Understanding safety aspects of gas mixing in low temperature electrolysers

TNO Public ❭ TNO 2025 R10381
14 February 2025

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TNO 2025 R10381 – 14 February 2025

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Classification report	TNO Public
Title	TNO Public
Report text	TNO Public
Number of pages	43 (excl. front and back cover)
Number of appendices	0
Sponsor	TNO
Project number	060.56176

Results are partly fed by ISPT-project H2-Safety2 which was co-funded by TKI-Energy with the supplementary grant 'TKI- Toeslag' for Topconsortia for Knowledge and Innovation (TKI’s) of the Ministry of Climate Policy and Green Growth.

Contents

Executive summary

As electrolysis technologies such as alkaline water electrolysis (AWE) and proton exchange membrane water electrolysis (PEMWE) are scaled up for large-scale green hydrogen production, new safety challenges emerge. Particularly, concerns are expressed regarding gas crossover, the phenomenon where hydrogen and oxygen permeate through the membrane separating the electrolyser compartments. While this issue is manageable under controlled, small-scale conditions, the transition to large-scale systems introduces complexities that must be addressed. This study aims to describe potential failure scenarios specific to electrolyser stack driven by gas crossover, focusing on how these risks evolve with operational parameters such as varying pressures, temperature and design parameters.

To investigate these failure scenarios, we employed a modelling framework developed in previous projects, which simulates the physical mechanisms of gas crossover and assesses their behaviour under different parameters. These models were mainly based on Trinke *et al.*[1] for PEMWE and De Groot *et al.*[2] for AWE. The results reveal that critical gas cross-over leading to unintended in-equipment mixing is hazardous especially when conditions such as **non-uniformity** and **degradation** are present. These conditions refer to situations where the electrolysers operation deviate from the intended **beginning of life** conditions, leading to hidden local failures, especially in a larger system. These findings highlight the critical need for advanced monitoring systems and optimized cell, stack and system design strategies to manage risks associated with gas crossover in large-scale electrolysis systems. Effective monitoring should notice how non-uniformities and degradation impact the system, while design improvements must limit design-specific failures.

1 Introduction

1.1 Project scope

As the large-scale deployment of green hydrogen appears crucial in meeting Europe's carbon neutrality objectives, electrolysis emerges as key enabler of this transition. In fact, over the past decade, the development of electrolyser technologies proceeded at an unprecedented pace, with an increasing number of demos and pilot projects spreading all across Europe.
This transition to large-scale deployment introduces new challenges, particularly in managing safety risks. In fact, unlike well-established industrial processes, large-scale electrolyser systems have not been extensively tested under real-world, high-capacity conditions, leaving critical questions about operational risks unanswered.
Among these, the phenomenon of ***gas crossover***, which refers to the mixing of **hydrogen (H_2) and oxygen (O_2)** inside the electrolyser, can represent a significant concern. Above certain concentrations, the mixture can lead to the **unintended in-equipment mixing of gases**, with a potentially explosive nature. However, the conditions under which such mixing might occur within electrolysis equipment remains yet partially unexplored, especially over the safety threshold. Combining lab-scale testing and modelling scenarios could help in addressing these gaps.

The objective of this current study is to offer a comprehensive understanding of which series of events and conditions can trigger the **abrupt mixing of these gases**. To address this, we developed a model that describes gas crossover under normal operating conditions. This model provides a foundation for understanding how gas behaviour changes as operational parameters shift, and it serves as a basis for assessing the likelihood of hazardous in-equipment mixing under specific scenarios. Therefore, this report builds on a comprehensive overview of scenarios developed during earlier phases of this project and related studies. By delving deeper into selected scenarios and their underlying mechanisms, this work outlines a number of mitigation barriers, the objective is to clarify which are the key actors in the acceleration and propagation of internal gas-mixing in alkaline water (AWE) and proton-exchange membrane water electrolysers (PEMWE). Failure scenario propagation from cell to cell and stack to stack is not addressed. However, with a thorough knowledge of mechanisms that influence individual cells, escalation scenarios could be developed.

1.2 Project approach

Gas cross-over is an inherent phenomenon of electrolyser technologies. Under normal conditions, when properly monitored and managed, it does not pose a safety threat for daily operations. However, certain factors can cause a sudden acceleration of this phenomenon, potentially turning it into a hazardous situation. We identified as critical elements two factors in particular: **non-uniformity** and **degradation**. In fact, it is shown that the key failure scenarios are usually driven by a combination of degradation processes and non-uniform operating conditions. To explore these aspects in depth and propose actionable insights, the report is structured as follows:

Section 2 offers a description of the gas cross-over phenomenon through the models developed. The major responsible for this phenomenon are the membrane (in PEMWE) and the diaphragm (in AWE). Therefore, this section outlines their intrinsic differences and how their characteristics contribute to gas cross-over.

Section 3 offers an in-depth exploration of the role of non-uniformity and degradation in the occurrence of failure scenarios, explaining how these elements contribute to unintended in-equipment mixing.

Section 4 aims to describe identified scenarios, systematically classifying them based on their specific characteristics and triggering parameters. Furthermore, this section provides a comprehensive overview of suited prevention and mitigation strategies.

Section 5 explains how the scenarios can be avoided by a good design of the electrolyser stacks and balance of plant, leading to a set of minimum design requirements for both elements.

2 Gas cross-over under normal operation

To assess whether gas cross-over under normal conditions can lead to concentrations which are regarded unsafe, TNO developed -as part of a previous project- a comprehensive model-suite, which simulates gas cross-over for different types of electrolysers[1,2] and different configurations. Before its description in section 2.3, a detailed overview of the main physical mechanisms used as base for the models is offered in section 2.2. As gas cross-over mainly happens in the electrolysers membrane or diaphragm, a particular focus is dedicated to these components, and their characteristics are outlined in the following section 2.1.

2.1 Membrane properties in Alkaline and PEM Water electrolysers

Alkaline water electrolysers feature a thin, porous layer which is filled with liquid, ion-conductive electrolyte. The separation function is obtained by the capillary forces which keep the small pores in the membrane filled with electrolyte. The solubility of hydrogen and oxygen in the electrolyte is low, resulting in a good barrier function of the membrane. Industry standard is the Zirfon© membrane supplied by AGFA.

PEM water electrolysers employ a non-porous membrane usually made of a polymeric, semipermeable proton conducting layer. Most membranes are based on a *perfluoro-sulfonic acid* backbone where sulfonic acid functionalities provide the necessary proton conductivity. Nafion© is the most common commercially available PEM membrane for electrolysis and is supplied by Chemours.

Inherently the gas flux through the PEM membrane is higher than for the alkaline diaphragm because the solubility of gases in the KOH electrolyte is much lower than in pure water used in the PEM electrolyser. However, this does not necessarily mean that gas cross-over is less of an issue in AWE than PEM electrolysers. In fact, in the PEM electrolyser, gas cross-over only happens across the membrane, while for AWE electrolyte mixing after the separation vessels (O_2 separator and H_2 separator), also contribute the gas mixing.

2.1.1 Proton Exchange Membrane: key properties and operational parameters

PEMWE are mostly operated at a temperature ranging from 50 to 80 °C and pressures of <70 bar. The proton exchange membrane acts as an ion-conductor by interacting with water: in fact, when the water molecules interact with the acidic sulfonic sites, protons are mobilized enabling their transport through the polymer matrix, while electrons and gases are mostly blocked. The choice of materials influences the membrane's ability to run efficiently within specific operational parameter ranges: a higher temperature gives a better performance because of an increased proton conductivity, but it also accelerates the membrane's degradation mechanisms, shortening its lifespan.

Given its crucial role in the gas separation process, it is very important to understand which factors require consideration to ensure the proper functioning. An overview of these aspects, together with the elements that lead to an accelerated increase of gas cross-over, is given in Table 2.1.

Table 2.1: An overview of the different parameters influencing gas cross-over and membrane degradation processes in PEM electrolysers.

	Parameter	Susceptibility to gas crossover	Factors which can accelerate leakage
OPERATING CONDITIONS	Pressure	Gas cross-over is driven by partial gas pressures (O_2 or H_2) and less so by absolute differential pressure. Higher operating pressures increase gas cross-over[3]. For example high pressure at cathode will increase H_2 gas crossover.	Higher pressure can lead to mechanical stress on the membrane. Deformation and creep of the membrane can lead to higher cross-over.
	Temperature	Higher temperatures increase gas cross-over due to higher solubility and diffusivity[4] and accelerate the degradation processes.	Higher temperatures can accelerate the chemical degradation processes[5] in PEM membranes, by influencing the rate at which degradation reactions occur.
	Relative Humidity	Water content controls proton conductivity. While fully wetted membranes have a better proton conductivity (efficiency) they also show higher gas cross-over, compared to dry state[6,7].	The uptake of water leads to swelling of membranes. This size expansion leads to mechanical stress. In particular cycles of drying and humidification cause mechanical stress that can lead to tears or pinholes, a well-known mechanism in fuel cells' degradation mechanism[8,9].
	Water purity	Cations in the feed water tend to block the proton conducting sites in the membrane[10]. Low purity water will decrease the performance of the electrolyser.	Impurities generally increase the rate of chemical degradation of the membrane polymer, leading to higher cross-over[10].
DESIGN CHOICES	Membrane Thickness	Influences mechanical strength, proton conductivity, and gas separation efficiency. Thinner membranes result in reduced ohmic losses, but their use at high pressures and low current density presents a safety hazard due to higher gas-crossover.	Membranes tend to become thinner with time due to chemical degradation[11]. Integrating a thin membrane in an electrolyser can shorten the operational lifetime of the electrolyser as unsafe levels of gas cross-over are reached sooner.
	Cell assembly	Choice of ionomer content in the catalyst layer[12] and Gas diffusion layer (GDL) (how compressed it is)[13] or even polymer chain length[14] can influence gas crossover.	The polymeric backbone of the electrolyser undergoes an inherent degradation process which can be further accelerated by operational conditions such as temperature, current and water purity.

2.1.3 Diaphragm in alkaline water electrolysers: key properties and operational parameters

As mentioned in the previous paragraph, in an alkaline water electrolyser the diaphragm consists of a porous matrix which contains the electrolyte in its pores. Zirfon®, the current industry standard, is a porous composite diaphragm material composed of a polysulfone matrix and Zirconia (ZrO_2). Given its hydrophilic nature, the ZrO_2 provides wettability and stiffness to the diaphragm, while the polysulfone acts as binder and imparts flexibility. Zirfon® exhibits high stability in an aqueous KOH solution.

They usually run at temperatures ranging from 70 to 90 °C and pressure spanning between 1 and 30 bar. Whilst the PEMWE degradation processes are mostly responsible for accelerated gas cross-over, for AWE the operational conditions play a critical role. In fact, the use porous diaphragm makes AWE extremely sensitive to pressure differentials.

An overview of the most important parameters considered for the scope of this study are presented in Table 2.2 together with the associated effects on gas cross-over.

Table 2.2: An overview of different parameters influencing gas cross-over and the degradation processes of the diaphragm in alkaline electrolysers.

	Parameter	Susceptibility to gas crossover	Factors contributing to leakage
OPERATING CONDITIONS	Pressure	Increases the gas concentration in the electrolyte and thus the gas crossover Differential pressure across the diaphragm causes a significant enhancement of gas cross-over.	
	Electrolyte flowrate	For mixed electrolyte systems, higher flow rates can significantly enhance gas cross-over[15] especially for pressurized systems. Electrolyte flow rates can show linear correlations to gas cross-over[15,16]	The presence of impurities or the formation of a sludge in different parts of the cell can affect the uniformity of flow of the electrolyte leading to hotspots
	Temperature	Operating temperature has an impact on gas cross-over. However, the reviewed literature shows contrasting effects with some saying increase in temperature increases gas cross-over[2] and others the opposite[16].	The operational range is limited to 80-100°C, because of the enhanced corrosion[2]. Also long-term diaphragm durability at high temperature is not well known.
	Electrolyte concentration	High concentrations benefit the system by providing a suitable proton conductivity and lower gas dissolution [16,17].	Higher electrolyte concentrations enhance the corrosion rates of materials.[2]
	Mixing of electrolyte	The contribution of gas cross-over due to electrolyte mixing may be reduced by applying a dynamic mixing strategy that alters separated and mixed electrolyte circuits.[1,16,18]	With thinner diaphragms and higher temperatures, the relative contribution of mixing becomes less dominant.[2]

DESIGN CHOICES	Diaphragm Material	The properties of the diaphragm material, such as its pore size, permeability impact gas cross-over	The material used in AWE is inherently more stable and less prone to degradation compared to PEM
	Diaphragm Thickness	Porous structure, commercially available diaphragms feature a thickness between 100 and 500 µm, where thinner diaphragms have higher gas cross-over.	
	Electrode-diaphragm gap	The distance between the electrode and the diaphragm has a significant contribution to overall gas crossover, where growing distance results in lower gas crossover[19]. It comes at the price of performance. Depending on the distance the AWE often gets categorized into finite gap or Zero-gap.	

2.2 The gas cross-over phenomenon and its mechanisms

Gas cross-over is the rate of gas (H_2 or O_2) permeation through membrane (or diaphragm, for AWE). This event occurs when H_2 migrates through the membrane to the O_2 side and vice versa. It is possible to identify three major underlying mechanisms leading to gas cross-over, valid for both PEMWE and AWE: *convection, diffusion,* and *electro-osmotic drag*.

Convection

Gas cross-over via a **convection mechanism** is a direct consequence of **differential pressure**. In fact, the flow moves from the higher-pressure side to the low-pressure side resulting in a convective transport of electrolyte and dissolved species, namely H_2 and O_2. Depending on the operation of the cell stack, the hydrogen flows to the oxygen side, or the oxygen flows to the hydrogen side of the cell. This phenomenon is described by Darcy's law (eq.1):

$$\Phi_{i,conv} = \frac{K\, c_i\, \Delta p}{\eta \delta} \quad (eq.\ 1)$$

K denotes the permeability of the medium and η the dynamic viscosity of the solvent. Due to their porous structure, diaphragms used in AWE, such as Zirfon©, are characterized by a permeability of several order of magnitude larger than Nafion® membranes (10^{-20} vs 10^{-16} m^2).[1] As such, AWE are often operated at equal anode/cathode pressure, due to the significant convective gas permeation under total pressure gradients. On the other hand, PEM electrolysers can operate under asymmetrical pressures, due to the much lower permeability of Nafion.

Diffusion

When gas cross-over is driven by a **diffusion mechanism**, it results in a flow of H_2 from the cathode, where the concentration is high, to the anode, where the concentration (or *chemical potential*) is lower, leading to a concentration gradient across the membrane or diaphragm. Instead, the opposite happens for the O_2, whose lower concentration is at the anode and therefore flows towards the cathode. This process is described by Fick's law (eq. 2) and it strongly depends on the concentration difference of the gas (Δc_i), on the thickness (δ) of the membrane/diaphragm and the effective diffusivity (D_i^{eff}) of the specie (i) through the membrane/diaphragm.

$$\Phi_{i,diff} = D_i^{eff} \frac{\Delta c_i}{\delta} \quad \text{(eq.2)}$$

To determine effective diffusivity we selected diffusion coefficient values and corrected them with membrane porosity and tortuosity.
For example for PEMWE the values for diffusion coefficient at 80 °C was 1e-8 m^2/s, membrane porosity 0.37 and tortuosity 1.5.

Electro-osmotic drag

Electro-osmotic drag is another mechanism influencing the gas cross-over. It is a phenomenon driven by the movement of ions that drag along water molecules including the dissolved gas species. As the ions are transferred in a different direction for AWE (OH^- from cathode to anode) and PEMWE (H^+ from anode to cathode), the effects are different as well: in PEMWE, the drag promotes oxygen transfer and hinders hydrogen transfer, while in AWE it is the opposite. Thus, in PEM electrolysis, the electroosmotic drag favours the **oxygen crossover**, while it hinders the hydrogen crossover, and vice versa in AWE.
The electroosmotic effect can be approximated using the following equation (eq. 3):

$$\Phi_{i,drag} = \frac{c_i}{c_{solv}} \frac{n_{drag}\, i}{F} \quad \text{(eq. 3)}$$

Where n_{drag} denotes the electroosmotic drag coefficient, defined as the ratio of dragged solvent molecules and ions moving under the effect of the applied bias. It is important to know that the absolute electro-osmotic drag is estimated to be lower in AWE than in PEMWE and even though the effects have not yet been quantified for AWE, it is not believed to play a significant role.[4]

Supersaturation

Concentrations of dissolved gas within the catalyst layer can be significantly larger than what the system pressure would otherwise suggest. This effect is called *supersaturation*[20] and it is caused by increased mass transport resistance. This effect is present in both AWE[1] and PEMWE, but is especially dominant in PEMWE at high current densities (>1 A/cm^2). The degree of supersaturation depends on the cell design. Although supersaturation can be minimized, for example by using less compression of the gas diffusion layer, there is trade-off between interfacial contact resistance (efficiency) and mass transport resistance (leading to higher gas cross-over).[21] This supersaturation can be accounted for by defining the concentration (c) of dissolved gases as a function of solubility (S), pressure (p), electrode mass transport coefficient (k_L) and current density (i) (eq. 4).

$$c_i = \frac{\frac{i}{2F} + k_L p_i S_i}{k_L + \frac{D_i^{eff}}{\delta}} \quad \text{(eq. 4)}$$

One of the main uncertainties is the mass transport coefficient. To calculate it we have assumed a linear relation of k_L with electric current I.

$$k_L = a + bI$$

where a = 0.002 and b = 0.001

In this work a fixed H_2 solubility was used S = 3.8 e-6 mol/(m3*Pa), but better results could be achieved with a temperature dependent solubility.

Electrolyte mixing

An additional mechanism, which only occurs in AWE is electrolyte mixing. This relates to the common practice used in AWE to mix the catholyte and anolyte via a communication line between cathode and anode gas-liquid separators. This line ensures equal electrolyte concentration and equalizes pressure between the two vessels. Mixing of both streams is necessary because water consumption at the cathode would otherwise lead to a difference in electrolyte concentration over time. Despite this process cannot be defined as *gas crossover*, mixing the flows contributes to increased concentrations of H_2 in O_2 and O_2 in H_2. The contribution for the crossover due to the mixing of the two electrolyte cycles depends on the anolyte (F_a) and catholyte (F_c) flow rate, and it can be defined as in eq. 5, accordingly to de Groot et al.[2]

$$\Phi_{i,mix} = S_i p_i \left(\frac{F_a}{F_c+F_a}\right) F_a \text{ (eq. 5)}$$

Depending on the flowrate, the mixing of the cathodic and anodic electrolyte flows can be the dominant mechanism in AWE[1,18,22]. However, as it depends on the design of the complete alkaline system, this assessment may not be valid for all (commercial) systems. As already observed for other mechanisms, gas cross-over due to electrolyte mixing also increases with higher pressures due to the higher gas dissolution[2].

For mixed electrolyte systems, higher electrolyte flow rates can lead to higher hydrogen crossover[2,15]. This effect is relevant if the gas crossover by mixing is high (i.e. for pressurized AWE systems operating at elevated flow rates).

2.3 Modelling gas cross-over

2.3.1 Contributions to gas crossover for PEMWE and AWE

In this section, by simulating crossover behaviour under varying pressures, we aim to determine which mechanisms (See section 2.2) dominate under specific conditions, for AWE and PEMWE systems.

Figure 2.1 shows the hydrogen concentration for the PEMWE reference system at different pressures (atmospheric, pressurized to 30 bar *balanced* -equal pressures on both sides of the membrane, and 30 bar differential pressure), at nominal (100%) and partial load (20%). Figure 2.2 shows the corresponding information for AWE.

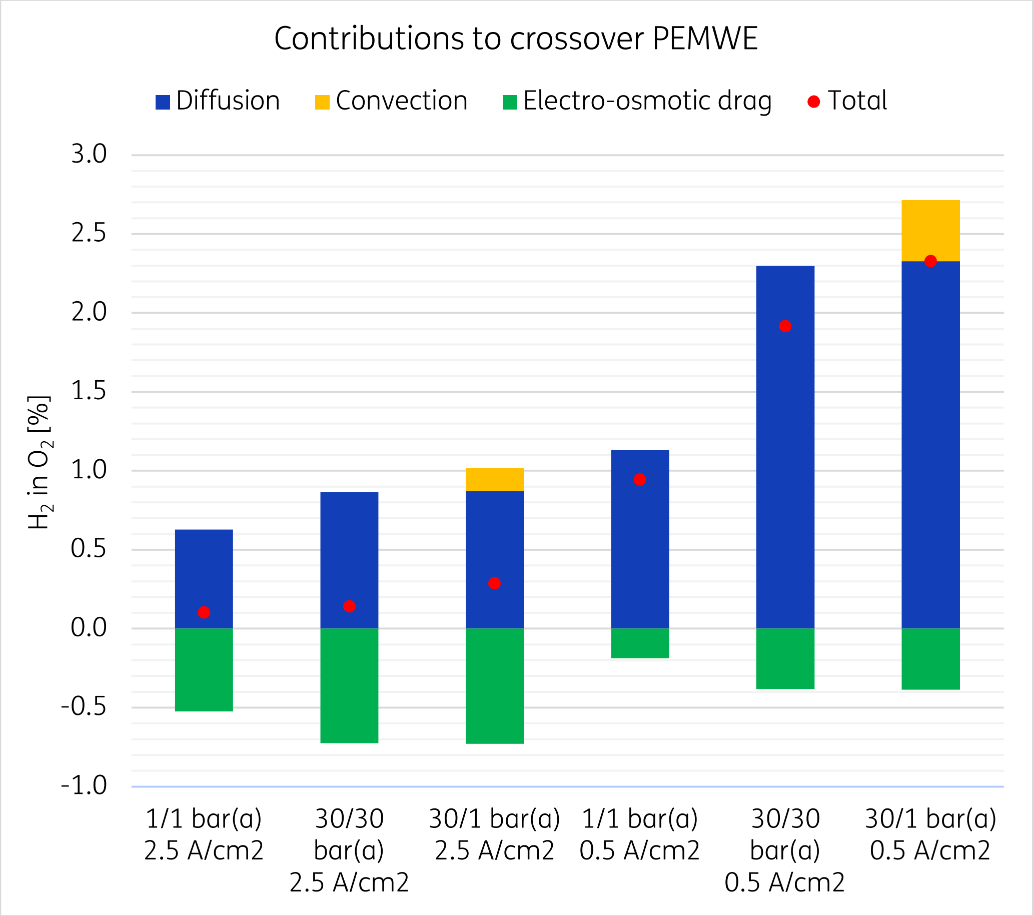

Figure 2.1: Results from the calculations in TNO gas cross-over model. The graphs show the different contribution of several operating conditions (pressure, load, current density) to the gas cross-over, for PEMWE technology at temperature = 80 °C and with Nafion 117 (membrane thickness is 180 µm).

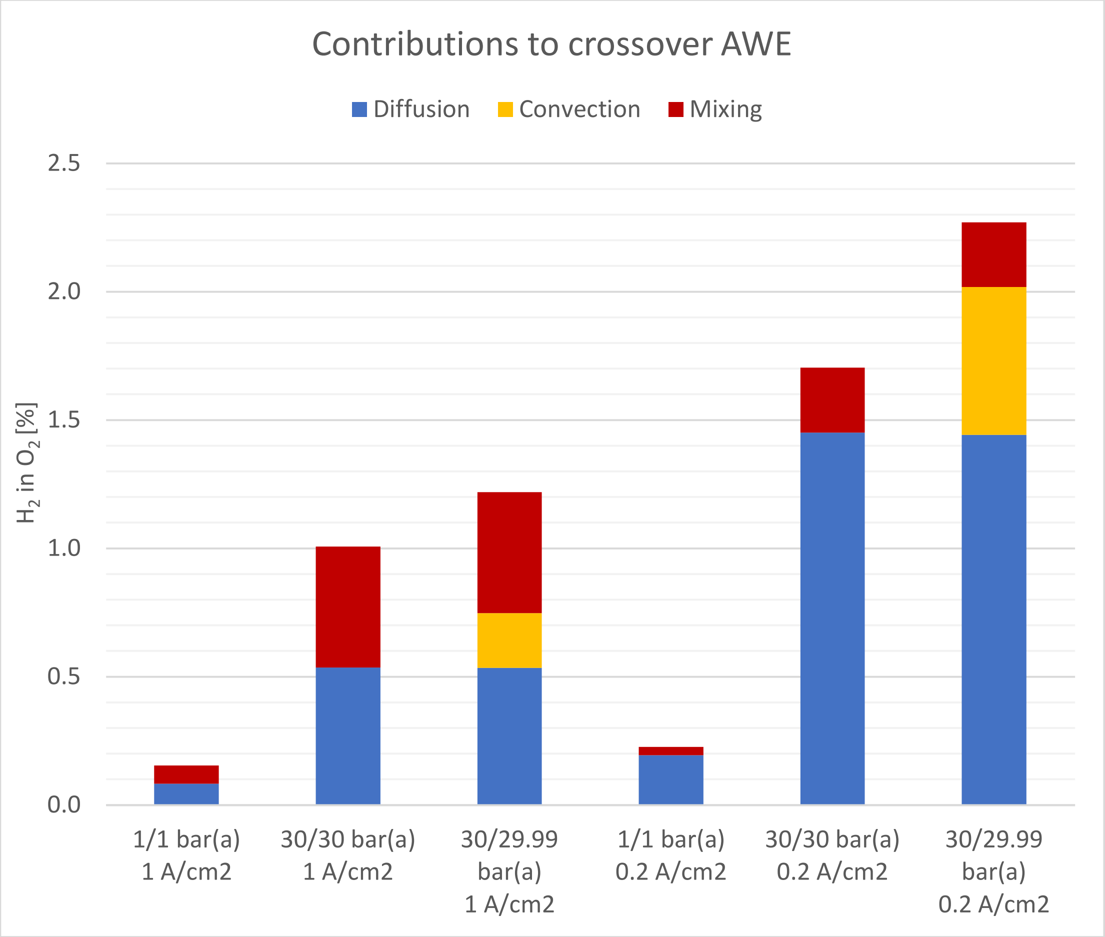

Figure 2.2: Results from the calculations in TNO gas cross-over model. The graphs show the different contribution of several operating conditions (pressure, load, current density) to the gas cross-over, for AWE technology at high performance zero-gap configuration, combined circuits, Temperature = 80 °C, p = 10 bar balanced (each side), Zirfon© membrane, thickness δ (200 µm), KOH (30 %), electrolyte flows ϕ (2.8 L/h) for a 100 cm2 cell area

Note that for PEM the differential pressure is equal to 29 bars (30 bar cathode and 1 bar anode), while for AWE the pressure difference across the diaphragm is only 0.01 bar (30 bar cathode and 29.99 bar anode).
The contribution of each *gas cross-over* mechanism is shown based on the color-coded legend on top of the graph. One should note:

- The supersaturation terms (cH2) are mostly included in the diffusion contribution (driven by concentration difference)
- In PEM electrolysis the electro-osmotic drag contribution to H_2 crossover is negative and lowers the hydrogen crossover correspondingly. Higher currents lead to increased electro-osmotic drag. The red dot in the diagram indicates the net effect.

There are important conclusions to draw from these graphs:

1. Operating at nominal load does not lead to hydrogen concentrations above the safety limit, even for pressurized systems.
2. Operating at partial load (<20%) and at high pressure is, however, potentially hazardous: both technologies require additional measures to ensure the safety of operations.
3. In AWE, small pressure imbalances (as low as 0.01 bar) can increase gas cross-over via pressure driven convection.

4. In PEMWE the convective contribution is less significant and, unless the membrane is damaged, it can withstand large pressure differentials. But the gas cross-over is high when operating at high pressure.

These conclusions should not be considered as a final assessment of the technology but as the starting point for the system design. As will be discussed in Section 5, measures can be introduced to reduce the impact of gas cross-over operate at high pressure. For AWE, for example it is shown that adapting the electrolyte flowrate to the operational current density can reduce the risk of reaching the critical safety limit for hydrogen concentration.[18] It is crucial to implement pressure control strategies. For PEMWE the use of a recombination catalyst makes operation at higher pressure possible. However, the results show the conditions under which a high gas cross-over needs to be taken into account.

2.3.2 Reference calculation for concentrations due to gas cross-over

Parameters

This model has been developed based on work previously published in literature and has been validated using TNO experimental data. The key parameters that influence gas crossover and are present in the model are:

- Electrolyte concentration (only for AWE)
- Diaphragm/membrane thickness
- Temperature
- Pressure and differential pressure
- Electrolyte flowrate

These crucial parameters are further explored and described in the sensitivity analysis (sections 2.3.3 and 2.3.4). It is important to note that there are other parameters which play a role in gas cross-over: for example, current quality (ripple)[23] is known to have an impact for AWE, but it is not considered the model, for simplification reasons.

The model simulates two selected reference cases, one per PEMWE and the second for AWE, for beginning of life conditions. These scenarios serve as basis for comparison in the following sensitivity analysis, where a few parameters were modified to assess their impact on gas crossover. The table below summarizes the main parameters used in the reference cases:

Table 2.3: Main operational and stack design parameters used for modelling the reference case scenarios.

	PEMWE	AWE
Temperature	80 °C	80 °C
Pressure	10 bar balanced (each side)	10 bar balanced (each side)
Membrane/diaphragm	Nafion 117 (membrane thickness 180 µm)	Zirfon© membrane, thickness δ (200 µm), KOH (30 %), 2.8 L/h electrolyte flows for a 100 cm^2 cell area.
Configuration		High performance zero-gap configuration, combined circuits

Reference scenarios results

Figure 2.3 shows the results for two base case calculations. As the nominal current density is different for both types of electrolysers, the horizontal axis in the figure has been normalized.

We have decided to focus this report only on the H_2 in O_2 concentrations due to the low reported concentrations of oxygen in hydrogen.[24] Oxygen crossover flux can be significant due to the effects of supersaturation, but recombination reaction at the cathode consumes most of it. Unless a catalyst with low activity towards the recombination of hydrogen and oxygen is used detected values at cathode will likely remain low.[25]

Note: The calculations in this chapter are meant to illustrate the different mechanisms and limitations, but of course are specific for the selected configuration and conditions and should not be interpreted as valid for all PEMWE or AWE setups and conditions.

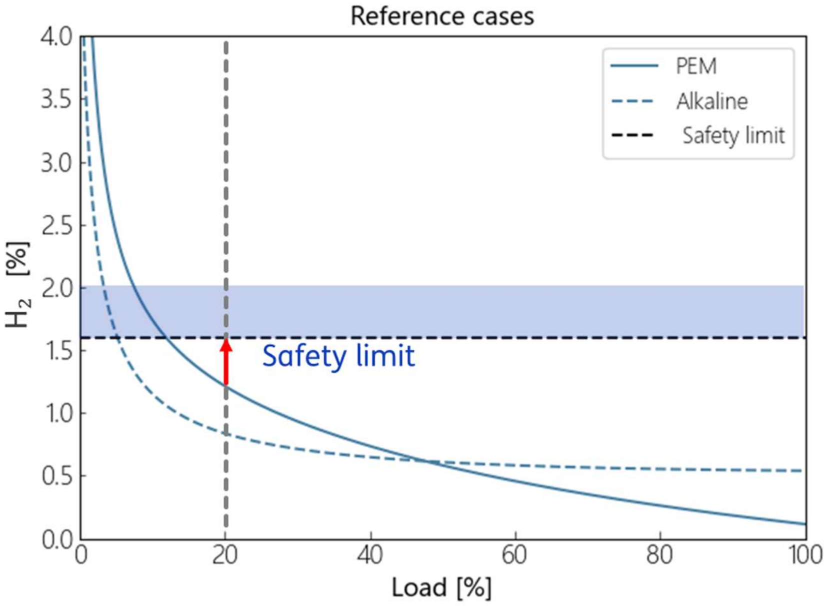

Figure 2.3: Results from the calculations in TNO gas cross-over model. The graphs show the hydrogen concentration on the oxygens side due to gas cross-over, for a reference system for both a PEMWE and an AWE electrolyser.

The reference case results suggest that hydrogen cross-over increases exponentially with decreasing load, as can be observed in Figure 2.3. above. This happens because, at low load, the oxygen production significantly decreases. In fact, it can be observed how even when the current density is zero there is a cross-over flow, despite no oxygen production. This implies that the hydrogen flow through the membrane is less diluted at low load, leading to higher concentrations than at nominal load. A practical consequence of the higher concentrations of hydrogen at lower loads is there is a minimum load at which no flammable mixtures are formed.

For the analysis in this report and practical application, we refer to the minimum load as the **minimum ratio of hydrogen-to-oxygen** (HTO). This safety threshold has been set to 1.6% hydrogen to oxygen. It Is important to note that the flammability range of a H_2/O_2 gas mixture is 4 – 94 % HTO (i.e., H_2 % in O_2 in dry conditions). In an actual design the safety threshold should assessed with the specific system in mind and can differ from the 1.6% chosen by us. To assess whether the concentrations in the electrolyser are below the safety limit under normal operating conditions, we have assumed the system is designed for 20% minimum load. For the PEMWE the current density ranges from 0.5 A/cm^2(min) to 2.5 (max)

A/cm^2. Correspondingly, for the AWE, which operates at a lower current density, the values are respectively 0.2 A/cm^2 (min) to 1.0 (max) A/cm^2.

Figure 2.3 shows that, under the indicated conditions, PEMWE and AWE manifest a similar behavior for HTO as a function of operating load. The HTO at low current densities is lower for AWE rather than for PEMWE, whilst the opposite is true at higher loads (above 50%), towards nominal conditions. This behavior is attributable to two main reasons:

- The solubility of hydrogen is higher in water than in the concentrate KOH solutions that AWE employs.
- At high load, as the current density increases, the hydrogen permeation rate decreases because of the countereffect offered by the electroosmotic drag. This effect is enhanced when using thicker membranes.

2.3.3 Sensitivity analysis for gas cross-over in PEM electrolysis

To understand the impact of variation of different parameters, a sensitivity analysis was conducted using the model. These results are a quantification of the mechanisms and processes described in Table 2.1 and Table 2.2.

2.3.3.1 Pressure

The operating pressure is one of the parameters with the largest impact on H_2 crossover in PEM water electrolysers. Increasing pressure reduces the requirement for mechanical H_2 compression to the delivery pressure and it has only a limited impact on the electrolyser performance (the reversible cell voltage increases with pressure).[26] *Higher operating pressure promotes gas cross-over.*[3]
Increasing the operating pressure from 1 to 30 bar (Figure 2.4) significantly limits the safe operating window effectively reducing load flexibility. At moderate differential pressures (< 5-10 bar) the impact on hydrogen crossover is small, as also described in literature.[7] Comparing the dotted (differential pressure) and solid lines (equal pressure on both sides) in Figure 2.4, it is clear that even at higher differential pressures (~30 bar) the impact of pressure difference remains limited. This indicates that *the crossover is mainly dependent on the cathodic pressure.* Diffusion, which is linked to the solubility and the absolute pressure, is the primarily contributing to gas-crossover mechanism whereas the convection mechanism driven by the the differential pressure . Thus, operating PEM electrolysers in differential pressure mode is practically possible, due to the limited impact on crossover (compared to similar balanced pressure) and the high mechanical strength of the membrane.[27]
Increased concentrations of hydrogen in oxygen can be readily reached at higher absolute cathode pressures (> 10 bar, both balanced and differential) and low current densities (< 1 A/cm^2).[28] This limits the minimum operating load due to safety issues, reducing the flexibility of the electrolyser.[3,29] For this reason, the adoption of recombination catalysts is highly recommended in combination with pressurized PEM electrolysis. A recombination catalyst is commonly employed as a layer close to anode catalyst with either a direct contact or separated by a thin layer of Nafion. This layer ensures that large part of hydrogen crossing over reacts with oxygen before it reaches the anode resulting in much lower hydrogen crossover.

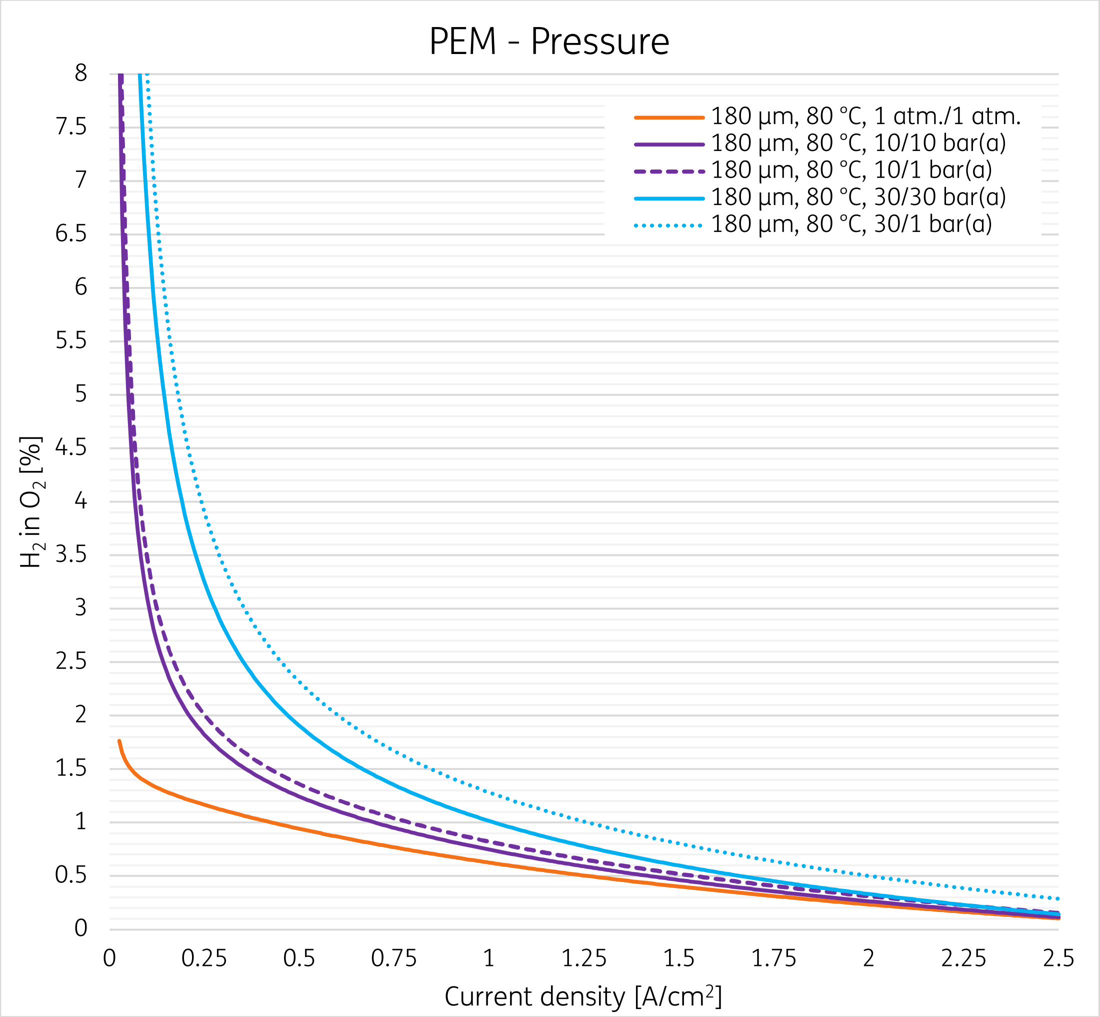

Figure 2.4: Effect of increasing pressure on the hydrogen concentration%. Graph shows the percentage of hydrogen in oxygen as a function of the current density, for a membrane with a 180 micron thickness. In orange, the pressure is balanced at 1 bar on both anodic and cathodic side. The dotted purple line represent a pressure of 10 and 1 bar on the cathodic and anodic side. The dotted blue line represents a differential pressure of 30 and 1 bar on the cathodic and anodic side. Finally, the blue and purple line represent a balanced pressure of 10 bar and 30 bar on both anodic and cathodic side.

2.3.3.2 Membrane

Thickness of the membrane greatly affects the permeability of both H_2 and O_2. The thickness of commercially available Nafion membranes for industrial scale PEMWE commonly ranges from 125 to 250 µm, even if Nafion membranes down to 25 µm are already being used for R&D applications.[30] Thinner membranes can produce H_2 more efficiently (i.e., lower ohmic losses); however, their use in combination with high operating pressures (> 4 bar) and low current density represent a tangible risk of explosive mixture at the anode.[3,28]

Gas cross-over in proton exchange membranes occurs primarily through the hydrated phase, thus fully wetted membranes are characterized by higher crossover, compared to the dry state.[6,7] Importantly, a good hydration level of the membrane is required to maintain a sufficient proton conductivity.

It should be noted that the formulation of the polymer is an important factor in the gas cross-over. It has for example been reported that H_2 crossover is reduced when using shorter polymer chains.[14,31] Polysulfone nanofibers have also been reported to effectively reduce the crossover of hydrogen.[14]

Similarly as with pressurized operation, thin membranes will require mitigation strategies such as recombination catalyst to combat gas crossover. Already 125 µm will result in a significantly constrained safe operating window.

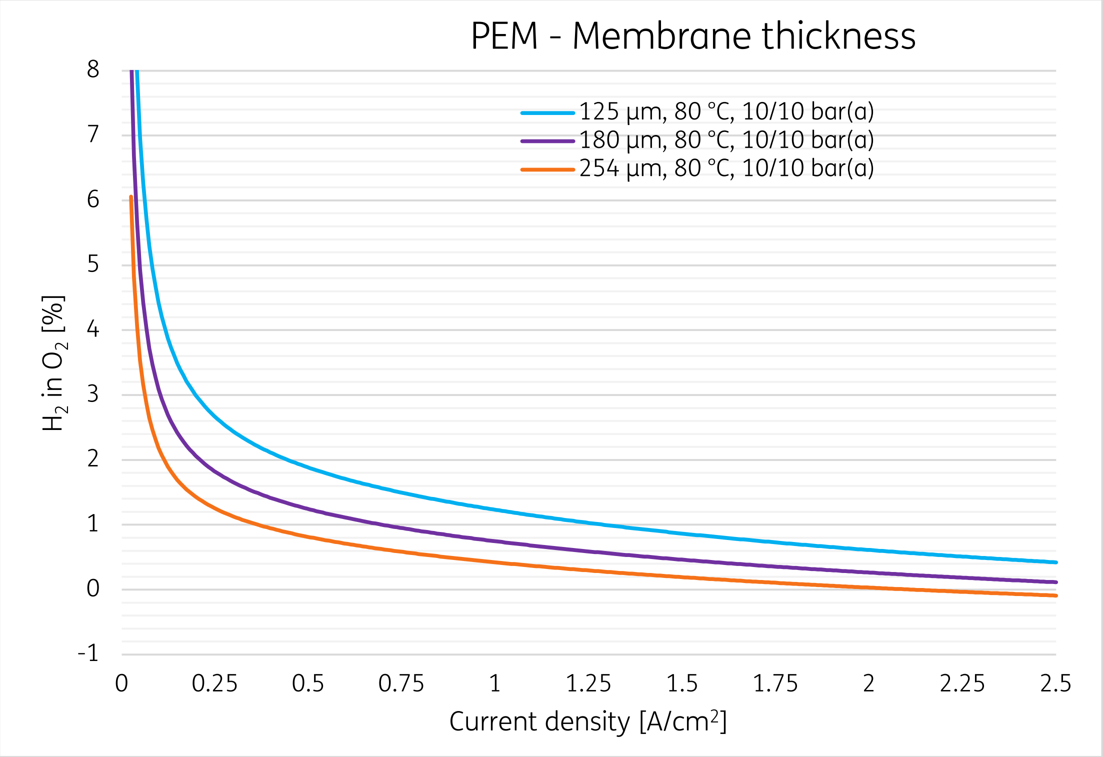

Figure 2.5: Effect of increasing membrane thickness on the hydrogen concentration%. It shows the percentage of hydrogen in oxygen as a function of the current density. The blue line represents the thinnest membrane of 125 micron, and the thickness increases to 180 micron (purple line) and 254 micron (orange line).

2.3.3.3 Temperature

Variations in the operating temperature between 60 and 100 ˚C lead to variations in hydrogen concentration in the produced oxygen (Figure 2.6). In general, a limited increase in operating temperature results in a reduced cell voltage (i.e., energy consumption), due to beneficial impact on multiple thermally activated and temperature dependent processes. The gas cross-over increases with temperature mainly due to larger diffusivity.[4] The model assumes a uniform temperature in the cell and does not consider a temperature profile across the membrane electrode assembly. However, during operation, as heat is generated close to the catalyst layer, the actual temperature in the membrane could end up being substantially higher than the temperature of the process flows[4,32]. Contrary to pressure and membrane thickness, temperature will not require the use of recombination catalysts just due to the temperature variation as it does not significantly constrain the safe operating window.

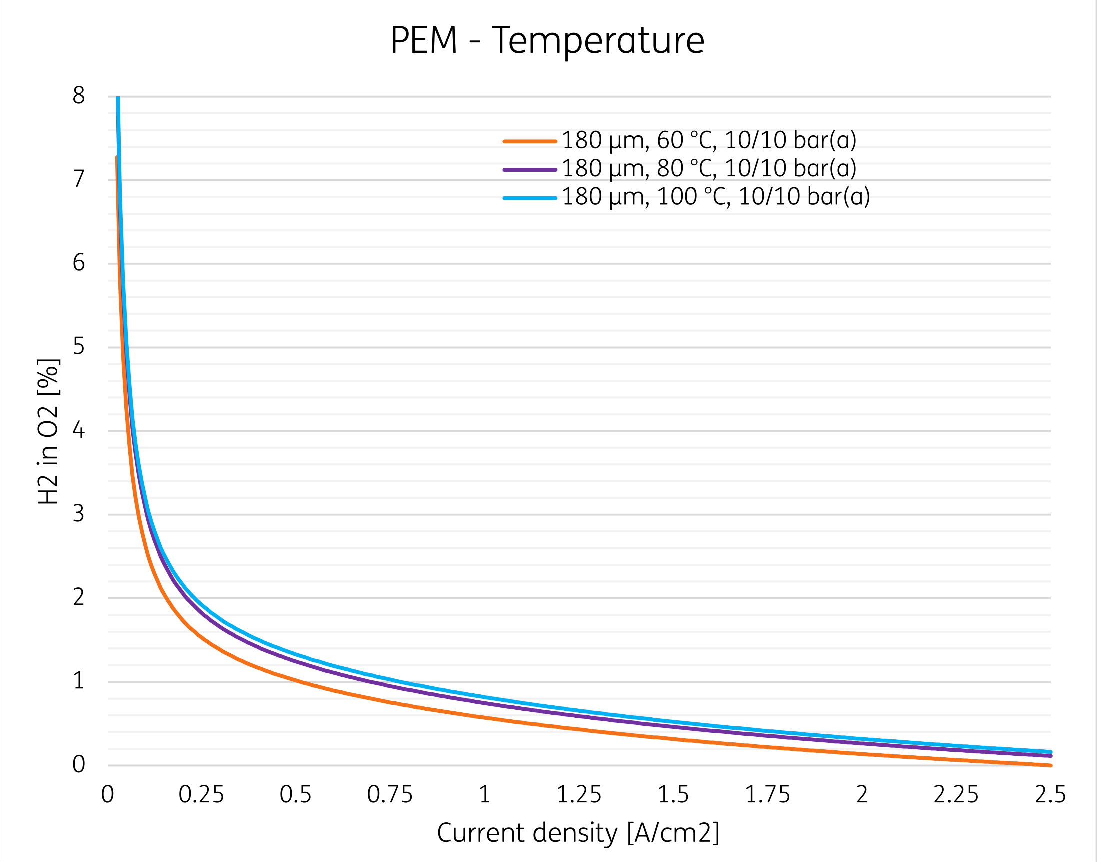

Figure 2.6: Effect of increasing temperature on the hydrogen concentration%. It shows the percentage of hydrogen in oxygen as a function of the current density. The reference case shows a membrane with a 180 micron thickness and a balanced pressured which features 10 bar on both cathodic and anodic side. The temperature increase goes from 60 °C (orange line) to 80 ° (purple line) and lastly 100 °C (blue line).

2.3.4 Sensitivity Analysis for gas cross-over in Alkaline Electrolysis

Similar calculations have been carried out to determine the impact of key parameters for gas cross-over in alkaline electrolysis. Parameters which have the most influence are the pressure and sepator thickness.

2.3.4.1 Pressure

Higher operating pressure increases the gas cross-over also in AWE.[2] The effect of pressure on gas cross-over becomes relevant especially when operating at partial load, with current densities lower than 0.4 A cm^{-2}. In AWE, the gas cross-over (H_2 and O_2) occurs primarily via the porous structure of the diaphragm, and the liquid phase within it.[33] As such, contrary to PEM, in AWE a differential pressure across the diaphragm, albeit of only few tens of millibar, causes a large increase in hydrogen crossover, and consequently higher hydrogen concentration (Figure 2.7Figure 2.7). The impact of pressure imbalance across the AWE diaphragm becomes more pronounced with increasing operating pressure due to the increasing amounts of dissolved hydrogen in the electrolyte. This trend is observable from the model calculations shown in Figure 2.7.

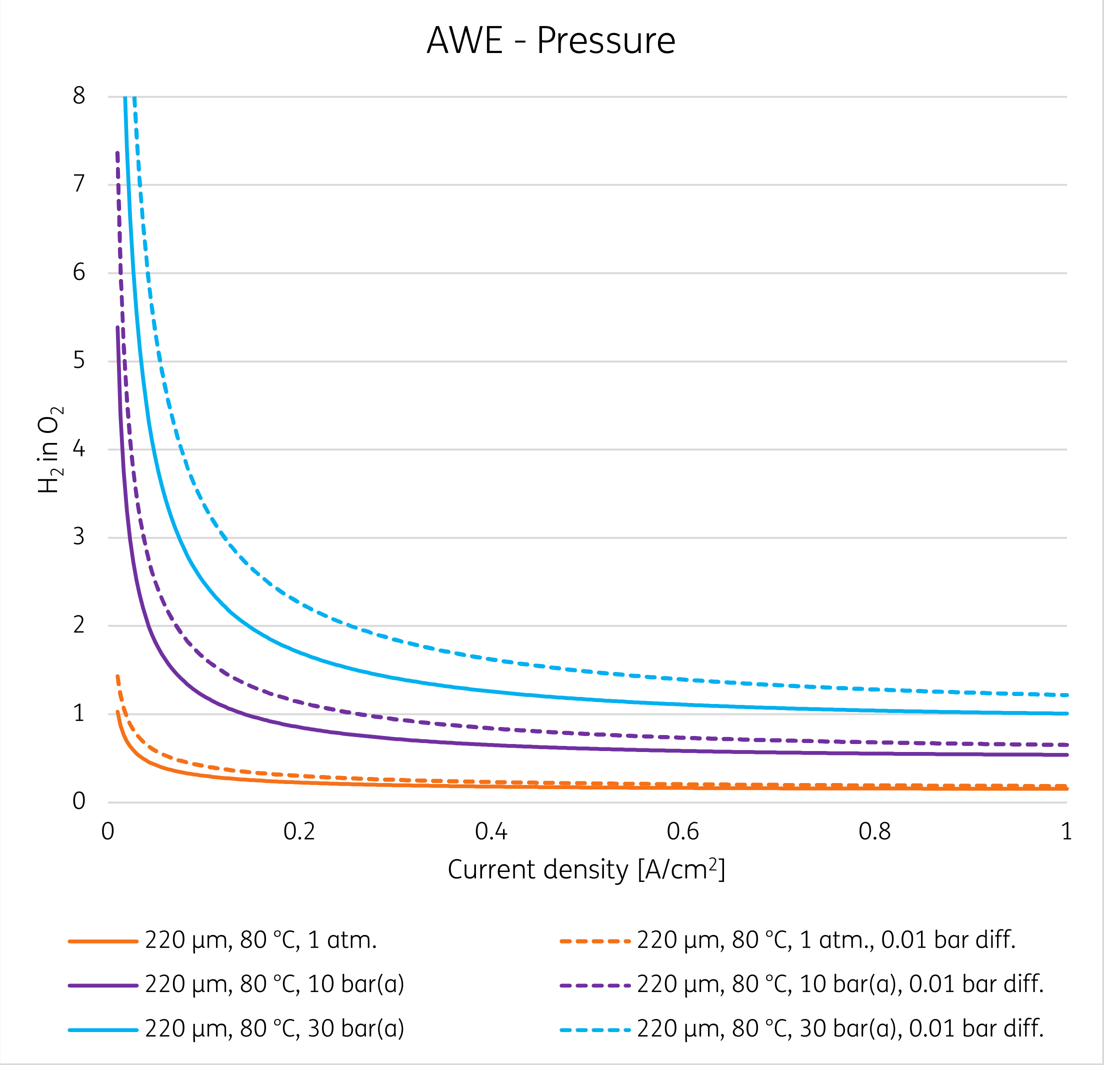

Figure 2.7: Effect of increasing pressure on the hydrogen concentration%. It shows the percentage of hydrogen in oxygen as a function of the current density. There are six cases displayed: The pressure is shown with an increase that goes from 1 atm (orange line) to 10 bar (purple line) and 30 bar (blue line). Differential pressure is more complex to achieve in AWE due to safety issues, therefore it is only considered a 0.01 bar differential (dotted lines).

In AWE with separated electrolytes, the diffusive crossover is dominant when operating at equal pressures, while already a limited differential pressure (> 0.01 bar)[33] results in a significant increase in convective transport through the diaphragm.[2] This suggests that even minimal deviations in the pressure control system of a AWE can result in a convective-dominated H_2 crossover regime. Therefore, an adequate pressure control in AWE is of critical importance. As such, improving the pressure control strategies and reducing the pore size has been shown to diminish the pressure driven convective gas cross-over.[34]

2.3.4.2 Diaphragm thickness

The most commonly adopted diaphragm for AWE in zero-gap configuration is known as Zirfon© supplied by AGFA, consisting of a porous polysulfone matrix with embedded ZrO_2 to enhance the hydrophilicity. Thickness of commercially available Zirfon© diaphragms for AWE commonly ranges from 100 to 500 µm. Thinner diaphragms enable operation at high current densities and efficiency, but enhance the gas cross-over and reduce the load flexibility of the electrolyser.[2]

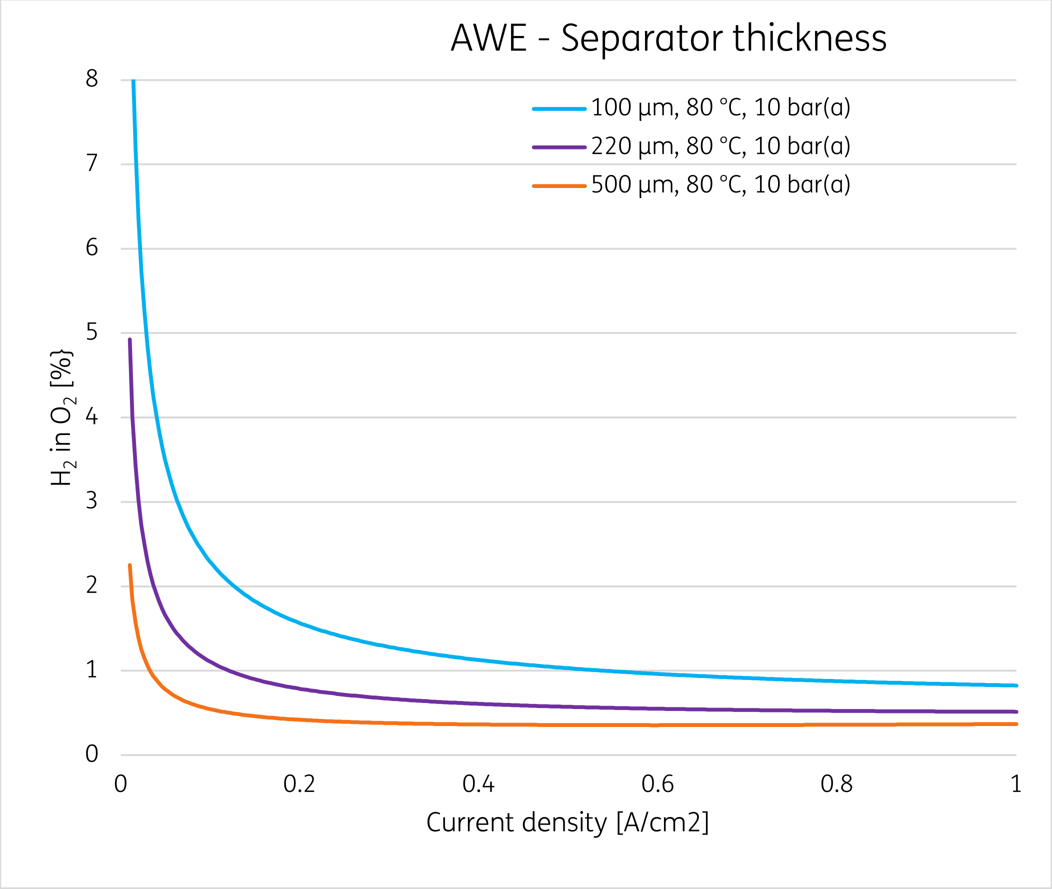

Figure 2.8: Effect of increasing pressure on the hydrogen concentration%. It shows the percentage of hydrogen in oxygen as a function of the Current density. The reference case shows a temperature of 80 °C. and a balanced pressure which features 10 bar on both cathodic and anodic side. The blue line represents the results for a 100 micron diaphragm. The results are also shown for a thickness of the diaphragm of 220 micron (purple line) and 500 micron (orange line).

2.3.4.3 Temperature effects

In AWE, temperature variations in the range 60 – 100 ˚C result in a considerable variation in hydrogen concentration (Figure 2.9). Higher temperature will result in an improved performance at the cost of increased gas crossover[35] and due to corrosion higher demands on the used materials.

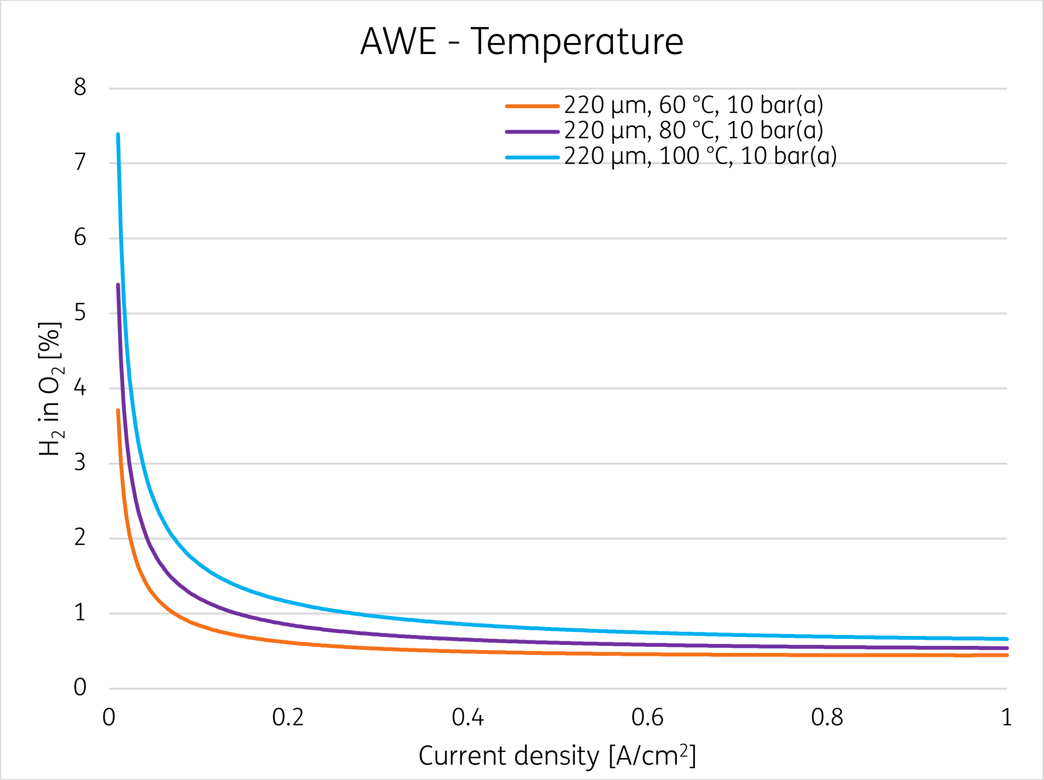

Figure 2.9: Effect of increasing temperature on the hydrogen concentration%. It shows the percentage of hydrogen in oxygen as a function of the current density. The pressure is kept constant at 10 bar and the reference case is calculated for a diaphragm with a thickness of 220 micron. There are three values chosen for the temperature: 60 °C (orange line), 80 °C (purple line) and 100 °C (blue line).

2.3.4.4 Hydrogen solubility

In AWE, hydroxide aqueous solutions, typically KOH or NaOH, are employed as electrolyte. High concentration are usually needed (about 30 wt.%) to ensure sufficient ionic conductivity, with a maximum between 30 and 33 wt.% for KOH. The poor solubility of H_2 and O_2 in concentrated hydroxide solutions limits greatly the diffusive crossover in AWE. Although a small variation (few percent) in the electrolyte concentration may influence the gas solubility, the impact on the gas cross-over remain limited (lower hydroxide concentration, higher gas cross-over).[15–17]

2.3.4.5 Electrolyte flow rate

The electrolyte flow rate has been reported to have a strong impact on both oxygen and hydrogen crossover in AWE.[15,36] The electrolyte flow rate shows a linear correlation with H_2 crossover.[15,16] Thus, slower electrolyte flow rate is preferred in terms of gas cross-over, but a suitable rate should be maintained for an efficient removal of bubbles from the surface of the electrode. A sufficient flow rate should also be maintained to remove the heat generated during the electrochemical reaction. A too small flow rate be detrimental to the electrolyser and could lead to failure.

3 Deviating from design conditions – degradation and non-uniformity

As shown in the previous sections, the conditions at which the electrolyser is operated have a substantial impact on the resulting gas crossover. The design choices of the electrolyser and balance of plant should be appropriate for the selected operating conditions and turn-down ratio. In this section we introduce concepts that are critical for the determination of safe operating window and which conditions can compromise it.

3.1 Trade-off efficiency and degradation

When operating an electrolyser, there is an important trade-off between efficiency and lifetime to consider. This trade-off makes the choice of operating parameters complex. One of the key parameters is the **temperature**. In fact, whilst on one hand high temperatures will improve efficiency, they will at the same time accelerate the degradation process. This complexity in balancing trade-offs does not only concern operating parameters, but also components and cell design. Thinner membranes/diaphragms show a lower ohmic resistance, but an increased gas cross-over, narrowing the operating window. Similarly, in AWE a smaller distance between the diaphragm and the electrode will improve performance, but also increase gas crossover[19]. As a result, a commercial electrolyser will ideally be operated at high efficiency but on the limit of what is an acceptable rate of degradation and gas crossover.

3.1.1 Membrane degradation in PEMWE

Many different degradation mechanisms are happening concurrently during operation in PEMWE, and while some will only have an impact on the efficiency and therefore economical aspects, others can directly influence the membrane, hence the gas cross-over. The degradation that impacts safety in PEMWE membranes follows two main mechanisms: chemical and mechanical membrane thinning.[37]

Although most degradation mechanisms will show as overpotential increase and lower performance, membrane thinning may show up as improvement in performance due to the thinner membrane. The most important mechanism for chemical thinning is the breakdown of the polymeric backbone, which occurs through three major steps:

1. **Formation of peroxides:** Due to the recombination of hydrogen and oxygen and/or (electro-)chemical reduction of O_2 to H_2O_2.
2. **Metal cations contamination:** Cation impurities coming from the stack or balance of plant from both cathode and anode are transported into the membrane close to the cathode interface.
3. **Radical attack**: Formed peroxide is catalytically converted by the metal impurities into radicals, with a mechanism similar to the Fenton reaction. Formed radicals attack the polymeric backbone leading to its gradual breakdown.

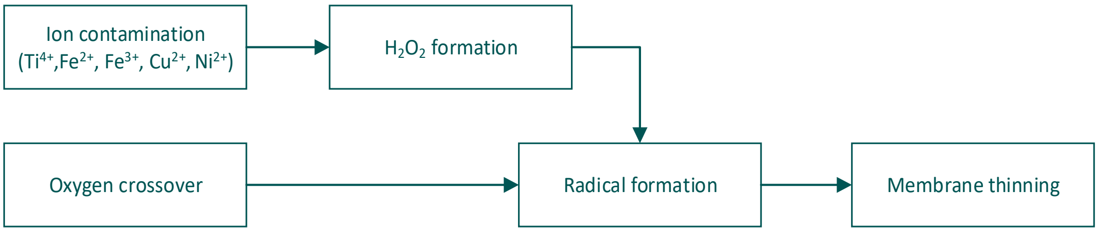

Figure 3.1: Membrane thinning due to water contamination.

When the polymer backbone of the membrane starts to degrade, it will start releasing fluorides (HF) and cleaving off polymeric chains[38,39]. It is therefore critical to minimize the number of contaminants, as already trace amounts of metals ($Ti^{4+,}$ Ni^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}) accelerate the rate of thinning.[5] The proposed mechanism in Figure 3.1, although generally accepted, is yet to be fully understood. Even though the reaction takes primarily place at the cathode, the contaminants from both the cathode and anode compartments cause problems. The cation-conductive properties of the proton conductive membrane cause cation impurities to travel through the membrane. In literature also other species such as Cl^- have been reported to cause an enhancement F^- release[40].
Cations (such as Ti^{4+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Na^+, Mg^{2+}, Ca^{2+}) will also degrade the performance. They block some of the protonic pathways of the membrane and ionomer present in the catalyst layer affecting the protonic conductivity.[10]

Apart from the already mentioned water impurities the rate of chemical membrane thinning can be influenced by low current and high temperature. At low current densities (<0,6 A cm^{-2}) [5,41,42] the rate of thinning is faster, because of a higher relative concentration of oxygen at the cathode (smaller hydrogen production). However, there are indications that current densities between 0,2 and 0,4 A cm^{-2} are the most damaging.[41,42] Dynamic operating profiles, such as a typical solar profile, with frequent operation close to 0 A cm^{-2} show faster membrane thinning rates. As a consequence, PEMWE that directly follows green energy profiles have to be more aware of the state of health of their membranes due to the significant difference in membrane material loss (fluoride release rates).

High temperature is another parameter that can significantly influence the membrane thinning rate and follows an exponential trend.[5,11,41,43,44] The actual rate of thinning will depend on the specific design of the electrolyser, such as membranes equivalent weight[45] and the usage of radical scavengers. This means that thinner membranes don't necessarily degrade faster than thicker membranes.

The mechanical membrane thinning mechanism is called creep. It is a process that manifests when membrane is compressed. The resulting force when applied on the active area of the membrane is called contact pressure. When membrane is subjected to contact pressure it shows a tendency to protrude into the porous structure of the porous transport layer (PTL). This protrusion as a consequence makes the membrane locally thinner making the distance between the electrodes shorter[46]. Higher temperature[47], coarser PTL[48] or higher contact pressure[46,48] will all cause the creep to become stronger. Contact pressure in particular needs attention as too little will result in poor electrical contact, while high contact pressure will improve performance[49], but also as mentioned make creep stronger.

3.1.2 Diaphragm degradation in AWE

As already mentioned in previous sections, Zirfon© is the most common commercial example of diaphragms for AWE. It relies on a polysulfone polymer backbone, which should remain stable up to 180 °C (the glass transition temperature). However, due to the presence of NaOH or KOH in the electrolyte, the environment in an AWE is highly corrosive. This significantly limits the safe temperature thresholds.

Depending on the electrolyser design, the diaphragm can have different degrees of support, which can influence the development of pinholes and tears. For example, in a finite-gap arrangement the diaphragm will experience over its lifetime significantly more mechanical stress than a zero-gap would. In some cases, during operation, the diaphragm can locally dry out (discussed further in section 4.3.2). This can cause significant issues as the diaphragm can not only lose some of its gas separation property, but also become brittle and develop cracks.

Unfortunately, the available information on the degradation mechanisms and durability is limited, especially so on long-term durability. This fact underlines the need for more research to be done on degradation and lifetime of diaphragms in AWE.

3.2 Non-uniformity

In previous sections we have defined degradation mechanisms and how they are influenced by different process conditions. In this section we would like to introduce the concept of non-uniformity.

Non-uniformity is a concept where the conditions of the electrolyser are not well distributed causing the electrolyser to either locally degrade faster or have an increased gas crossover. They are often interlinked, and one non-uniformity can result in another possibly originating from a stack design, or by process conditions set by the balance of plant (BoP) design. Examples of these hypothetical scenarios are described in Figure 3.2.

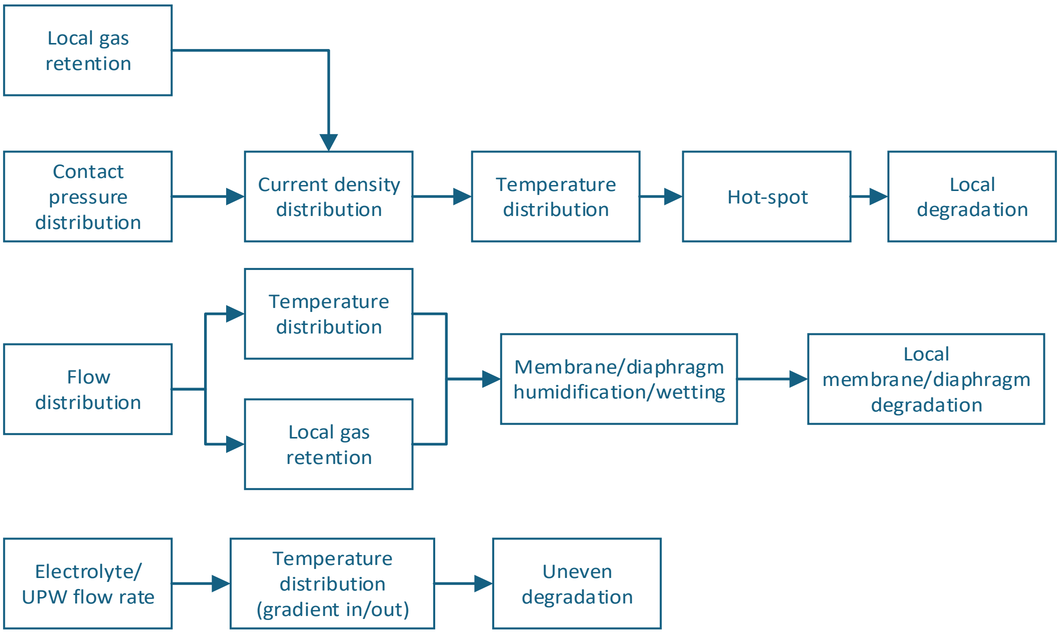

Figure 3.2: Example interactions between non-uniformity conditions and their consequences.

The interactions between the design, process parameters and degradation are often hard to distinguish, and information is still lacking in literature, but some indications can be found.

One such example is reported in literature, where the membranes from a 100 kW PEMWE pilot plant operating on renewable energy profiles were analyzed after H_2 in O_2 concentrations exceeded 3% during operation. Membrane analysis showed severe non-uniform membrane degradation likely caused by local mechanical and/or temperature effects. As the operating pressure was low (1-2 bar) the resulting gas crossover through the severely damaged membranes was not enough to reach an explosive atmosphere.[50]

Current density distribution is one of the key indicators for uniform conditions inside of the electrolyser. Factors such as contact pressure distribution[51] or local gas retention[52], caused by poor flow distribution or flow-field design, can result in uneven current density distribution and as a consequence can indicate local hotspots. These hotspots can then become the weak points of the electrolyser and have locally accelerated degradation. In PEMWE the hotspots will then follow the non-linear degradation profile similar to what is described in section 3.1.1.

Poor gas removal for AWE can stem from too low electrolyte flow rate and/or uneven flow distribution. The challenge is to obtain a uniform flow distribution over different cells but also, because of the large area of commercial system, a uniform flow distribution within the cells. In AWE a too slow flow rate or non-uniform distribution can have significant consequences. It can result in:

- Temperature increase due to the imperfect removal of gas bubbles, leading to locally reduced cooling.
- Gas hold-up creating gas pockets and dry spots that can potentially damage the diaphragm and/or reduce the separating function of the diaphragm which relies on the pores in the membrane being fully filled with liquid.

Unfortunately lack of available evidence makes this scenario a hypothesis.

4 Critical failures

With large scale deployment of electrolysers and highly competitive market the need for credible scenarios is growing. Although attempts have been made in describing the present hazard scenarios[53–55], due to lack of reported incidents defining credible scenarios remains difficult[56,57]. Although, the failure scenarios described are based on a combination of literature and interviews with industry experts, they are in the end hypothetical. For the scenarios to become credible more data and validation is necessary.

Because of what was discussed until now, it is crucial to understand *what makes a scenario critical* and *what marks the distinction between a safe and a hazardous scenario*. Thus, what are the additional conditions that can accelerate the degradation processes to a point where they become high-risk. A critical failure scenario is thus a failure scenario that has escalated due to the specific design and/or process flaws promoting degradation and/or non-uniformity.

4.1 Failure classification and selected scenarios

Degradation processes alone, when manifesting under uniform operating conditions, can be noticed in time with monitoring tools such as gas analyzers, cell voltage monitoring, conductivity, temperature and promptly tackled. However, it is clear, especially from interviews with experts and review of incidents, that non-uniformity plays an important role and often appears as the factor discriminating between a hazardous and a non-hazardous event. There are three different implications related to non-uniformity which make it crucial in the context of critical failures:

- Non-uniformity can lead to **local** conditions upset which are beyond the operational limits (e.g. hotspot), but which are difficult to observe.
- Non-uniformity, especially because it can remain hidden, can contribute to the *abruptness of a critical failure*, making the failure unexpected and therefore unpredictable. For example, if you have multiple stacks connected to one separator and several cells of a single stack are failing measured concentration may be (far) below LEL, while a combustible mixture occurs in a stack, cell or tubing.
- System design, such as system volumes and sensor response time, can determine the effectiveness of sensors at prevention of hazards. For example, in the case of PEM electrolysis the operating differential pressures can lead to rapid mixing in the case of a critical membrane failure. In the case of a pressurized alkaline system, pressure loss on either side can lead to a rapid increase in concentration making gas analyzers too slow to react.

Based on these considerations, we have identified four critical scenarios:
1. Critical pinhole (PEM)
2. Short circuit (PEM)
3. Pressure difference (AWE)
4. Dry spots (AWE)

These four scenarios are chosen to represent the outcome of the combination of non-uniformity and degradation.

4.2 Failures in PEM electrolysers

4.2.1 Critical pinholes

Based on the experience from fuel cells, the occurrence of small pinholes in a membrane is likely. When these holes do not exceed the critical size, they can be regarded as non-hazardous, and it is expected that their presence will not interfere with the electrolyser operation. In the figure below, it is possible to observe some identified steps that can lead to membrane perforation. The introduction of foreign material during, for example, assembly or maintenance can play a crucial role in this scenario.

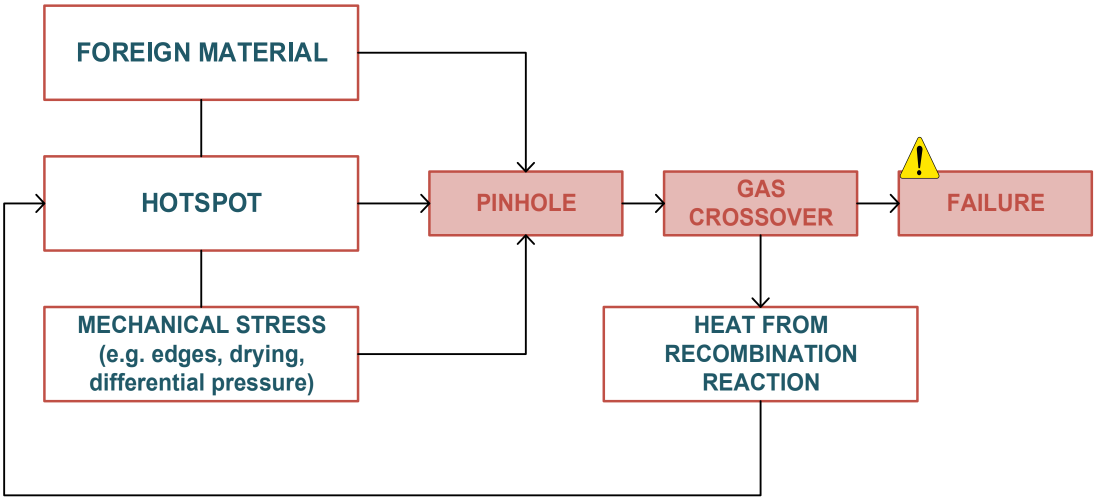

Figure 4.1: Possible scenarios for development of critical pinholes

Uneven clamping, sharp edges and gaps[58,59] where membrane is unsupported could result in a quick development of tears and pinholes, whilst drying and humidification cycles such as nitrogen purging during shut downs will lead to pinholes over time.

As the pinhole grows larger, the subsequent flowing hydrogen may begin to react with the oxygen, generating small hotspots[56]. The hotspots resulting from local heating caused by the gas reaction could accelerate membrane's breakdown processes. This effect is well-researched in PEM fuel cells[60], but not so much in PEM water electrolysis. The role of recombination catalysts, which are often employed to combat excessive gas crossover, is not known and could negatively influence the previously mentioned hot-spot formation.
This situation may result in a loss of control and therefore escalate rapidly to a hazardous scenario.

4.2.2 Short circuit

The puncturing of the membrane could be further accelerated by a “short-circuit”.
A short circuit occurs when anode and cathode make a direct connection while a potential is still applied: this causes local heating that could destroy the membrane[56]. In the picture below, the scenarios leading to this failure are identified and displayed.
There are three main mechanisms leading to this failure:

- Direct membrane puncture for example by a stray PTL fiber or sharp edges

- Proton exchange membranes show a tendency to creep. When creep occurs, the distance between the electrodes is reduced.
- Proton exchange membranes get thinner during their lifetime. Operating the electrolyser at high temperatures can accelerate this process, leading the electrodes to come closer together.

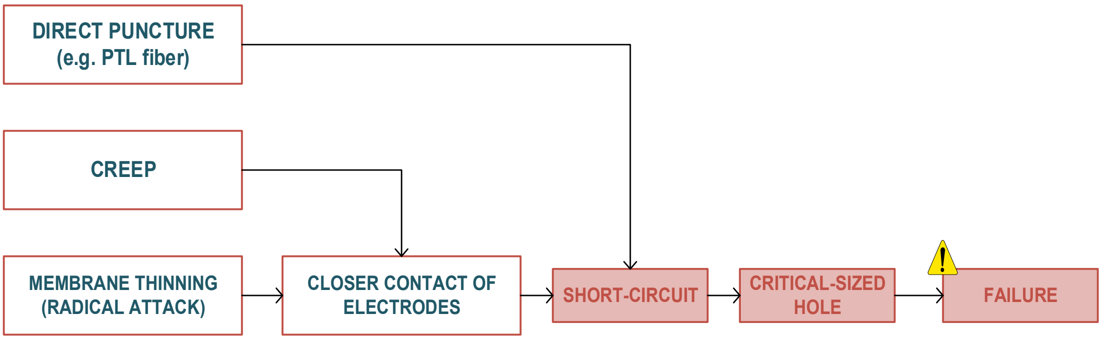

Figure 4.2: Possible scenarios for development of a short circuit in a PEM electrolyser

When healthy, the membrane acts as an electric isolator between the electrodes, but degradation can cause the electrodes to quickly come closer together.
Similarly, as with the pinhole discussion during operation small shorts-circuits can also be observed, but these do not necessarily pose an immediate risk.

4.3 Failures in alkaline water electrolysers

4.3.1 Critical differential pressure

Pressure differences between the two sides of the cell have a limited impact for PEM electrolysers, which feature a solid membrane. However, this aspect becomes crucial when discussing in-equipment mixing in alkaline technologies, since they feature a porous diaphragm. Due to the porous nature of the diaphragm the pressure differential at which the electrolyser can operate is small and only becomes more critical when combined with a diaphragm with pinholes, cracks and tears. These can be caused for example by wear and tear, overtightening of the electrolyser, or drying of the diaphragm.

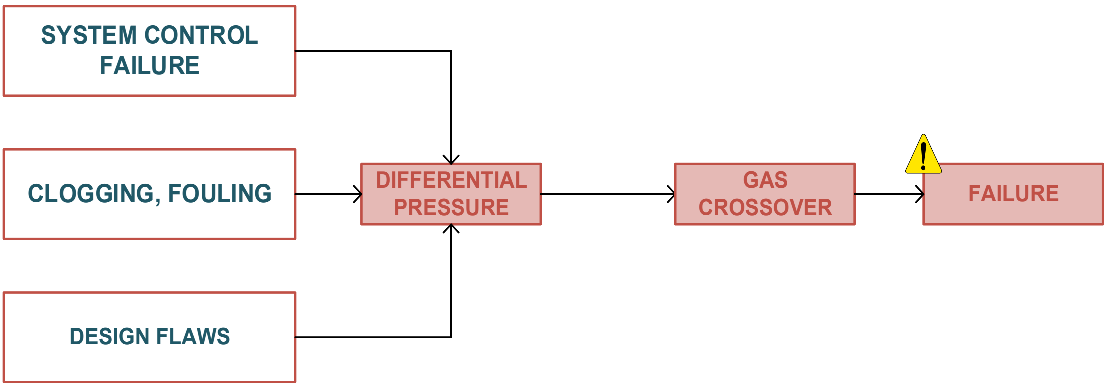

Figure 4.3: Possible scenarios for development of critical different pressure in an alkaline electrolyser

Having a strict pressure control system and optimized hydraulic design is of utmost importance in prevention of critically high differential pressure.

4.3.2 Dry spots

A dry spot in an AWE is an event that occurs when the diaphragm dries out due to the formation of a gas pocket. They generally form in locations with poor gas removal or in locations prone to gas accumulation. In the scheme Figure 4.4, we show the factors contributing to this failure:

- Flow restriction (e.g. blockage caused by impurities such as sludge) appears as one of the crucial factors. In fact, a proper flow distribution is necessary to maintain a proper bubble evacuation and uniform temperature across the cell.
- Design flaws in the cell design can result in having an area with too much accumulated gas ultimately leading to dry spots. One such example is the top of the cell, where due to the higher gas content a gas pocket can occur.

When a gas pocket is formed, the local temperature will start to increase, resulting in the formation of hotspots. A hotspot in combination with a gas pocket, can lead to loss of liquid from the pores in the membrane resulting in a significant gas crossover increase. Drying and an increased local temperature can also lead to damage to the diaphragm.

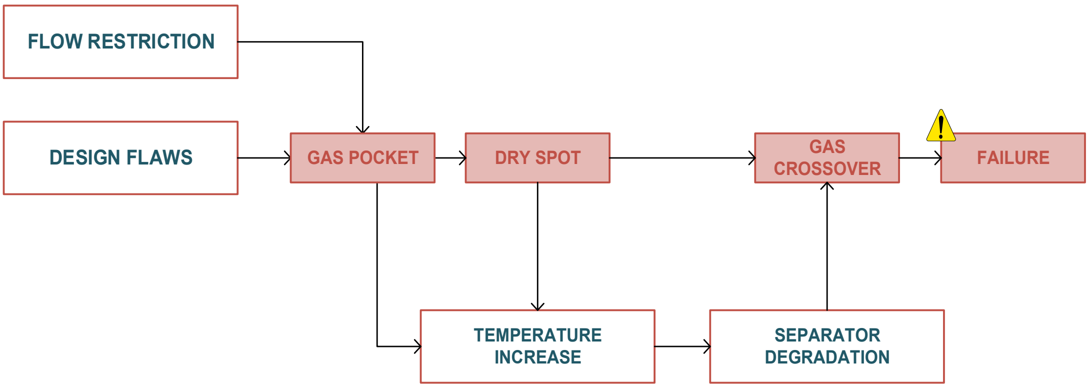

Figure 4.4: Possible scenarios for development of a dry spot in an alkaline electrolyser

5 Design Requirements for Safe Operation

It is generally understood that an electrolyser will degrade over the course of its lifetime: For this very reason, it is important to strictly follow a proper maintenance- and operations program, which can assure the purity of the water and the electrolyte solution, and the right functioning of equipment such as valves and compressors.

The foregoing sections extensively discuss the risks related to gas crossover both in normal and abnormal operating conditions. Based on the selection of critical failures in the previous section, several critical aspects in the ***electrolyser stack design*** and in the ***system design*** can be indicated. Although a full systematic analysis of barriers is out of scope, in this section, we consider which are the key requirements for both PEM and alkaline water electrolysis stacks and system to minimize the critical failures.

5.1 Stack design requirements

5.1.1 PEM stack design requirements

From the discussion on potential critical failures, it is possible to derive requirements for the electrolyser stack design. An example of such a requirement is that design (and operation) should guarantee that the membrane remains well humidified. As indicated, repeated cycles of drying and humidification can lead to the formation of pinholes which is one of the potential failure mechanisms.
Depending on the cell design, the water can be supplied to the electrolyser stack at the oxygen side and/or hydrogen side and is distributed over the individual cells. In each cell the water moves from the channels of the flow field through the PTL to the membrane. However, at the same time the gas, which is formed at the interface of the anode electrode and the membrane, has to move from the interface to the channel, in counterflow with the liquid. One challenge is to design the electrolyser cell in such a way that the oxygen does not accumulate in the electrode thus blocking the water from reaching the electrode and (locally) drying the membrane.

As the heat generated in the catalyst layer and membrane needs to be removed through the PTL, gas accumulation might lead to local hotspots. Low water flow rates and high current densities are the operating conditions at which blocking gas hold-up may occur. Avoiding local hotspots requires[61]:

- A uniform distribution of flows over cells and channels to avoid that some channels have low flow.
- A matching design of the electrode geometry with the flow field design (i.e. the dimensions and pattern of the channels).
- An appropriate compression to ensure good mass transport in the system.

More general, the two scenarios identified which could lead to a sudden failure in the PEM electrolyser are related to membrane integrity. Therefore, all design aspect which relate membrane degradation are important. Most importantly the following factors:

- The membrane needs to be evenly supported to prevent mechanical damage. In particular areas where the membrane is clamped or where different components connect (for example the boundaries between the flow-field and the frame or sealing area) are critical locations.
- Well-designed flow distribution (flow-field design, manifold design) to prevent maldistribution of liquid to avoid either temperature differences or low flow conditions in parts of the cell.
- Appropriate cell compression is necessary to avoid bad (electrical) contact, excessive mechanical loads (creep) and increased gas crossover.
- The design of the catalyst layer is important. For example, excessive ionomer content in CL can lead to mass transport limitations and in turn higher gas crossover.[62,63]
- PTL should have appropriate porosity, pore size and contact angle to avoid creep and drying.
- Sharp edges and foreign material need to be avoided as they can cause punctures and pinholes.

Use of recombination catalyst in high pressure PEM electrolysers

As the calculations in Section 2 demonstrate, for PEM electrolysers operating at high pressure (e.g. 30 bar at the hydrogen side), the gas crossover will significantly limit the safe operating window especially since aging will increase the crossover further. Therefore, for these systems incorporation of a recombination catalyst to avoid high hydrogen concentrations at the oxygen side is essential. Generally, the catalyst will be either with or without anode contact in the membrane. Based on discussion with experts, we conclude that it is possible to create a recombination catalyst layer which will be stable and highly efficient. Although long-term behavior of such a catalyst layer is not yet well-known, potential degradation mechanisms such as dissolution of the catalyst will occur gradually and can be detected by gas analyzers before leading to safety issues.

5.1.2 Alkaline stack design requirements

The diaphragm used in the alkaline electrolyser stack is mechanically robust and under normal conditions mechanical damage leading to a critical failure is unlikely. However, conditions such as overtightening, drying, hotspots and pressure imbalances can make the diaphragm more susceptible to mechanical damage and critical failure, especially so when thinner diaphragms are to be used. Careful design of the electrolyser and the system plays a key role in avoiding failures. Most importantly:

- Good flow-distribution over cell and stack is critical and needs to be kept even during start-up and shutdown.
- The diaphragm should always be immersed in liquid to keep its function as a barrier. If gas is allowed to accumulate this can lead to dry spots with potentially uncontrolled gas crossover as a result. Avoiding such gas pockets depends on the system operation (see Section 5.2) but also on the hydrodynamic design of the electrolyser.
- Electrode design and mounting is critical as uneven contact can lead to hotspots (e.g., as a result of bubble retention) and subsequent pinhole formation.

5.2 System design requirements

In addition to a good design of the electrolyser stack, the whole system around the electrolyser needs to be designed in such a way that the plant can be operated in a safe manner. The main functions of the system include:

- Supplying a clean flow of electrolyte to both anode and cathode compartments;
- Controlling the temperature of the electrolyser by regulation of the process cooling;
- Maintaining the desired absolute system pressure and maintaining the desired pressure difference between the anode and cathode;
- Separating oxygen from the anode flow and hydrogen from the cathode flow;
- Conditioning (drying, compressing, purifying) the produced hydrogen.

The pumps, compressors, heat exchanger, reactors and other process equipment used to enable the operation of the electrolyser stack is often denoted as the “balance-of-plant”. This system consists of conventional components which are widely used in the petrochemical process industry. Therefore, the safety related characteristics of the system can be assessed with data from conventional tools and databases. In this analysis we therefore focus specifically on the functional requirements to safeguard the safe operation of the electrolyser. In other words, which specific events in the system could lead to failures in the electrolyser stack.

5.2.1 PEMWE balance of plant requirements

Analysis of the failure scenarios discussed in Section 4.2 leads to the following requirements for the PEM electrolyser system.

- Operation at low loads (<50 %) and at high pressures is critical and it requires attention to avoid high concentration of hydrogen in the oxygen. A minimum safe load must be determined depending on the specific design and operating conditions. At nominal load the hydrogen in oxygen concentrations and vice versa are expected to be low. It is expected that with widespread recombination catalyst layer use, minimum load of 10% is going to be normal practice.
- High water purity is required because already trace amounts (ppm) of metal ions can accelerate membrane thinning due to chemical degradation. This requires the feed water to have the required purity. However, this does not guarantee high purity at the inlet of the electrolyser; ions leaching from the metal parts in contact with the process water, for example in the recycle loop, can reduce the purity. Therefore, purification of the recycled flows may be required to achieve the proper specifications at the inlet of the electrolyser. Best practice in the industry is to keep the process water conductivity < 0.1 µS/cm at 25 °C.
- The required flowrate may be varied based on applied current. However, low process water flow rates should be avoided to prevent water starvation. The minimum flows should take into account non-uniformities, such as the flow distribution inside the electrolyser, compression, etc.
- Temperature gradient across the cell should be kept small to avoid differences in degradation, while avoiding excessive flow rates. Good practice is to set the gradient at ≤ 5 °C.
- Given the gradual degradation of performance and potentially increasing gas crossover it is important to monitor the state-of-health with methods such as gas analyzer, temperature gradient and stack operating voltage.
- As shown, the PEM electrolyser is robust against pressure variations in a well-designed electrolyser and the system design is not critical with respect to maintaining a given pressure difference between the anode and cathode side of the electrolyser.
- DC current should not contain excessive residual ripples to prevent efficiency losses.

5.2.2 AWE balance of plant requirements

The two critical failure scenarios for the AWE are both based on excessive gas crossover. While the challenge to avoid dry spots leading to excessive gas crossover sets requirements mainly on the electrolyser stack, the challenge to keep the pressure differences within strict limits requires an appropriate balance-of-plant or system design. As shown in the model analysis and confirmed in the expert interviews, already pressure differences of 10s of millibars can lead to substantial gas crossover. Note that pressure difference of 10 mbars used in our calculations in section 2 will likely be exceeded in a real large scale system and will change with the load.

In general, the design of an AWE system uses a passive method to limit the pressure difference between anode and cathode. This is achieved by adding a balancing line, which is a connection between the hydrogen and oxygen separators connecting the liquid volumes in both vessels. If a pressure difference occurs between the two sides in the electrolyser, a flow will result to compensate for the pressure difference. As long as there is a very limited pressure drop between the electrolyser and both separation vessels, an almost equal pressure can be assumed at the outlet of the electrolyser between the anode and cathode side. However, some designs consider valve in the balancing line to battle crossover at low loads and some use two pump system instead of a single pump. Avoiding mixing of anolyte and catholyte is called split electrolyte circulation, while the more traditional that mixes the two streams is called mixed electrolyte circulation. With these designs special care should be taken to prevent differential pressure at the level of the diaphragm.

A list of requirements for a safe design of the electrolyser plant includes:

- Precise balance pressure control to avoid high crossover and damage to the zero-gap configuration. Especially during dynamic load changes, where stability is difficult to maintain.[64]
- Operation at low loading (depending on the exact design of the electrodes and electrolyser but indicatively <50%) and at high pressures is critical due to the higher solubility of hydrogen and oxygen at higher pressures. It requires attention to avoid high hydrogen concentration at the anode and vice versa.
- Different measures have been discussed to keep concentrations well below the explosion limits:
  - To limit the gas crossover due to mixing of the electrolyte streams, alternating split/mixed electrolyte cycles, and regulation of the flowrate can be used to reduce concentrations.
  - Temperature control can be leveraged to limit the impact of crossover at low loads. As shown, this can be part of an operating strategy to enable safe operation even at low loads and high pressure.
- DC current should not contain excessive residual ripples to prevent efficiency losses and potentially gas crossover.
- Potential maldistribution of electrolyte flows is a key factor which can contribute to hotspots and gas pockets. An important aspect is to handle impurities (e.g., corrosion products) to prevent blockage (sludge) in the electrolyser system.

5.2.3 Measuring H_2 in O_2 and O_2 in H_2

An important part of safe operation of an electrolyser plant is monitoring critical parameters. Evidently, mixing of hydrogen and oxygen is an important concern, measuring concentrations is essential. Gas analysis is thus widely used. Measuring hydrogen concentration in oxygen and vice versa can help track gradual processes and prevent dangerous mixture from building up in the separator and in the downstream components.

With the ignition probability unknown, two situations need to be considered:

- Ignition before the mixture reaches the separator with either an explosion or a flame within the electrolyser stack.
- Ignition after an explosive mixture is formed in the separator.

Looking at the two scenarios, it can be said that the first scenario is likelier to occur, while the second is significantly more hazardous.

To reduce cost when scaling up, often the use of a single separator for several stacks is considered, with measurement of the concentrations at the outlet of a separation vessel. In this situation, concentrations at the point of measurement will be different than the actual concentration occurring upstream.

There are different types of gas analyzers and sensors available even though oxygen rich environment places some restriction on the selection. Sensors such as binary gas thermal conductivity sensors can be used to continuously analyze a gas mixture in a humid gas, but they can be less precise. On the other hand, gas analyzers such as gas chromatograph can precisely measure, but the sample frequency can be slow and their use as a safety device can be questionable.

Monitoring of individual stacks can be achieved with a limit on the number of stacks connected to a single separator but measuring closer to the stack can only be done with novel designs. Example of such a design can either be sensors that can measure in a two-phase flow (e.g., optical sensors for dissolved gases) or use traditional sensors and separate the liquid with a mini separator. However, such systems are currently not yet commercially available.

5.2.4 Limitations to monitoring gas concentration

Gas composition monitoring is an effective way to assess whether the gradual increase in gas cross-over leads to concentrations which exceed the safety limits. Therefore, gas analysis is considered a standard practice, when operating electrolysers, as it can help track the development of potentially hazardous situations.

However, for an accurate measurement the flow should not contain liquid, while the flows coming from the electrolyser contain a large amount of water. Therefore, it is common practice to monitor the concentrations at the outlet of the gas/liquid separation vessel. This means that there is considerable time-lag in the measurements. In addition, depending on the choice of the type of gas analyzers, an additional delay may occur in the measurements.

The degradation processes described in the previous section are gradual processes. As long as the right value is selected for the threshold, there will be sufficient time to bring the system into a safe state when the degradation becomes too high. However, there are two important conditions for concentration monitoring as safeguarding option. *It is only sufficient:*

1. *if the increase in gas cross-over is indeed longer than the time-lag in the measurement:* If the increase in cross-over is fast or sudden, accumulation of a gas mixture with concentrations beyond the safety limit can occur before the event is registered by the measuring device.
2. *if the degradation is uniformly distributed over the electrolyser stack:* If the membrane in a single cell in a stack has degraded more strongly than in the rest of the cells, the concentrations in this cell could even exceed the LEL, but downstream mixing of the flow of the different cells could dilute the concentration before reaching the separator. Therefore, it is important to understand to what extent degradation and gas cross-over will be non-uniform.

5.2.5 Other measurements

Although direct measurement of concentrations at the relevant locations would be preferable, there are considerable challenges in monitoring, for example because of dilutions (e.g., multiple cells feeding a single header or multiple stacks feeding a single separation vessel) and, because of the challenges measuring concentrations in a gas/liquid mixture. Therefore, indirect methods are used as well to assess whether critical mixing occurs or might occur. The most important methods are described below.

Cell voltage measurement

The use of cell voltage monitoring is currently a highly debated topic. Some experts consider cell voltage monitoring as potentially beneficial in terms of safety while others consider it only useful for performance tracking. Although it is possible to identify a hole in the membrane beyond a certain size and short-circuit, smaller issues such as pinholes will be hard to identify.[65] To be able to identify deviations in performance in an early stage, cell voltage monitoring will need to be based on comparison of the cell voltage of an individual cell with the expected value and therefore requires some form of modelling of the expected behavior. Another consideration should be that cell voltage monitoring reacts only after the failure and is therefore not a preventive measure. However, it might allow a quicker response than in the case of a monitoring system in the downstream vessels.

For companies the price of single cell voltage monitoring often outweighs the questionable benefits. With that being said cell voltage monitoring is a mainstay in chlor-alkali industry and is considered as a crucial measurement for safe operation.

Particles

Due to aging of the system or due to maintenance, particles of foreign material (e.g. sand, sludge) can be introduced into the system. This foreign material can cause consequences ranging from clogging of flow channels to damage of the membrane. For that reason, it is a standard practice to have a particle filter installed. To monitor the state of health of the filter can be done in regular maintenance intervals or with a simple differential pressure measurement.

Dissolved species

Keeping the process water pure to prevent contamination is crucial in PEMWE. This can be done by continuous purification of the process water in combination with, for example, conductivity measurement.

Water sampling is often used to track degradation speeds of a PEMWE in a lab environment. As discussed in section 3.1.2, during membrane degradation fluorine is released and that can be tracked with regular water sampling. As fluorine affects the conductivity of the liquid it may also be possible to track the rate of release with standard conductivity sensors. The advantage of such measurement is that it is relatively simple, and the sensor type is well known.[41]

Differential pressure

Differential pressure measurement is considered important in AWE where even small differential pressures can cause a significant gas crossover. It is important to keep in mind that it is not possible to measure individual cells and differences might appear at a cell level.

Pressure

It is attractive to produce hydrogen at high pressure to avoid the need for compression of the product. In PEMWE, it is possible to achieve this while the oxygen side operates at near atmospheric pressure. However, due to the risk of a rapid mixing on hydrogen in oxygen in case of a critical scenario some PEMWE system suppliers design critical components in anode (e.g. separator vessel) explosion proof. This serves as a barrier against scenarios that cause internal mixing that is faster than the system's reaction time. This is an essential difference with the AWE system, where a high pressure of the hydrogen needs to be accompanied by a high pressure on the oxygen side and the approach of designing for detonation is challenging.

Temperature and flow

Temperature and flow can both play a role. Overheating of a stack can always become hazardous, especially in PEMWE where it significantly accelerates the degradation of the membrane. A good way to know that the flow is sufficient is through comparison of inlet and outlet temperatures. Keeping the temperature gradient within acceptable levels is a good way to keep degradation in check. Controlling the inlet temperature is also crucial as temperature and degradation are directly linked.

6 Bibliography

1. Trinke, P. *et al.* Hydrogen Crossover in PEM and Alkaline Water Electrolysis : Mechanisms , Direct Comparison and Mitigation Strategies Hydrogen Crossover in PEM and Alkaline Water Electrolysis : Mechanisms , Direct Comparison and Mitigation Strategies. (2018) doi:10.1149/2.0541807jes.
2. de Groot, M. T., Kraakman, J. & Garcia Barros, R. L. Optimal operating parameters for advanced alkaline water electrolysis. *Int. J. Hydrogen Energy* **47**, 34773–34783 (2022).
3. Wrubel, J. A. *et al.* Estimating the energy requirement for hydrogen production in proton exchange membrane electrolysis cells using rapid operando hydrogen crossover analysis. *Int. J. Hydrogen Energy* **47**, 28244–28253 (2022).
4. Omrani, R. & Shabani, B. Hydrogen crossover in proton exchange membrane electrolysers: The effect of current density, pressure, temperature, and compression. *Electrochim. Acta* **377**, 138085 (2021).
5. Frensch, S. H. *et al.* Impact of iron and hydrogen peroxide on membrane degradation for polymer electrolyte membrane water electrolysis: Computational and experimental investigation on fluoride emission. *J. Power Sources* **420**, 54–62 (2019).
6. Sakai, T., Takenaka, H. & Torikai, E. Gas Diffusion in the Dried and Hydrated Nafions. *J. Electrochem. Soc.* **133**, 88–92 (1986).
7. Schalenbach, M. *et al.* Gas Permeation through Nafion. Part 1: Measurements. *J. Phys. Chem. C* **119**, 25145–25155 (2015).
8. Feng, C., Li, Y., Qu, K., Zhang, Z. & He, P. Mechanical behavior of a hydrated perfluorosulfonic acid membrane at meso and nano scales. *RSC Adv.* **9**, 9594–9603 (2019).
9. Ngo, P. M., Karimata, T., Saitou, T. & Ito, K. Effect of current density on membrane degradation under the combined chemical and mechanical stress test in the PEMFCs. *J. Power Sources* **556**, 232446 (2023).
10. Becker, H. *et al.* Impact of impurities on water electrolysis: a review. *Sustain. Energy Fuels* 1565–1603 (2023) doi:10.1039/d2se01517j.
11. Frensch, S. H. *et al.* Influence of the operation mode on PEM water electrolysis degradation. *Int. J. Hydrogen Energy* **44**, 29889–29898 (2019).
12. Trinke, P., Keeley, G. P., Carmo, M., Bensmann, B. & Hanke-Rauschenbach, R. Elucidating the Effect of Mass Transport Resistances on Hydrogen Crossover and Cell Performance in PEM Water Electrolyzers by Varying the Cathode Ionomer Content. *J. Electrochem. Soc.* **166**, F465–F471 (2019).
13. Stähler, M. *et al.* Impact of porous transport layer compression on hydrogen permeation in PEM water electrolysis. *Int. J. Hydrogen Energy* **45**, 4008–4014 (2020).
14. Giancola, S. *et al.* Composite short side chain PFSA membranes for PEM water electrolysis. *J. Memb. Sci.* **570–571**, 69–76 (2019).
15. Haug, P., Kreitz, B., Koj, M. & Turek, T. Process modelling of an alkaline water electrolyzer. *Int. J. Hydrogen Energy* **42**, 15689–15707 (2017).
16. Haug, P., Koj, M. & Turek, T. Influence of process conditions on gas purity in alkaline water electrolysis. *Int. J. Hydrogen Energy* **42**, 9406–9418 (2017).
17. Ruetschi, P. & Amlie, R. F. Solubility of hydrogen in potassium hydroxide and sulfuric acid. Salting-out and hydration. *J. Phys. Chem.* **70**, 718–723 (1966).
18. Brauns, J. & Turek, T. Experimental evaluation of dynamic operating concepts for alkaline water electrolyzers powered by renewable energy. *Electrochim. Acta* **404**, 139715 (2022).
19. Lira Garcia Barros, R., Kraakman, J. T., Sebregts, C., van der Schaaf, J. & de Groot, M. T.

Impact of an electrode-diaphragm gap on diffusive hydrogen crossover in alkaline water electrolysis. *Int. J. Hydrogen Energy* **49**, 886–896 (2024).

20. Trinke, P., Bensmann, B. & Hanke-Rauschenbach, R. Current density effect on hydrogen permeation in PEM water electrolyzers. *Int. J. Hydrogen Energy* **42**, 14355–14366 (2017).
21. Martin, A. *et al.* The Effect of Cell Compression and Cathode Pressure on Hydrogen Crossover in PEM Water Electrolysis. *J. Electrochem. Soc.* **169**, (2022).
22. Brauns, J. *et al.* Evaluation of Diaphragms and Membranes as Separators for Alkaline Water Electrolysis. *J. Electrochem. Soc.* **168**, 014510 (2021).
23. Speckmann, F. W., Bintz, S. & Birke, K. P. Influence of rectifiers on the energy demand and gas quality of alkaline electrolysis systems in dynamic operation. *Appl. Energy* **250**, 855–863 (2019).
24. Grigoriev, S. A. *et al.* High-pressure PEM water electrolysis and corresponding safety issues. *Int. J. Hydrogen Energy* **36**, 2721–2728 (2011).
25. Trinke, P., Bensmann, B. & Hanke-Rauschenbach, R. Experimental evidence of increasing oxygen crossover with increasing current density during PEM water electrolysis. *Electrochem. commun.* **82**, 98–102 (2017).
26. Abe, I., Fujimaki, T. & Matsubara, M. Hydrogen production by high temperature, high pressure water electrolysis, results of test plant operation. *Int. J. Hydrogen Energy* **9**, 753–758 (1984).
27. Mališ, J., Mazúr, P., Paidar, M., Bystron, T. & Bouzek, K. Nafion 117 stability under conditions of PEM water electrolysis at elevated temperature and pressure. *Int. J. Hydrogen Energy* **41**, 2177–2188 (2016).
28. Martin, A., Trinke, P., Bensmann, B. & Hanke-Rauschenbach, R. Hydrogen Crossover in PEM Water Electrolysis at Current Densities up to 10 A cm −2 . *J. Electrochem. Soc.* **169**, 094507 (2022).
29. Afshari, E., Khodabakhsh, S., Jahantigh, N. & Toghyani, S. Performance assessment of gas crossover phenomenon and water transport mechanism in high pressure PEM electrolyzer. (2020) doi:10.1016/j.ijhydene.2020.10.180.
30. Park, J. E. *et al.* High-performance proton-exchange membrane water electrolysis using a sulfonated poly(arylene ether sulfone) membrane and ionomer. *J. Memb. Sci.* **620**, 118871 (2021).
31. Siracusano, S. *et al.* Chemically stabilised extruded and recast short side chain Aquivion® proton exchange membranes for high current density operation in water electrolysis. *J. Memb. Sci.* **578**, 136–148 (2019).
32. Bock, R. *et al.* Measuring the thermal conductivity of membrane and porous transport layer in proton and anion exchange membrane water electrolyzers for temperature distribution modeling. *Int. J. Hydrogen Energy* **45**, 1236–1254 (2020).
33. Schalenbach, M., Lueke, W. & Stolten, D. Hydrogen Diffusivity and Electrolyte Permeability of the Zirfon PERL Separator for Alkaline Water Electrolysis. *J. Electrochem. Soc.* **163**, F1480–F1488 (2016).
34. In Lee, H. *et al.* The synthesis of a Zirfon-type porous separator with reduced gas crossover for alkaline electrolyzer. *Int. J. Energy Res.* **44**, 1875–1885 (2020).
35. Jang, D. *et al.* Investigation of the operation characteristics and optimization of an alkaline water electrolysis system at high temperature and a high current density. *J. Clean. Prod.* **424**, 138862 (2023).
36. Lopata, J. S. *et al.* Investigating influence of geometry and operating conditions on local current, concentration, and crossover in alkaline water electrolysis using computational fluid dynamics. *Electrochim. Acta* **390**, 138802 (2021).
37. Khatib, F. N. *et al.* Material degradation of components in polymer electrolyte membrane (PEM) electrolytic cell and mitigation mechanisms: A review. *Renew. Sustain. Energy Rev.* **111**, 1–14 (2019).
38. Feng, Q. *et al.* A review of proton exchange membrane water electrolysis on degradation mechanisms and mitigation strategies. *J. Power Sources* **366**, 33–55

(2017).
39. Zatoń, M., Rozière, J. & Jones, D. J. Current understanding of chemical degradation mechanisms of perfluorosulfonic acid membranes and their mitigation strategies: A review. *Sustain. Energy Fuels* 1, 409–438 (2017).
40. Kuhnert, E., Kiziltan, O., Hacker, V. & Bodner, M. Investigation of the Impact of Chloride Contamination on Degradation in PEM Water Electrolyzer Cells. *ECS Meet. Abstr.* MA2023-02, 2130–2130 (2023).
41. Marocco, P. *et al.* Online measurements of fluoride ions in proton exchange membrane water electrolysis through ion chromatography. *J. Power Sources* 483, 229179 (2021).
42. Voronova, A. *et al.* Systematic Degradation Analysis in Renewable Energy-Powered Proton Exchange Membrane Water Electrolysis. *Energy Environ. Sci.* (2023) doi:10.1039/d3ee01959d.
43. Chandesris, M. *et al.* Membrane degradation in PEM water electrolyzer: Numerical modeling and experimental evidence of the influence of temperature and current density. *Int. J. Hydrogen Energy* 40, 1353–1366 (2015).
44. Garbe, S. *et al.* Understanding Degradation Effects of Elevated Temperature Operating Conditions in Polymer Electrolyte Water Electrolyzers. *J. Electrochem. Soc.* 168, 044515 (2021).
45. Rodgers, M. P., Pearman, B. P., Mohajeri, N., Bonville, L. J. & Slattery, D. K. Effect of perfluorosulfonic acid membrane equivalent weight on degradation under accelerated stress conditions. *Electrochim. Acta* 100, 180–187 (2013).
46. Arthurs, C. & Kusoglu, A. Compressive Creep of Polymer Electrolyte Membranes : A Case Study for Electrolyzers. (2021) doi:10.1021/acsaem.0c03024.
47. Zhang, Z., Tian, C., Yuan, Z., Li, J. & Wu, W. Temperature and loading sensitivity investigation of nanoindentation short-term creep behavior in Nafion ® Temperature and loading sensitivity investigation of nanoindentation short-term creep behavior in Na fi on ®. (2017).
48. Schuler, T., De Bruycker, R., Schmidt, T. J. & Büchi, F. N. Polymer Electrolyte Water Electrolysis: Correlating Porous Transport Layer Structural Properties and Performance: Part I. Tomographic Analysis of Morphology and Topology. *J. Electrochem. Soc.* 166, F270–F281 (2019).
49. Borgardt, E. *et al.* Impact of clamping pressure and stress relaxation on the performance of different polymer electrolyte membrane water electrolysis cell designs. *Int. J. Hydrogen Energy* 44, 23556–23567 (2019).
50. Stucki, S., Scherer, G. G., Schlagowski, S. & Fischer, E. PEM water electrolysers: Evidence for membrane failure in 100 kW demonstration plants. *J. Appl. Electrochem.* 28, 1041–1049 (1998).
51. Verdin, B. *et al.* Operando current mapping on PEM water electrolysis cells. Influence of mechanical stress. *Int. J. Hydrogen Energy* 42, 25848–25859 (2017).
52. Minnaar, C., De Beer, F. & Bessarabov, D. Current Density Distribution of Electrolyzer Flow Fields: In Situ Current Mapping and Neutron Radiography. *Energy and Fuels* 34, 1014–1023 (2020).
53. Muthiah, M., Elnashar, M., Afzal, W. & Tan, H. Safety assessment of hydrogen production using alkaline water electrolysis. *Int. J. Hydrogen Energy* 84, 803–821 (2024).
54. Wismer, S. E., Jimenez, A., Al-Douri, A., Grabovetska, V. & Groth, K. M. PEM electrolyzer failure scenarios identified by failure modes and effects analysis (FMEA). *Int. J. Hydrogen Energy* 89, 1280–1289 (2024).
55. Mohsen, R., Olewski, T., Badreldin, A., Abdel-Wahab, A. & Véchot, L. Explosive mixture formation in PEM electrolyzers: A safety review using fault tree analysis. *Renew. Sustain. Energy Rev.* 211, (2025).
56. Millet, P., Ranjbari, A., De Guglielmo, F., Grigoriev, S. A. & Auprêtre, F. Cell failure mechanisms in PEM water electrolyzers. *Int. J. Hydrogen Energy* 37, 17478–17487

(2012).
57. HM Factory Inspectorate. The explosion at Laporte Industries Ltd., Ilford, 5 April 1975. 24 (1976).
58. Kink, J. *et al.* Reinforcing membranes with subgaskets in proton exchange membrane water electrolysis: A model-based analysis. *J. Power Sources* **614**, 234987 (2024).
59. Kink, J., Ise, M., Bensmann, B. & Hanke-Rauschenbach, R. Modeling Mechanical Behavior of Membranes in Proton Exchange Membrane Water Electrolyzers. *J. Electrochem. Soc.* **170**, 054507 (2023).
60. Ding, F. *et al.* The pinhole effect on proton exchange membrane fuel cell (PEMFC) current density distribution and temperature distribution. *Appl. Energy* **342**, 121136 (2023).
61. Lee, J. K. *et al.* Critical Current Density as a Performance Indicator for Gas-Evolving Electrochemical Devices. *Cell Reports Phys. Sci.* **1**, 100147 (2020).
62. Franz, T., Papakonstantinou, G. & Sundmacher, K. Transient hydrogen crossover in dynamically operated PEM water electrolysis cells - A model-based analysis. *J. Power Sources* **559**, 232582 (2023).
63. Zhang, Z., Baudy, A., Testino, A. & Gubler, L. Cathode Catalyst Layer Design in PEM Water Electrolysis toward Reduced Pt Loading and Hydrogen Crossover. *ACS Appl. Mater. Interfaces* (2024) doi:10.1021/acsami.4c01827.
64. Gu, J. *et al.* Experimental studies on dynamic performance of 250-kW alkaline electrolytic system. *J. Power Sources* **592**, 233920 (2024).
65. Liu, C., Wrubel, J., Padgett, E. & Bender, G. The impacts of membrane pinholes on PEM water electrolysis. *J. Power Sources* **581**, 233507 (2023).

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