, the process is analogous but reversed.



Figure 2.2: Strategy to allocate increasing wind power load among 4 electrolyser stacks [52]

It is recognisable from Figure 2.2, that the lower current density limit of the stack affects the control strategy and the switching dynamics between electrolysers to a great extent. Reducing this limit allows for more effective coordination of resources and decreases stack standby and off time. Shutting electrolysers down or keeping them in standby mode is detrimental to the OPEX, partly because the electrolyte has to be kept at operating temperature and the pumps need to be started up again when a necessity arises. In addition to this, frequent switching also causes a severe drop in efficiency, as depicted in 2.3, resulting from recently initiated stacks not operating at the nominal efficiency level [52].



Figure 2.3: Stack efficiency of 2.2 Control Strategy [52]

Due to these shortcomings in terms of process management and flexibility, a handful of innovative cell concepts were developed. Some of them led to commercially available stacks, while others ended as promising lab-scale attempts to revolutionise the industry. In any case, their strategy and cell architecture are of great interest when constructing a cell to accomplish the same feat.

2.3. Innovative Concepts aiming to increase Felixibility

The capillary Fed Electrolyser (CFE)

One of the latest and most disruptive cell designs is attributed to Hodges et al. and implemented by the Australian company Hysata, which claims a measured efficiency of 98% [17]. Their design takes advantage of several aspects of previous concepts and of capillary forces to suck the electrolyte from a lower reservoir [17]. This process is made possible by the use of a porous membrane confined between the two electrodes. The permeable fabric delivers the electrolyte solution through the capillaries to the anode and cathode, while maintaining an effective ion conduction capability, resulting in hydrogen and oxygen separation from the liquid phase at the production site.



Figure 2.4: The Capillary Fed Electrolyser (CFE) Concept[17]

The study proposed the use of Polyethersulfone (PES) as a separator, which is thinner, more porous, and thus has lower ionic resistance compared to Zirfon membranes, the most widely used commercial

alkaline separator. Hodges et al. undertook a search to select the best interelectrode separator capable of drawing up an aqueous KOH electrolyte through capillary rise only. The PES structures submitted to the test were differentiated by their average pore diameter: $0.45 \,\mu\text{m}$, $1.2 \,\mu\text{m}$, $5 \,\mu\text{m}$, and $8 \,\mu\text{m}$. The capillary flow rates were measured at different heights and led to the observation that the $8 \,\mu\text{m}$ pore diameter is the most favourable option for the task at hand. Further improvements were pursued to maximise efficiency; these include the welding of the anode to the bipolar plate to minimise contact resistances and the addition of PTFE to the anode to avoid bubble formation. A reduction in resistance is visible for each modification and is illustrated in Figure 2.6.



Figure 2.5: Increase in performance through various modifications

Although exhibiting phenomenal performance, the fundamental weakness of the construction is its low heat dissipation capacity as a result of the low flow velocity of the electrolyte through the tortuous geometry. This is further aggravated as the height increases or the pore size decreases. Resulting in a maximal cell height of 18 cm for stable water electrolysis at 1 A/cm^2 and $\geq 80^\circ$ with an average pore diameter of $8 \ \mu m$ [17]. Consequently, the design of a CFE is constrained to expand its surface area per cell horizontally to achieve lower costs per installed capacity.

A further reduction in the CAPEX of the CFE can be achieved through its simplified BoP and process management. The reason is mainly due to the unnecessity of pumps and gas/liquid separators since there are no gas bubbles enveloped by liquid that need to be removed from the electrodes. Furthermore, there is no need for excessively large volumes of water, which is essential for the removal and separation of gas bubbles in conventional commercial cell stacks. This volume amounts to $\sim 10\ 000\ L$ of water per MW for conventional commercial cell stacks, which is incomparable to the modest $\sim 500\ L$ of water per MW of a CFE system. Furthermore, a significant benefit of the capillary-fed cell system is its ability to prevent the inefficient and corrosive high-voltage shunt currents that typically occur between cells along the catholyte and anolyte return lines in traditional alkaline electrolysers.

The Reselyser

A further concept aimed at increasing the flexibility of AWE can be attributed to an EU-funded research project codenamed Reselyser titled "Hydrogen from RES: Pressurised alkaline electrolyser with high efficiency and wide operating range" [34]. This undertaking aims to tackle the same issue as the CFE, although with a different approach.

The electrolyte is pumped between and through the adjacent separator layers, thus, in essence, creating a flow-through electrolyser, with an anolyte and a catholyte circuit that is then remixed after phase separation and before reinjection into the cell (2.7). The electrolyte influx is carried out at high-pressure levels of 10,15 and 30 bar. The developed separator has been baptised "e-bypass separator", which is one of the crucial elements for the cell stack to perform at the expected level, and it features a three-layer separator composite. The middle layer binds the two separator layers together, while also acting as a spacer to keep them at a regulated distance from each other. This structure is created by impregnating the outer layers of the 3D spacer fabric with a Zirfon organomineral layer [34]. The internal channel serves as a third compartment in the electrolyser, along with the anolyte and catholyte compartments. During the electrolysis process, this third compartment (the internal channel between the adjacent Zirfon separator layers) must be filled with electrolyte. The distinctive aspect of this design is its ability to create an electrolyte flow from the third compartment toward both the anolyte and catholyte compartments through the two separator layers. Using operational mode, it is anticipated that the diffusion of dissolved gases to the opposite compartment is either significantly reduced or nearly eliminated. Achieving this is one of the primary objectives of the Reselyser project.



Figure 2.6: The Reselyser concept [34]

The performance of the cell stack has been demonstrated through J-V curves at various system pressures. It shows impressive performance with maximum efficiencies reaching 82 %, although this value significantly drops compared to the same cell after 1500 on/off cycles. However, compared to the single membrane stack, the efficiency based on HHV decreases from 81 % to 72 % at the stack level over 36 % of the total life cycle. This degradation time window is equivalent to 90 % of the lifespan of a single membrane commercial stack (S1000) of the same era (2015). Notably, with the bypass membrane, the spacing is increased to 3 mm (compared to the 500 μ m of the Zirfon in a single membrane stack); the resulting rise in cell voltage in the high-pressure stack is minimal. This indicates that the catalytic activity effectively offsets a fair share of the additional ohmic resistance, calculated to be 300 mV at the highest current density.



Figure 2.7: J-V curves of the e-bypass stack before and after cycling (1500 on/off at 30 bar and 0.433A/cm²) [34]

In terms of crossover concentrations, the HTO of the stack at different pressure levels is again compared to a conventional single membrane cell stack (S1000) 2.8. Moderately high pressures of 10-15 bars allow for lower HTO levels, while operating at 30 bars results in a sharper increase at lower current densities, but remain within the industrial safety measures of 2%. It should be noted that all gas crossover measurements were conducted until the lower limit of (1 A/cm^2) . The region of interest being below this threshold, further measurements at lower current densities would have been insightful. The authors of the project also observed that the gas impurity depends not only on the separator used but also on the dissolved gas and microbubble concentration of the recirculated KOH solution. To decrease this concentration, the use of larger gas separators and the possible application of Zirfon-like membranes were proposed to enhance the degassing process. This demonstrates the importance of well-designed and operated electrolyte flow management, while also recognising the outstanding simplicity and efficiency of the Capillary-Fed Electrolyser's gas withdrawal management.



Figure 2.8: Hydrogen content of the oxygen stream of the high pressure (HP) stack at different pressures compared to the single membrane baseline.

The Gravity Fed Laminar Electrolyser

Accumulating the knowledge and observation of the Reselyser and the Capillary-Fed Electrolyser, a new unproven design has emerged aiming to achieve the same goal of improved flexibility and reduced crossover concentration. In addition, taking inspiration from membraneless electrolysers' working principles by merging the flow-through and flow-by concepts led to the gravity-fed laminar electrolyser. It comprises an electrolyte flow channel, similar to the Reselyser's, but several factors thinner and fed from an upper reservoir. The channel is confined between two porous electroles positioned parallel to the flow direction [9]. This thin channel dimension allows the electrolyte to flow unperturbed along the electrodes while remaining in the laminar flow regime. This smooth and orderly movement of the fluid is essential in avoiding the advection of gaseous or dissolved products from the surface and pores of the electrodes. The optimal electrode material would be a combination of a large active area catalyst layer applied on a gas diffusion substrate. The electrolyte must enter the pore system; once the evolution reaction is concluded, the products must be transported through the gas diffusion layer to the gas phase side. Thus, similarly to the capillary-fed electrolyser, the gaseous products are ideally separated at the reaction site, and no phase separators are necessary. This simplifies the BoP, and the electrolyte can be directly recirculated.



Figure 2.9: Schematic illustration of the Gravity-Fed Laminar Electrolyser concept

2.4. Aim of Work

This project aims to demonstrate the feasibility and assess both the performance and design limitations of the Gravity Fed Laminar Electrolyser concept, while also examining the purity of the product at lower current densities. This brings about the objective of this project:

"Design and manufacture a cell based on the Gravity-Fed Laminar Electrolyser concept, improve its performance using available resources, and assess the purity of its gas output for various channel widths and current densities."

3

Theoretical Background

This chapter describes the fundamentals of electrochemistry, parameters that affect the concentration of dissolved gas and their behaviour in fluid flow regimes, and finally a section that outlines the gas crossover mechanisms that occur in alkaline water electrolysis cells.

3.1. AWE fundamentals

It is essential to understand the various factors influencing the total cell voltage to assess how the performance of a cell can be improved. In an AWE cell, the total cell voltage originates from separate components: equilibrium potential (E_{eq}), activation overpotential (η_{eq}), concentration overpotential (η_{conc}), and ohmic losses (IR). The aggregate of these factors determines the overall cell voltage:

$$E_{\text{cell}} \approx E_{\text{eq}} + \eta_{\text{act}} + \eta_{\text{conc}} + IR$$
 (3.1)

Figure 3.1 demonstrates the dependence of these losses on the current density. The y-axis begins at the equilibrium potential. In this instance, bubble effects are evaluated separately, despite their impact on the three distinct losses. The following sections will dive into each component mentioned in Equation 3.1.



Figure 3.1: Graph illustrating relationships between current density and total cell voltage, including concentration, activation, ohmic, and bubble losses within a zero-gap cell at room temperature [15]

Equilibrium Potential

Equilibrium thermodynamics defines the minimum voltage necessary for water electrolysis, there is no net current under these conditions, indicating the absence of concentration gradients. Despite the lack of net current, a dynamic equilibrium is present at each electrode/electrolyte interface, with charges traversing in both directions. The exchange current density (j_0) reflects this balanced faradaic process.

To determine the equilibrium potential (E_{cell}°) for the overall water splitting reaction, it is calculated using the difference in Gibbs free energy (ΔG°) under standard conditions:

$$E_{\text{cell}}^{\circ} = -\frac{\Delta G^{\circ}}{nF} \approx \frac{237}{2 \cdot 96485} \approx 1.23 \text{V}$$
(3.2)

In this context, n denotes the moles of electrons transferred per mole of product, while F is the Faraday constant (96485 $C \cdot mol^{-1}$), which represents the charge per mole of electrons. Operating near the equilibrium voltage leads to an endothermic reaction, inducing cooling through heat absorption. The reaction enthalpy ΔH accounts for supplementary heat required to equalise the temperatures of the products to that of the reactants [2].

$$\Delta H = \Delta G + T \cdot \Delta S \tag{3.3}$$

 ΔS denotes the variation in entropy for the reaction, where gases possess greater entropy than liquids. Running the cell at the thermoneutral potential of 1.48 V at ambient temperature leads to the total heat necessary to drive the reaction being provided by the applied electrical current. In an operating cell stack, the thermoneutral potential is exceeded, generating excess heat compared to what is strictly necessary to convert the reactants to products.

Activation overpotential

Electrochemical reactions frequently involve a series of steps with multiple electron transfers. In these series, a particular step often proceeds at a slower rate, known as the rate-determining step, which governs the reaction kinetics overall. In this context, the activation overpotential is the extra potential required to surpass the energy barrier of this step. The Butler–Volmer equation describes the correlation between current density (*j*) and overpotential (η) [3].

$$j = j_0 \left[\frac{C_{\rm R}}{C_{\rm R,eq}} \exp\left(\frac{\alpha F \eta}{RT}\right) - \frac{C_{\rm O}}{C_{\rm O,eq}} \exp\left(\frac{-(1-\alpha)F \eta}{RT}\right) \right]$$
(3.4)

The transfer coefficient α reflects the energy barrier's symmetry and typically lies between 0.3 and 0.7. $C_{O,eq}$ and $C_{R,eq}$ represent the equilibrium surface concentrations of the oxidising and reducing species, respectively, while C_O and C_R indicate deviations from these equilibrium states. The exchange current density (j_0) depends on the concentration and can be described by:

$$j_0 = Fk_0 C_{\text{O,eq}}^{(1-\alpha)} C_{\text{R,eq}}^{\alpha}$$
(3.5)

A catalyst is considered effective if it has a high standard rate constant k_0 which corresponds to a low activation overpotential. In contrast, low values of k_0 (and therefore implicitly j_0) result in a high activation overpotential, which requires greater potentials compared to E_{eq} to drive the reaction. For considerable overpotentials, either the first or second term in the Butler-Volmer equation 3.4 can be ignored, depending on the current's sign. With anodic currents, the expression becomes:

$$j = j_0 \frac{C_{\rm R}}{C_{\rm R, eq}} \exp\left(\frac{\alpha F\eta}{RT}\right)$$
(3.6)

The concentration-independent Tafel equation is applicable when the cell is operated at high current densities and when concentration gradients are negligible :

$$\eta_{\text{act}} = \frac{RT}{\alpha F} \ln(j_0) - \frac{RT}{\alpha F} \ln(j) = a + b \cdot \log(j)$$
(3.7)

Tafel characteristics are indicative of irreversible kinetic processes with a predominantly unidirectional faradaic reaction. The Tafel slope (b) is associated with the rate-determining step and is frequently used for kinetic evaluations.

Ohmic Overpotential

Ohmic losses in an electrochemical cell are the result of ionic and electronic resistances within the cell and its configuration. Governed by Ohm's law, these resistances correspond to the current-resistance product: I \cdot R. The main loss contributors are high-current pathways, especially the electrolyte, which stem from the resistance hydroxide ions face traversing through it. The ohmic resistance of the electrolyte R_Ω, under the absence of bubbles, is related to the gap 1 [m] between the electrodes of area A [m²] and the limiting ionic conductivity κ [$\Omega^{(-1)} \cdot m^{(-1)}$]:

$$R_{\Omega} = \frac{l}{\kappa A} \tag{3.8}$$

Correlations and experimental data on the conductivity of the electrolyte as a function of temperature and KOH mass fraction are detailed in Le Bideau et al.'s extensive report [25]. Additionally, the ohmic resistance incorporates resistances from cables, electrodes, the diaphragm, and other connections.

3.2. Flow Regimes

The flow regime in a channel significantly influences the crossover of dissolved products between electrodes. In laminar flow, the fluid layers move in thin parallel layers with minimal mixing, which leads to a defined concentration gradient across the channel. This structured flow limits the convective transport of dissolved species, relying primarily on diffusion products that move across the channel[5]. As a result, dissolved gases produced at one electrode tend to accumulate near their source, creating higher local concentrations adjacent to the electrode surface. This increases the magnitude of crossover in stagnant velocity regions, as the concentration gradient drives the diffusion of products toward the opposite electrode. However, turbulent flow causes rapid mixing of the electrolyte, which dilutes the products into the bulk of the flow through convection. This would reduce local concentrations near the electrodes and promote the crossing of dissolved species dominated by mixing rather than diffusion. Thus, the controlled, steady nature of laminar flow promotes a stable environment where diffusion dominates, it also inherently limits convective mass transport, which could have a higher impact on crossover concentration.

The flow regime of a channel can be characterised by the Reynolds number, which is the ratio of inertial resistance to viscous resistance for a flowing fluid. It can be expressed as follows [5]:

$$\operatorname{Re} = \frac{\rho \, v \, l}{\eta} \tag{3.9}$$

where:

 $\mathrm{Re} = \text{Reynolds number}$

- $\rho = \text{density of the fluid}$
- v = velocity of the fluid
- l = characteristic length
- $\eta = dynamic viscosity of the fluid$

Considering membraneless electrolysers, reaching exceedingly low Reynolds numbers causes the diffusion term to dominate, and thus high crossover flux becomes a threat once again. This relation is further described in the following figure:



Figure 3.2: Relation between hydrogen crossover concentration and Reynolds number in a membraneless electrolyser [32].

3.3. Solubility

Another factor that has a major influence on the crossover flux rate is the solubility of hydrogen in KOH, for which Henry's law provides the fundamental equation as follows [12][4]:

$$C = k_H \cdot P \tag{3.10}$$

where:

C = Concentration of the dissolved gas in the liquid $k_H =$ Henry's constant P = The partial pressure of the gas

However, in non-equilibrium, additional factors such as diffusion and the ionic strength of KOH should be considered. The salting-out effect emerges when the increased ionic strength decreases the capacity of the solvent to solvate gas molecules because the electrolyte ions compete with the gas molecules for solvation, leading to a lower gas solubility. Thus, increasing the weight percentage of KOH in the solution reduces the solubility of hydrogen gas. This is visible from the experiments conducted by Ruetschi and Amlie [36].



Figure 3.3: Relation between solubility and KOH concentration [36]

Another parameter that strongly influences solubility is temperature. The more recent study by Schalenbach et al. shows the solubility of hydrogen as a function of temperature and KOH concentration [38].



Figure 3.4: Solubility of hydrogen in KOH as a function of temperature and concentration [38]

In conclusion of the measurements by Ruetschi et al. [35] and Knaster et al. [56], it can be established that the solubility of hydrogen in potassium hydroxide is inversely correlated with concentration and the research by Schalenbach et al. confirms that at concentrations greater than 10 w%, solubility increases with temperature. [38][16].

3.4. Gas Crossover Mechanisms

In literature, HTO (also denoted as anodic hydrogen fraction) is used as the reference value to assess the safety of the electrolysis process, as the hydrogen diffusion coefficient is approximately 3 times higher compared to oxygen in 30 w% KOH at a temperature of 60° C [38]. However, the same derivation can be done for oxygen. Equation 3.11 describes the hydrogen to oxygen ratio in percentages, in terms of N_{H2}^{perm} , which sums up the crossover flux of all transport mechanisms and N_{O2}^{prod} defining the oxygen production rate at the anode.

$$HTO[\%] = \frac{N_{H_2}^{\text{perm}}}{N_{O_2}^{\text{prod}} + N_{H_2}^{\text{perm}}}$$
(3.11)

 N_{O2}^{prod} , assuming 100 % faradaic efficiency, can be accurately estimated with equation 3.12, where *i* describes the current density and *F* the Faraday constant.

1

$$N_{O_2}^{\mathsf{prod}} = \frac{j}{4F} \tag{3.12}$$

In terms of these two equations, it is now possible to derive the hydrogen permeation flux with the experimentally measured anodic hydrogen fraction, first by rearranging 3.11 and then substituting equation 3.12. This leads to the final form of the total of all crossover transport mechanisms defined in terms of oxygen production rate and measured HTO concentration.

$$N_{H_2}^{\text{perm}} = N_{O_2}^{\text{prod}} \cdot \frac{HTO}{1 - HTO} = \frac{j}{4F} \cdot \frac{HTO}{1 - HTO}$$
(3.13)

The equations mentioned above are restricted to the condition that the separator area must be identical to that of the electrodes, otherwise, a $\frac{A_{el}}{A_{sep}}$ factor must be implemented in equation 3.13.

The hydrogen crossover to the anodic compartment can be divided into 3 transport mechanisms: diffusion, convection, and electrolyte mixing. These will be further detailed in the following sections.

Diffusion

Among the potential crossover mechanisms is the migration of electrolysis products through the separator (and in the case of the Gravity Fed Laminar Electrolyser through the electrolyte) to the opposite half-cell compartment. Typically, these products can migrate through both the solid and liquid phases of the membrane. However, it has been observed that the diffusion through the solid phase of Zirfon is several orders of magnitude lower than through the liquid phase [49], thus these are considered insignificant. Furthermore, it is assumed that the separator remains impermeable to gas bubbles at atmospheric pressure, indicating that only the species dissolved in the KOH solution are taken into account for diffusion across the separator unit. To describe this transport phenomenon through the Zirfon layer, Fick's law is used [5], as presented in equation 3.14.

$$N_{H2}^{\text{diff}} = D_{H2}^{\text{eff}} \cdot \frac{\Delta c_{H2}}{\delta_{sep}}$$
(3.14)

Where:

 $D_{H2}^{\text{eff}} = \text{effective diffusion coefficient}$ $\Delta c_{H2} = \text{difference in dissolved hydrogen concentration across } \delta_{sep}$ $\delta_{sep} = \text{thickness of the separator}$ Estimating the effective diffusion coefficient in porous materials, such as zirfon, generally involves adjusting the molecular diffusion coefficient with D_{H2}^{eff} , which accounts for the tortuous nature of the channels in the porous medium and the limited cross-sectional area available for flow.

$$D_{H2}^{\text{eff}} = \frac{\epsilon}{\tau} D_{H_2} \tag{3.15}$$

Where:

$\epsilon={\rm fractional}$ void space in the porous material

$\tau =$ tortuosity factor

Assuming total electrolyte degassing takes place in the stirred reservoir, the concentration gradient across the cathodic membrane, Δc_{H2} , can be approximated using the cathodic concentration of dissolved hydrogen, c_{H2}^{cat} , since the concentration in the electrolyte flow, c_{H2}^{elyte} , is assumed to be zero.

$$\Delta c_{H_2} \approx c_{H_2}^{\text{cat}} - c_{H_2}^{\text{elyte}} \approx c_{H_2}^{\text{cat}}$$
(3.16)

The solubility of hydrogen significantly affects its concentration in the electrolyte and, consequently, its diffusion as well. Experimental data is covered by Young et al.'s lengthy compilation of solubility data series in various fluids [56]. Although Ruetschi, Amlie, Knaster, and Apelbaum's experimental results are the few that specifically focus on hydrogen solubility in KOH solutions, the study by Schalenbach et al. is among the limited recent literature on the topic. As already mentioned in figure 3.4 and 3.3, the experiments give insight into the variation as a function of the concentration and temperature of the solution [56][35]. These are parameters necessary to consider when the objective is to minimise the anodic hydrogen concentration of an experimental setup.

Ultimately, the hydrogen flux by diffusion through the separation unit can be approximated with the subsequent equation.

$$N_{H2}^{\text{diff}} \approx D_{H2}^{\text{eff}} \cdot \frac{c_{H_2}^{\text{cat}}}{\delta_{sep}}$$
(3.17)

Through the above equation, it is clearly visible that the flux is inversely proportional to the thickness and tortuosity of the separator material and proportional to its porosity since it directly influences D_{H2}^{eff} .

Convection

Convection refers to the process of transporting mass (such as dissolved gases, solutes, or reactants) through the fluid as a result of the effect of fluid motion. In convective mass transfer, fluid flow enhances the rate at which substances move within the system, allowing mass transfer to occur more rapidly than it would through diffusion alone. It can be further divided into three causing occurrences: pressure gradient, electro-osmotic drag, and electrolyte mixing.

A. Pressure Gradient

Pressure differentials across the anodic separator can drive the convective movement of a solution containing dissolved hydrogen with velocity v_{sol} (perpendicular to the separator unit), resulting in a hydrogen crossover flux. The velocity of the solution v_{sol} within porous media can be described using Darcy's law [5]. Substituting these relationships, the resulting hydrogen flux depends on the permeability of the diaphragm K_{sep} , the dynamic viscosity η and, critically, the pressure difference Δp between the two sides of the separator (3.18). This pressure difference determines the direction of convective flow across the separator, with flux directed toward either side depending on the sign of Δp . The hydrodynamic pressure in the channel being higher than atmospheric pressure directs the flow toward the gas phase side of the separator.

$$N_{H_2}^{\text{conv}} \sim v_{sol} = \underbrace{\frac{K_{\text{sep}}}{\eta} \cdot \frac{\Delta p}{d_{\text{sep}}}}_{\text{Darcy's law}}$$
(3.18)

The permeability of the diaphragm K_{sep} is mainly influenced by the pore structure and pore size, with a secondary dependence on other characteristics, such as porosity and tortuosity. The permeability K_{sep} can be estimated using the Hagen-Poiseuille law, which describes the volumetric flux through a pore of diameter d_{pore} and the pore length of the separator. This approach models the separator as an array of parallel cylindrical pores orientated perpendicularly or slightly oblique to the separator surface. By assuming a uniform pore size and incorporating corrections for porosity and tortuosity, the permeability K_{sep} is expressed as shown in Equation 3.19 [30].

$$K_{\mathsf{sep}} = \frac{\epsilon \cdot d_{\mathsf{pore}}^2}{32\tau} \tag{3.19}$$

B. Electro-osmotic Drag

The movement of fluid caused by friction between charged ions that migrate under the influence of an electric field is called electro-osmotic drag [43]. Consequently, the dissolved gas may be transported through the resulting convective flow [39]. In the context of alkaline electrolysis, being dissociated in the solvent, the migration of K^+ and OH^- ions in response to the electric field is facilitated.

C. Electrolyte Mixing

The electrochemical reactions result in changes in electrolyte concentration because water is consumed at the cathode, while it is produced in the anodic half-cell. To mitigate this concentration gradient, anodic and cathodic electrolyte cycles are typically mixed. However, this process management can lead to a decrease in the purity of the resultant product gases, as the electrolyte becomes saturated with dissolved products. Consequently, the electrolysis cell is continuously supplied with dissolved hydrogen and oxygen if degassing is not effective or accounted for. Although separation of the electrolyte cycles can prevent this crossover mechanism entirely, it may lead to a reduction in cell efficiency over time because of the shifts in the anodic and cathodic electrolyte concentrations as prolonged operation decreases the electrolyte's conductivity. In a ZGE at atmospheric pressure, the contribution of electrolyte mixing to the total permeation of hydrogen in the anodic compartment is reported to be 90%, which makes other crossover mechanisms almost negligible [49].

4

Design Considerations

Several parameters must be taken into account to design and build a performance-optimised cell and achieve a low crossover concentration. Building on the previous chapter on theory, the cell geometry and specifications are defined.

4.1. Inter-electrode Distance

The Gravity-Fed Laminar Electrolyser restricts the electrolyte flow between two electrodes, where their spacing dictates both the volumetric flow and the flow regime. According to Fox et al., a Reynolds number below the 2300 threshold is typically required to maintain a laminar flow regime [10]. In the laminar regime, the flow is characterised by parallel streamlines, which minimises turbulence and mixing. As a result, the mass transfer perpendicular to the electrodes caused by the bulk motion of the fluid is limited, leading to reduced mixing of the electrolyte.

The velocity profile is computed by assuming a fully laminar flow between two vertical parallel plates. In this configuration, we can assume that the *z* component of the velocity field (v_z) is constant with respect to *y* (spanwise coordinates) and thus only depends on the *x* coordinate, the distance from the electrode. However, this initial assumption will be refined in the Analytical Model section (6.3), where the velocity domain $v_z(x, y)$ of the channel is estimated more accurately with a Fourier sum. Currently, neglecting all the velocity components of the flow except the vertical element v_z , the equation describing the velocity profile is defined as:

$$\frac{\delta^2 v}{\delta x^2} = \frac{g}{\nu} \tag{4.1}$$

Where:

v = velocity of the electrolyte q = gravitational acceleration

 $\nu =$ kinematic viscosity of the electrolyte

With the following boundary conditions:

$$v|_{x=0} = 0$$
 and $v|_{x=l} = 0$ (4.2)

With the no-slip boundary condition, the velocity at the wall is zero, and the porous electrode's suction effect is not taken into account.

Solving this equation for w and averaging it over the width of the channel leads to the following parametrical form of the average velocity.

$$\overline{v} = \frac{g \cdot L^2}{12\nu} \tag{4.3}$$

Where:

 $\overline{v}=\mbox{average}$ velocity of flow

g = gravitational acceleration

L = width of the channel restricting the flow

 $\nu =$ kinematic viscosity of the electrolyte

The average velocity within the channel being defined, another alteration to the general form of the Reynolds number has to be made. Since the channel profile is rectangular, the hydraulic diameter of the channel must be employed:

$$D_h = \frac{4A}{P} = \frac{2 \cdot L \cdot W}{(L+W)} \tag{4.4}$$

Where:

 D_h = hydraulic diameter A = cross-section area of the duct P = wetted perimeter of the duct L = width of the channel W = spanwise length of the channel

Finally, the Reynolds number adjusted for the specific case of the gravity-fed membraneless electrolyser can be described with equation 4.5, using 4.3 and 4.4:

$$Re = \frac{|\overline{\nu}| \cdot D_h}{\nu} = \frac{1}{6} \cdot \frac{g \cdot L^3 \cdot W}{\nu^2 \cdot (L+W)}$$
(4.5)

Since the width of the channel is more than an order of magnitude smaller than the spanwise dimension, the following simplification can be made:

$$\frac{W}{(L+W)} \approx 1 \tag{4.6}$$

Thus, the relationship between Reynolds number, kinematic viscosity, and channel width is clearly visible.

$$Re \sim \frac{1}{\nu^2} \tag{4.7}$$

$$Re \sim L^3$$
 (4.8)

4.2. Hydrodynamic Entrance Length

Another important factor that influences the flow regime in the inlet section of the channel is the Hydrodynamic Entrance Length. At a sufficiently far distance from the leading edge of the channel, the boundary layer forming on the wall reaches the centerline. The distance from the entrance of a flow channel to the point where the flow becomes fully developed is known as the entrance length. Shah and London define L_{hy} as the point where the developing centerline velocity equals 99 % of the fully developed magnitude [42]. The shape of the fully developed velocity profile depends on whether the flow is laminar or turbulent [10]. Furthermore, the shape of the duct and its aspect ratio are also decisive parameters when characterising the entrance length. McComas et al. [29] have conducted a thorough examination of this matter including different duct dimensions and geometries. In the case at hand, a rectangular duct is the fitting profile of the channel, thus the following table is of relevance:

| | | U_m | | |
|---------------|--------|----------------|--------|--------------------------------|
| $\beta = b/a$ | C | \overline{U} | K | $\overline{D \cdot \text{Re}}$ |
| 0 | 96.000 | 1.5000 | 0.6857 | 0.00588 |
| 0.05 | 89.908 | 1.5488 | 0.7613 | 0.00709 |
| 0.10 | 84.675 | 1.6009 | 0.8392 | 0.00855 |
| 0.125 | 82.339 | 1.6283 | 0.8788 | 0.00938 |
| 0.1667 | 78.809 | 1.6758 | 0.9451 | 0.0110 |
| 0.25 | 72.931 | 1.7737 | 1.0759 | 0.0147 |
| 0.40 | 65.472 | 1.9236 | 1.2815 | 0.0217 |
| 0.50 | 62.192 | 1.9918 | 1.3829 | 0.0255 |
| 0.75 | 57.886 | 2.0774 | 1.5203 | 0.0310 |
| 1.00 | 56.908 | 2.0962 | 1.5515 | 0.0328 |

Figure 4.1: Dimensionless entrance lengths of rectangular ducts [29].

Where:

 $\beta =$ aspect ratio of the rectangular duct $X_e =$ dimensionless hydraulic entrance length

$$D = hydraulic diameter$$

Re = Reynolds number

In this specific case, a channel width of $L=1\,\rm{mm}$ and a spanwise length of $C=20\,\rm{mm}$ are assumed to define the necessary parameters:

$$D_h = \frac{4A}{P} = \frac{2 \cdot LW}{L+W} = 1.9 \cdot 10^{-3} \,[\text{m}]$$
 (4.9)

$$\beta = \frac{b}{a} = \frac{L}{W} = \frac{1}{20} = 0.05 \tag{4.10}$$

$$Re = \frac{|\overline{v}|D_h}{\nu} = \frac{1}{6} \cdot \frac{gL^3W}{\nu^2(L+W)} = 1177$$
(4.11)

Where the kinematic viscosity $\nu = \frac{\mu}{\rho}$ of KOH has been calculated using the experimental data of Zaytsev et al. [57][25].



Figure 4.2: Thermophysical properties of KOH [25].

With these variables defined and the values from table 4.1, the hydrodynamic entrance length can be expressed as follows:

$$X_e = 0.00709 \cdot D_h \cdot Re = 0.00709 \cdot 1.9 \cdot 10^{-3} \cdot 1177.42 = 0.01586 \,[\text{m}] = 15.86 \,[\text{mm}]$$
(4.12)

To ensure a fully developed flow, a developing region of approximately 16 mm is allocated in the upstream section of the flow channel prior to the electrode installation location.

4.3. Cell Design

The cell was designed and engineered with the goal of allowing rapid exchange of electrodes between experiments and minimising the risk of leakage during operation. In addition, keeping the two electrodes 1 mm or 0.7 mm apart(depending on the chosen spacer) on a surface of 25 cm^2 is an ambitious task. Incorporating them into the core of the cell and avoiding any possible shunt at the inlet and outlet interface of the electrode and the framework is a further strenuous task. Reaching this challenging goal has meant continuous enhancement of the design until it reaches its final format. The following section will dive into the architecture of the cell and detail the components which compile the cell. The outlook will first focus on the modules that surround the channel and progressively outline the other parts until the outermost gas phase container. The cell is symmetrical except for the compressing nuts, bolts, excess flow duct perforation, and the gas-phase containers' outlet connection geometry. Further detailed descriptions of the cell components can be found in the Appendix (A.2).



Figure 4.3: Exploded view of the cell with part denotation.

Figure 4.3 shows the exploded view of the cell with ePTFE electrodes, which makes it easy to recognise each component and their purpose within the unit. At the core lies the channel-defining T-shaped PMMA layer (1), which gives the channel its width and can be conveniently interchanged between measurements. The sides of this layer and all the following parts are perforated to allow the structural bolts to cross and the current-feeding ones to reach the electrodes. The electrodes (2) are fitted in plane with the T-shaped gaskets (3), which, after compression, reach about the same thickness. Through this design, the necessity for the electrodes to have a segment reaching outward of the cell for the current feeding clamps to be connected is excluded. Because these interfaces, where the electrode strips are compressed between two gaskets, are usually the most vulnerable to leaks. The next parts in line are the T-shaped phase-dividing structural components (4). The upper cutout section is the reservoir profile (A), the middle rectangular cutout is the exit pathway for the gas phases (B), and the lower circular cutout (C) is the exit of the electrolyte after it travels through the channel. To this module are the upper and lower parts of the electrode glued to with hardened resin. In the case of Zirfon configurations, the Zirfon layer, which is in direct contact with the flow, has to overlap the mesh when glueing it to the PMMA to avoid leaking through the frontal area (perpendicular to the flowing fluid) of the mesh. Subsequently, another identical element is annexed with an additional T-shaped gasket (5), which features bridges between each cutout region to ensure that leaks do not propagate through the reservoir, gas phase, or outlet conduit cutout. Next, the enclosure (6), separated by another gasket, integrates the electrolyte outlet (D) and is the boundary wall of the reservoir, of which one is perforated to lodge the excess flow duct's inlet (E). It also features 16 tapped holes, into which the current feeding bolts are screwed in, wrapped in Teflon to ensure leak tightness. Finally, we have the gas phase container (8), which collects the gaseous product before being sent for analysis to the GC. This outermost part was manufactured with Formlab's Form 3+ 3D printer, making it easier to produce the nonmetric threaded outlet (F) that accommodates the gas chromatograph's inlet line. To compress the layers, ensuring that the gaskets offer leak tightness, the bolts (10) and nuts (11) are fastened with a torque wrench to monitor the pressure applied and prevent cracking of the PMMA layers.

Enabling contact between the current feeding bolts and the electrodes requires a precise and meticulous assembly. In the case of an ePTFE or GDE configuration, it has to make contact with the inside of the electrode, where the current collector distributing the current towards the electrode mesh is located. Due to this reason, the electrodes have to be cut in a staggered manner, allowing the bolts to pass to the opposite electrode. A miscut of the electrode by a fraction of a millimetre can cause it to contact the crossing bolt and cause a short circuit, leaving the cell inoperable. When experiments are performed with Zirfon electrodes, the bolt makes contact with the back of the electrode assembly; thus, the channel-defining PMMA layer is not perforated and must support the electrode to avoid bulging in and establish a more effective contact quality. The perforated and non-perforated versions have variants with and without spacer (see figure 4.5). Figure 4.4(a) shows the trajectory of the bolt to reach the back panel of the electrodes. The bolts have been chosen shorter on purpose to have a better understanding and overview of the assembly, except for the lowest M4 bolt which demonstrates the contact between its tip and the electrode.



(a) Cell in imploded view, detailing the current feeding bolt and the electrodes contact.

(b) Staggered electrode.





(a) Flow defining layer without perforations and spacer



(b) Flow defining layer perforated with spacer

Figure 4.5: Flow Defining PMMA Layers

Methodology

This chapter delves into the methodology, details the components employed in assembling the BoP of the Gravity-Fed Laminar Electrolyser, and the procedures used to retrieve the data from the conducted experiments. Furthermore, it shows the experimental groundwork necessary to answer the main research question described in the Introduction 2.4.

5.1. Experimental Setup

The experimental setup consists of three distinct control circuits: electrolyte flow, current, and gas analysis circuit. Their smooth coordination is necessary to keep the transient time to a minimum when shifting between measurement points and to retrieve accurate data from the measurements. Figure 5.1 displays the block flow diagram of the Gravity Fed Laminar Electrolyser and its components. Furthermore, a table containing all the details of the components comprising the BoP can also be found in Appendix A.1.



Figure 5.1: Block flow diagram of the experimental setup.

Electrolyte Flow Control

The electrolyte has been gradually heated to a temperature with a magnetic hot plate stirrer connected to a thermocouple to keep track of the temperature in the bulk of the fluid throughout the process. Once the desired value is reached, with the aid of the peristaltic pump, it is then supplied to the top reservoir, from where it is fed contrived by gravity into the cavity of the channel. An excess flow duct has been fitted to the reservoir to keep the electrolyte level constant and independent of the pump's RPM, and the surplus is dispensed back to the beaker located on the magnetic stirrer hot plate. The electrolyte used is an aqueous KOH solution of 30 w%, prepared from KOH pellets of 85% purity manufactured by Sigma-Aldrich mixed with demineralised water; the remaining 15% of the pellets consist of water and various impurities. These considerations were carefully taken into account during the preparation of the solution. Furthermore, a magnetic inductive flow metre was fitted after the outlet to validate the analytically derived volumetric flow rate for different channel widths, temperatures, and experiments run with a spacer.



Figure 5.2: The experimental setup with denotation.

Current Control

Upon reaching the upper reservoir, the electrolyte flows laminarly through the electrolyser powered by the OWON SPE6103 power supply which is connected to the PC. The computer serves to perform voltammetry sweeps using a Python script to observe the performance of the various electrode configurations. The sweeps were conducted between 1 and 4 Volts (except for the low-performing electrode configurations, which have a steep curve) with 100 intervals separated by 1-second time steps. Oftentimes, due to the high fraction of bubbles within the channel, especially for ePTFE configurations, high volatility can be observed in the curves with sudden spikes and plunges deviating from the curve's trendline. A shorter time-step interval was taken for the affected electrodes, allowing for fewer disruptions in the continuity of the graphs and better readability of the measured values. When measuring anodic hydrogen concentration, four setpoints of current density were selected: 0.13 A/cm^2 , 0.09 A/cm^2 , 0.06 A/cm^2 and 0.03 A/cm^2 . These are translated into current values by accounting for the electrode surface to 3.25 A, 2.25 A, 1.5 A and 0.75 A, respectively. Minor deviations from the set currents were observed, especially when testing ePTFE configurations at high current densities. The most excessive percentage deviations were: 1.3%, 2%, 2.22%, and 2.4% respectively. These minor fluctuations are temporal and fade out after a brief period of time. Hence, they have a negligible effect on the produced gas quantity, and the accuracy of the gas purity measurements.

Gas Analysis

Once the reactions occur and gaseous products diffuse through the gas phase compartment, their composition can be analysed using a gas chromatograph. The gas phase diffusing through the cathode is by means of a T junction directed either to the gas chromatograph for crossover concentration analysis or to the ambient air. This is because the gas phase container must first be completely flushed from the gas produced by the previous current density setpoint. For each current density, a flush time is calculated; these can be found in Appendix A.0.4. To investigate HTO levels at various current densities, the capabilities of the Varian CP-4900 Micro-GC were exploited. The compound examination time of the Sabatier column was chosen to $50 \, s$, for quick sequential measurements but also for the oxygen and hydrogen retention time to remain within the measurement time limit. Each peak in the chromatogram corresponds to a different compound in the sample, with the retention time indicating the time elapsed for a compound to reach the detector at the other end of the column. The area under each peak is proportional to the concentration of the compound in the sample. An important observation is that oxygen and nitrogen possess nearly identical retention times, resulting in a single peak on the chromatogram. Any other compound, such as carbon dioxide and other elements that have a retention time above this threshold, is irrelevant to the calculation of HTO; thus, their exclusion does not affect the results. The results sheet for each measurement is compiled and displayed in the form of a chromatogram; an example is presented in the Appendix (A.1).

5.2. Electrode Configurations

This section describes the material composition of the electrodes tested, detailing the dimensions and specifications of the various configurations. The table below summarises the configurations that are focused on in the Results section (6), this is a narrow but necessary selection of all configurations to highlight the key improvements made throughout the process. The sum of all combinations of electrode configurations that can be tested is 15. These are possible by coupling the 5 electrode materials: Nickel felt 1, Nickel felt 2, Nickel mesh, Nickel mesh (open) and Stainless Steel with Zirfon 500, Zirfon 220 or ePTFE. Furthermore, the addition of possibly hot pressing two layers also adds another layer of possible combinations. A GDE was also acquired for testing, featuring a nickel catalyst on a gaspermeable, non-conductive PTFE film with a nickel mesh current collector. During the long process of manufacturing, hot pressing and testing the electrodes with different materials, several proved to be unviable due to leaking (typically due to hot pressing Zirfon) or showed subpar performance and were deemed not worthy of further exploration. Therefore, during the pursuit of improved performance, certain configurations were rejected to narrow down the potential candidates for increased efficiency and to save time in testing the assemblies that are worth further investigation.

| | Zirfon 500 | Zirfon 220 | ePTFE |
|--------------------|------------|------------|-------|
| Nickel felt 1 | Х | | |
| Nickel felt 2 | X HP | | Х |
| Nickel mesh | HP | Х | Х |
| Nickel mesh (open) | | Х | X HP |
| Stainless Steel | | Х | X HP |

 Table 5.1: Selection of electrode configurations, X: superposed HP: Hot Pressed

| | OEM/Supplier | Thickness [mm] | Open Area Ratio [%] / Porosity [%] | Fibre Diameter [µm] / Hole Size [mm] |
|-----------------------|----------------------|----------------|---------------------------------------|---|
| Nickel felt 1 | Hebei Aegis Co., Ltd | 0.4 | 60 | 40 |
| Nickel felt 2 | Hebei Aegis Co., Ltd | 0.4 | 82.5 | 30 |
| Nickel mesh | Hebei Aegis Co., Ltd | 0.2032 | 75 | 0.2032 |
| Nickel mesh (open) | Hebei Aegis Co., Ltd | 0.0508 | 90 | 1.3208 |
| Stainless Steel | BOPP Co. AG | 0.16 | 40 | 0.09 |
| GDE | Gaskatel | 0.4 | - | - |

Table 5.2: Specifications of the electrode materials

5.3. Assembly/Reproducibility

The assembly of the cell is a delicate and tedious process that requires high precision. When the electrodes are glued or the gaskets are cut, a slight misalignment can cause the two in-plane layers to press against each other, causing tension. As a result, the bulging in of the electrode within the channel is common, which is only discernable once the cell is assembled and the compressing bolts have been tightened. Tightening them too much leads to the lateral expansion of the gasket, again leading to the identical outcome as mentioned above. Furthermore, it also results in the warping of the components, and over several cyclic strain periods, the components tend to protrude along the vertical axis, losing the pressurised contact between the PMMA layers and gaskets, and bringing about the flooding of the gas phase compartment. Of course, tightening the bolts loosely has the same consequence, the sweet spot has to be met. Thus, the use of a torque wrench is indispensable to consistently reproduce a similar pressure distribution along the planes of the cell's components. In addition, regular exchange of components to avoid material fatigue is also worth considering.

Moreover, leak testing Zirfon configurations with narrow channel widths is not feasible, due to the suction effects of the pores; the two layers stick together and cannot be separated by the flow. The introduction of material into the cavity of the channel with the intention of separating the electrode leads to the tearing of the Zirfon surface, creating an opening for the electrolyte to flow through with lowered flow resistance.

The use of current collectors is advantageous not only in terms of current distribution but also in terms of protection of the electrodes, enabling them to be reused in subsequent measurements. Their possible damage comes from the pressure applied by the current-feeding bolts since they have to contact the electrode without applying too much pressure. In addition, their rotation while they are screwed in can cause surface damage due to abrasive wear, which again can be mitigated with the implementation of current collectors.

6

Results and Discussion

This part consists of three distinct subsections. First, advances in electrode materials and layouts that affect performance enhancement are discussed. The relationship between crossover concentration and current densities is then explored in different electrode setups and operating conditions. Lastly, it compares the measured and analytical volumetric flow rates for different channel widths, both with and without vertical spacers.

6.1. Performance

Zirfon Configurations

As presented in the Methodology chapter (5), one of the promising electrode configurations features zirfon layers adjacent to the electrolyte flow, while the electrode mesh layer is located on the gas side. The performance of this electrode family is shown in Figure 6.1. The steps taken to increase the cell's performance have been divided into separate paragraphs, and their incremental improvement is mirrored in the flattening of the J-V curves below.



Figure 6.1: Performance of Zirfon electrode configurations; Nickel mesh: 75% open area ratio, Nickel (open) mesh: 90 % open area ratio, further material specifications in table 5.2; current collectors reduce the contact resistance between current feeding bolts and the electrode; a: anode, c: cathode.

Nickel Felt: Initial Configuration and Performance Optimisation

The initial configuration used a nickel felt layer combined with a Zirfon 500, which produced suboptimal performance characterised by high resistances across all polarisation regions. This high resistance is likely due to gas accumulation at the interface, which hinders ion transport and introduces additional inefficiencies. The original nickel felt had moderate porosity (60%), which limited the escape of the hydrogen and oxygen gases produced, contributing to increased resistance and reduced efficiency. A subsequent test used a nickel felt with a higher porosity (82.5%), leading to a moderate improvement in performance due to enhanced gas release. To further improve interfacial contact and reduce resistance, hot pressing of the layers was considered to optimise surface interaction between the nickel and Zirfon materials.

Hot Pressing: Manufacturing Under High Temperature and Pressure

Hot pressing is an advanced technique that applies controlled temperature and pressure to create an improved interface between two surfaces. For nickel felt and zirfon layers, the optimal temperature and pressure are critical to avoid structural degradation, as excessive heat or pressure can weaken the integrity of the material, alter porosity, and reduce mechanical strength. With optimal control, hot pressing softens the Zirfon, allowing it to adapt to the nickel surface, creating a tighter interface that facilitates smoother gas and ionic transport. The result is a more stable polarisation curve, as seen in Figure 6.1. This enhancement in gas diffusion and contact quality improves reaction efficiency, particularly in high current density regions. Additional gains could be achieved by optimising the transport pathways for gaseous products, leading to the selection of improved electrode materials that support better gas escape.

Nickel Mesh: Improved Gas Transport and Structural Considerations

The use of a nickel mesh offers distinct advantages for gas transport, although it also introduces the challenge of maintaining structural separation of the electrolyte and gas phases. In contrast to felt, the more open mesh design allows hydrogen and oxygen to escape freely, reducing the risk of gas entrapment. However, the elimination of felt as a barrier places an increased reliance on the Zirfon layer to prevent electrolyte leakage into the gas phase compartment. By achieving optimal contact quality and controlling the Darcy flow through the zirfon layer, it is possible to maintain phase separation effectively if an excessive pressure difference across the zirfon is kept at bay. Although this setup improves current density across the spectrum, significant ohmic resistances at higher polarisation still indicate room for further enhancements. This led to the substitution of Zirfon 500 with the more porous Zirfon 220 to reduce overall resistance and improve performance.

Zirfon 220: Increased Porosity and Gas Diffusion

Replacement of Zirfon 500 with Zirfon 220, a thinner and more porous separator, substantially reduced the ohmic resistance, lowering the slope of the J-V curve in the ohmic region. However, this adjustment also increased the trigger voltage, potentially due to gas accumulation or pore-clogging at the interface with the nickel mesh. The higher porosity of Zirfon 220 facilitates greater electrolyte permeability, allowing for more efficient diffusion. However, the increased pore count and shorter pore pathways can allow gas bubbles to become trapped, obstructing electrolyte flow and reducing the reactant transport efficiency. An interesting observation was that over time, performance gradually improved, probably because of the progressive saturation of the Zirfon layer by the electrolyte seeping in, which enhanced the hydroxide ion delivery to the reaction sites. Despite attempts to improve results by hot pressing Zirfon 220, it was found that this process increased the separator's permeability too much, resulting in flooding of the gas compartment, which compromised the setup's safety and functionality.



Figure 6.2: Increasing performance of Zirfon configuration with subsequent measurements, a: anode, c: cathode.

Interelectrode Gap Reduction: Enhanced Ion Transport Efficiency

Narrowing the interelectrode gap from 1 mm to 0.7 mm mainly affected the ohmic region of the J-V curve, as activation overpotentials remained unaffected. By decreasing the gap, the reaction sites on the anode and cathode were brought closer together, reducing the migration distance for hydroxide ions through the electrolyte. According to Fick's law, this narrower channel also creates a steeper concentration gradient, which proportionally increases ion diffusion flux, further improving current density and improving performance in the ohmic region.

Open Nickel Mesh: Optimising Bubble Detachment and Gas Escape

Switching to an open nickel mesh with a larger open area (from 75% to 90%) allowed improved gas escape from the electrode surface. This modification facilitated the detachment of gas bubbles, preserving the active surface area and preventing performance losses at high current densities. The increased openness also dispersed gas bubbles more effectively, reducing the likelihood of bubble coalescence and clogging, which can impede efficient gas release. This improvement is particularly noticeable at lower current densities, where reactants are better able to access reaction sites because of the reduction in obstructive gas bubbles.

Current Collectors: Enhanced Electrical Contact with Platinised Titanium Felt

To improve current distribution and reduce contact resistance, an intermediate layer of platinised titanium fibre felt was introduced between the current feed bolts and the nickel mesh. This addition improved contact quality and expanded the effective contact area between the metals, significantly lowering contact resistance. The uniform distribution of current along the mesh minimised localised resistance, thus enhancing the overall electrical performance of the cell.

Temperature Increase: Improved Reaction Kinetics and Reduced Resistance

Preheating the electrolyte was implemented as a final measure to enhance cell performance. The elevation of temperature positively affects the reaction kinetics by increasing the reaction rate and lowering the activation energy requirements. In the ohmic region, the reduced slope of the J-V curve with increased temperature can be attributed to improved electrolyte conductivity, as well as a decrease in Zirfon's ionic resistance [45]. Furthermore, elevated temperature is beneficial in terms of catalytic activity, contributing to enhanced reaction efficiency and lower overall cell resistance across all polarisation regions.

ePTFE Configurations

Similarly, as for the Zirfon configuration, ePTFE MEAs went through an iterative process to achieve the best possible performance. The experiments were run in parallel, and the choices made followed a similar reasoning; thus, the first choice for the electrode was the same as for the Zirfon configuration: Nickel felt.



Figure 6.3: Performance of ePTFE Electrode Configurations, Nickel mesh: 75% open area ratio, Nickel (open) mesh: 90 % open area ratio, further material specifications in table 5.2; current collectors reduce contact resistance between current feeding bolts and electrode; a: anode, c: cathode.

Nickel Felt: Limitations in Gas Diffusion and Performance

The nickel felt electrode showed limited improvement potential, as evidenced by the steep slope in the J-V curve, which reflects high resistance and restricted gas diffusion. The primary issue arises from the thick and porous structure of the felt, which slows gas escape, leading to bubble accumulation and coalescence within the channel. This buildup of gas bubbles reduces the surface area available for reactions, increasing the ohmic resistance, and reducing overall performance. Although slight improvements were observed with continuous electrolyte flow, which eventually wetted more of the porous volume of the felt, the performance gains remained marginal. The high gas fraction in the channel and limited diffusion prompted the shift to a different electrode material to minimise overpotentials and improve efficiency.

Open Nickel Mesh: Enhanced Performance

The replacement of nickel felt with nickel mesh yielded a substantial performance improvement. The overpotentials were significantly reduced, allowing current densities to reach $0.4 \,\mathrm{A/cm^2}$ below $4 \,\mathrm{V}$, still a far cry from industrial standards, but a promising advance. The open structure of the nickel mesh provides a larger effective surface area and facilitates access of the electrolyte to the reaction sites, resulting in a greater number of nucleation sites and a more efficient gas evolution. Compared to nickel felt, the mesh design minimises gas bubble accumulation by promoting faster detachment and flow of bubbles away from the reaction surface and ideally through the pores of the ePTFE layer. However, at higher current densities, the J-V curve displayed increased volatility as a result of rising gas fractions within the channel, causing detectable noise. However, this improvement underscores the advantage of the mesh in enhancing mass transport and reducing clogging.

Interelectrode Gap: Optimisation Challenges in Channel Width Reduction

Initially, reducing the interelectrode gap from 1 mm to 0.7 mm showed an increase in efficiency, especially at higher current densities. The closer proximity of reaction sites reduced the ion migration distance, thereby enhancing the performance. However, further reduction to a 0.5 mm gap led to unintended resistance increases, particularly in ePTFE-nickel mesh configurations. This effect likely results from intensified bubble nucleation on the mesh surface within the narrower channel, leading to excessive gas buildup that compromises efficiency. Although reducing the channel width can improve performance until a certain limit, excessive narrowing appears counterproductive in ePTFE setups because of the excessive gas fraction within the channel, highlighting the need for optimised channel dimensions to balance ion transport with gas management.

Temperature Increase and Open Nickel Mesh: Improved Mass Transport and Reaction Kinetics

Experimental results demonstrated that increased operating temperatures significantly improved performance by flattening the J-V curve and reducing fluctuations caused by bubble dynamics. Higher temperatures reduce the viscosity of the electrolyte, thereby increasing ionic mobility and improving ion exchange throughout the cell [25]. Furthermore, increased solubility of gases at higher temperatures leads to a higher concentration of dissolved species, further reducing the volume of the bubble but at the cost of increased crossover rate [38]. The increase in thermal energy also improves reaction kinetics, resulting in a significant reduction in the trigger voltage for the Zirfon configuration, a change oddly not observed in their ePTFE counterparts. Elevated temperatures also promote smaller bubble formation [31], allowing consistent gas release, which decreases surface coverage and stabilises system performance. However, recent investigation questions the general belief that decreasing departure diameters enhances electrolysis efficiency [54]. The upgrade to an open nickel mesh also had a beneficial effect, contributing to a smoother evacuation of the bubbles through the larger open area of the mesh matrix. To enhance gas access and diffusion through the ePTFE, hot pressing was explored as an option.

Hot Pressing with ePTFE: Enhancing Gas Diffusion and Reducing Resistance

Attempts to improve performance by hot pressing Zirfon 220 were largely unsuccessful; however, the same process with ePTFE provided more promising results. The ability of ePTFE to maintain liquid impermeability while supporting mesh integration yielded a slight performance improvement, as shown in Figure 6.3. The increased contact area between the ePTFE and nickel mesh created a more effective pathway for gas diffusion toward the gas-phase containers, reducing bubble retention within the channel. At high current densities, the improved gas withdrawal capability decreased the bubble accumulation, which, in turn, lowered the ohmic resistance and stabilised the J-V curve. This configuration demonstrated reduced fluctuations, highlighting ePTFE's potential as a robust material for efficient gas transport when hot pressed. Looking for further improvement in bubble management, which is so crucial when electrode meshes are submerged within the channel, a new material was chosen to enhance catalytic performance and bubble detachment from the anode, which is usually more susceptible to high surface coverage [24].

Stainless Steel Mesh: Bubble Management and Catalytic Performance

The use of stainless steel mesh was evaluated as a possible means to reduce bubble size and detachment rate, particularly at high current densities. Although the smoother surface of stainless steel relative to that of nickel should contribute to a reduction in bubble coalescence, helping to lower the gas fraction within the channel. Its denser mesh can have the negative effect of blocking the gas bubbles from diffusing through the ePTFE layer and are rather retained in the channel. Hot pressing proved to be a possible solution by enhancing contact quality between the mesh and the ePTFE while also boosting the cell's performance. This gain in efficiency may be attributed to other factors, as several studies show the promising catalytic activity of stainless steel, especially when pretreated [58][21]. Therefore, superior performance can likely be credited to its ability for efficient oxygen evolution, rather than its gas release. This hypothesis is further confirmed by the higher crossover rate observed compared to that of nickel mesh (6.8).

Gas Diffusion Electrode - Nickel Mesh - Zirfon 220

For the GDE, an impressively low activation overpotential was achieved, resulting in a relatively low onset voltage of approximately 1.4 V. However, its initial great performance at low current densities gradually decreases compared to its ePTFE and Zirfon counterparts. Above 0.15 A/cm^2 , the efficiency drop became more pronounced, making it the least effective of the three assemblies. Figure 6.4 compares the best-performing versions of each electrode configuration, incorporating all iterative enhancements made throughout the project.

Voltammetry sweeps revealed that the GDE exhibited better performance as a cathode than as an anode, likely because the OER typically produces larger and more numerous bubbles compared to the HER. As a result, the combination of Zirfon 220 and nickel mesh as the anode was more effective in limiting bubble formation within the channel, thus enhancing overall performance.



Figure 6.4: Best performance of each electrode configuration

6.2. Crossover Concentration

This section evaluates the impact of current density on hydrogen crossover concentration (HTO) between different electrode configurations, an essential metric to comply with safety standards in the hydrogen industry. Although the safety threshold for hydrogen crossover is set at 2% HTO, some configurations exceeded this limit. However, controlled experimentation, aided by low flow rates at the cell gas outlets and the fume hood's effective suction, allowed tests to proceed safely. The tests were carried out with nickel mesh as both electrodes or with nickel mesh as the cathode and stainless steel as the anode for both the Zirfon and ePTFE configurations. Finally, the GDE - Zirfon 220 - Nickel Mesh configuration was also subjected to evaluation, which had the best performance at low current densities.

All HTO tests were performed at 80° C with channel widths of 1 mm and 0.7 mm, focussing on lowpolarisation regions at current densities of 0.03 A/cm^2 , 0.06 A/cm^2 , 0.09 A/cm^2 , and (except for the Nickel Mesh - Stainless Steel - Zirfon 220 configuration) 0.13 A/cm^2 . The box plots, derived from a sample of five HTO measurements for each current density, were taken once the values stabilised and converged after the current adjustment. The colour gradient represents values from 0 to the industrial safety threshold of 2%, with any exceeding values marked in black.

Zirfon Configurations

The nickel mesh-Zirfon 220 configuration exhibited consistent performance within safety limits across both 1 mm and 0.7 mm channel widths. HTO levels remained stable, with median values below 0.03 % and 0.035 % for the respective channel widths at current densities of 0.13 A/cm^2 and 0.09 A/cm^2 . A critical threshold was observed near 0.09 A/cm^2 , consistent with the findings of Lira Garcia Barros et al. [27] for ZGEs. A surge is visible below this value where HTO levels peaked, reaching 0.05 % and 0.065 % at 0.06 A/cm^2 for the 1 mm and 0.7 mm channels, respectively. Below this peak, HTO levels slightly decreased diverging from those obtained in measurements with conventional zero-gap electrolysers, which makes this setup promising for maintaining low crossover concentrations across a range of current densities.



Figure 6.5: HTO values of nickel mesh(anode, cathode) - Zirfon configurations at various current densities

The replacement of the nickel-mesh anode with a stainless steel mesh in the previous setup significantly decreased crossover. HTO levels followed a trend similar to the nickel mesh-only setup and peaked at 0.06 A/cm^2 before declining to levels comparable to those at the highest current densities tested. However, in the 0.7 mm channel, the HTO values did not fully recover to the baseline level of the first measurement point. This suggests that the 1 mm channel possibly benefits from a more effective electrolyte flushing effect, which is detailed in the analytical model chapter (6.3), leading to lower crossover concentrations at 0.03 A/cm^2 .



Figure 6.6: HTO values of nickel mesh(cathode) - Zirfon 220 - stainless steel(anode) configurations at various current densities.

ePTFE Configurations

In the ePTFE-nickel mesh configuration, HTO levels increased significantly with current density, ranging from 0.27 % at lower current densities to close to 2 % at 0.06 A/cm². The trend was more pronounced in the thinner, 0.7 mm channel, where HTO levels reached a median value of 3 %, exceeding 2 % and would require shutdown for compliance with industrial safety measures. This behaviour is attributed to the structural configuration of ePTFE assemblies, where the electrode is placed within the flow channel, leading to increased hydrogen supersaturation and more numerous nucleation sites, causing abundant bubble production. Although the crossover curve peaked between 0.09 and 0.13 A/cm², further increases in current density led to reduced HTO levels, hypothetically due to the large gas coverage and bubble production on the anode surface, hindering contamination.



Figure 6.7: HTO values of nickel mesh(anode,cathode) - ePTFE configurations at various current densities

Substituting the anode in the ePTFE-Nickel Mesh configuration with stainless steel resulted in even higher crossover levels, with HTO values for the 1 mm channel width ranging from 1.54 % at 0.03 A/cm² to an excessive 5.28 % at higher current densities. This trend was amplified in the 0.7 mm channel, where HTO levels reached 8.5 %, far exceeding safety limits. As already mentioned, the smoother surface of stainless steel contributes to swift bubble detachment with a decreased diameter, reducing their ohmic resistance in the channel. In addition, this facilitates their diffusion through the ePTFE layer and their mobility in the electrolyte. These results indicate that ePTFE configurations are unsuitable for applications such as the gravity-fed electrolyser concept, particularly when paired with similarly thin channel geometries.



Figure 6.8: HTO values of nickel mesh(cathode) - ePTFE - stainless steel(anode) configurations at various current densities

GDE Configuration

Finally, the configuration with NiH33 GDE as a cathode and a combination of Zirfon 220 and nickel mesh as an anode was also evaluated using the GC (6.9). The anodic hydrogen concentration is safely within limits across the measured range. Displaying a gradual rise in HTO levels with increasing current density, starting at 0.22 % and plateauing at 0.09 A/cm^2 with 0.51 %. In this configuration, anodic crossover occurs as a result of the hydrogen diffusing from the surface or back through the GDE pores into the bulk electrolyte. The plateau observed beyond 0.09 A/cm^2 may be the result of the accumulation of oxygen bubbles at the separator mesh interface, which promotes the clogging of the zirfon pores, hindering the path of dissolved hydrogen to the anode.



Figure 6.9: HTO values of GDE(cathode) - Zirfon 220 - nickel mesh(anode) configuration at various current densities with a channel width of 1 mm.

Experiments on crossover concentration have provided insight into the safety and purity of various configurations. EPTFE setups exceeded the safety threshold for anodic hydrogen concentration even at minimal current densities. In contrast, Zirfon assemblies showed HTO values well below the limit, selecting it as a candidate for integrating its data into the analytical model in the following chapter.

6.3. Analytical Model

This section details the formulated analytical model, employing HTO measurements and literature to estimate mass fluxes and interface concentrations using a system of equations. Furthermore, it gives insight into the train of thought and assumptions made to estimate the crossover flux through the electrolyte and the mass transport phenomena that govern the process.

Mass flux and Crossover Model

The subsequent section will detail the equation linking mass transfer flux and concentration values, together with the values acquired from measurements and the parameter approximations obtained from the literature that are required for evaluation. The analysis of the equations will be done only for hydrogen since the system is symmetrical, and as a result the equations for hydrogen mass transfer also hold for their oxygen counterpart, of course, defined with different constants regarding the specific gas in question. The MEA chosen for the analysis is Zirfon 220 combined with nickel mesh as both anode and cathode. A schematic representation of the fluxes and concentrations is presented below(6.10). Hydrogen generated at the cathode (N_{fH2}) can be transported to the gas phase container as a gas (N_{GH2}) or remain dissolved, diffusing through Zirfon pores to the electrolyte stream (N_{ZH2}) . At this junction, hydrogen has two potential passages: convection to the electrolyte bulk or diffusion through the channel's stagnant flow zone, illustrated in the top cross-sectional channel view. Convection to the bulk, results in the flushing of the hydrogen by the electrolyte flow. However, diffusive transport along the inert walls of the cell can reach the anodic Zirfon layer, where further diffusion can be facilitated through its pores reaching the anodic side of the cell. The model seeks to quantitatively evaluate the mechanisms to estimate gas evolution efficiency and the diffusive hydrogen fraction traversing the channel.



Figure 6.10: Schematic representation of the model: side cross-sectional view and top cross-sectional view.

Gas Convection

To model mass transfer between the electrode surface and the bulk of the container, it is assumed that the gas composition in the bulk is the same as the sample aspired from the bulk to the injector of the GC. The input data provided to the model are the measured crossover concentrations (HTO and OTH) at their respective current density (j). By means of these and the faradaic equation, the mass balance at the electrode surfaces, and the hydrogen and oxygen concentrations in the bulk of the gas container were determined.

$$N_{fH2} = N_{H2G} + N_{H2Z} (6.1)$$

 N_{fH2} = produced hydrogen flux at the electrode N_{H2G} = gas mass flux towards the gas container N_{H2Z} = hydrogen mass flux at the Zirfon interface

The temperature and pressure of the gas sample were collected from the GC's software, a snippet of the interface can be seen in Appendix A.2. Assuming the sample aspirated by the gas chromatograph to be an ideal gas, the following equations were written:

$$n_T = \frac{V_S \cdot P}{R \cdot T} \tag{6.2}$$

$$C_{H2GB} = X_c \cdot n_T \cdot \frac{1}{V_S} \tag{6.3}$$

$$C_{H2CB} = X_a \cdot n_T \cdot \frac{1}{V_S} \tag{6.4}$$

Where:

$$\begin{split} X_c &= \text{cathodic molar ratio of hydrogen} \\ X_a &= \text{anodic molar ratio of hydrogen} \\ V_S &= \text{sample volume} \\ R &= \text{ideal gas constant} \\ n_T &= \text{moles of gas in the volume} \\ P &= \text{pressure in the GC column} \\ C_{H2GB} &= \text{hydrogen concentration in the cathodic gas bulk} \\ C_{H2CB} &= \text{hydrogen concentration in the anodic gas bulk} \end{split}$$

Upon estimating the hydrogen and oxygen concentrations in the gas container bulk via experimental data, the gaseous mass flux is evaluated.

$$N_{H2G} = k_{GHH} \cdot (C_{H2EW} - C_{H2GB})$$
(6.5)

Where:

 $k_{GHH} =$ gas mass transfer coefficient of hydrogen in hydrogen $C_{H2EW} =$ hydrogen concentration at the electrode surface $C_{H2GB} =$ hydrogen concentration in the cathodic gas bulk

The mass transfer coefficient can be defined as related to the Schmidt number.

$$k_{GHH} = \frac{D_{GHH}}{L_{EWGB}} \cdot Sc_G^{-\frac{1}{2}}$$
(6.6)

Where:

 $D_{GHH} =$ diffusion coefficient of hydrogen in hydrogen $L_{EWGB} =$ distance between the electrode surface and gas bulk $Sc_G =$ Schmidt number for hydrogen gas

Diffusion Through the Zirfon Layer

The mass flux through the Zirfon layer (N_{H2Z}) is assumed to be constant since there are no sources or sinks present, that is, the flux at the electrode-Zirfon interface is equal to the flux at the electrolyte-Zirfon interface. Its relation to the concentration at these interfaces (C_{H2EW} and C_{H2ZW}) respectively, can be defined as follows.

$$N_{H2Z} = D_{H2}^{\text{eff}} \cdot (C_{H2EW} - C_{H2ZW})$$
(6.7)

Where D_{H2}^{eff} is the effective diffusion coefficient through the Zirfon, which accounts for its porosity (ϵ) and tortuosity (τ), as mentioned in the Theoretical Background chapter (3.15):

$$D_{H2}^{\mathsf{eff}} = \frac{\epsilon}{\tau} \cdot D_{H2} \tag{6.8}$$

Convection to the Electrolyte

The following mass transfer step for hydrogen to reach the anodic chamber would be through the electrolyte flow by a convective-diffusive mechanism. To simplify the reasoning process, all mass transfer interfaces and surfaces are made equal, which is in fact true for all except the electrolyte flow outlet surface. By presuming all surfaces to be equal, the mass transfer processes can be compared solely based on their flux. Hypothetically considering that hydrogen from the Zirfon surface is transported solely by convection to the electrolyte and subsequently evacuated through the outlet of the channel, the mass flux at the Zirfon surface would match the outlet flux ($N_{H2Z}=N_{H2O}$). Given these premises, the hydrogen concentration in the bulk of the electrolyte is estimated to be zero and the convective mass transfer can be written as follows.

$$N_{H2Z} = N_{H2O} = k_{LH2} \cdot (C_{H2ZW} - C_{H2EB})$$
(6.9)

Where:

 N_{H2Z} = mass flux at the Zirfon surface N_{H2O} = mass flux through the theoretical outlet surface C_{H2ZW} = hydrogen concentration at the Zirfon surface C_{H2EB} = hydrogen concentration in the electrolyte bulk k_{LH2} = liquid mass tranfer coefficient

Then, the liquid mass transfer coefficient is defined using the Sherwood number.

$$K_{LH2} = \frac{Sh_{H2} \cdot D_{H2}}{L}$$
(6.10)

Where:

 $Sh_{H2} =$ Sherwood number $D_{H2} =$ hydrogen diffusion coefficient L = characteristic length The Sherwood number is described in the literature as a correlation of the Schmidt and Reynolds numbers [4]. The Schmidt number links the kinematic viscosity to the mass diffusivity, characterising fluid flows where both momentum and mass diffusion are occurring, providing insight into the relative rates of these processes.

$$Sh_{H2} = 0.664 \cdot (Re)^{\frac{1}{2}} \cdot Sc_{H2}^{\frac{1}{3}}$$
 (6.11)

$$Sc_{H2} = \frac{\nu}{D_{H2}} \tag{6.12}$$

Taking into account the velocity domain and the variation in the Peclet number within the channel (see 6.12(b), 6.14(b)), it is evident that convection is not the dominant transfer mechanism in all sections of the channel. The mass transfer to the anode can be dictated by diffusion through the stagnant flow zones in the vicinity of the inert walls. Thus, based on this assumption, the flux at the Zirfon wall can be split into two components:

$$N_{H2Z} = N_{H2C} + N_{H2O} \tag{6.13}$$

 N_{H2C} represents the crossover flux to the anode, while N_{H2O} is the hydrogen flux that is transported to the electrolyte by convection and exits the cell through the outlet. These fluxes are proportional to the channel geometry and are accounted for with a multiplication factor that will be introduced to the model in the next section.

Advection and Diffusion in the Channel

The proportionality of N_{H2C} and N_{H2O} to the geometry of the channel can be conveniently explained by figure 6.13. The viscous boundary layer (δ) is the section of the channel through which the crossover is assumed to occur through diffusion; therefore, taking this into account, the crossover flux can be defined.

$$N_{H2C} = D_{H2} \cdot \frac{C_{H2ZW} - C_{H2CZ}}{L} \cdot X$$
 (6.14)

Where:

 C_{H2ZW} = hydrogen concentration at the cathodic Zirfon wall C_{H2CZ} = hydrogen concentration at the anodic Zirfon wall (crossover)

X is the fraction that relates the diffusive cross-sectional area to the surface of the Zirfon, since the z dimensions are identical the y dimensions are sufficient to express the ratio. Whereas δ is the viscous boundary layer along the inert walls and is averaged along the height of the channel.

$$X = \frac{2 \cdot \overline{\delta}}{W} \tag{6.15}$$

$$\delta(z) = 4.64 \cdot \left(\frac{\nu z}{\overline{v}}\right)^{\frac{1}{2}} = 1.31 \,[\text{mm}]$$
 (6.16)

$$\overline{\delta} = \frac{1}{L_z} \cdot \int_0^{L_z} \delta(z) \, dz = 0.864 \, \text{[mm]}$$
 (6.17)

The remaining surface of the Zirfon is considered to convey the mass to the electrolyte by convection, which then escapes through the outlet of the channel. This area is scaled to the electrode surface by the factor Y.

$$N_{H2O} = Y \cdot N_{H2Z} \tag{6.18}$$

$$Y = \frac{W - 2 \cdot \delta}{W} \tag{6.19}$$

Through these assumptions, the mass flux at the Zirfon wall is allocated to either two auxiliary fluxes, and the crossover flux at the anodic Zirfon wall can be computed. The flux through the Zirfon to the anode is constant and can be defined in the same manner as on the cathodic side of the channel 6.3, therefore, it will not be restated.

Crossover Convection to the Anodic Gas Bulk

The crossover flux from the electrode to the gas bulk of the container proceeds similarly to the gas convection in the cathodic gas compartment (see 6.3). However, in this case, the gas mass transfer coefficient k_{GHO} is expressed with D_{GHO} , which is the diffusion coefficient of hydrogen in oxygen since the anodic compartment predominantly contains oxygen.

$$N_{H2C} = k_{GHO} \cdot (C_{H2CE} - C_{H2CB})$$
(6.20)

Here, C_{H2CE} is the hydrogen concentration at the electrode (anode) and C_{H2CB} is the hydrogen concentration in the anodic gas bulk. With this equation, the system is rounded off, constrained, and can be solved with the aid of Maxima, a powerful software package capable of performing extensive computer algebra calculations.

Velocity Profile and No Flow Region

This section seeks to investigate the hypothesis that a stagnant flow is present at the inert walls of the channel by mapping its velocity domain. An analytical solution to the Navier-Stokes equation is notoriously difficult to derive for the general case. For some geometries and cases, an analytical solution can be found, however, in the case of a Poiseuille flow in a rectangular duct, the best approximation is in the form of a Fourier sum, described by equation 6.21 [7].

$$v_x(y,z) = \frac{4h^2 \Delta p}{\pi^3 \eta L} \sum_{n,\text{odd}}^{\infty} \frac{1}{n^3} \left[1 - \frac{\cosh\left(n\pi\frac{y}{h}\right)}{\cosh\left(n\pi\frac{w}{2h}\right)} \right] \sin\left(n\pi\frac{z}{h}\right)$$
(6.21)



Figure 6.11: Contour lines for the velocity field for the Poiseuille-flow problem in a rectangular channel [7].

Adapting the equation to a vertical gravity-driven Poiseuille flow and substituting the parameters of the channel, the velocity domain and contour lines of the channel can be depicted. Here, the origin of the

Cartesian coordinate system has been chosen so that the inter-electrode distance is defined along x from 0 to L (= 1 mm) and the spanwise dimension of the channel extends along y between -W/2 and W/2 (W = 25 mm). Naturally, the intervals on the x and y axes are not on the same scale, to enhance the plot's clarity. Furthermore, the figure is intentionally plotted in the inverse direction of the flow to achieve a concave surface, making the gradients easier on the eye and discernible.

$$v_z(x,y) = \frac{4L^2 \rho g}{\pi^3 \eta} \sum_{n,\text{odd}}^{\infty} \frac{1}{n^3} \left[1 - \frac{\cosh\left(n\pi\frac{x}{L}\right)}{\cosh\left(n\pi\frac{W}{2L}\right)} \right] \sin\left(n\pi\frac{y}{L}\right)$$
(6.22)



Figure 6.12: Velocity domain of the channel.

It is visible that the maximum velocity is reached in the centre of the channel along the x = 0.5 mm plane. At this distance from the electrodes is the bulk movement of the fluid fully developed. This also implies that this cross-section of the channel is where the viscous boundary layer is the thinnest near the inert walls. Along both inert walls, these section areas are considered as a no-flow region, and thus diffusion dominates, and convection towards the bulk of the fluid can be neglected. Viewing the velocity profile at x = 0.5 mm from a perpendicular perspective to the Y axis provides an understanding of the relationship between fluid velocity and the boundary layer thickness (see 6.13 below), which has been averaged over the height of the channel for simplified data processing and understanding.



Figure 6.13: Velocity profile and averaged viscous boundary layer (as illustration) thickness at x=0.5 mm

The velocity domain of the channel being mapped, it is clearly visible that the until now presumably thin low flow velocity regions in the vicinity of the inert walls are thinner than expected. This finding supports the low crossover values reported in the previous section. To acquire additional understanding, the Peclet number is introduced to evaluate and compare the magnitude of diffusive and advective mass transport through the channel, and is defined in the following manner:

$$Pe = \frac{Lv}{D_{H2}} \tag{6.23}$$

Where:

Pe = Peclet number L = characteristic length v = velocity of the fluid $D_{H2} =$ diffusion coefficient of hydrogen

The characteristic length in this context is specified as the distance to the nearest wall from the coordinates where the Peclet number is calculated. Similarly to the velocity profile, the cross section x = 0.5 mm is of interest in relation to the viscous boundary layer where diffusion dominates. Using the Peclet number as a metric, the diffusion term is shown to be responsible for crossovers through only a fraction of the cross-section of the channel.



Figure 6.14: The Peclet number variation throughout the domain of the channel.

6.4. Discussion

This section aims to explore the relationships among the input parameters and the output parameters of the analytical model, examining the interaction of various parameters and their impact on crossover concentration and performance.

In order to assess gas evolution efficiency across different current densities, the input parameters in the code are altered, evidently the current density along with the concentrations of hydrogen and oxygen in the anodic and cathodic gas chambers, based on HTO measurements. These were then plotted using this updated input data.



Figure 6.15: Gas evolution efficiency in function of current density.

The measured HTO levels can be contextualised by analysing gas evolution efficiencies at various current density levels. These efficiencies provide essential insights, as the primary cause of crossovers is the fraction of produced hydrogen that remains in dissolved form. This occurs because Zirfon membranes are impermeable to gaseous species, allowing only dissolved species to permeate to the Zirfonelectrolyte interface.

The model outputs of the Zirfon 220 nickel mesh configuration reveal that the gas evolution efficiency increases with current density. This indicates that a larger proportion of the total hydrogen produced is collected in the gaseous phase, reducing the dissolved fraction. Additionally, HTO levels are significantly influenced by the gas evolution efficiency of the oxygen reaction, which exhibits a trend similar to that of hydrogen evolution, albeit with slightly higher efficiency values. Higher oxygen gas evolution efficiency leads to an increased proportion of the gas phase product, diluting the hydrogen crossover, thereby reducing HTO levels. This phenomenon explains the observed decrease in HTO values when comparing 0.06 A/cm^2 and 0.09 A/cm^2 levels. However, the lower HTO at 0.03 A/cm^2 requires further investigation.

In conventional electrolysers, crossovers at low current densities are typically attributed to limited convection through the separator, driven by lower-pressure differentials. Additionally, the effect of electroosmotic drag diminishes at lower current densities and is therefore negligible. In a gravity-fed laminar electrolyser, these factors have further reduced influence due to the steady-state nature of the electrolyte flow, which maintains close to constant pressure gradients regardless of current density. The electro-osmotic drag is similarly insignificant compared to the dominant effect of convection between electrodes. Consequently, diffusion and electrolyte mixing emerge as the main potential crossover mechanisms. Diffusion is induced by concentration gradients, consequently, at diminished current densities, hydrogen production declines, leading to a reduced concentration gradient across the channel. This results in a correlation between current density and the contribution to crossover from the diffusion mechanism, even in the presence of reduced gas evolution efficiency. When comparing 0.03 A/cm^2 to 0.06 A/cm^2 , the halving of the current density has a more pronounced effect on the amount of dissolved hydrogen than the 16% decrease in gas evolution efficiency.

In terms of mixing, dissolved hydrogen has sufficient time for degassing because of the oversized electrolyte reservoir, the substantial electrolyte volume, and the reduced recirculation rate. These factors ensure the effective flushing of dissolved hydrogen. To conclude, the observed decrease in crossover concentration at lower current densities can be attributed to the reduced concentration gradient, the thinner than anticipated viscous boundary layer along the inert wall, and consistent electrolyte flushing effects.

In terms of performance, Zirfon configurations consistently outperformed their ePTFE counterparts, with one notable exception: when stainless steel mesh was employed as the anode. In the ePTFE configuration, the stainless steel mesh demonstrated remarkable performance, due to the presence of iron compounds that have a beneficial effect on the catalytic reaction at the anode [44]. Its submersion in the electrolyte facilitated enhanced ionic transport, which increased the number of accessible reaction sites. Furthermore, its smooth surface makes it more difficult for gas bubbles to form and adhere [26]. Consequently, bubbles on smoother surfaces tend to detach more readily and with a smaller diameter, which can be advantageous for reducing the accumulation of gas bubbles on the electrode surface. However, the same anode material yielded average results when used in Zirfon assemblies.

The primary issue lies in the stainless steel mesh's low open area ratio of 40%, which obstructs the escape of gases produced during operation. This leads to gas accumulation at the mesh-Zirfon interface, forming bubbles that reduce the effective contact area between the mesh and the electrolyte. As a result, performance declines significantly. In addition, this accumulation of bubbles creates uneven contact along the surface, causing the electrolyte to leak. Furthermore, the trapped gas makes the situation worse by clogging the electrolyte-feeding pores in the Zirfon layer, further restricting the transport of ions to the reaction sites.

The superior performance in ePTFE can likely be credited to its ability for efficient oxygen evolution, rather than its gas release. Despite its improved efficiency in the ePTFE configuration, this still does not make it a viable alternative. A critical limitation is the rapid increase in gas crossover concentration with current density, which renders the system inoperable at values exceeding $0.09 \,\mathrm{A/cm^2}$. Above these rates, the gas fraction in the channel becomes excessive. This constraint highlights the challenges of achieving stable and efficient operation with ePTFE-based designs, reinforcing the need for continued optimisation of Zirfon-based configurations for better gas management and ionic transport.

Another important point of discussion is the discrepancy between the calculated and actual volumetric flow rates. As mentioned in Chapter 4 the average flow velocity can be analytically derived and defined with 4.3. Figure 6.16 compares the measured volumetric flow rates performed with and without spacers at 80° C and room temperature. These are carried out for all channel widths (0.5, 0.7 and 1 mm) and are compared to the analytical solution. The primary reason for observing higher volumetric flow rates at elevated temperatures is the reduction in viscosity. At the interelectrode spacing of 0.5 mm, flow was often nonexistent. This was attributed to the suction effect of the Zirfon layer causing the electrodes to stick to each other or, in the case of ePTFE configurations, to the obstruction of electrolyte flow by the electrode meshes. Analytical approximations tend to overestimate flow rates because they do not account for real-world occurrences, such as Zirfon bulging, leakages, or flow disturbances caused by the frontal area of the electrodes.



Figure 6.16: Flow rate vs channel thickness at room temperature and 80° C.

Finally, the highest product purity results are compared with those of a conventional electrolyser modified to reduce anodic hydrogen levels. Recent strategies to mitigate crossover in traditional ZGEs include implementing a finite gap between the Zirfon separator and electrodes, leading to encouraging outcomes. Although this introduces additional resistance, it effectively reduces the anodic hydrogen concentration. Barros et al. [27] constructed and evaluated such a design, with their findings compared to the nickel mesh - Zirfon 220 configuration illustrated in figure 6.17.



(a) Stationary anodic gas impurity, Conditions: 25 $^\circ$ C, 12 w% KOH, Zirfon UTP 500 (blue data) and UTP 220 (red data)



(b) HTO values of Nickel Mesh (a,c) - Zirfon Configuration with 1 mm channel width

Figure 6.17: Comparison between the crossover values of the finite gap and the gravity-fed laminar electrolyser cell.

Conclusion and Recommendation

Although flexibility and restricted load range remain the main limitations of contemporary modern alkaline water electrolysis cells, this project aimed to design, manufacture, and evaluate the performance and gas crossover of the prototype based on the gravity-fed laminar electrolyser concept. Upon testing numerous electrode configurations, involving various mesh materials and polymer membranes, the following findings and conclusions are drawn:

- The iterative process of narrowing down the electrode configurations and tuning the parameters to achieve the best performance has led to the combination of Zirfon 220 and the open nickel mesh as the highest-performing configuration, which includes a diaphragm in the liquid side and an active electrode on the gas phase side, see section 6.4.
- Counterintuitively, the use of active electrodes on the inner side and ePTFE on the outer side led to lower performance, particularly at higher current density, which is explained by the appearance of bubbles in the liquid channel.
- The gas diffusion electrode as a cathode showed promising performance at low current densities, although exhibiting a strong linear resistance rise with increasing current densities, vastly underperforming the most efficient compositions of ePTFE and Zirfon configurations. The final ePTFE setup exhibited high efficiency, featuring the open nickel mesh as cathode and the stainless steel mesh as anode. However, its performance diminished slightly with rising current density compared with the ultimate iteration of the Zirfon configuration, employing open nickel mesh for both the anode and cathode.
- The use of stainless steel as an anode showed superior performance when combined with ePTFE, and the additional hot pressing procedure improved contact quality. In contrast, when implemented in conjuncture with Zirfon at the outer side, it had an adverse effect, displaying diminished performance across the whole current density range which can be attributed to the excessive bubble build-up at the mesh-Zirfon interface. This clogging effect is related to the low open area ratio of the stainless steel mesh, which obstructs the convection of the gas bubbles towards the gas container.
- The hot pressing procedure had a beneficial effect on the ePTFE and Zirfon 500 subjects. When using the very same technique on Zirfon 220, severe leaks and floods were detectable, which is due to loss of surface integrity and permeability when exposed to the high compressing pressure and temperature. Furthermore, the thinner membrane revealed a lower performance in the activation region compared to the Zirfon 500 series, which is surprising considering its superior porosity.
- Increasing the temperature proved to be one of the most rewarding undertakings, while selfevident when inspecting the catalytic activity and electrolyte conductivity. However, it also has its drawbacks: first, elevated temperature leads to lower product purity as a result of the higher fraction of vapour and KOH fumes in the gaseous product flux. Secondly, the higher solubility

of the products in the electrolyte has an unfavourable effect on the diffused ratio of the products, further promoting increased crossover rates and deteriorating gas evolution efficiency.

- In terms of crossover, the Zirfon assemblies exhibit outstanding values. They show an inverse correlation with current density, except for the measurements carried out at the lowest current density, unveiling a peculiar drop in the anodic hydrogen content. While the ePTFE configurations emerged as unviable, exceeding the 2% safety limit already at moderate current densities. Their anodic hydrogen concentration is directly correlated with the current density and shows no sign of halting its growth when stainless steel is employed as the anode. Regarding the variant where both electrodes are nickel meshes, a maximum is reached at $0.09 \, {\rm A/cm^2}$, followed by a subtle decline.
- The measured and analytically approximated volumetric flow rates do not coincide and have, due to the simple fact that the thin and flexible Zirfon layers tend to bulge into the channel and constrict the cross-section available for electrolyte flow.
- Reducing the channel width leads to a performance increase for Zirfon configurations, although an optimal value seems to exist between 0.5 and 1 mm for their ePTFE counterparts. In terms of assembly, the thinner the channel the higher the failure rate, and the lowered distance between the electrodes leads to a higher possibility for the zirfon layers to stick together and impede the flow of electrolyte, due to their porous hydrophilic characteristic.

The following recommendations provide insight into further research that seeks to undertake a similar demanding challenge in the design, manufacture, and experimenting of a cell that relies on the gravity-fed laminar electrolyser concept. In addition, further aspects and possible developments that merit consideration are mentioned.

- Pre-soaking: Extended exposure to the electrolyte prior to the experiments facilitates the seeping
 of KOH into the pores of the Zirfon membrane. As visible in figure 6.2, subsequent measurements
 showed enhanced performance, due to the increase in surface contact of the electrolyte with the
 mesh, resulting in better transport in the vicinity of the electrodes.
- Oversizing and agitation of the electrolyte reservoir: As realised in this experimental setup, opting for a larger electrolyte container than would be required by the volumetric flow and dimensions of the cell enables the additional time for the degassing of the dissolved products. In addition, the implementation of stirring and agitation of the liquid further amplifies the process.
- Cell Design: From a more pragmatic perspective, the adhesion of the electrode to the cells' framework employing hardened resin is highly recommended. An alternative solution avoiding adhesive materials was considered for the sake of straightforward replacement of the electrodes, although these did not resolve the issue and led to extensive time delay. To facilitate the assembly and experiment process, it is advised to reduce the spanwise width of the channel to avoid the protrusion of the MEA along the channel width. In addition, the use of a more expansive spacer structure reduces the failure rate and leads to more consistent testing. Contemplating the reduction of channel width below 0.5 mm is an ambitious undertaking, although can be achieved by relying on the cutting precision of the laser cutter instead of the PMMA layer's thickness. This procedure could result in channel widths as low as 0.2 mm.
- Electrochemical Impedance Spectroscopy: The use of EIS provides insight into charge transfer, mass transport, and reaction kinetics, offering a deeper understanding of the magnitude of resistances and their contribution to the total cell potential. This further highlights which aspects of the design need improvement.
- Exploring additional polymer membrane materials: Experimenting with the variation of the porosity and thickness of the membrane has the potential to significantly increase performance. This involves an examination of the effect of the channel width on the flow through materials with various porosities and thicknesses (Darcy flow) to find the optimal combination of parameters.
- Investigation of gas diffusion electrodes: Testing and further research in gas diffusion electrodes would undoubtedly yield enhanced performance. MEAs have far reduced potential to maximise efficiency compared to GDEs, which are specifically manufactured for these types of applications.

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A.O.1. Table of parts

Table A.1 summarises the supplier and model numbers of the components that were required to assemble the experimental setup.

| Component Specifications | | | | | |
|-------------------------------|--------------|-------------------|--|--|--|
| Component | OEM/Supplier | Model Number | | | |
| Magnetic Stirrer Hot Plate | Cole-Parmer | US152 | | | |
| Peristaltic Pump | Heidolph | Hei-FLOW Core 120 | | | |
| Excess Flow Duct | Swagelok | SS-PB8-TM12 | | | |
| DC Power Source | OWON | SPE6103 | | | |
| Gas Chromatographer | VARIAN | CP-4900 Micro-GC | | | |
| Magnetic Inductive Flow Meter | Kobold | MIM-1305HG4C3T0 | | | |
| T-Junction | Swagelok | T4MF20 | | | |

Table A.1: Overview of the Components that comprise the BoP.

A.0.2. Cell Component Description

| | Cell Component Specifications | | | | | |
|----|------------------------------------|---------------|---------------|---------------|--|--|
| | Component | OEM/Supplier | Material | Dimension | | |
| 1 | Channel Defining Layer | Laserbeest | PMMA | 1 mm | | |
| 2 | Electrode | Various (5.2) | Various (5.2) | Various (5.2) | | |
| 3 | T-shape Gasket without bridge | PremiumFol | EPDM | 0.5 mm | | |
| 4 | T-shaped phase divider | Laserbeest | PMMA | 6 mm | | |
| 5 | T-shaped gasket with bridge | PremiumFol | EPDM | 1 mm | | |
| 6 | T-shaped foundation & liquid phase | Formlabs | Clear V4 | | | |
| | outlet | | Resin | | | |
| 7 | Gas phase container gasket | PremiumFol | EPDM | 1 mm | | |
| 8 | Gas phase container | Formlabs | Clear Resin | | | |
| | | | V4 | | | |
| 9 | Current feeding bolts | Dresselhaus | Stainless | M4 DIN84 | | |
| | | | Steel | | | |
| 10 | Tightening M8 Bolts | Dresselhaus | Stainless | 8X40 DIN933 | | |
| | | | Steel | | | |
| 11 | Tightening M8 Hex Nuts | Dresselhaus | Stainless | DIN 934 | | |
| | | | Steel | | | |

Table A.2: Overview of the components that comprise the cell.

A.0.3. GC file output example



Figure A.1: Extract of the GC's output

Because of similar retention times for oxygen and nitrogen, their peaks in the chromatogram are intertwined.

A.0.4. Gas container flush time calculation

$$\dot{V}_g = \frac{IV_m}{zF} \left[\frac{m^3}{s}\right] \tag{A.1}$$

$$V = 8.95 \cdot 10^{-5} [m^3] \tag{A.2}$$

$$T_f = \frac{V}{\dot{V}_g}[s] \tag{A.3}$$

| j [A/cm ²] | 0.03 | 0.06 | 0.09 |
|---------------------------|-----------------------|------------------------------|------------------------|
| $\dot{V_g}[rac{m^3}{s}]$ | $1.127 \cdot 10^{-7}$ | 2.254 $\cdot 10^{-7}$ | $3.3814 \cdot 10^{-7}$ |
| $T_f[s]$ | 794 | 397 | 265 |

Table A.3: Gas container flush time calculation for 0.03, 0.06 and $0.09 \ A/cm^2$

A.0.5. GC sample's temperature and pressure

| Agilere 490 Micro GC | | | | | | | | | | |
|-------------------------|--------|-----------|----------|-----------|----------------------|--------|-----------|----------|-----------|--|
| strument | | | | | | | | | | |
| Charpel 1 | | | | | Channel 2 | | | | | |
| Injector temperature | Actual | 110.0 °C | Setpoint | 110.0 °C | Injector temperature | Actual | 110.1 °C | Setpoint | 110.0 °C | |
| Column temperature | Actual | 100.0 °C | Setpoint | 100.0 °C | Column temperature | Actual | 100.0 °C | Setpoint | 100.0 °C | |
| Column pressure | Actual | 199.4 kPa | Setpoint | 200.0 kPa | Column pressure | Actual | 148.7 kPa | Setpoint | 150.0 kPa | |
| Autozero | Actual | 11.924 mV | | | Autozero | Actual | -3.523 mV | | | |
| Instrument | | | | | | | | | | |
| State | | Ready | | | Connection type | IP 1 | 190 65 11 | | | |
| Status | | | | | Serial rumber | | 1012607 | | | |
| Semple line temperature | Actual | 110.0 °C | Setpoint | 110.0 °C | | | | | | |
| Miscelleneous | | | | | | | | | | |
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Figure A.2: GC sample's temperature and pressure