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# Electrolyzer System Modeling - Experimental Testing of PEM Electrolyzer Degradation

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Master's thesis  
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Energy

**Title:**

Electrolyzer System Modeling - Experimental  
Testing of PEM Electrolyzer Degradation

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**Abstract:**

Green hydrogen is crucial for the development of sustainable energy systems and their integration into the market. Proton exchange membrane (PEM) electrolyzers stand out as one of the most promising technologies for producing green hydrogen. However, there is a lack of research in long-term degradation models. Modeling has become a vital tool to study PEM electrolyzer functioning and optimization. This project develops a simulation model in Python that couples mass transport phenomena with the thermodynamic and electrochemical characteristics of the cell. Degradation mechanisms are implemented to provide a high-fidelity prediction of the PEM electrolyzer's lifespan and operation over time. An experimental cell was assembled and subjected to 500 h operation in a Greenlight test station. Additional data were obtained through EIS and XRD tests. The experimental data were implemented into the model, forming a 1D semi-empirical model. The model's flexibility and robustness were validated by simulating performance under different operating conditions: temperatures, pressures, current densities, symmetric/asymmetric configuration. The results revealed an interesting counterintuitive behavior at high temperatures: when operating at low isobaric pressure or with elevated pressure in the cathode, membrane thinning can be mitigated by controlling the oxygen crossover and the oxygen solubility in water. This model serves as a tool for optimization, prediction, and phenomena study purposes.

# Preface

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This Master's Thesis was prepared by Javier Bermúdez Blanco (Student No. 20241850) during the 4th semester of the Fuel Cells and Hydrogen Technology program at Aalborg University. The research project is entitled *Electrolyzer System Modeling – Experimental Testing of PEM Electrolyzer Degradation*.

The supervisor in charge of this project is Vincenzo Liso, and the co-supervisor is Hamilton Delaney Miller, who guided the laboratory experiments. I would like to express my gratitude for all the work both supervisors put into this project.

Artificial Intelligence (AI) was used as a supportive tool for programming, accelerating literature research, and refining the academic writing and formatting of this project.

## Reading Guide

Throughout this report, sources are cited in sequential numerical order. All references are compiled at the end of the document. This report uses the Anglo-Saxon standard, points are used to separate decimals, and commas are used as thousands separators.

Figures, tables, and equations follow a chapter-based numbering system, i.e. the first figure in Chapter 4 would be Figure 4.1, the next one would be Figure 4.2, and so on. Figures and tables have a caption that describes them.

Appendices are included at the end of the document. Appendix A summarizes the simulation parameters and libraries in tables. Appendix B shows figures of key variables obtained from a simulation.

Aalborg University, May 26, 2026



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# Summary

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Following Aalborg University guidelines, a summary in a foreign language is provided. The summary is written in Spanish.

El hidrógeno verde se ha erigido como una de las formas más prometedoras de almacenar energía renovable. Uno de los mayores desafíos de estas energías es su intermitencia; el hidrógeno puede ser la clave para resolver este problema, ya que permite almacenar la energía producida de forma limpia hasta que se requiera su uso.

Los electrolizadores de membrana de intercambio de protones (PEM) son una de las tecnologías empleadas para obtener hidrógeno a partir de fuentes de energía renovables. De forma simplificada, en el ánodo el agua se divide en presencia de un catalizador al aplicar un voltaje. La membrana de intercambio de protones actúa como filtro, permitiendo únicamente el paso de los protones. Finalmente, los protones de hidrógeno se recombinan con electrones en el cátodo, en presencia de otro catalizador, para formar hidrógeno.

Esta tecnología aún está bajo desarrollo, más investigación debe ser realizada para el correcto desarrollo de los electrolizadores PEM y su implementación en el mercado. En el ámbito del modelado, existe una carencia de modelos predictivos que implementen diversos mecanismos de degradación.

El modelo de simulación desarrollado en este proyecto es un gemelo digital 1D semi-empírico. El modelo acopla datos experimentales con principios teóricos, integrando dinámica de fluidos, termodinámica, electroquímica y fenómenos de degradación que ocurren dentro de la celda.

Se realizaron ensayos experimentales con el objetivo de obtener datos de degradación. Un electrolizador PEM fue sometido a operación durante 500 h en una estación Greenlight. Tests de espectroscopía de impedancia electroquímica (EIS) fueron realizados periódicamente para obtener datos sobre la evolución de la resistencia óhmica y del catalizador. Por último, una membrana virgen y la membrana utilizada en el electrolizador fueron sometidas a un análisis de difracción de rayos X (XRD) para estudiar la evolución estructural de las partículas de Pt y de la membrana. Los datos experimentales fueron integrados en el modelo. Sin embargo, estos datos indican el funcionamiento no ideal de la celda.

Las ecuaciones teóricas fueron implementadas con el fin de calcular los parámetros termodinámicos y electroquímicos de la celda, así como para predecir la vida útil de la misma. Los resultados obtenidos mostraron la evolución de los parámetros de rendimiento de la celda y la influencia de las condiciones de operación en estos parámetros y en la vida útil.

Se halló que, contraintuitivamente, operar la celda a altas temperaturas puede ser beneficioso para reducir la degradación de la membrana bajo ciertas condiciones. Al operar a presiones simétricas bajas, la solubilidad del oxígeno en el agua se reduce a mayores temperaturas, generando una limitación de transferencia de masa del ánodo al cátodo. En consecuencia, la cantidad de oxígeno que cruza al cátodo es menor, ralentizando el adelgazamiento de la

membrana. Este fenómeno también ocurre cuando se opera con una presión diferencial más alta en el cátodo. Así, el modelo es capaz de predecir las condiciones óptimas de operación para diferentes escenarios, minimizando la degradación de la membrana y maximizando tanto la producción de hidrógeno como la vida útil del electrolizador PEM.

El modelo fue validado simulando un gran abanico de condiciones: diferentes temperaturas, densidades de corriente, presiones y configuraciones (presión simétrica o presión asimétrica). Así, se demostró la gran robustez y flexibilidad del modelo, capaz de adaptarse a diferentes condiciones de operación. Además, el modelo también incluye un factor industrial, ya que su operación se detiene cuando se alcanza un límite de seguridad, dictado por el contenido de hidrógeno en oxígeno. Este parámetro puede ser modificado para futuras variaciones de la simulación.

Como conclusión, el modelo desarrollado en este proyecto sirve como una avanzada herramienta de predicción y optimización de electrolizadores de membrana de intercambio de protones. Gracias al acoplamiento de la dinámica de fluidos, termodinámica, electroquímica, y su impacto al rendimiento y degradación de la celda, el modelo sirve como plataforma para el estudio de diversos fenómenos de degradación y dinámica de fluidos.

# Nomenclature

## List of symbols

| Symbol       | Definition                      | Unit                                         |
|--------------|---------------------------------|----------------------------------------------|
| $\Delta H_f$ | Reaction formation enthalpy     | $\frac{\text{kJ}}{\text{mol}}$               |
| $\Delta G$   | Gibbs free energy               | $\frac{\text{kJ}}{\text{mol}}$               |
| $V_{th}$     | Thermoneutral potential         | V                                            |
| $V_{rev}$    | Reversible potential            | V                                            |
| V            | Voltage or potential            | V                                            |
| $\eta$       | Efficiency                      | %                                            |
| z            | Number of electrons transferred | -                                            |
| F            | Faraday constant                | $\frac{\text{C}}{\text{mol}}$                |
| T            | Temperature                     | K                                            |
| S            | Entropy                         | $\frac{\text{J}}{\text{mol}\cdot\text{K}}$   |
| t            | Time                            | s                                            |
| m            | Mass                            | g                                            |
| $M$          | Molar mass                      | $\frac{\text{g}}{\text{mol}}$                |
| $\omega$     | Mass fraction                   | %                                            |
| EW           | Equivalent weight               | $\frac{\text{g}}{\text{mol}}$                |
| $\lambda$    | Water uptake                    | -                                            |
| $\kappa$     | Proton conductivity             | $\frac{\text{S}}{\text{cm}}$                 |
| $k_{drag}$   | Electro-osmotic drag flux       | $\frac{\text{mol}}{\text{m}^2\cdot\text{s}}$ |
| $k_{drag}$   | Drag coefficient                | -                                            |
| $\dot{n}$    | Molar flow                      | $\frac{\text{mol}}{\text{s}}$                |
| $k_{specie}$ | Water permeability              | $\text{cm}^2$                                |
| A            | Area                            | $\text{cm}^2$                                |
| P            | Pressure                        | bar                                          |
| $t_{mem}$    | Membrane thickness              | cm                                           |
| $\mu$        | Viscosity                       | $\text{Pa}\cdot\text{s}$                     |
| $D_i$        | Diffusion coefficient           | $\frac{\text{m}^2}{\text{s}}$                |
| C            | Concentration                   | $\frac{\text{mol}}{\text{L}}$                |
| v            | Velocity                        | $\frac{\text{m}}{\text{s}}$                  |
| i            | Current density                 | $\frac{\text{A}}{\text{cm}^2}$               |
| x            | Mole fraction                   | %                                            |
| $\alpha$     | Charge transfer coefficient     | -                                            |
| R            | Universal gas constant          | $\frac{\text{J}}{\text{mol}\cdot\text{K}}$   |
| $\beta$      | Symmetry factor                 | -                                            |
| $\delta_e$   | Diffusive layer thickness       | cm                                           |
| Q            | Electrical charge               | C                                            |
| I            | Electrical current              | A                                            |
| $W_t$        | Work                            | J                                            |

## List of symbols

| Symbol           | Definition                 | Unit                                            |
|------------------|----------------------------|-------------------------------------------------|
| H                | Henry solubility           | $\frac{\text{mol}}{\text{m}^3 \cdot \text{Pa}}$ |
| K                | Constants                  | -                                               |
| $\dot{V}$        | Volume flow rate           | $\frac{\text{m}^3}{\text{s}}$                   |
| $R_{ohm}$        | Electrical resistance      | $\Omega$                                        |
| $\epsilon$       | Porosity                   | %                                               |
| $\Theta$         | Bubble coverage            | %                                               |
| $\tau$           | Membrane thickness ratio   | -                                               |
| D                | Damage factor              | %                                               |
| $k_{rxn}$        | Reaction rate constant     | -                                               |
| $R_{rxn}$        | Reaction                   | -                                               |
| $\rho$           | Density                    | $\frac{\text{kg}}{\text{m}^3}$                  |
| Sc               | Scherrer constant          | -                                               |
| $\lambda_{wave}$ | Wavelength                 | nm                                              |
| $\beta_{FWHM}$   | Full width at half maximum | nm                                              |
| $\theta$         | Bragg angle                | rad                                             |
| $Q_{gen}$        | Heat generated             | kW                                              |

## Abbreviations

| Abbreviation | Definition                             |
|--------------|----------------------------------------|
| AEM          | Anion exchange membrane                |
| ASR          | Active surface area                    |
| BPP          | Bipolar plate                          |
| CL           | Catalyst layer                         |
| EEC          | Equivalent electrical circuit          |
| EIS          | Electrochemical impedance spectroscopy |
| FWHM         | Full width at half maximum             |
| GDL          | Gas diffusion layer                    |
| HER          | Hydrogen evolution reaction            |
| LHV          | Lower heating value                    |
| M            | Metal surface                          |
| MEM          | Membrane                               |
| NLPM         | Normal liters per minute               |
| OCV          | Open circuit voltage                   |
| OER          | Oxygen evolution reaction              |
| PEM          | Proton exchange membrane               |
| PTFE         | Polytetrafluoroethylene                |
| PTL          | Porous transport layer                 |
| SOEC         | Solid oxide electrolysis cell          |
| XRD          | X-ray diffraction                      |

## Subindexes and Superindexex

| Subscript     | Meaning              |
|---------------|----------------------|
| 0             | Standard conditions  |
| <i>th</i>     | Thermoneutral        |
| <i>rev</i>    | Reversible           |
| <i>l</i>      | Liquid phase         |
| <i>g</i>      | Gaseous phase        |
| <i>ads</i>    | Adsorbed             |
| <i>eod</i>    | Electro-osmotic drag |
| <i>hyp</i>    | Hydraulic permeation |
| <i>diff</i>   | Diffusion            |
| <i>i</i>      | Substance "i"        |
| <i>conv</i>   | Convection           |
| <i>an</i>     | Anode                |
| <i>cat</i>    | Cathode              |
| <i>crit</i>   | Critical             |
| <i>loss</i>   | Loss                 |
| <i>act</i>    | Activation           |
| <i>ohm</i>    | Ohmic                |
| <i>conc</i>   | Concentration        |
| <i>0</i>      | Initial              |
| <i>mem</i>    | Membrane             |
| <i>ref</i>    | Reference            |
| <i>ch</i>     | Vhannel              |
| <i>op</i>     | Operation            |
| <i>prod</i>   | Produced             |
| <i>theo</i>   | Theoretical          |
| <i>diss</i>   | Dissolved            |
| <i>p</i>      | Prelocation          |
| <i>su</i>     | Summit               |
| <i>eff</i>    | Effective            |
| <i>s</i>      | Surface              |
| <i>lim</i>    | Limit                |
| <i>transf</i> | Transferred          |
| <i>cons</i>   | Consumed             |
| <i>p</i>      | Particle             |

## Chemical compounds

| Chemical representation              | Meaning                        |
|--------------------------------------|--------------------------------|
| $\text{H}_2\text{O}$                 | Water                          |
| $\text{H}_2$                         | Hydrogen                       |
| $\text{H}^+$                         | Hydrogen proton                |
| $\text{O}_2$                         | Oxygen                         |
| $\text{OH}^-$                        | Hydroxide                      |
| $\text{OOH}$                         | Hydroperoxyl                   |
| $\text{H}_3\text{O}^+$               | Hydronium ion                  |
| $\text{SO}_3\text{H}$                | Sulfonic acid                  |
| $\text{H}_5\text{O}_2^+$             | Zundel ion                     |
| $\text{H}_9\text{O}_4^+$             | Eigen ion                      |
| $\text{IrO}_2$                       | Iridium dioxide                |
| $\text{Ir}$                          | Iridium                        |
| $\text{RuO}_2$                       | Ruthenium dioxide              |
| $\text{Ru}$                          | Ruthenium                      |
| $\text{Pt}$                          | Platinum                       |
| $\text{Pt/C}$                        | Platinum supported with carbon |
| $\text{Ti}$                          | Titanium                       |
| $\text{Fe}$                          | Iron                           |
| $\text{H}_2\text{O}_2$               | Hydrogen peroxide              |
| $\text{HO}\bullet$                   | Hydroxyl radical               |
| $\text{HOO}\bullet$                  | Hydroperoxyl radical           |
| $\text{HF}$                          | Hydrogen fluoride              |
| $\text{R}_f\text{-CF}_2\text{-COOH}$ | Perfluorocarboxylic acid       |
| $\text{IrO}_x$                       | Iridium oxides                 |
| $\text{Ir}^{3+}$                     | Iridium ion                    |
| $\text{IrO}_4^{2-}$                  | Iridate ion                    |
| $\text{Ir}_2\text{O}_7^{2-}$         | Diiridate ion                  |
| $\text{TiO}_2$                       | Titanium dioxide               |
| $\text{CO}_2$                        | Carbon Dioxide                 |
| $\text{Cu}$                          | Copper                         |
| $\text{Al}$                          | Aluminium                      |
| $\text{M}$                           | Electrochemical active site    |

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# Introduction

# 1

The global energy paradigm is shifting away from fossil fuels, as renewable energy sources are stepping in and becoming an important energy source. But these sources face a challenge: they are highly unsteady over time as a result of their dependency on natural conditions.

There are different technologies that aim to address this issue, such as thermal energy storage, batteries, or compressed air energy storage. One of the most promising alternatives to fossil fuels is green hydrogen, which acts as a versatile energy carrier. It is a net-zero carbon emission alternative when produced from electricity obtained from renewable energy sources, such as solar or wind energy. [1]

Despite its immense potential, green hydrogen currently represents only a marginal fraction of the global market. The hydrogen industry remains heavily dependent on fossil fuels, with the vast majority of production derived from natural gas rather than renewable energy sources. Hydrogen only constituted 2% of the total energy consumption of Europe in 2022 and its main use was as a chemical reactant to manufacture products such as plastics. 96% of this hydrogen was obtained from natural gas, producing considerable CO<sub>2</sub> emissions. [2]

7.8 Mt of H<sub>2</sub> were consumed in Europe in 2024, but the RePowerEU strategy aims to produce 10 Mt and import another 10 Mt by 2030. 10% of Europe's total energy consumption is expected to be covered by green hydrogen by 2050. [2][3]

Water electrolysis is the main process used to produce green hydrogen. However, it only represents 4% of the total hydrogen produced, since other low-cost processes are preferred, such as steam reforming. Water electrolysis is an electrochemical process in which water is split into hydrogen and oxygen by applying electricity. [1]

This technology market is growing very fast, Europe reached an energy production capacity of 571 MW in 2025. 288 MW out of the total were installed from June 2024 to June 2025, and the first two +50MW electrolyzers were built in Germany and Denmark. [3]

## 1.1 Technology comparison

As the development of water electrolysis technologies accelerates, different technologies have been invented or perfected. Each one of these technologies present different characteristics, advantages, and disadvantages.

### 1.1.1 Alkaline

Alkaline water electrolysis is a well-known proven technology that was invented over 200 years ago, it is the most widely used technology at the commercial level.

It consists of two electrodes submerged in a liquid alkaline electrolyte aqueous solution of

20-30% KOH/NaOH. It also has a diaphragm that separates the gasses and allows hydroxide ions and water molecules to permeate through. Nickel based materials are usually used for this purpose.[4] [5]

It can be operated at low temperatures (30-90°C), has a low capital cost, long lifetime, and low degradation rates. However, it works at low current densities (0.25 - 0.8 A/cm<sup>2</sup>), and presents a slow start-up time which results in moderate flexibility. [5] [6]

### 1.1.2 PEM

Proton Exchange Membrane (PEM) electrolysis or polymer electrolyte membrane electrolysis uses a thin solid ion-conducting membrane, which is made of solid sulfonated polystyrene. It is a technology that is around 60 years old. It was invented by General Electric. [1][5]

It presents a compact design, high responsiveness, and a fast start-up time. It can also operate at high pressures, and high current densities (1-6 A/cm<sup>2</sup>), with a high hydrogen production rate and purity.

It is very suitable for the use of renewable energy sources. Nonetheless, it presents high capital and maintenance costs due to the noble metals used as catalysts. The degradation rates also impact significantly to the electrolyzer performance over time.

### 1.1.3 SOEC

Solid Oxide Electrolysis (SOEC) is a more recent technology invented in 1980s. It uses a solid high-temperature oxygen-ion conductor as an electrolyte, being yttria-stabilized zirconia the most used one. [4][5]

It operates at high temperatures (700-900°C), which significantly accelerates the degradation of the electrolyzer, reducing its lifetime. This makes this kind of electrolyzers to have a low flexibility, but very high efficiency (around 100%), and very low specific energy consumption. [6]

### 1.1.4 AEM

Anion Exchange Membrane (AEM) is an emerging technology that is in the early stages of development. It is composed of a hydrocarbon anion exchange membrane and two transition metal-catalyst electrodes. It combines the principles of alkaline and PEM electrolysis.[6] [7]

Despite being a very immature technology, it has a promising future, as it could be a cheaper alternative to PEM electrolyzers. AEM electrolysis has low capital cost, full load flexibility, and quick cold start. However, it is still under development and presents low durability and performance. The studies of catalyst development, degradation, stability, and optimization are of great importance for the future of this technology. [6] [7]

A comparison table of operation and some performance parameters of the different technologies is presented in Table 1.1:

**Table 1.1.** Comparison of water electrolysis technologies [6]

| Parameters                                     | Alkaline | AEM      | PEM       | SOEC      |
|------------------------------------------------|----------|----------|-----------|-----------|
| <b>Operating conditions</b>                    |          |          |           |           |
| Temperature [°C]                               | 70–90    | 60–80    | 50–80     | 700–900   |
| Pressure [bar]                                 | 30       | 35       | 50        | 15        |
| Current density [A/cm <sup>2</sup> ]           | 0.25–0.8 | 0.2–2    | 1–6       | 0.3–1.0   |
| <b>Flexibility</b>                             |          |          |           |           |
| Load flexibility (%)                           | 10–100   | 0–100    | 0–100     | -100/+100 |
| Cold start                                     | 1–2 h    | 5–10 min | 5–10 min  | ≥1h       |
| Hot start                                      | 1–5 min  | <10 s    | <10 s     | 15 min    |
| <b>Efficiency</b>                              |          |          |           |           |
| Stack efficiency (LHV)                         | 63–71 %  | 60–83 %  | 60–68 %   | ~100 %    |
| Stack spec. energy [kWh/Nm <sup>3</sup> ]      | 3.8–5.2  | 3.95–5.2 | 4.3–5.8   | 3         |
| System efficiency                              | 51–60 %  | <75 %    | 46–60 %   | 76–81 %   |
| <b>Production</b>                              |          |          |           |           |
| Stack power [MW]                               | 6.5      | 2        | 5         | <0.01     |
| H <sub>2</sub> production [Nm <sup>3</sup> /h] | 1400     | 462      | 1255      | <10       |
| Cell surface area [m <sup>2</sup> ]            | <3.6     | <0.03    | <0.3      | <0.06     |
| <b>Durability</b>                              |          |          |           |           |
| Lifetime [kh]                                  | 55–120   | <2       | 60–100    | 8–20      |
| Degradation [%/year]                           | 0.25–1.5 | –        | 0.5–2.5   | 3–50      |
| <b>Economics</b>                               |          |          |           |           |
| Capital cost [€/kW]                            | 500–800  | 200      | 1400–2100 | >2000     |

The chart in Figure 1.1 shows the advantages and disadvantages of each technology with respect to each other in the main performance and market factors. [6]

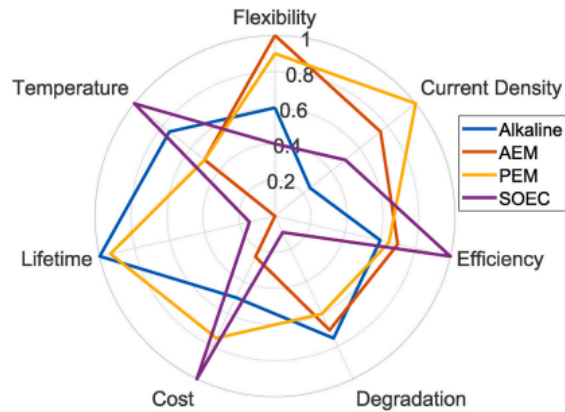


**Figure 1.1.** Comparative chart of technologies [6]

The most important characteristics of a PEM electrolyzer are presented in the graph. The aim is to minimize temperature, cost, and degradation, while maximizing lifetime, flexibility, current density, and efficiency. Degradation is a key factor in determining the lifetime and efficiency over time. It measures how different mechanisms affect the performance and durability of an electrolyzer. The temperature must be optimized to achieve the best efficiency while keeping costs and degradation rates low.

Flexibility and current density limit are also key factors. Flexibility allows the cell to be operated with a rapid response to changes and under different conditions, and the higher the current density operation limit, the higher  $H_2$  production rates could be obtained.

## 1.2 PEM electrolysis

PEM electrolysis is a promising technology that is worth developing for the future. It is very flexible, works at relatively low temperature, and has a long lifetime. However, the main drawbacks that must be addressed to make this technology proliferate in the commercial markets are its high cost, high degradation, and efficiency, although it is a decent one.

It is the technology that fits best to the dynamic behavior of renewable energy sources. [1]

For these reasons, PEM electrolysis has awakened the interest of many researchers and companies. Figure 1.2 shows the volume of scientific publications dedicated to PEM electrolysis, an exponential increase over the last years can be observed: [8]

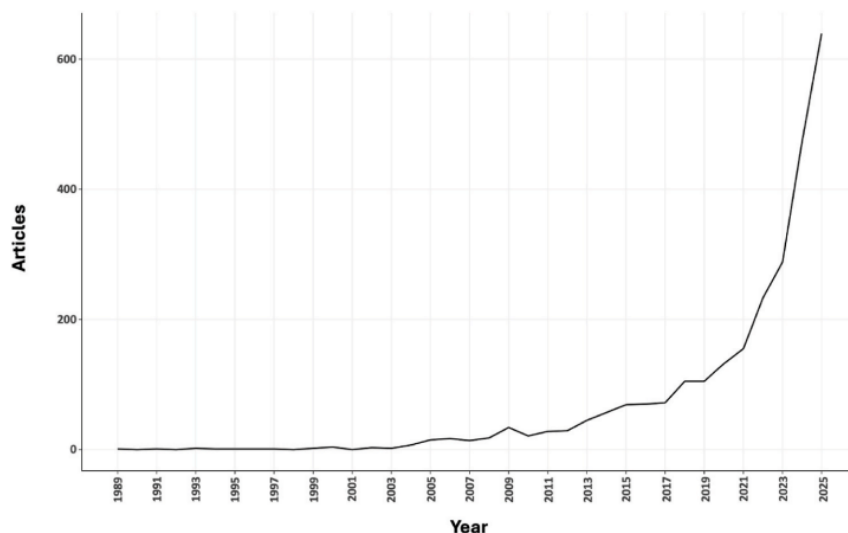


*Figure 1.2.* PEM electrolysis papers published [8]

These articles mainly focus on the study of the conditions, materials, and degradation mechanisms that affect the performance of PEM electrolyzers. Optimization studies are also a subject of interest in this field

PEM electrolyzer modeling has also become of great importance for this field because it is a tool that is used to study the electrolyzer behavior and performance efficiently, understanding the physico-chemical phenomena that occur during its operation. However, there is a lack of investigation in this matter nowadays, especially regarding the coupling of performance models with physical degradation mechanisms. Accurately simulating phenomena such as catalyst dissolution and membrane thinning over time remains a significant challenge that must be addressed to predict the true lifetime and performance of PEM electrolyzers.

The theory behind the PEM electrolyzer functioning and modeling will be studied in depth in this master thesis project. A life prediction model will be developed.

# Problem Statement 2

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Based on the introduction (Chapter 1), the primary research question of this thesis is formulated as follows:

*How can a predictive model of a PEM electrolyzer be developed to accurately account for diverse, coupled degradation mechanisms over time?*

To address this question, the following specific objectives were established:

1. Theoretical description of the principles of PEM electrolyzer operation and degradation.
2. Development of a simulation model, including experimental data and degradation phenomena.
3. Simulation of the model and discussion of results.

## 2.1 Project Limitations

This scope of this project is limited by different factors:

- Experimental duration: The total operational time of the experimental PEM electrolyzer was limited to 500 hours, restricting the observation of extreme long-term aging phenomena.
- Sample size: The limited number of experimental test runs restricts the statistical validation of the data.
- Equipment constraints: Limitations and detection thresholds in the laboratory measurement devices.
- Modeling assumptions: The necessary simplifications required to establish dynamic degradation constants without causing a model crash.

## 3.1 PEM Electrolyzer

Water electrolysis is a well known technology which was discovered more than 200 years ago. Nicholson and Carlisle discovered the possibility of splitting water by electrolysis during the industrial revolution, in the year 1800.

A century later, more than 400 industrial water electrolyzers were in operation. The first large water electrolyzer was developed in 1939, and the first pressurized industrial electrolyzer was built in 1948. [9]

Alkaline water electrolyzers were the ones used, but PEM electrolyzers emerged as a possible replacement when the first solid polymer electrolyte system was built in 1966 by General Electrics. [9]

Since, new electrolyzer technologies have been invented and studied, and PEM electrolysis still remains one of the most promising electrolysis technologies. They were first used to produce oxygen in anaerobic or space environments, but with the increasing worldwide demand for energy storage, they began to be used to produce hydrogen. However, their implementation in the market is challenging. Therefore, the study of the PEM electrolysis performance over time and materials used is crucial for its implementation. [4][1]

One of the earliest, most comprehensive, and often cited books on the topic of PEM electrolysis was published in 2015 by D. Bessarabov et al.[1]. This book explains in depth the PEM electrolyzer functioning, providing extensive information on the fundamentals of the PEM electrolyzer, the materials used, the modeling, and other topics related to PEM electrolysis.

More recent studies, such as the one conducted by T.Wang et al.[5] in 2022, also summarize and review the fundamentals, advances, and future prospects of PEM electrolysis. Previous publications on the topic were limited to research articles.

Studies about PEM electrolyzer performance have become more precise over time. Optimization and specific degradation mechanisms are being studied in depth. The aim is to reduce capital and operational costs by studying the materials used and the electrolyzer performance under different conditions.

Different studies summarize the degradation mechanisms that occur in PEM electrolyzers. In 2025, A.Bernhardt et al. [10] presented a review of the PEM electrolyzer's components degradation, summarizing measurement techniques to study different degradation mechanisms, and a discussion of less-studied degradation mechanisms.

Eva Wallnofer-Ogris et al.[11] also presented a review of the most influential degradation mechanisms, explaining their influential factors, consequences, and mitigation strategies.

Regarding chemical degradation of the membrane, Zhiyan Rui. et al [12] presented in 2023 a document on new insights into membrane thinning. It was observed that  $\text{H}_2\text{O}_2$  was produced either in the anode and in the cathode.

Na Li et al. [13] studied the effects of cationic impurities on PEM electrolyzer performance in 2020.  $\text{Fe}^{+3}$ ,  $\text{Cu}^{+2}$ , and  $\text{Al}^{+3}$  were studied, showing that these cations negatively impact the PEM electrolyzer, even causing sudden cell failure for  $\text{Al}^{+3}$ .

In 2024, E.Padgett et al. [14] also studied the cationic contamination impact coming from the water. They showed near-fully recovery of cell for sodium and calcium, and partial recovery for iron contaminants.

A very recent study from 2026, conducted by Fahad Maoulida et al. [6], reviews the dynamic degradation mechanisms under energy intermittency, focusing on electric, thermal, and cycling-induced aging phenomena. Equations for a mathematical model are presented. High current densities were found to accelerate internal degradation, high temperatures accelerate membrane thinning, hotspot development, and bubbles accumulation, and on/off cycles cause considerable voltage drifts. Some mitigation strategies such as dynamic electrical control or advanced thermal regulation are presented.

## 3.2 Modeling

H. Görgün introduced the first dynamic model of a PEM electrolyzer in 2006. This model is based on the mole balance of species between the anode and the cathode, taking into account the water electro-osmotic drag and diffusion through the membrane. It models the dynamics of a PEM electrolyzer and can be integrated to renewable energy sources to design and optimize systems.[15]

R.Garcia-Valverde et al. [16] presented a simple model with experimental validation for a PEM electrolyzer in 2011. The developed model is capable of simulating electrochemical, thermal, and  $\text{H}_2$  output flows with precision for atmospheric or low pressure PEM electrolyzers. The effects of pressure are neglected, uniform temperature, and 100% water saturation in the membrane are assumed. The model is divided into 3 sub-models: electrochemical, thermal, and  $\text{H}_2$  production.

Different models have been developed to study the PEM electrolyzer performance at different conditions. In 2018, V. Liso et al. [17] conducted an experimentally validated model to study the PEM electrolyzer performance at different temperatures. The methodology for modeling potential losses and mass transfer is clearly presented in this study.

Yanxi Zhu et al.[18] developed an experimentally validated model in 2024. This investigation studies the effects of key parameters and operating conditions on PEM electrolyzers. It was observed how the membrane thickness is the most influential factor, followed by temperature and ending with pressure.

An investigation with modeling equations on the effect of pressure on PEM electrolyzers was conducted by D.Saebea et al. [19] in 2017. At high cathode pressures, a slight effect on electrolyzer performance, and hydrogen crossover from cathode to anode was observed

Jian Dang et al. [20] developed a PEM electrolyzer mathematical model considering transient behaviors. Differential equation based transients models of the RC equivalent circuit are presented. The cation degradation highlights in transient operations.

A paper on the increase in ohmic resistances as a consequence of gas bubbles stacked inside the cell was published by H.Vogt in 2012 [21]. Different equations are presented to calculate the electrochemically inactive fraction of the electrode surface, at either low or high values of nominal current density. It can be easily calculated by knowing the nominal current density and the actual current density.

More recent studies have developed optimization models for a long PEM electrolyzer lifetime, studying degradation mechanisms and control. In 2025, Zerrougui et al.[22] summarized optimization techniques for PEM electrolyzer, considering different degradation mechanisms, advanced modeling approaches, diagnostic tools, and control strategies.

L.Bornemann et al[23] also conducted an optimization model for the operating temperature and pressure of PEM electrolyzers in 2025. The optimization applied was shown to improve 5% of the maximum system efficiency, and reduce energy consumption by 4% and operating costs by 7%.

Industrial models of PEM electrolyzers are also being developed. M.Pfennig et al [24] presented a comprehensive model of a PEM electrolyzer plant in 2025. The model successfully simulates a PEM electrolyzer with a 100MW capacity, it is divided into a time dependent thermal sub-model and a time independent electrochemical sub-model.

### 3.3 Degradation modeling

PEM electrolyzer degradation models have been developed to estimate the lifetime and performance of the electrolyzer. These models usually focus on one kind of degradation.

Chandesris et al. [25] developed a model to study the dependence of membrane degradation on temperature and current density in 2014. This paper focuses on the chemical ionomer degradation of the membrane. Gas crossover and Fenton reactions were presented and studied to model the impact of free radical attacks on the membrane. The results obtained were experimentally validated.

In 2025, Arthur R.Dizon and Adam Z.Weber developed a 1-D, non-isothermal, multiphase continuum model to simulate the effects of cation contamination on PEM electrolyzers [26]. The model predicts a performance decrease as a result of the replacement of protons with  $\text{Na}^+$  and  $\text{Ca}^{+2}$  cations on the membrane.

Regarding catalyst contamination, a physico-chemical model of a PEM electrolyzer considering the dissolution of Iridium catalyst was developed in 2022 by A.A. Kalinnikov et al. [27]. The rates of Iridium loss and voltage increase were studied in this paper.

New modeling techniques are also being used to model the PEM electrolyzer degradation. In 2025, A.Polo-Molina et al. [28] implemented physics-informed neural networks to model membrane degradation in PEM electrolyzers.

Table 3.1 summarizes the most important simulation models of PEM electrolyzer utilized in this project:

**Table 3.1.** Summary of the most relevant state-of-the-art models for PEM electrolyzers.

| Study                       | Model Scope                   | Key Contribution                                                                      |
|-----------------------------|-------------------------------|---------------------------------------------------------------------------------------|
| García-Valverde et al. [16] | Semi-empirical                | Developed a highly adaptable model that can be extrapolated for any PEM electrolyzer. |
| Abdin et al. [29]           | Mathematical                  | Developed a detailed model for PEM electrolyzer performance.                          |
| Ratib et al. [30]           | Electrical equivalent circuit | Summary of the different equivalent electrical circuits for PEM electrolyzers.        |
| Marangio et al. [31]        | Electrochemical theoretical   | Developed a model for high-pressure operation focusing on mass transfer mechanisms.   |
| Chandesris et al. [25]      | 1D degradation model          | Focused on membrane thinning and reaction mechanisms.                                 |
| Vogt et al. [32]            | Empirical                     | Analyzed bubble impact on the electrodes.                                             |
| Marefat et al. [33]         | Dynamic linear model          | Developed an electrical and aging model including degradation.                        |
| Xu et al. [34]              | 2D model                      | Developed a model based on the effects of catalyst layer agglomeration.               |

There is still room for advancement in the PEM electrolyzer modeling field. Current models rarely implement more than one degradation mechanism simultaneously. Furthermore, secondary degradation mechanisms are rarely considered in current models, but do play a role in the overall aging of the electrolyzer.

# Theory 4

## PEM Electrolyzer Overview

The water electrolysis reaction is an endothermic reaction in which a potential is applied to water ( $\text{H}_2\text{O}$ ) on a catalyst surface to split the water molecule into molecular hydrogen ( $\text{H}_2$ ) and molecular oxygen ( $\text{O}_2$ ): [1]



The formation enthalpy under standard conditions ( $\Delta H_f^0$ ), at 25 °C and 1 atm, represents the energy that must be supplied to water for the reaction to occur. The thermoneutral voltage can be calculated by knowing the Faraday constant ( $F = 96485 \text{ C/mol}$ ) and the number of electrons transferred during the reaction ( $z = 2$ ). The thermoneutral voltage refers to the potential that must be applied for the reaction to occur without having an external energy source. It can be calculated using the following equation:[1]

$$V_{th}^0 = \frac{\Delta H_f^0}{z \cdot F} = 1.48V \quad (4.1)$$

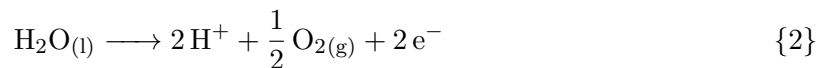
Since the water splitting reaction converts the liquid phase into a gas phase, there is a significant positive change in the entropy of the system ( $\Delta S$ ). The reaction is endothermic and can absorb thermal energy from the surroundings at an operating temperature ( $T$ ). This entropic contribution ( $T \cdot \Delta S$ ) means that part of the total energy required is provided by heat, reducing the amount of electrical work needed. The Gibbs free energy ( $\Delta G^0$ ) represents the minimum energy or electrical work that must be applied for the reaction to occur. [1]

$$\Delta H_f^0 = \Delta G^0 + T \cdot \Delta S \quad (4.2)$$

The reversible potential or the minimum voltage needed ( $V_{rev}^0$ ) at standard conditions can be calculated knowing the value of Gibbs free energy:

$$V_{rev}^0 = \frac{\Delta G^0}{z \cdot F} = 1.23V \quad (4.3)$$

The reaction mechanism of water electrolysis consists of two reactions. First, the water is split into oxygen and hydrogen protons, freeing electrons, as shown in reaction 2. This reaction is a catalyzed electrochemical reaction called the oxygen evolution reaction (OER); it is the rate determining step in water electrolysis:[1]



The hydrogen protons then cross the membrane to the other side of the PEM electrolyzer, and the hydrogen evolution reaction (HER) occurs. Hydrogen protons react with the electrons to form molecular hydrogen, following reaction 3.



The structure of a PEM electrolyzer can be divided into three different regions: anode, membrane, and cathode. Similarly, the anode and cathode are each composed of a bipolar plate, a current collector, and a catalyst layer. The parts of a PEM electrolyzer will be described in the following. Figure 4.1 shows an overview of the PEM electrolyzer structure:

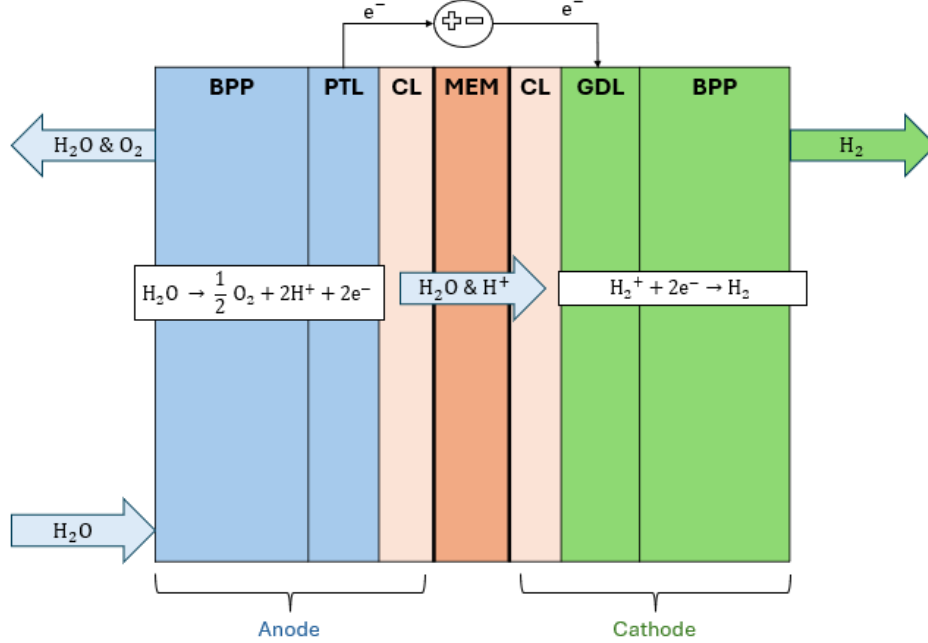
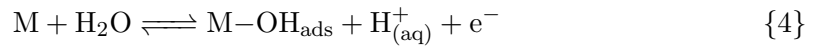


Figure 4.1. Electrolyzer overview

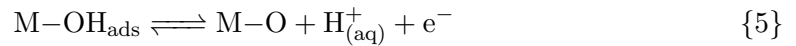
## 4.1 Anode

The anode side of the PEM electrolyzer is where the OER occurs. The reaction mechanism that describes the steps for splitting water into molecular oxygen, hydrogen protons, and electrons has been studied over the years. Different mechanisms with different Tafel slopes and reaction orders have been studied to characterize this reaction, but the one presented by Rossmeisl et al. (2007) is considered accurate and widely accepted. This mechanism consists of: [1] [35]

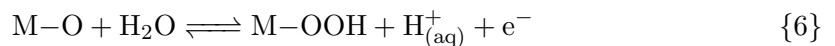
1. Water adsorption: A water molecule adsorbs to an active site ( $M$ ) on the surface of the metal catalyst, releasing one hydrogen proton and one electron to form adsorbed hydroxyl.



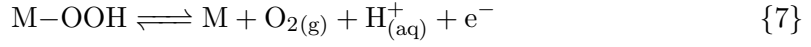
2. Hydroxyl oxidation: The adsorbed hydroxyl species is further oxidized. It loses a second hydrogen proton and an electron, leaving atomic oxygen attached to the catalyst surface.



3. Hydroperoxyl formation: A second water molecule attacks the adsorbed oxygen. Adsorbed hydroperoxyl species ( $OOH_{ads}$ ) are formed and a hydrogen proton and an electron are released. This step is often considered the rate-determining step (RDS). [35]



4. Final oxidation: The adsorbed hydroperoxyl species undergoes the final oxidation step. Molecular gaseous oxygen ( $O_2$ ), a hydrogen proton, and an electron are released. The empty catalyst active site is regenerated for the next cycle.



## 4.2 Proton Exchange Membrane

The proton exchange membrane is the core component of a PEM electrolyzer, as it selectively allows for transport of protons from the anode side to the cathode side.

It is made of perfluorosulfonic acid (PFSA) ionomers. Nafion<sup>TM</sup> has long been the favorite choice due to its good mechanical, chemical, and thermodynamic properties. However, it presents some disadvantages, such as temperature limitation and cost. [1][36]

Due to the low gas crossover rate through the membrane and the high proton conductivity, the PEM electrolyzer can be operated at high current densities, increasing its performance. High purity hydrogen is obtained using this technology. These characteristics play a key role in the economical aspects of PEM electrolyzers. [1]

PFSA membranes must be hydrated for their function. The proton conductivity increases with more hydration, so full hydration is essential to reduce losses and obtain higher performance. Water uptake can be calculated and represented differently. Using the relation between the wet sample weight ( $\omega_{wet}$ ) and the dry sample weight ( $\omega_{dry}$ ):[1]

$$\omega = \frac{\omega_{wet} - \omega_{dry}}{\omega_{dry}} \quad (4.4)$$

And calculating the number of water molecules per sulfonic acid site, knowing the relationship between the wet and dry sample weight, the equivalent weight (EW) or mass of dry polymer per mole of sulfonic acid group, and the molar mass of water ( $M_{H_2O}$ ):

$$\lambda = \frac{\omega \cdot EW}{M_{H_2O}} \quad (4.5)$$

High water uptake can also decrease the mechanical toughness and decrease the gas permeability through the membrane. Local dry outs of the membrane can occur when operating at high current densities. These concerns must be addressed to achieve optimal cell performance. [37]

Figure 4.2 shows a representation of the chemical structure of the membrane when hydrated. It consists of a backbone made of polytetrafluoroethylene (PTFE) with double ether perfluoro side chains that terminate in a sulfonic acid group ( $SO_3^-$ ). [1]

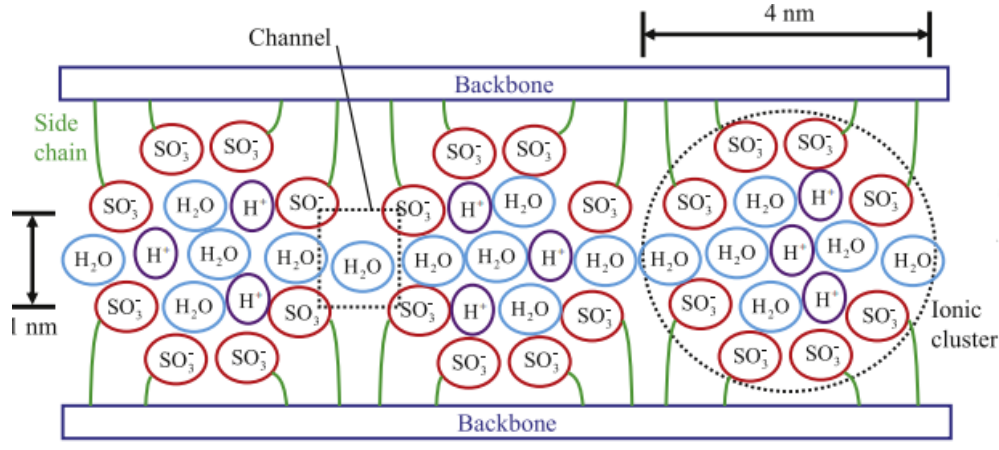


*Figure 4.2.* Membrane chemical structure [38]

### 4.2.1 Transport Mechanisms

Membranes must provide efficient proton transport; different transport mechanisms occur at the same time to facilitate this process. However, not all of them are beneficial for the PEM electrolyzer performance. Some involve the transport of water or oxygen.

The transport mechanism must be studied in detail to understand the physics behind the membrane functioning, and to be able to optimize the membrane conditions and its performance. The different transport mechanisms that occur during the PEM electrolyzer operation are presented in the following:

#### 4.2.1.1 Proton Conductivity

Proton conductivity is the ability of the membrane to transport protons. There are two main mechanisms that explain the movement of protons through the membrane: [36]

- Grotthuss mechanism (proton hopping): Hydronium ( $\text{H}_3\text{O}^+$ ) is formed by hydrogen protons when they dissociate hydrated sulfonate groups. The proton then jumps from one water molecule to another, forming new hydroniums and transporting the hydrogen proton. This mechanism is dominant at high water content and weak bonding water regions, when there are more water molecules and more hydroniums can be formed. [36][39]
- Vehicle mechanism: It is a diffusion mechanism in which hydrogen protons are dissolved in water to produce hydrated ions, such as hydronium ( $\text{H}_3\text{O}^+$ ), Zundel ( $\text{H}_5\text{O}_2^+$ ), or Eigen ( $\text{H}_9\text{O}_4^+$ ). This transport causes electro-osmotic drag. The hydrated ions move through the membrane from the anode to the cathode. This mechanism is dominant at low temperatures and low hydration levels of the membrane. [36] [40]

Figure 4.3 shows a simple representation of these two mechanisms:

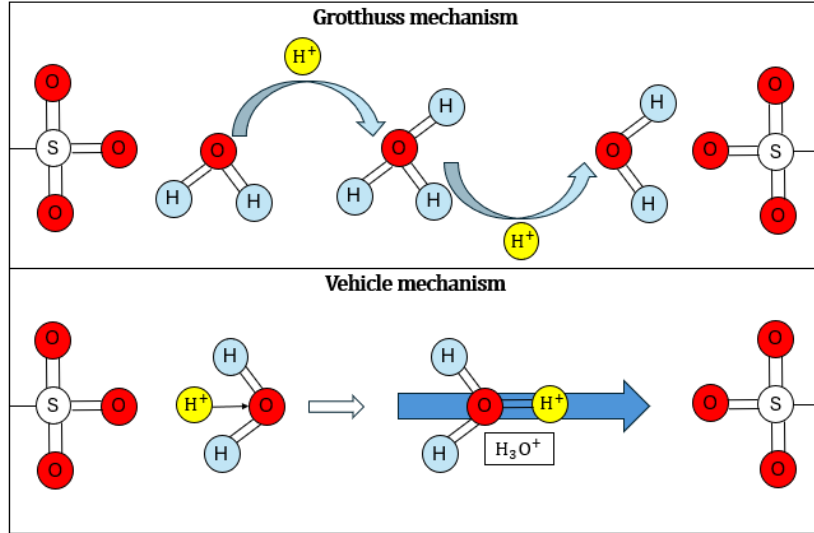


**Figure 4.3.** Grotthuss and Vehicle mechanisms

The proton conductivity ( $\kappa$ ) is the parameter that measures the electrical conductance of the membrane, it is usually expressed in S/cm.

This parameter is highly dependent on the temperature and water content of the membrane. The proton conductivity is directly proportional to the water uptake ( $\lambda$ ), in the range of  $2 < \lambda < 22$ , where 22 represents a fully hydrated membrane. Springer et al. (1991) developed the equation (4.6), which correlates the water uptake and temperature to the proton conductivity: [1]

$$\kappa = (0.005139\lambda - 0.00326) \cdot \exp \left[ 1268 \cdot \left( \frac{1}{303} - \frac{1}{T} \right) \right] \quad (4.6)$$

#### 4.2.1.2 Electro-osmotic drag

Electro-osmotic drag is a phenomenon that occurs in PEM water electrolysis. The water is dragged through the membrane as a result of the electro-osmotic drag caused by the hydrogen proton transport, from anode to cathode.

The presence of water in the output hydrogen would reduce the hydrogen purity and could cause some problems in the compression treatment of the hydrogen output stream, as well as in the storage of hydrogen. This can be reduced by using hydrophobic GDLs. [1] [37]

The electro-osmotic drag coefficient ( $k_{drag}$ ) is the parameter that measures the relation between the number of water molecules and the hydrogen protons transported. It is linearly dependent on the water uptake, the value of the electro-osmotic drag coefficient for fully hydrated membrane ( $\lambda = 22$ ) is in the range of 2.5 to 2.9.

It also depends on the temperature and current density. The experimentally determined correlation as a function of temperature (in °C), was found to be: [1] [41]

$$k_{drag} = 0.0134 \cdot T + 0.03 \quad (4.7)$$

It can also be calculated knowing the ratio between the water molecules transported by electro-osmotic drag ( $\dot{n}_{H_2O,eod}$ ) and the hydrogen protons ( $\dot{n}_{H^+}$ ): [41]

$$k_{drag} = \frac{\dot{n}_{H_2O,eod}}{\dot{n}_{H^+}} \quad (4.8)$$

### 4.2.1.3 Permeation

Permeation is also a transport mechanism inside the PEM electrolyzer. It consists of molecules of water, hydrogen, or oxygen crossing from one side of the membrane to the other. This phenomenon causes inefficiencies, and even safety problems.

Permeation is usually attributed to molecules in the vapor phase (hydrogen and oxygen), but water can also be transported by permeation from the cathode to the anode as a result of hydraulic permeation. [1][41]

Hydraulic permeation (*hyp*) of water from the cathode to the anode can be easily calculated by using Darcy's Law for water transport through porous materials. It is valid for Reynolds values lower than 10: [42]

$$\dot{n}_{H_2O, hyp} = \frac{-k_{H_2O} \cdot A \cdot \Delta P}{t_{mem} \cdot \mu_{H_2O}} \quad (4.9)$$

Where  $k_{H_2O}$  is the permeability of water through the membrane,  $A$  is the area,  $\Delta P$  is the pressure difference between the cathode and the anode,  $t_{mem}$  is the thickness of the membrane and  $\mu_{H_2O}$  is the viscosity of water.

Regarding gases, gas permeation causes  $O_2$  to cross from the anode to the cathode, and  $H_2$  from the cathode to the anode. This causes more cell degradation, lower efficiency, and less pure hydrogen production. These effects are more noticeable when operating at high pressures, since the oxygen consumes the membrane in the cathode and the accelerated crossover of hydrogen to the anode can create an explosive mixture. There are two main causes that contribute to permeation: [1]

- Diffusion:  $O_2$  and  $H_2$  are dissolved either in the water or in the membrane and then cross to the other side of the cell. However, diffusion through the polymer phase of the membrane is so slow that it is usually not considered. Only diffusion in water is considered.

Molecules go from the side with higher concentration to the side with lower concentration. Fick's Law describes the rate of permeation of species  $i$  ( $n_{diff,i}$ ):[1][43]

$$n_{diff,i} = D_i^{eff} \cdot \frac{\Delta C_i}{t_{mem}} \quad (4.10)$$

Where  $D_i^{eff}$  is the diffusion coefficient of the membrane, and  $\Delta C_i$  the concentration difference from anode to cathode, of species  $i$ .

Henry's law correlates the concentration of gases and their partial pressures, which is very useful when operating at changing or different conditions. [44]

- Convection: convective transport refers to the movement of gases dissolved in the water crossing the membrane, there are two factors that contribute to this phenomenon: pressure differences, and electro-osmotic drag.

The convective transport of species  $i$ , when they are dissolved in water, can be calculated knowing the water velocity ( $v_{H_2O}$ ), and the concentration of species  $i$  in water ( $C_i$ ): [43]

$$\dot{n}_i^{conv} = v_{H_2O} \cdot C_i \quad (4.11)$$

The convection driven by the pressure difference ( $\Delta P$ ) can be calculated using the following equation:

$$\dot{n}_i^{\Delta P} = n_i^{\Delta P} \cdot \frac{p_{i,cat} \cdot \Delta P}{t_{mem}} \quad (4.12)$$

Where  $n_i^{\Delta P}$  is a transport coefficient which depends on the membrane permeability, and ( $p_i$ ) is the partial pressure of species  $i$  at the cathode.

The electro-osmotic drag convection can be calculated as: [43]

$$\dot{n}_i^{drag} = n_{drag,i} \cdot p_{i,an} \cdot i \quad (4.13)$$

#### 4.2.2 Safety Limit

Gas crossover inside the PEM electrolyzer also plays an important role in cell safety. It can cause a dangerous situation during PEM electrolysis operation. The hydrogen content in oxygen must be kept below the ignition composition. This limitation is established for safety reasons, since an explosion could occur if this limit is exceeded. The maximum hydrogen content in oxygen is equal to 0.04 ( $x_{H_2,crit} \approx 0.04$ ).[1]

This condition also limits the co-compression or operation pressure that can be achieved. The critical hydrogen pressure or the maximum hydrogen partial pressure in the cathode at which the electrolyzer can be operated can be calculated using the following equation, where  $k_{H_2}$  is hydrogen permeability: [1]

$$P_{H_2,cat,crit} = t_{mem} \cdot \left( \frac{1}{4 \cdot F \cdot k_{H_2}} \cdot \frac{x_{H_2,crit}}{1 - x_{H_2,crit}} \right) \cdot i \quad (4.14)$$

This equation shows the dependence of the cathode critical hydrogen partial pressure on the current density, which is the only non-constant variable in the equation. At higher current densities, the critical value increases because more hydrogen can be diluted as a result of the increase in oxygen production. It can also be increased by using a thicker membrane.

Only hydrogen crossover is taken into account to calculate the critical point, since the oxygen crossover is less critical than hydrogen crossover due to the lower permeability of  $O_2$ , and the oxygen consumption before it reaches the cathode. [1] Figure 4.4 shows a simple overview of the permeation of the different substances in the cell. In the modeling part (Chapter 5), another image, which summarizes all the corresponding transport mechanism, is introduced.

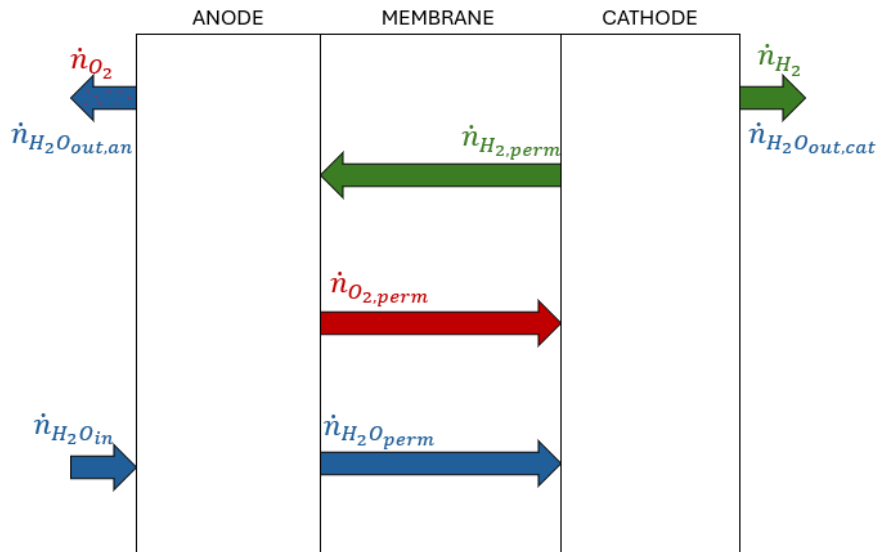


Figure 4.4. Permeation overview

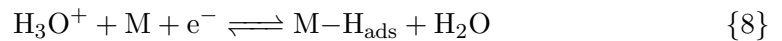
## 4.3 Cathode

The cathode side of the PEM electrolyzer is where HER occurs. This reaction is characterized by the electron transfer step being the only step reaction, with no parallel or consecutive steps. No products, intermediates, or starting materials are absorbed on the electrode, and no chemical bonds are formed or broken through the reaction. The geometry of the species is constant.

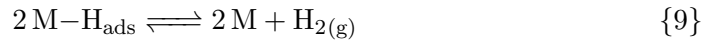
These features make the reaction a simple electrode reaction. However, the HER mechanism is highly dependent on the operating conditions and electrode materials. A general accepted mechanism has been developed to characterize the HER, it consists of a two-electron reaction:[1]

1. Mass transport of reactants (hydronium) from the membrane to the catalyst layer.
2. Charge transfer and adsorption: The reaction kinetics are described by the Volmer-Tafel mechanism, consisting of two consecutive steps:

- 2.1. Volmer step (electrochemical discharge): A hydrated proton accepts an electron to form an adsorbed hydrogen atom ( $H_{ads}$ ) on the catalyst active site ( $M$ ).

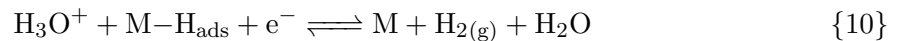


- 2.2. Tafel step (chemical recombination): Two adsorbed hydrogen atoms recombine to form a hydrogen molecule, releasing the catalyst active sites.



3. Desorption of molecular hydrogen ( $H_2$ ) from the catalyst surface.
4. Mass transport of the product gas away from the catalyst layer via diffusion, convection, and gas bubble formation.

It should be mentioned that there is another step that can occur and can be combined with the Volmer and Tafel steps. This is the Heyrovsky step, in which an adsorbed hydrogen atom reacts with a hydrated proton. The proton accepts an electron, freeing a hydrogen proton, which combines with the adsorbed hydrogen to form molecular hydrogen. Then, it is deattached from the metal surface, regenerating the active site. [1]



## 4.4 Bipolar Plates

The bipolar plates (BPP) are the components responsible for providing structure to the cell and flow channels to distribute the water uniformly over the cell. They are located at the outer boundaries on the anode and cathode sides. Furthermore, they remove the oxygen and hydrogen produced out of the cell, and their thermal conductivity allows for easier temperature management. They also act as electron conductors to complete the circuit and connect individual cells in series when configured as a stack. [1]

Bipolar plates must have high thermal and electrical conductivity, high corrosion resistance, mechanical strength, and low gas permeability. Different materials, such as titanium, graphite, or coated stainless steel, have been studied over the years to fulfill all these requirements. Titanium is the most widely used material for bipolar plates, but it also presents some drawbacks, such as susceptibility to oxidation and high cost. Bipolar plates and current collectors are the most expensive parts of a PEM electrolyzer. [1]

## 4.5 Terminal Current Collectors

Terminal current collectors are metal plates that are used to transfer and collect electrons directly from the external power supply. They must be made of electrically conductive materials with high corrosion resistance, as they operate in the same harsh environment as bipolar plates. [1]

## 4.6 Transport Layers

Transport layers play a crucial role in the operation of a PEM electrolyzer. They are responsible for conducting electrons from the catalyst layers to the bipolar plates and removing oxygen and hydrogen from the catalytic layers in an efficient way.

Because they work in the same environment as the bipolar plates, characteristics such as corrosion resistance or electrical conductivity are very important. They must also present adequate porosity, and the pore size and structure must be optimized. Inadequate porosity can significantly increase the cell overpotential. [1]

There are two transport layers in the PEM electrolyzer. They present different characteristics depending on whether they are located on the anode or cathode side:

### 4.6.1 PTL

The porous transport layer (PTL) is placed on the anode side. In addition to collecting electrons and removing the gases, it also serves as a pathway to deliver water from the anode bipolar plate to the catalyst layer.

The materials used for this purpose are usually titanium or sintered titanium.[45]

Optimizing the PTL thickness and porosity is vital to achieve high efficiencies. The PTL thickness significantly affects the liquid water access to the catalyst layer and, consequently, the cell's performance. Thin PTLs with small pores are generally preferred. They present a more uniform pore distribution and porosity, and a higher interface contact between layers, which reduces the ohmic resistances and increases the performance. The optimized pore diameter was found to be 10–13  $\mu\text{m}$ , and the optimized porosity is around 30%. These values would maximize gas/water transport and improve cell performance. [45] [46]

Coating PTLs is a critical strategy for mitigating corrosion and ensuring the long-term durability and high performance of PEM electrolyzers. Platinum coating is the industrial standard. However, different materials, such as gold, and techniques, such as plasma spraying, are being studied to improve PEM electrolyzer performance or reduce its cost. [46]

### 4.6.2 GDL

The gas diffusion layer (GDL) is the name attributed to the porous transport layer or current collector placed on the cathode side. Its functioning is the same as that of the PTL, but it is adapted for cathode conditions, which primarily involve gas-phase transport from the catalyst layer to the bipolar plate.

Therefore, carbon paper and carbon cloth are used for this purpose because they are significantly cheaper than Ti-based PTLs and can operate on the cathode due to the low potential. They usually have a high porosity, which facilitates the hydrogen flow and reduces the concentration overpotentials. They are treated with PTFE to facilitate the removal of transported water. [1][47]

## 4.7 Catalysts

Electrocatalysts are fundamental to the operation of PEM electrolyzers, serving to lower the activation energy for both the OER and the HER. The investigation of catalyst materials is still a major topic nowadays, since they have a major impact on the performance, lifetime, and cost of the cell. Different materials are used depending on where the catalyst is used, in the anode for the OER, or in the cathode for the HER. [1]

### 4.7.1 Anode Catalyst

$\text{IrO}_2$  and Ir black have been the industrial standard for anode catalysts since they were discovered in 1973. They are highly stable and resistant to corrosion, making them suitable for work in anode conditions. Although there are other catalysts with higher electrochemical activity, such as  $\text{RuO}_4$ , the stability properties of  $\text{IrO}_2$  made it the number one option for PEM electrolysis. [1]

Different techniques and catalysts have been studied to try to increase the electrochemical activity of the anode without decreasing the stability or lifetime of the cell and, consequently, increase the performance of the cell. Mixtures with Ru and ternary materials have been tested for this purpose, as well as the use of support materials and nanostructuring of catalysts to increase their active area.[1]

### 4.7.2 Cathode Catalyst

Pt has always been considered to be the best electrocatalyst for the HER. It presents a high stability, resisting corrosive low pH conditions. It also allows the operation at high current densities. [1]

Because of the non-oxidizing environment of the cathode, Pt/C has become the industry standard cathode catalyst, because Pt is a well-known catalyst and carbon maximizes its surface area, increasing the efficiency and reducing the price.

Nevertheless, the reduction of Pt loading or the usage of new catalysts is of great interest for the development of large-scale PEM electrolyzers. The structural design of the cathode catalyst plays a key role in the hydrogen crossover, and consequently, the performance of the PEM electrolyzer. [1][48]

## 4.8 PEM Electrolyzer Characterization

The most important characteristics and parameters that are used to study the performance of a PEM electrolyzer will be presented in this section.

### 4.8.1 I-V curve

The I-V curve or polarization curve is the representation of the cell voltage over the current density. This curve shows all the voltage losses from the anode to the cathode summarized in one curve.

Then, the voltage can be calculated as the sum of all the voltages that must be applied to overcome the voltage losses, these voltages are called voltage overpotentials. There are three main loss mechanism that contribute to the cell polarization, these are: [1]

- **Activation losses:** These are the losses attributed to the slow reaction kinetics. They are mainly faradaic losses, caused by the direct transfer of electrons between redox couples of OER and HER. These losses are more pronounced at low values of current density, when the cell is being activated, and can be divided into anode and cathode activation losses. [1]
- **Ohmic losses:** The ohmic losses are non-faradaic losses which occur due to the resistance of electrons to go through the electrodes and cell components, and due to the resistance of proton transport through the membrane. Materials play an important role here. The ohmic losses are directly proportional to the current, following Ohm's Law. [1]
- **Mass transport losses:** Diffusion and gas bubble accumulation are the two main factors that contribute to these non-faradaic losses. Diffusion losses occur when there is a mass transfer limitation caused by bubbles preventing water from reaching the active sites. Gas bubble losses are attributed to the reduction of the effective catalyst surface area due to large bubbles adhering to the electrode surface. The voltage applied to compensate for these losses is called concentration overpotential, and it increases exponentially at high current densities when gas generation rates are high and there is a higher concentration gradient. [1]

Figure 4.5 shows a representation of the behavior of the different overpotentials depending on the current density regions. It can be observed how the activation losses increase exponentially and dominate in the initial zone, and the concentration losses behave similarly but in the final region. The linearity of ohmic losses, and its domination on the central zone can also be observed.

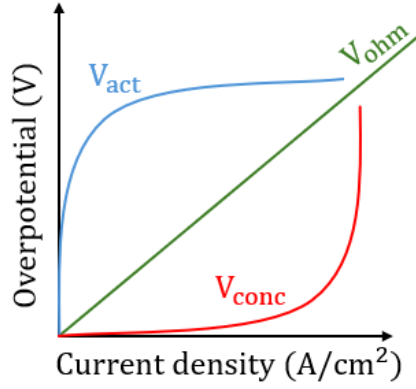


**Figure 4.5.** Voltage overpotentials behavior

The total voltage that must be applied to the cell, the one that represents the electrical energy needed for the water decomposition, can be calculated as:[1] [16]

$$V = V^0 + V_{loss} = V^0 + V_{act} + V_{ohm} + V_{conc} \quad (4.15)$$

Where  $V^0$  is the reversible voltage,  $V_{loss}$  is the sum of the overpotentials,  $V_{act}$  is the activation overpotential or the voltage attributed to the activation losses,  $V_{ohm}$  is the ohmic overpotential, and  $V_{conc}$  is the concentration overpotential.

$V_{act}$  can be calculated by using the following equation: [1][16]

$$V_{act} = V_{act,an} + V_{act,cat} = \frac{R \cdot T}{\alpha_{an} \cdot F} \ln \left( \frac{i}{i_{0,an}} \right) + \frac{R \cdot T}{\alpha_{cat} \cdot F} \ln \left( \frac{i}{i_{0,cat}} \right) \quad (4.16)$$

The first term of the sum is the anode activation overpotential  $V_{act,an}$ , and the second one is the cathode activation overpotential  $V_{act,cat}$ .

$R$  is the universal constant for gases ( $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$ ),  $T$  is the temperature,  $\alpha$  is the charge transfer coefficient,  $F$  is the Faradaic constant, and  $i$  is the current density.

The Butler-Volmer equation is used in electrochemical reactions to relate the electrode potential and the current density. It is used to model the activation region, until the reaction rate of the electrochemical reactions reaches an equilibrium: [1][49]

$$i = i_0 \cdot \left[ e^{\left( \frac{\alpha \beta F V_{act}}{RT} \right)} - e^{\left( -\frac{\alpha(1-\beta) F V_{act}}{RT} \right)} \right] \quad (4.17)$$

The first term refers to the OER and the second term refers to the HER.  $i_0$  is the exchange current density, which determines the rate of the electrochemical reaction at equilibrium. It must be optimized to increase the kinetics of the OER. It can be done by reducing the activation barrier, using different materials, or setting optimal operating conditions.

$\alpha$  is the number of electrons transferred in the OER or in the HER.  $\beta$  is the symmetry factor and represents an electron transfer coefficient within a range of  $0 < \beta < 1$ . Quantifies the impact of the electrical energy input on the redox process. [1] [49]

When the overpotential is very high, the reverse reaction can be assumed to have no impact on the current density, so the second term of the equation can be ignored and the equation can be simplified. [1]

The Tafel relationship shows the relationship between the overpotentials and the reaction rate. Even though the Tafel equation does not fit perfectly with overpotential behavior in reality due to mass transport limitations when operating at high current densities, it is widely used to approximate the overpotentials that compose the IV-curve. It is especially useful for the activation region, in which the overpotential can linearly fit with the logarithmic current density values. The Tafel equation is the following: [1] [50]

$$V_{act} = \frac{R \cdot T}{\alpha \cdot \beta \cdot F} \cdot \ln(i) - \frac{R \cdot T}{\alpha \cdot \beta \cdot F} \cdot \ln(i_0) = a \cdot \ln(i) - b \quad (4.18)$$

$a$  is the so called Tafel slope, it provides an idea about the reaction rate and the rate-determining step of the reaction mechanisms.  $b$  is intercept of the Tafel fit. It is a constant value that can be used with the Tafel slope to calculate the exchange current.

These Tafel constants ( $a$  and  $b$ ) are determined experimentally. [1]

$V_{ohm}$  or the overpotential caused by ohmic losses can be calculated applying Ohm's law: [1]

$$V_{ohm} = i \cdot ASR \quad (4.19)$$

Where  $ASR$  is the overall area-specific resistance of the cell.  $V_{ohm}$  can be divided into two terms, the electrical resistance and the membrane resistance: [1] [19]

$$V_{ohm} = V_{ohm,e} + V_{ohm,mem} = \frac{I}{A} \sum R_i + t_{mem} \cdot \frac{i}{\kappa} \quad (4.20)$$

Where  $I/A$  is the current density calculation, total current divided by the area, and  $\sum R_i$  is the sum of the electrical resistances that contribute to ohmic losses. The ohmic overpotential attributed to the membrane and its resistance to proton transport is calculated with the second term, using the membrane thickness and its proton conductivity.

Fick's law can be used to calculate the concentration of species and then the overpotential, by applying the Nernst equation: [1] [19]

$$V_{conc} = \frac{R \cdot T}{z \cdot F} \cdot \ln\left(\frac{C_i}{C_{ref}}\right) \quad (4.21)$$

Where  $c_i$  is the concentration at the electrode interface and  $c_{ref}$  is the concentration at a reference position. The following equation can be derived:

$$V_{conc} = \frac{R \cdot T_{an}}{4 \cdot F} \ln\left(\frac{C_{an,O}}{C_{0,O,an}}\right) + \frac{R \cdot T_{cat}}{2 \cdot F} \ln\left(\frac{C_{cat,H}}{C_{0,H,cat}}\right) \quad (4.22)$$

The equation is divided into two different terms, the first one for the anode concentration overpotential and the second one for the cathode. The concentration losses in the anode only take into account the losses caused by the oxygen, and the concentration losses in the cathode the ones generated by the hydrogen. This consideration is done due to the assumption that only the gas crossover of oxygen from the anode to the cathode, and gas crossover of hydrogen from the cathode to the anode are considered.

The concentrations of oxygen and hydrogen, in the anode and in the cathode respectively, can be calculated using the following equations: [19]

$$C_{0,O,an} = C_{O_2,ch} + \frac{\delta_{e,an}}{D_{eff,an}} \cdot \dot{n}_{O_2} \quad (4.23)$$

$$C_{O_2,ch} = \frac{\dot{n}_{O_2}}{\dot{n}_{O_2} + \dot{n}_{H_2O,an}} \cdot \frac{P_{an}}{R \cdot T_{an}} \quad (4.24)$$

$$C_{0,H,cat} = C_{H_2,ch} + \frac{\delta_{e,cat}}{D_{eff,cat}} \cdot \dot{n}_{H_2} \quad (4.25)$$

$$C_{H_2,ch} = \frac{\dot{n}_{H_2}}{\dot{n}_{H_2} + \dot{n}_{H_2O,cat}} \cdot \frac{P_{cat}}{R \cdot T_{cat}} \quad (4.26)$$

Where  $P$  is the pressure,  $\delta_e$  is the thickness of the diffusive layers (PTL and GDL),  $D_{eff}$  is the diffusion coefficient and  $\dot{n}$  is the flow rate of the species.

#### 4.8.2 Nernst Equation

The Nernst equation is used to calculate the reversible voltage of the water splitting process, using the reversible voltage under standard conditions. It considers the effects of temperature and species activity, which are represented by their partial pressures ( $p$ ). The water activity based on the partial pressure is assumed to have a value of 1. [1] [19]

$$V_{rev} = V_{rev}^0 - \frac{R \cdot T}{2 \cdot F} \cdot \ln \left[ \frac{1}{\left( \frac{p_{H_2}}{p_{op}} \right) \cdot \left( \frac{p_{O_2}}{p_{op}} \right)^{0.5}} \right] \quad (4.27)$$

This equation is also derived for use it to calculate the concentration overpotential, as shown in Equation 4.21.

### 4.9 Hydrogen Production

Hydrogen production is usually expressed in normal cubic meters per hour ( $N \cdot m^3/h$ ) or in normal liters per minute (NLPM). Units are referred to standard conditions of temperature and pressure (273.15K and 101.325KPa), and a relative humidity of 0%. It can also be expressed in kg/h. [1]

Faraday's law is usually used to calculate hydrogen production. The electrical charge consumed by the cell ( $Q$ ) can be used to calculate the hydrogen produced in water electrolysis: [1]

$$Q = n_{H_2} \cdot z \cdot F \quad (4.28)$$

Where  $n_{H_2}$  represents the number of moles of hydrogen produced. The equation can be derived to calculate the mass of hydrogen produced ( $m_{H_2}$ ) over a specific period of time ( $t$ ), using the applied current ( $I$ ) and the molar mass of hydrogen ( $M_{H_2}$ ): [1]

$$m_{H_2} = \frac{I \cdot t \cdot M_{H_2}}{z \cdot F} \quad (4.29)$$

Hydrogen purity is another important aspect of hydrogen production. Hydrogen usually comes out of the PEM electrolyzer with traces of water, oxygen, and other contaminants. More steps can be added to the process for further purification, such as pressure swing adsorption. However, this would increase the energy needed and the cost of the process. It is important to achieve high hydrogen purity directly. [1]

## 4.10 Efficiency

The efficiency can be measured following different approaches, depending on how many steps of hydrogen production by water electrolysis process are taken into account, or which energy is measured. An overview of the most important efficiencies is shown in the following: [1] [23] [45]

- Faradaic efficiency: It is the efficiency that relates the hydrogen output ( $\dot{n}_{H_2}$ ) to the total hydrogen produced ( $\dot{n}_{H_2,prod}$ ). This efficiency is usually around 99.9%, it decreases when operating at higher pressures, due to the increase in hydrogen crossover from cathode to anode. It can be calculated using the following equation: [1][23]

$$\eta_{faraday} = \frac{\dot{n}_{H_2}}{\dot{n}_{H_2,prod}} \quad (4.30)$$

- Energy content efficiency: The energy content of the hydrogen produced is used to calculate the efficiency with respect to the electrical power applied to obtain hydrogen ( $P_{el}$ ), similar to the first law efficiency. The lower heating value (LHV) of hydrogen is used for this purpose. An assumption of 100% Faradaic efficiency is usually made, as is shown for the simplified equation in the right side: [23] [45]

$$\eta_{LHV} = \frac{\dot{n}_{H_2} \cdot LHV_{H_2}}{P_{el}} = \frac{LHV_{H_2}}{2 \cdot F \cdot V} \quad (4.31)$$

- First law efficiency: Relates the specific energy consumption ( $\Delta H_{OR} = Q + W_t$ ), with the electrical work applied: [1]

$$\eta_{\Delta H} = \frac{\Delta H_{OR}}{W_t} \quad (4.32)$$

- Second law efficiency: Similar to the first law efficiency, but only considering the reversible electrical work ( $\Delta G_{OR}$ ) and not all the energy consumption: [1]

$$\eta_{\Delta G} = \frac{\Delta G_{OR}}{W_t} \quad (4.33)$$

- Voltage efficiency: Relates the real cell voltage to the ideal open-circuit voltage  $V_{OCV}$ . [1]

$$\eta_V = \frac{V_{OCV}}{V_{cell}} \quad (4.34)$$

- Overall energy efficiency: Faradaic efficiency and voltage efficiency can be used to calculate the overall energy efficiency, since they consider the faradaic losses and the electrical energy losses caused by the cell's activation, ohmic, and mass transport overpotentials.:

$$\eta_E = \eta_{faraday} \cdot \eta_V \quad (4.35)$$

- Thermodynamic efficiency: It is the relation between the reversible voltage and the thermoneutral voltage: [1]

$$\eta_{th} = \frac{V^0}{V_{th}} \quad (4.36)$$

- Stack and process efficiencies: These efficiencies are important when trying to get the total efficiency of a stack of PEM electrolyzers, or the efficiency of the water electrolysis processes, including external steps such as compression. [23]

## 4.11 Lifetime

Operational lifetime is the total duration a device can function continuously until interruption due to a complete failure or the requirement to replace a core component of the system. The lifetime limit is reached when a component failure makes further operation not possible, when maintenance costs become too high to economically justify continued operation, or when limited useful life of the device is reached. [1]

The standard end-of-life criterion for PEM electrolyzers is the loss of membrane thickness. For safety reasons, when the membrane loses 20% of its original thickness, the lifetime limit is reached. At this point, gas crossover could surpass the safety limit, causing explosions, as well as operation inefficiencies. [1]

Original equipment manufacturers usually establish another end-of-life criterion, more economically-related. PEM electrolyzers reach their lifetime limit when the voltage or power required is 20% higher than the one needed at the start of life or initial operation. This criterion is based on a trade-off with electricity costs. [51].

Degradation plays a crucial role in determining the end-of-life of PEM electrolyzers. The minimization of these degradation mechanisms impact, by optimizing the operation conditions and the selection of materials, is of great importance to increase the lifetime of PEM electrolyzers and make them profitable over time. [1]

Increasing the lifetime of the PEM electrolyzer has always been a challenge in the field. When using high Pt-loadings, the targeted lifetime of an electrolyzer is greater than 60,000 hours, according to U.S.DOE. [1] [52]

## 4.12 Degradation

Degradation plays a crucial role in the determination of the performance of a PEM electrolyzer over time. Degradation mechanisms attack the different components of the cell, degrading them and making them less efficient. It can also affect the purity of the hydrogen produced.

It is of great importance to understand how these mechanisms behave, and what their impact on the cell is under different conditions. Optimization techniques and mitigation strategies must be applied to minimize the effects of degradation. This is essential for the development of this technology and for the commercialization of PEM electrolyzers. [1]

The degradation can be divided into two types, reversible and irreversible degradation:

- **Reversible degradation:** Degradation that can be recovered or, at least, partially recovered. It is usually reversed by changing the operating conditions or turning off the operation. These mechanisms are frequently overlooked because the associated performance losses can be recovered. However, they notably affect the efficiency of PEM electrolyzers and can stimulate irreversible degradation. During operation, these reversible phenomena can contribute to voltage increases on the order of hundreds of millivolts. [1][53]

- Irreversible degradation: Degradation that cannot be recovered. Once it happens, the component is permanently degraded. It is the most concerning kind of degradation, due to its impact over time. There is a wide range of factors and degradation mechanisms that contribute to irreversible degradation. [10]

Figure 4.6 summarizes the most important irreversible degradation mechanisms. They are divided into three groups: low, medium, and high concern. The impact is calculated on the basis of the severity of the mechanism and its frequency: [54]

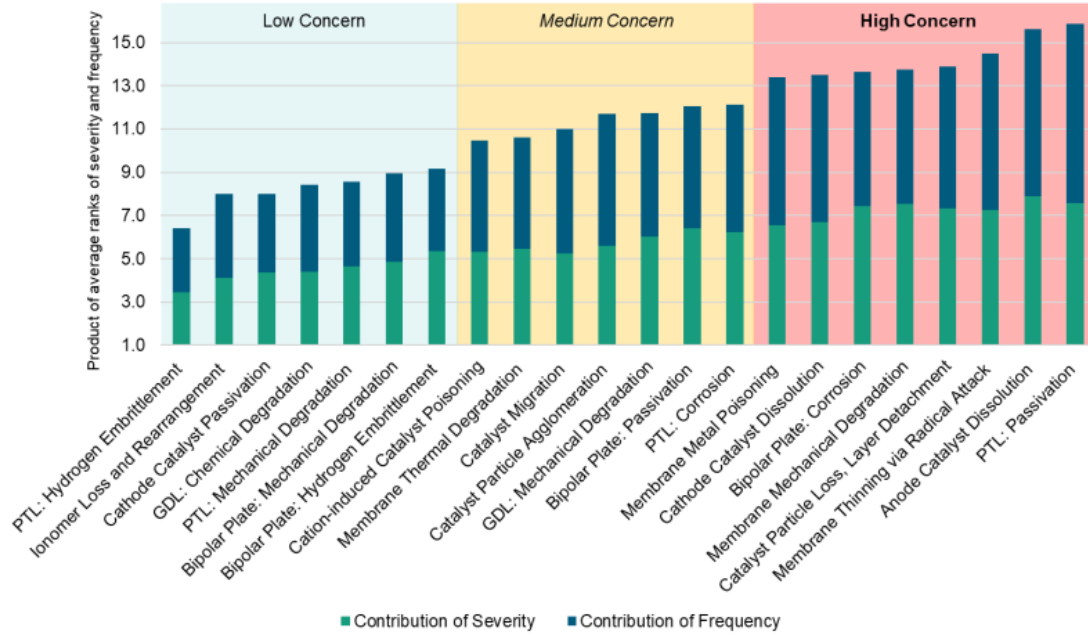


**Figure 4.6.** Degradation mechanism overview [54]

The most important mechanisms will be explained in the following, describing their working principles, their impact on the PEM electrolyzer components and performance, and some mitigation strategies. The degradation mechanisms present in the developed model will be explained in more detail.

#### 4.12.1 Reversible Degradation

There are different reversible degradation mechanisms that affect the performance of the PEM electrolyzer. However, the most notable one is the accumulation of bubbles inside the cell, which cause significant reversible losses.

Moreover, the permanent accumulation of bubbles can accelerate irreversible degradation mechanisms. They can cause local hotspots in cell components or accelerate other mechanisms. [1] [55]

Bubbles are generated in the anode with the OER producing oxygen bubbles and in the cathode with the HER producing hydrogen bubbles. Although hydrogen bubbles can flow efficiently out of the cell, oxygen bubbles cannot easily leave the anode, and they can cause some reversible degradation mechanisms. Oxygen bubbles are produced in the anode catalyst layer and follow three steps before leaving the surface: nucleation, growth, and detachment. Slow bubble detachment, the coverage of the catalyst active surface, and insufficient bubble

generation sites provoke an increment in the activation, ohmic, and mass transport losses. [55]

After being detached from the catalyst surface, the oxygen bubbles cross the PTL to reach the bipolar plate and leave the cell with the output water stream. This could cause gas accumulation, which increases the ohmic and mass transport losses, reducing the cell efficiency. Bubbles can also cause mechanical degradation, especially at high current densities and on the catalyst. [55]

A shutdown of the operation is usually enough to remove the bubbles inside the cell and reduce this kind of reversible degradation. Figure 4.7 shows a visual representation of the main issues that bubbles cause inside the PEM electrolyzer. [55]

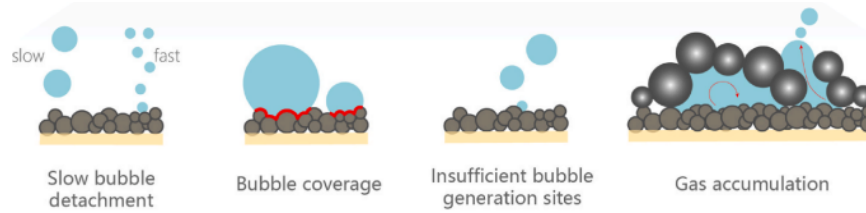


**Figure 4.7.** Overview of bubble issues [55]

The effects of bubbles on cell performance are particularly pronounced at high current densities when more oxygen is being produced. This bubble impact can be reduced by using a catalyst structure that increases the number of bubble nucleation sites and, consequently, reduces the bubble detachment size and increases the detachment frequency. The selection of materials and the control of operating conditions are also important in reducing the impact of bubbles. [55]

Other examples of reversible degradation, which have a lower impact on the cell performance, are:

- Membrane reversible degradation: Deionized water is used as input for PEM electrolysis. It can dissolve metallic ions when in contact with stainless steel, such as in the input stream pipes. This can reduce the ionic conductivity of the membrane. [1]
- Catalyst degradation: The metallic ions are also attached to the Pt catalyst surface, reducing the active area of it. This causes an increase in the overpotential needed for the HER, and consequently, for the water electrolysis process. [1]

These examples also accelerate other mechanisms as corrosion. They are difficult to reverse because the metallic ions would be removed by soaking the membrane in an acidic aqueous solution. It is expensive and slow. [1]

The operating conditions and components properties are of great importance for this kind of degradation. Low anode loading, low temperatures, low anode coating quality, and water contamination are some examples of parameters that increment the reversible degradation. [1] [53]

### 4.12.2 Chemical Ionomer Degradation

Chemical ionomer degradation occurs when a side reaction mechanism consumes the membrane compounds, making it thinner. This kind of degradation is also known as membrane thinning. [25] [10]

This phenomenon occurs when molecular oxygen crosses over from the anode to the cathode and is reduced to hydrogen peroxide ( $H_2O_2$ ). The hydrogen peroxide then initiates a radical chain reaction, a process described by Fenton's reaction mechanism.

Hydrogen peroxide also reacts with metallic contaminants to produce more radicals, mainly with iron ions ( $Fe^{+2}$  and  $Fe^{+3}$ ). The radicals produced are hydroxyl radicals ( $HO^\bullet$ ) and hydroperoxyl radicals ( $HOO^\bullet$ ). [25]

The hydroxyl radicals react with the PFSA membrane, breaking the fluorinated carbon backbone bonds. The membrane structure is decomposed, releasing fluoride ions, which combine with hydrogen protons to form hydrogen fluoride (HF). This is a crucial step in membrane thinning, as the measurement of the hydrogen fluoride released, also known as fluoride emission rate (FER), provides a measurement reference for the rate of chemical ionomer degradation of the membrane. [25] [56]

Table 5.3 shows the reaction mechanisms presented by Chandesris et al. [25], which can be used as a reference to understand the reactions involved in the radicals formation and attack to the membrane.

**Table 4.1.** Main chemical and electrochemical degradation reactions

| No. | Reaction                                                   | Rate constant                                                     |
|-----|------------------------------------------------------------|-------------------------------------------------------------------|
| 1   | $O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$              | -                                                                 |
| 2   | $H_2O_2 \rightarrow 2HO^\bullet$                           | $k_2 = 1.2 \times 10^{-7} (s^{-1})$                               |
| 3   | $H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^\bullet + HO^-$ | $k_3 = 1.05 \times 10^8 \exp(-9460/RT) (l \cdot mol^{-1} s^{-1})$ |
| 4   | $H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HOO^\bullet + H^+$ | $k_4 = 4 \times 10^{-5} (l \cdot mol^{-1} s^{-1})$                |
| 5   | $HO^\bullet + Fe^{2+} \rightarrow HO^- + Fe^{3+}$          | $k_5 = 2.3 \times 10^8 (l \cdot mol^{-1} s^{-1})$                 |
| 6   | $HO^\bullet + H_2O_2 \rightarrow HOO^\bullet + H_2O$       | $k_6 = 2.7 \times 10^7 (l \cdot mol^{-1} s^{-1})$                 |
| 7   | $HO^\bullet + O_2 \rightarrow HOO^\bullet$                 | $k_7 = 1.2 \times 10^{10} (l \cdot mol^{-1} s^{-1})$              |
| 8   | $HOO^\bullet + Fe^{3+} \rightarrow Fe^{2+} + O_2 + H^+$    | $k_8 = 2 \times 10^4 (l \cdot mol^{-1} s^{-1})$                   |
| 9   | $HOO^\bullet + Fe^{2+} + H^+ \rightarrow Fe^{3+} + H_2O_2$ | $k_9 = 1.2 \times 10^6 (l \cdot mol^{-1} s^{-1})$                 |
| 10  | $HO^\bullet + R_f-CF_2-COOH \rightarrow \text{products}$   | $k_{10} \leq 10^6 (l \cdot mol^{-1} s^{-1})$                      |

Other reactions can also take place, as other contaminants, such as Copper ions ( $Cu^{+2}$ ), can also contribute to membrane thinning. [56]

Although chemical ionomer degradation does not have a significant impact on the overpotential, this is the primary factor determining the operational lifetime of PEM electrolyzers. Thinner membranes present lower mechanical stability, and pinholes are formed

due to the appearance of preferential sites, the increase of initial thin spots, or mechanical weaknesses. This increases gas crossover and can cause safety problems.

Paradoxically, membrane thinning can even increase cell performance and efficiency. The path of the protons becomes shorter, reducing the ohmic losses and the cell overpotential. [1] [25] [10]

### 4.12.3 Catalyst Dissolution

Catalyst dissolution is another irreversible degradation mechanism that occurs in PEM water electrolysis. It takes place for both the Iridium in the anode and the Platinum in the cathode. However, Iridium dissolution has a greater impact on cell performance than Platinum dissolution. This degradation mechanism consists of the catalysts reacting to end being dissolved in water, different reaction mechanisms take place. [10][54]

#### 4.12.3.1 Iridium Dissolution

Iridium dissolution is one of the most impactful degradation mechanisms during PEM water electrolysis operation. Depending on the applied potential, Iridium and iridium oxide can react to form  $\text{Ir}^{3+}$ ,  $\text{IrO}_4^{2-}$ , and  $\text{Ir}_2\text{O}_7^{2-}$ , which are soluble in water. The iridium oxides ions come from a previously formed  $\text{IrO}_3$ . Figure 4.8 shows an overview of the Iridium dissolution pathways. These reactions are thermodynamically favored in acidic environments ( $\text{pH} < 7$ ). [10]

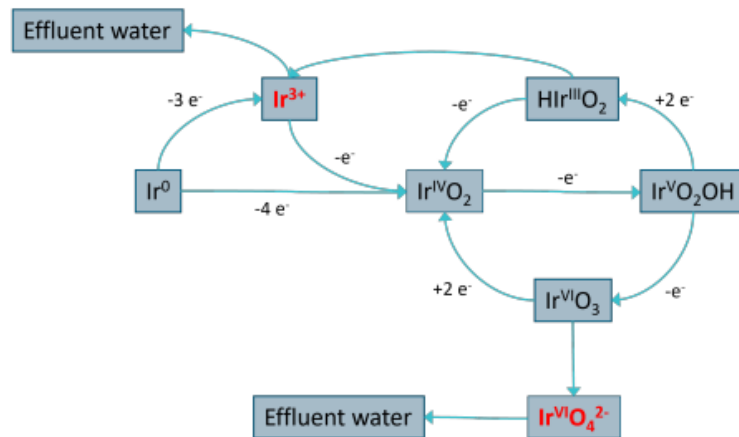


Figure 4.8. Iridium dissolution overview [10]

High Iridium loads, high temperatures, impurities, and transient operation accelerate the dissolution of Iridium. Cycling the voltage constantly shifts the Ir between stable and unstable oxidation states. However, Iridium dissolution can be mitigated by selecting an appropriate catalyst support, such as inert oxides, by optimizing the operation conditions, and by avoiding contaminants. [10]

### 4.12.4 Passivation

Passivation is the phenomenon that occurs when a metal is oxidized, forming a growing layer of this passivated metal, which is attached to the surface of one of the cell components. It is another of the most impactful degradation mechanisms in PEM electrolyzers. It has a more

significant effect on the PTL, although it also considerably degrades the bipolar plates. It is more significant in long term operations of the PEM electrolyzer[10] [54]

Under specific conditions, such as high humidity, potential, and an oxidizing and acidic environment, the Titanium placed in the anode is oxidized, forming a layer of titanium dioxide ( $\text{TiO}_2$ ). This layer presents low electrical conductivity and also causes a higher contact resistance between layers. Consequently, there are more ohmic losses, and the efficiency of the cell decreases.

The passivation layer also has some advantages; it works as protection barrier against hydrogen embrittlement. Passivation is more noticeable at high current densities. [10]

The right choice in the coating materials used is crucial for the minimization of the negative effects of passivation. [10]

#### 4.12.5 Agglomeration and Ostwald Ripening

Agglomeration and Ostwald ripening are degradation mechanisms that affect the performance of the catalyst. They reduce the catalyst active area by reducing the surface-to-volume ratio of the catalyst: [1]

- Agglomeration: this is the accumulation of particles in the catalyst surface. Nanoparticles migrate through the catalyst layer, collide, and form larger accumulations of nanoparticles, called agglomerations. [57]
- Ostwald ripening: metal ions are dissolved from smaller particles, they diffuse through the electrolyzer, and redeposit to be combined to form larger particles. The active area of the catalyst decreases as its size grows, causing a decrease in the catalyst efficiency. [1]

The catalyst surface can also be deactivated by foreign compounds that poison the cell, such as iron or copper ions. [1]

# Model Methodology 5

In this chapter, the simulation model developed and the experimental data acquisition will be described. The proposed approach is a hybrid semi-empirical 1D model, in which experimental data is coupled with theoretical equations, enabling the calculation of the performance parameters and degradation of a PEM electrolyzer over time. Python was selected as the coding language. This chapter intends to summarize all the used equations to replicate the model.

Lab work was done to obtain data for the model. A 25 cm<sup>2</sup> PEM electrolyzer was operated for 500 h. IV-curve and EIS measurements were also conducted throughout the experiment and a post-mortem XRD test was performed.

The model is divided into different computational modules to have a clearer and more practical view and manageability. Each of the modules has a function, and they were integrated to drive the simulation. Table 5.1 shows an overview of the different blocks present in the model:

**Table 5.1.** Overview of the computational modules and their respective functions.

| Module                      | Function                                          |
|-----------------------------|---------------------------------------------------|
| Parameters                  | Input and cell parameters                         |
| Water properties            | Water properties calculation                      |
| Production                  | Species production and mass transfer calculations |
| EEC                         | Equivalent electrical circuit                     |
| Performance and degradation | Performance and degradation simulation            |

The chronology of the development of the model is shown in Figure 5.1:

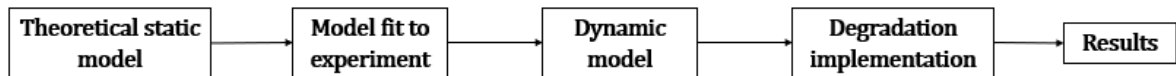


**Figure 5.1.** Model Flow Diagram

Firstly, a static theoretical model of a PEM electrolyzer was developed. This model simulates the cell performance as a function of current density, and calculates the voltage losses, hydrogen production, mass transfer, and efficiencies.

After verifying that the model worked as intended, the cell parameters and performance were fitted to the experimental data and the obtained results. This was done by implementing the parameters and characteristics of the experimental cell to the model and fitting the simulated I-V curves with the experimental I-V curves.

Finally, the different degradation mechanisms were integrated into the model. In the

beginning, initial static constants were used to check the functioning of the model. Experimental degradation data was obtained from EIS measurements, effluent water chemical analyses, and catalyst particle size characterization. These data give enough information to develop a semi-empirical degradation model of a PEM electrolyzer at the beginning of life. Furthermore, theoretical equations were implemented to obtain a more flexible and robust model.

The model was developed to run over time, but was modified to stop at fixed times of operation and run simulations at current densities in the range of 0–4 A/cm<sup>2</sup>. This approach allows for the obtainment IV curves that illustrate the effects of the degradation at different times of operation.

## 5.1 Parameters and Water Properties Blocks

These two initial modules form the basis of the model. The parameters block stores all the variables needed to run the model, such as temperature and pressures. It also contains the electrolyzer characterization parameters, such as active area and membrane thickness. It works as a control block that allows the efficient manipulation of variables.

The water properties block is a module with two functions that calculate the exact values for different water properties, such as viscosity and density, depending on the operating conditions. They are calculated based on the IAPWS97 library. [58]

## 5.2 Production Block

In the Production block of the model, the hydrogen and oxygen production is calculated, as well as the outlet and input streams of the electrolyzer. The transport mechanisms taken into account for modeling the transport of species through the membrane are of great importance for the development of the model. Figure 5.2 summarizes the modeled transport mechanisms and their behaviour:

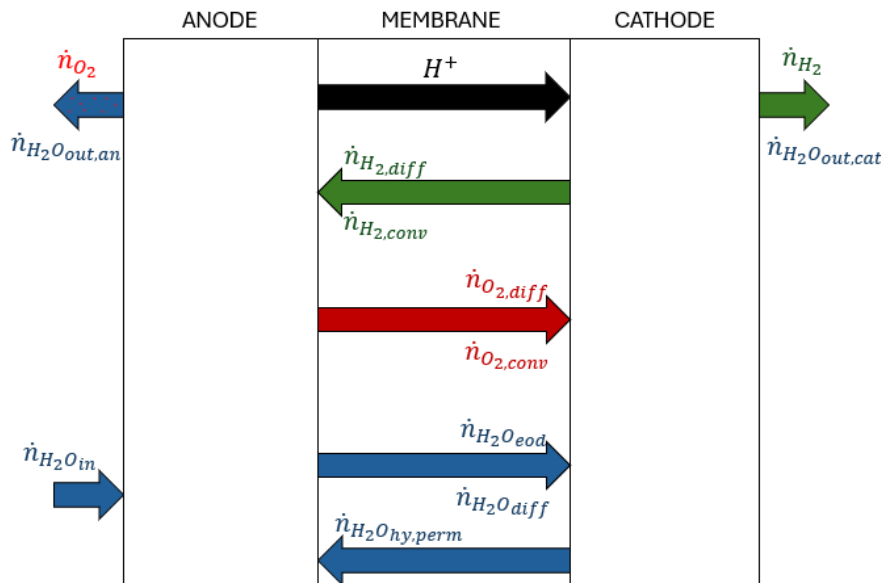


Figure 5.2. Permeation mechanisms overview

The total theoretical hydrogen produced is first calculated by applying Faraday's law with the current density of operation:

$$\dot{n}_{H_2,theo} = \frac{i \cdot A}{z \cdot F} \quad (5.1)$$

The real value of the species  $i$  produced is the theoretical value minus the amount lost by diffusion and convection:

$$\dot{n}_{i,real} = \dot{n}_{i,theo} - \dot{n}_{i,diff} - \dot{n}_{i,conv} - \dot{n}_{i,diss} \quad (5.2)$$

### 5.2.1 Diffusion

To calculate the hydrogen diffusion flow, Fick's Law (Equation 4.10) is applied. The concentration of hydrogen in the anode is assumed to be 0, and the diffusion coefficient for hydrogen is calculated following the equation presented by Chandesaris et al.: [25]

$$D_{H_2} = 3 \cdot 1.23 \cdot 10^{-2} \cdot \exp\left(\frac{-2602}{T}\right) \quad (5.3)$$

However, the value obtained for the diffusion coefficient of oxygen using the equations was not in the expected range. The equation calculated a diffusion 4 times higher for oxygen than for hydrogen. Therefore, a value of 1/3 of the hydrogen diffusion coefficient is taken as the oxygen diffusion coefficient, based on an extrapolation from the literature. [59]

Then, the solubility for each of the species ( $H_i$ ) is calculated using Henry's Law. First, the Henry solubility constant is calculated:

$$H_i = H_{i,ref} \cdot \exp\left(K_{henry,i} \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (5.4)$$

Where  $K_{henry,i}$  and  $H_{i,ref}$  are constant reference values of species  $i$  at a reference temperature, which are used to calculate the solubility value dependent on the temperature. The concentration of hydrogen and oxygen in water is calculated applying Henry's Law: [60] [1]

$$C_i = H_i \cdot P_i \quad (5.5)$$

Finally, Fick's Law is applied to calculate the amount of hydrogen and oxygen crossing by diffusion:

$$\dot{n}_{diff,i} = D_i \cdot A \cdot \frac{C_i}{t_{mem}} \quad (5.6)$$

### 5.2.2 Convection

Convection has no impact on the simulation since the anode and the cathode operate under isobaric conditions. However, it was modeled following Darcy's Law, presented in Equation 4.9:

$$\dot{n}_{i,conv} = \frac{k_{i,perm} \cdot \Delta P \cdot A}{t_{mem}} \quad (5.7)$$

### 5.2.3 Water Transport

The electro osmotic drag for water is calculated by using a drag coefficient of 2.5, which is a typical value for fully hydrated membranes. The water flow dragged by electro-osmosis is

calculated using Faraday's law: [43]

$$\dot{n}_{H_2O,eod} = n_{drag} \cdot \frac{i \cdot A}{F} \quad (5.8)$$

The water flow that crosses from the cathode to the anode by hydraulic permeation is calculated only when there is a pressure difference, using Equation 4.9.

Lastly, the hydrogen flow that crosses from the cathode to the anode dissolved in the water, and the oxygen flow that crosses from the anode to the cathode also dissolved in water are calculated, after knowing the water flow crossing the membrane:

$$\dot{n}_{H_2,diss} = \dot{V}_{H_2O,hyd} \cdot C_{H_2} \quad (5.9)$$

Additionally, the back-diffusion of water driven by the concentration gradient across the membrane is calculated using Fick's Law and added to the net water transfer flow from the anode to the cathode.

$$\dot{n}_{O_2,diss} = (\dot{V}_{H_2O,eod} + \dot{V}_{H_2O,diff}) \cdot C_{O_2} \quad (5.10)$$

All the flows are now calculated, and the total outlet flows can be determined.

### 5.3 Cell Performance and Degradation Block

The main block is the one in which all the time-dependent calculations are performed. The time of operation is defined, and the fluxes of species, voltages, and membrane degradation rate are calculated for each iteration of time.

The model uses the experimental data obtained from the EIS and XRD tests to model the first 322h of operation with the EIS data and 500h with the XRD data. The data management, analysis, and implementation to the model are explained in the following sections.

#### 5.3.1 Ohmic and Activation Losses

The ohmic and activation losses are clearly separated into two regimes, an initial empirical phase and one modeled theoretically. The first 322 h are modeled using experimental data obtained from the EIS test. A mathematical fit was obtained from this data. Section 5.4 explains the process and the equations obtained to model degradation in the first 322h. The ohmic and activation overpotentials are affected by parameters calculated from the EIS data. Table 5.2 shows the ohmic resistance and the exchange current density calculations:

**Table 5.2.** Ohmic resistance and exchange current density modeling

| Parameter  | Experimental data ( $t \leq 322$ h)            | Theoretical equation ( $t > 322$ h)               |
|------------|------------------------------------------------|---------------------------------------------------|
| $i_{0,an}$ | $i_{0,initial} \cdot \exp(-K_{decay} \cdot t)$ | $i_{0,an}(322) - 2 \cdot 10^{-7} \cdot (t - 322)$ |
| $R_0$      | $K_0 \cdot \exp(\alpha \cdot t)$               | $R_0(322) + 4 \cdot 10^{-7} \cdot (t - 322)$      |

The parameter  $i_{0,initial}$  is obtained by calibrating and forcing the IV curve of the model electrolyzer at 0 h to be the same as the experimental IV curve at 0 h. The other parameters at  $t < 322$  h are obtained from the EIS fitting.

After 322 h, a linear dependency on a degradation factor is applied. Values from literature are taken for this purpose.

The US Department of Energy (DOE) estimates a total voltage degradation of 2–6 mV/1000 h, or 2–6  $\mu\text{V}/\text{h}$ , for modern proton exchange water electrolyzers. However, some studies have reported higher degradation rates, in the order of 12–30  $\mu\text{V}/\text{h}$ . A value in this range will be taken as a reference to approximate the voltage loss due to ohmic resistances. [52] [61] [62]

A value of ohmic potential loss of 20  $\mu\text{V}/\text{h}$  was selected. To know the resistance increase over time, the ohmic potential loss must be multiplied by the current of operation.

#### 5.3.1.1 Activation Overpotential

The activation overpotential is calculated following the inverse Butler-Volmer equation, based on the exchange current density calculation: [29]

$$V_{act} = V_{act,an} + V_{act,cat} \quad (5.11)$$

$$V_{act,an} = \frac{R \cdot T}{\alpha_{an} \cdot F} \cdot \operatorname{arcsinh} \left( \frac{i}{2 \cdot i_{0,an}} \right) \quad (5.12)$$

$$V_{act,cat} = \frac{R \cdot T}{\alpha_{cat} \cdot F} \cdot \operatorname{arcsinh} \left( \frac{i}{2 \cdot i_{0,cat}} \right) \quad (5.13)$$

The activation overpotential caused by Pt particle agglomeration is calculated from the XRD data, explained in Section 5.5. The reversible degradation caused by bubbles is also added to the total activation overpotential.

#### 5.3.1.2 Ohmic Overpotential

The ohmic losses can easily be calculated by knowing the ohmic resistance of the electrolyzer. The ohmic overpotential is calculated using Ohm's law, where  $R_0$  is the ohmic resistance dependent on time, previously modeled, and  $I$  is the applied current: [1]

$$V_{ohm} = I \cdot R_0 \quad (5.14)$$

#### 5.3.2 Concentration Overpotential

The concentration overpotential is modeled using the Nernst equation and a diffusion-driven approach. While the diffusion, concentrations, and initial concentration overpotential of both oxygen and hydrogen are calculated, only the concentration overpotential penalty caused by oxygen mass transfer is taken into account. This simplification is justified by the assumption of negligible accumulation of hydrogen at the cathode due to its rapid diffusivity.

The experimental initial porosity of the PTL is 0.56. A degradation factor ( $k_\epsilon$ ) was set to account for the loss of porosity over time. However, there is a lack of study on this topic, so a simple linear relation is used for this purpose. A porosity loss of 0.035 over the life of the PEM electrolyzer was assumed: [62]

$$\epsilon(t) = \epsilon_0 - k_\epsilon \cdot t \quad (5.15)$$

The effective porosity is calculated by knowing the blocked fraction due bubbles, as presented in Equation 5.23.

The effective diffusion coefficient is calculated by applying a correction suggested in literature: [31]

$$D_{eff,an} = D_{A-B} \cdot \left( \frac{\epsilon - \epsilon_p}{1 - \epsilon_p} \right)^\alpha \quad (5.16)$$

Where  $D_{A-B}$  is the bulk coefficient,  $\epsilon_p$  is the prelocation threshold, with a value of 0.11, and  $\alpha$  is an empirical coefficient with a value of 0.785.

Then, the concentration of oxygen is calculated, following Equation 4.23. The final equation for the concentration overpotential is reduced to:

$$V_{conc} = \frac{R \cdot T}{4 \cdot F} \cdot \ln \left( \frac{C_{O_2}}{C_{ref}} \right) \quad (5.17)$$

Where  $C_{ref}$  is the concentration reference for the PEM electrolyzer, with a value of 0.005 mol/cm<sup>3</sup>.

### 5.3.3 Reversible Degradation

The modeled reversible degradation is attributed to the production and accumulation of bubbles inside the PEM electrolyzer, in the anode electrode. Bubbles affect the system in two different ways. They cause a small overpotential due to the attachment of bubbles in the electrode, which is part of the activation overpotential. However, the large production of bubbles at high current density causes mass transport limitations that dictate the maximum current density at which the electrolyzer can operate.

#### 5.3.3.1 Reversible Activation Overpotential

The following equation is a semi-empirical equation developed to calculate the fractional bubble coverage in the electrode ( $\Theta$ ): [21]

$$\frac{I/A - i_0}{(I/A)_{su}} = 3.08 \cdot \Theta^{1.5} \cdot (1 - \Theta)^{0.5} \quad (5.18)$$

The subindex  $_{su}$  refers to the summit current density, which is the limiting current density determined by the electrolyzer operation failure caused by the limitations in mass transport due to large amount of bubbles. The bubbles form a continuous insulating film that prevents current flow. The summit current density value was found to be around 30 A/cm<sup>2</sup> for the experimental cell. [32]

The bubble coverage can be calculated by using a solver. Then, the effective current density can be calculated from the exchange current density, assuming a percent relation with the bubble coverage:

$$i_{0,eff,b} = i_{0,an} \cdot (1 - \Theta) \quad (5.19)$$

Finally, the Butler-Volmer equation, presented in Equation 4.17, can be rearrange to calculate the overpotential based on the ideal and effective current density relation. Assuming symmetry in the charge transfer coefficients, the inverse Butler-Volmer equation is as the following: [1] [63]

$$V_{act,b} = \frac{R \cdot T}{\alpha \cdot F} \cdot \operatorname{arcsinh} \left( \frac{i}{2 \cdot i_{0,eff,b}} \right) \quad (5.20)$$

To isolate the bubble impact on the voltage losses, the ideal activation overpotential is calculated:

$$V_{act,ideal} = \frac{R \cdot T}{\alpha \cdot F} \cdot \operatorname{arcsinh} \left( \frac{i}{2 \cdot i_0} \right) \quad (5.21)$$

Then, the bubbles overpotential is calculated as the difference between the ideal and the real activation overpotential:

$$V_{act,bubble} = V_{act,b} - V_{act,ideal} \quad (5.22)$$

### 5.3.3.2 Reversible Concentration Overpotential

The production and attachment of bubbles to the catalyst surface is one of the limiting factors of the electrolyzer operation. At high current densities, oxygen bubbles cause huge mass transport limitations that can end the PEM electrolyzer operation. Bubbles have a direct impact on the porosity of the electrodes, since they occupy their surface and block flow paths. The effective porosity can be determined by knowing the bubble coverage for the current density of operation, which can be calculated using Equation 5.18. The available porosity ( $\epsilon_{eff}$ ) is proportionally reduced by the blocked fraction: [32]

$$\epsilon_{eff} = \epsilon \cdot (1 - \Theta) \quad (5.23)$$

Consequently, the available void space of the porous layer is restricted by accumulation of bubbles. This reduction in porosity leads to a decrease in the diffusion coefficient:

$$D_{eff,an} = D_{A-B} \cdot \left( \frac{\epsilon_{eff} - \epsilon_p}{1 - \epsilon_p} \right)^\alpha \quad (5.24)$$

The diffusion reduction causes mass transport limitations, which negatively affect the species concentration at the catalyst surface and increase the concentration overpotential.

### 5.3.4 Iridium dissolution

The dissolution of iridium and the loss of surface is one of the most important factors to consider to predict the PEM electrolyzer total failure. The iridium is dissolved over time when the electrolyzer is operating, reaching a point where the potential that must be applied to the cell is too high, producing catastrophic failure.

The iridium dissolution can be modeled by calculating a surface degradation ratio ( $\tau_s$ ). It has a value between 0 and 1, and represents the ratio between the surface at time  $t$  and the initial area. A model from literature was simplified to predict the iridium dissolution impact on the overpotential, based on the membrane thickness ratio ( $\tau_{mem}$ ): [33]

$$\tau_s = \frac{A(t)}{A_0} = \frac{1 + D}{1 - D} \cdot \frac{C}{\tau_{mem}} \quad (5.25)$$

Where  $D$  is a damage factor, with values between 0 and 1, which is related to the membrane thickness ratio. They are defined as:

$$\tau_{mem} = \frac{t_{mem}(t)}{t_{mem,0}} \quad (5.26)$$

$$D = 1 - \tau_{mem} \quad (5.27)$$

C is a dimensionless factor that relates the equivalent current density crossover factor ( $K_n$ ) to the initial surface and the limiting current density: [33]

$$C = \frac{K_n}{A_0 \cdot i_{lim}} \quad (5.28)$$

$K_n$  is dependent on the partial pressure of the hydrogen and the hydrogen permeability through the membrane. It is defined as: [33]

$$K_n = \frac{2 \cdot F \cdot p_{H_2} \cdot K_{H_2}}{t_{mem,0}} \quad (5.29)$$

Finally, the surface degradation ratio is applied every iteration to calculate the resistance caused by the iridium dissolution ( $R_{Ir,0}$ ) and the overpotential that must be applied to overcome this resistance ( $V_{Ir}$ ), using Ohm's Law. A linear relation between the area loss and resistance increase is assumed:

$$V_{Ir} = (R_{Ir,0} \cdot \tau_s) \cdot I \quad (5.30)$$

The iridium dissolution is more noticeable when the membrane is thinner because of the higher gas crossover. This causes a higher potential in the anode, which exponentially accelerates the iridium dissolution. The calculated iridium dissolution potential penalty takes into account the impact on the activation losses and on the ohmic losses.

### 5.3.5 Membrane Thinning

Water samples were taken at specific intervals during operation of PEM electrolyzer to study the water composition. The goal is to obtain the concentration of fluoride and construct a model based on these data. Unfortunately, the concentration measurement values were below the detection limit of the analytical equipment used to measure the fluoride composition. Therefore, a fully theoretical model of membrane thinning is developed.

A simplified model based on the membrane thinning model presented by Chandesris et al.[25] is developed. Only three reactions are taken into account to calculate the membrane consumption and the fluoride released, reducing the system of reactions to hydrogen peroxide formation and ionomer degradation reactions and an intermediate radical generation reaction. This approach neglects the contamination of external metal ions, which are of great importance for the radical forming reactions:

**Table 5.3.** Chemical reactions involved in the membrane degradation mechanism

| Description                 | Reaction                                                 | Rate Constant ( $k$ )                           |
|-----------------------------|----------------------------------------------------------|-------------------------------------------------|
| Hydrogen peroxide formation | $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$                   | $k_1$                                           |
| Radical generation          | $H_2O_2 \rightarrow 2HO^\bullet$                         | $k_2 = 1.2 \times 10^{-7} \text{ s}^{-1}$       |
| Ionomer degradation         | $HO^\bullet + R_f-CF_2-COOH \rightarrow \text{products}$ | $k_3 \leq 10^6 \text{ L mol}^{-1}\text{s}^{-1}$ |

$k_1$  is calculated for the operating temperature using the following equation: [64] [65]

$$k_1 = k_1^0 \cdot \exp\left(-\frac{E_{A_{H_2O_2}}}{R \cdot T}\right) \cdot \exp\left(\frac{-\alpha_{H_2O_2} \cdot F}{R \cdot T^0} \cdot V_{act,cat}\right) \quad (5.31)$$

Where  $k_1^0$  is a kinetic constant at  $T^0$  (298K) ( $k_1^0 = 2.56e-5 \text{ cm}^7\text{mol}^{-2}\text{s}^{-1}$ ).  $EA_{H_2O_2}$  is the activation energy of the electrochemical reaction ( $EA_{H_2O_2} = 42450 \text{ J/mol}$ ). [64] [65]

For the development of this model, reverse reactions are neglected, and a radical Quasi-Steady-State-Approximation (QSSA) model is assumed for the radicals. That is, radicals are produced at the same rate that they are consumed. The model is simplified by assuming that highly reactive hydroxyl radicals ( $HO^\bullet$ ) react fast enough to be produced by the radical generation reaction and consumed by the ionomer degradation reaction at exactly the same rate. The complex and micro-kinetic radical reaction can then be omitted, linking membrane thinning only to the hydrogen peroxide formation reaction rate ( $R_1$ ): [1] [25]

$$R_1 = R_2 = k_1 \cdot C_{O_2,cat} \cdot C_{H^+}^2 \quad (5.32)$$

$$2R_1 = 2R_2 = R_3 \quad (5.33)$$

$$R_3 = 2 \cdot k_1 \cdot C_{O_2,cat} \cdot C_{H^+}^2 \quad (5.34)$$

Where  $C_{O_2,cat}$  and  $C_{H^+}$  are the concentrations of oxygen and hydrogen protons in the cathode, respectively.

To calculate the concentration of hydrogen protons in the cathode, the density and the equivalent weight ( $EW = 1100 \text{ g/mol}$ ) of the ionomer, which is the mass of dry polymer required to provide one mole of protons ( $H^+$ ), are used: [25] [65]

$$C_{H^+} = \frac{\rho}{EW} = \frac{1.98 + 0.0324 \cdot \lambda}{(1 + 0.0648 \cdot \lambda) \cdot EW} \quad (5.35)$$

A steady-state mass balance is assumed for the oxygen when it reaches the cathode catalyst layer after crossing the membrane. When the PEM electrolyzer is operating under isobaric conditions, the oxygen transfer through the membrane can be calculated using the Fick's Law as:

$$\dot{n}_{O_2,transf} = \frac{D_{O_2}}{t_{mem}} \cdot (C_{O_2,an} - C_{O_2,cat}) + \dot{n}_{O_2,eod} \quad (5.36)$$

In conventional model, only the oxygen transferred by convection and diffusion from anode to cathode is used to calculate the membrane thinning. In this model, oxygen that travels through the membrane dissolved in water by electro-osmotic drag is also taken into account. The oxygen consumed by the reaction is calculated with the reaction rate and the thickness of the catalyst layer:

$$\dot{n}_{O_2,cons} = R_1 \cdot t_{CL} = k_1 \cdot C_{O_2,cat} \cdot C_{H^+}^2 \cdot t_{CL} \quad (5.37)$$

These parameters are equalized, and the concentration of oxygen in the cathode can be calculated taking into account the voltage overpotential and temperature in the kinetic constant:

$$\dot{n}_{O_2,transf} = \dot{n}_{O_2,cons} \quad (5.38)$$

$$C_{O_2,cat} = \frac{\frac{D_{O_2}}{t_{mem}} \cdot C_{O_2,an} + \dot{n}_{O_2,eod}}{\frac{D_{O_2}}{t_{mem}} + k_1 \cdot C_{H^+}^2 \cdot t_{CL}} \quad (5.39)$$

Now,  $R_3$  can be calculated by the Equation 5.34. The reaction rate of the reaction consuming the membrane is obtained and the fluor released rate can be calculated as: [25]

$$R_{fluor} = 3.6 \cdot R_3 \quad (5.40)$$

The membrane thinning can be calculated by relating the fluoride release to the membrane thinning with a factor ( $\Delta t_M$ ), which represents the thinning membrane per mol of fluor released: [25]

$$\Delta t_{mem} = \Delta t_M \cdot R_{fluor} \cdot dt \quad (5.41)$$

The factor  $\Delta t_M$  was calculated from the geometry and kinetics of the electrolyzer. 1 mol of consumed membrane releases 3.6 mol of fluoride. Knowing the molar volume of the membrane ( $M_{V,mem}$ ), the membrane volumetric loss factor can be calculated, and when divided by the surface of the membrane, the membrane thinning factor is obtained:

$$\Delta t_M = \frac{M_{V,mem}/3.6}{A} \quad (5.42)$$

## 5.4 Electrochemistry Impedance Spectroscopy (EIS)

The data obtained from the EIS test is used to study the different degradation mechanisms that occur during cell operation. EIS tests were performed at 0, 170, 253, 323, and 500 h of operation. The methodology for performing the tests is as follows:

1. EIS setup: a Gamry Reference 3000 potentiostat is used to perform the EIS test. Current is applied with the Greenlight Station, while the EIS test is performed, from 100 kHz to 0.4 Hz.
2. Points measured: the EIS was performed at the same time that I-V curve was measured. 15 points from 0 A to 25 A were measured to obtain a clearer view of the activation overpotential and low current density behavior. 5 points between 25 A and 100 A were also measured, obtaining a total of 20 points for a range of current density from 0 to 4 A/cm<sup>2</sup>.
3. Data filtering: EIS data were filtered to remove the parasitic inductance effect on the result, as well as the bubble mass transport limitations at low frequencies. Figure 5.3 shows a Nyquist plot of all EIS data obtained from the test:

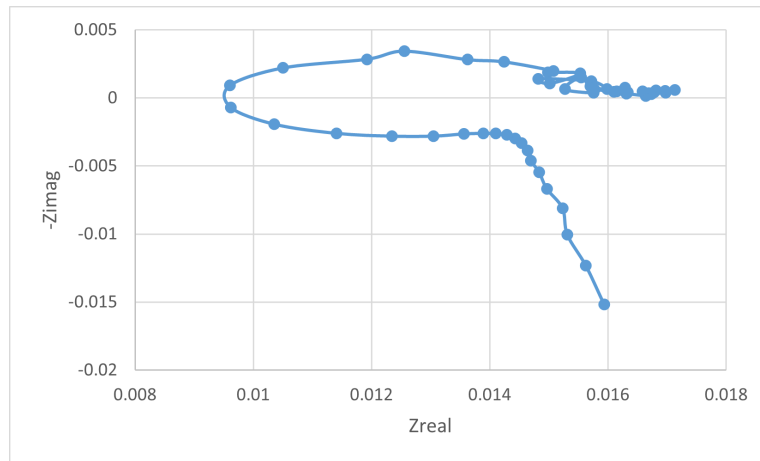


**Figure 5.3.** Nyquist plot for 170 h at 70°C and 1 A/cm<sup>2</sup>

Inductance is removed by filtering the high frequency data, and low frequency mass transport limitations due to bubbles effects are also eliminated. The mass transport limitations caused by large amounts of bubbles can be minimized by performing the

EIS test at low current densities. So, only the positive values of  $-Z_{\text{imag}}$  are plotted for the analysis, since the negative values are parasitic inductance. Figure 5.8 shows examples of the Nyquist plot after data filtering at 70 °C and 1 A/cm<sup>2</sup>:

4. Data analysis: EIS data were analyzed at different current densities, depending on which degradation mechanism was targeted. The results of the EIS at different times reveal the evolution of the resistance of the different components of the electrolyzer over time.
5. Incorporation to the model: Finally, the parameters obtained from the data analysis were processed to obtain semi-empirical degradation parameters, which were implemented to the code. The degradation parameters were obtained from an experimental fitting curve to the EIS results. The curve is an exponential curve as the following:

$$k_R = k_{0,R} \cdot e^{(\alpha \cdot t)} \quad (5.43)$$

Where  $k$  is the resistance due to degradation over time,  $k_0$  is the intercept,  $\alpha$  is the fitting parameter and  $t$  is the time in h. The resistances and current densities can be modeled over time using this equation.

To process the data, it is necessary to have an Equivalent Electrical Circuit of the PEM electrolyzer that corresponds with the cell composition.

#### 5.4.1 Equivalent Electrical Circuit

Figure 5.4 shows an image of the cell components of a PEM electrolyzer, and how the different layers would be represented in the EEC. Where 1 is the membrane, 2 are the catalyst layers, 3 are the current distributors, 4 are the spacers or gaskets, and 5 are the bipolar plates. [1]

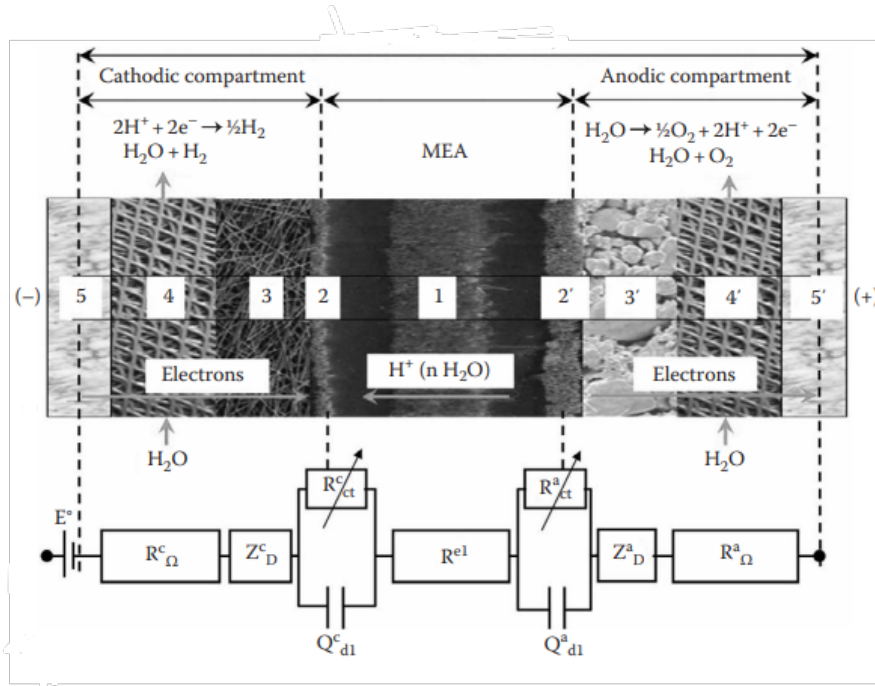


Figure 5.4. EEC PEM electrolyzer overview [1]

The complex EEC circuit that takes all mechanisms into account is shown in Figure 5.4. The EEC circuit can be simplified to avoid over-parametrization and to obtain information about specific degradation mechanisms.

A simplified version of the EEC is presented in Figure 5.5. This EEC model is simplified by omitting the charge transfer resistances in the cathode because they are very small in comparison with the anode charge transfer resistances. The mass transport impedance ( $Z_D$ ) is also omitted, by assuming that porous transport layers with proper porosity are used. [1].

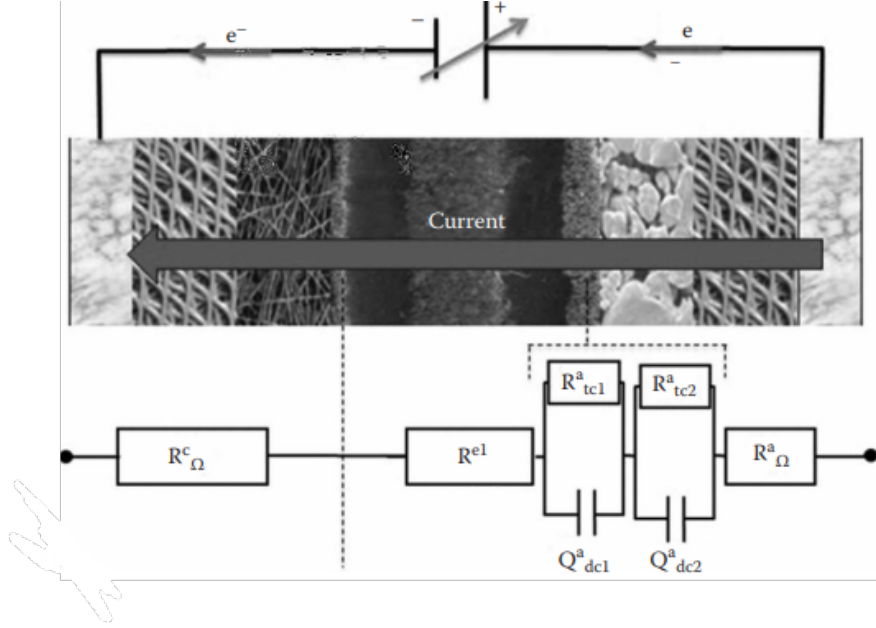


**Figure 5.5.** EEC PEM electrolyzer simplified [1]

The final EEC model is composed of two series ohmic resistance blocks, for the anode and the cathode, another series ohmic resistance block referred to the electrolyte, and two series of blocks with activation resistances in the anode and in the anode in parallel with a capacitor. A representation of the EEC used to analyze the data is shown in Figure 5.6: [30]

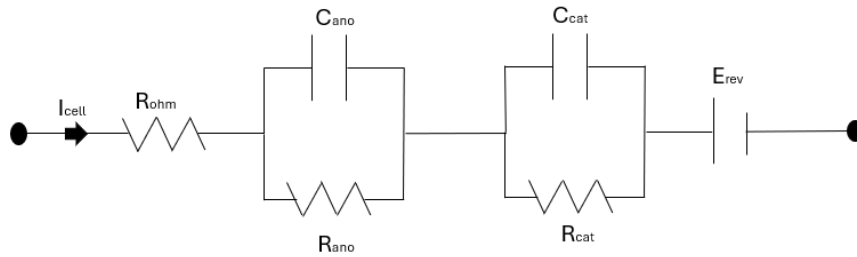


**Figure 5.6.** EEC used for the model

The circuit is defined in Python as 'R0-p(R1,CPE1)-p(R2,CPE2)'. Where "R0" represents the ohmic resistances, comprising the the anode, the cathode, and the membrane, "-" is the connection in series, and "p(R1,CPE1)" is the connection in parallel of the cathode activation or charge transfer resistance ("R1"), and the constant phase element ("CPE") which represents the capacitor. "R2" and "CPE2" refer to the anode side.

The library "impedance.py" is used to do the data analysis by defining the circuit previously mentioned, and some initial guesses for the optimization to start. The circuit is fitted to the

frequency array and the complex impedance consisting of the real and imaginary values, both acquired during the EIS measurements.

The results of the fitting parameters obtained are in the form of numerical values and their standard errors, corresponding to  $R_0$ ,  $R_1$ ,  $R_2$ ,  $CPE1$ ,  $CPE1_0$ ,  $CPE2$ , and  $CPE2_0$ .  $R_0$  is the initial point on the x-axis,  $R_1$  is the width of the first semicircle, and  $R_2$  is the width of the second semicircle. The EIS data and the fitting can be plotted in a Nyquist plot to gain a clearer view of the results. The fitting parameters were calculated for  $0.01 \text{ A/cm}^2$  and for  $1 \text{ A/cm}^2$ . Data obtained at higher current densities was considered to not be valid due to the significant negative impact and instability caused by the large amount of bubbles inside the PEM electrolyzer.

Figure 5.7 shows the visual representations of the results obtained from the EIS performed at  $0.01 \text{ A/cm}^2$  at 0, 170, 253, 322, and 500 h. As well as the fit with the simplified EEC presented before. Points are a bit scattered in the right side of the graphs, in the low frequency region. This can be attributed to bubble disturbances in the cell, since the EIS test was performed right after normal cell operation. It can be also due to small changes in the PEM electrolyzer operation or due to perturbations between the Greenlight station and the Gamry Potentiostat.

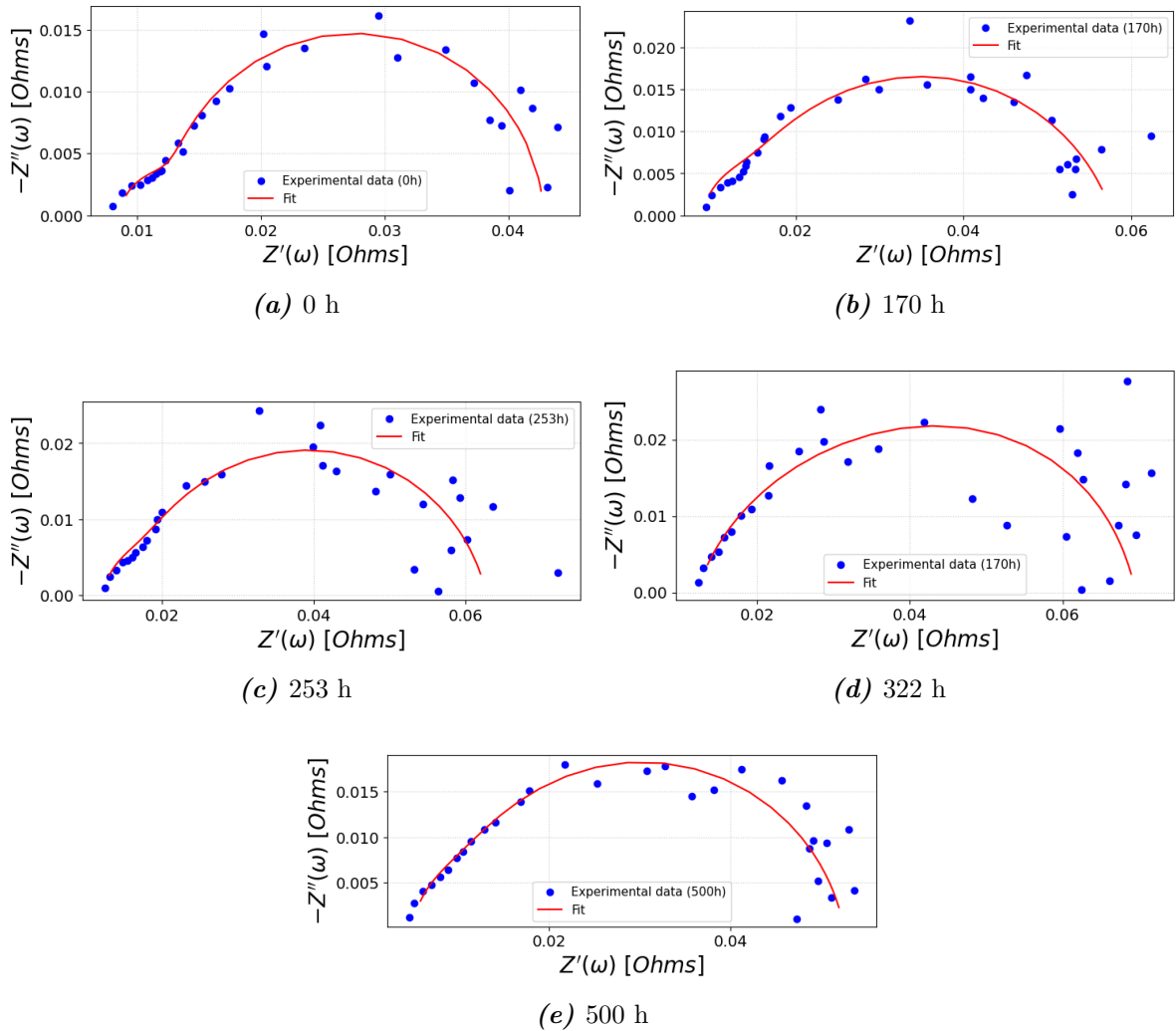


**Figure 5.7.** EIS fit at  $0.01 \text{ A/cm}^2$  for 0 h (a), 170 h (b), 253 h (c), 322 h (d), and 500 h (e)

The data obtained must be further processed before implementation in the degradation model. The evolution over time of the fitting parameters  $R_0$ ,  $R_1$ ,  $R_2$ , representing the ohmic losses and the activation losses, respectively, is studied.

The EIS data form two distinct semicircles, that can be appreciated in the early operation of the PEM electrolyzer. The first corresponds to the cathode side, and the second corresponds to the anode side. The cathode semicircle is small as a result of the low resistance in the cathode and the good stability of the HER in the Pt catalyst. In contrast, the anode side presents a larger semicircle due to the resistances caused by the mass transport limitations and the slow kinetics of the reaction at  $0.01 \text{ A/cm}^2$ .

Additionally, due to the nature of the reactions and the stability of the anode and cathode catalysts, the degradation is much more noticeable on the anode side, causing resistance to increase and a larger semicircle over time, which eclipses the small cathode semicircle. That is the reason why it is not observed at first sight at high times of operation. The cathode side was iterated until the solver could fit it without the influence of the anode side.

At longer times of operation, the points in the low frequency range are more scattered. This can be attributed to diffusion. However, Warburg impedance ( $W$ ) was added to the EEC to model concentration-diffusion losses, obtaining ' $R_0\text{-p}(R_1,\text{CPE1})\text{-p}(R_2+W,\text{CPE2})$ '. As a result, the model failed to converge, and the Warburg value obtained was the lower limit established. This shows that the instability of the points is not caused by diffusion losses, but by noise inside the cell that can be caused by bubbles. [30]

To study the EIS data obtained when operating the cell with current, the same methodology previously described was used. However, the OER in the anode side is the one that contributes more to the overpotential at high current densities. The anode covers a wider frequency range than before, making the cathode side negligible. The anode and cathode processes have more similar time constants, which make them more difficult to differentiate in the EIS data. The model results in mathematical overparameterization when trying to fit ' $R_0\text{-p}(R_1,\text{CPE1})\text{-p}(R_2,\text{CPE2})$ ', so it is simplified to ' $R_0\text{-p}(R_{act},\text{CPE}_{act})$ ', where  $R_{act}$  represents the total activation losses of the anode and the cathode. The fitting curve was anchored to the calibrated parameters of the experimental IV-curve, resulting in a limitation in the fitting to the initial points. Only the evolution of resistance over time is sought for these EIS data. Figure 5.8 shows the fitting results for the data obtained at  $1 \text{ A/cm}^2$ : [66] [67]

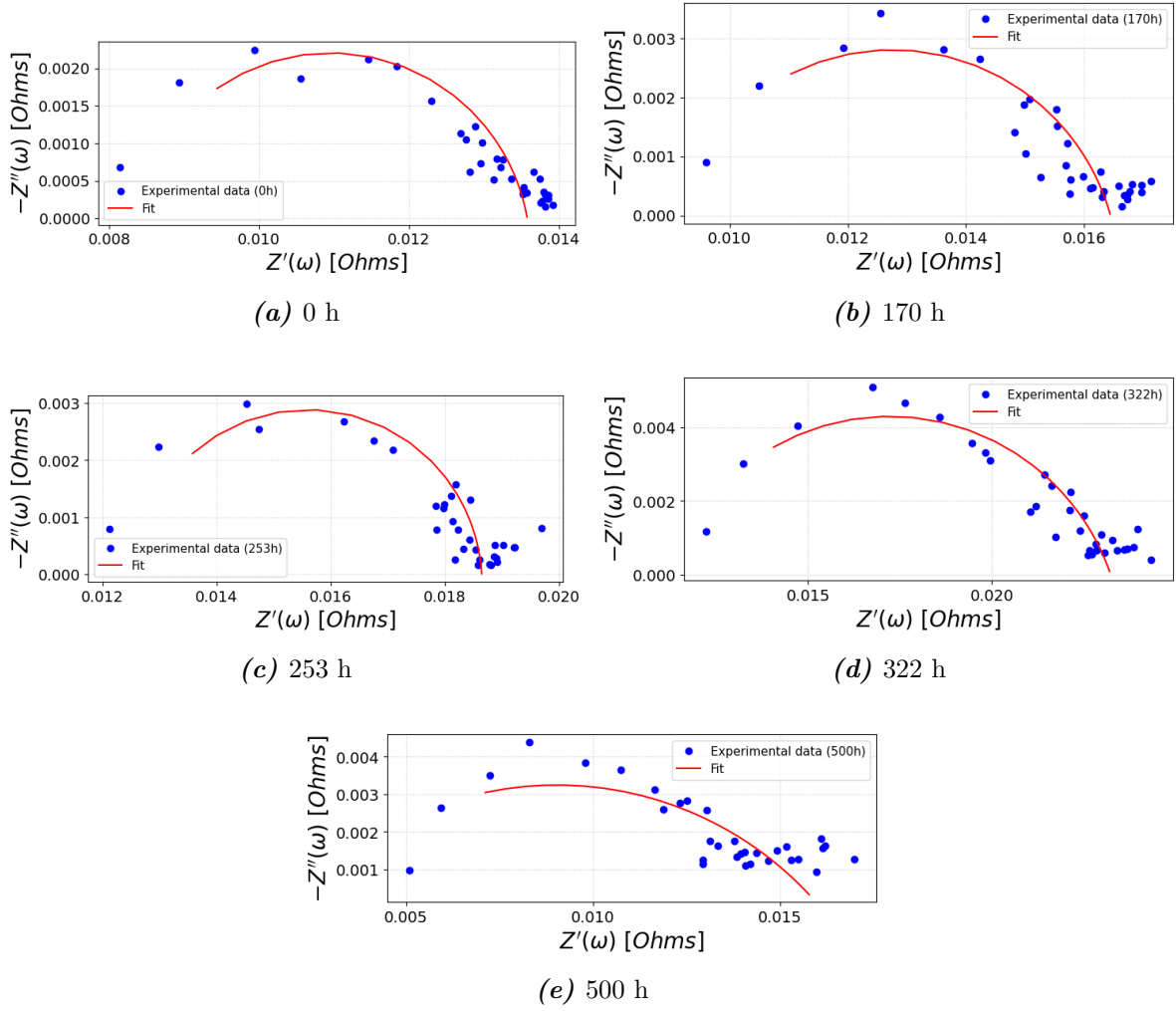


**Figure 5.8.** EIS fit at 1 A/cm<sup>2</sup> for 0 h (a), 170 h (b), 253 h (c), 322 h (d), and 500 h (e)

The results obtained show the resistance increase over time, from 0 to 322 h, probably dominated by passivation, oxidation, and catalyst restructuring mechanisms. After 322 h, the resistance decreases, reaching the peak performance point of the cell before 500 h. The 500 h data can be used as a reference for the long-term operation, since it can be considered to be the steady state operation of the cell. However, due to concerns about the viability of these data, it is not used. EIS data were used only to calculate the temporal degradation rates, then anchored to the initial parameters obtained for the experimental IV curve and the calibration.

To accurately obtain the degradation parameters, only the data before the steady-state point are processed (0-322 h). This would give an empirical equation that models the resistance evolution over time in the initial stage of the PEM electrolyzer operation. The data for 0.01 A/cm<sup>2</sup> were used to determine the activation losses, since the catalyst behavior can be most clearly observed at low current densities. Figure 5.9 shows the degradation of the catalyst layer in the anode and cathode and its fitting of the  $R_{act}$  values.  $R_{act}$  represents total losses, which is the sum of  $R_1$  and  $R_2$ :

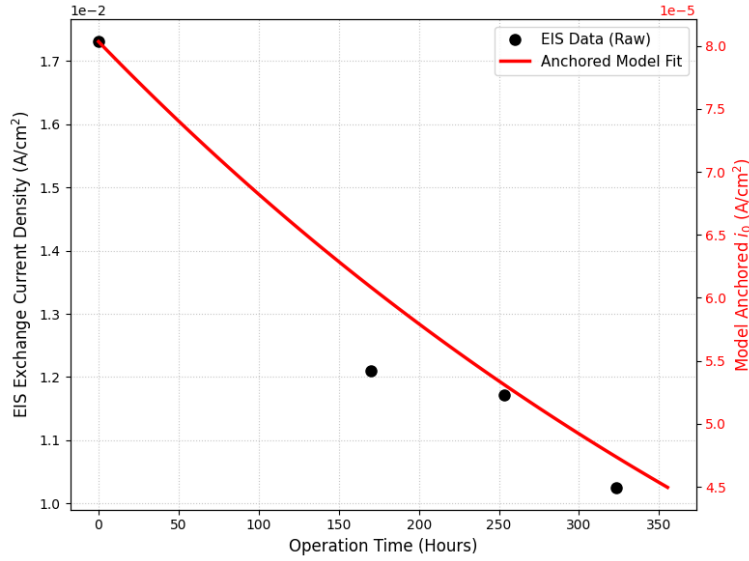


**Figure 5.9.** Activation resistance fit

The parameters of the exponential fitting curve presented in Equation 5.43 were found for these data points after converting the resistance increase to the anode exchange current density using the Butler-Volmer equation. The value of the intercept  $i_{0,an}$  is  $8.03 \cdot 10^{-5}$  A/cm<sup>2</sup> and the value of the fitting parameter  $\alpha$  is  $0.00163 \text{ h}^{-1}$ . These values can easily be integrated into the model to simulate the first 322 h according to the experimental data:

$$i_{0,an} = 8.03 \cdot 10^{-5} \cdot e^{(-0.00163 \cdot t)} \quad (5.44)$$

The evolution of the resistance of the activation overpotential was converted to exchange current density to normalize the values and be able to scale them to higher current densities.

To obtain the evolution of the ohmic losses, the data at 1 A/cm<sup>2</sup> was used. The ohmic losses can be studied at this current density due to the fact that the reaction is being performed at a fully hydrated and thermally active state, and bubbles do not significantly affect the EIS measurements. Figure 5.10 shows the  $R_{ohm}$  values from 0 to 322 h and the fitting curve.

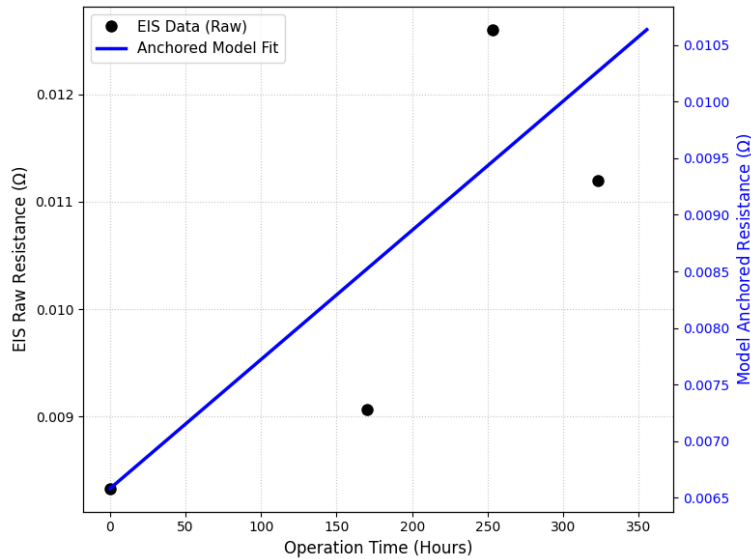


**Figure 5.10.** Ohmic resistance fit

The intercept found for the model ( $R_{ohm}$ ) is  $6.58 \cdot 10^{-3}$  O hms and  $\alpha$  is  $1.14 \cdot 10^{-5} \frac{\Omega}{h}$ .

$$R_{ohm} = 6.58 \cdot 10^{-3} + 1.14 \cdot 10^{-5} \cdot t \quad (5.45)$$

The fitting equations are obtained for calculating the resistances. After applying this experimentally obtained degradation parameters, the electrolyzer operation is modeled theoretically to calculate the end of life estimation.

## 5.5 XRD

The membrane was subjected to an X-ray diffraction (XRD) test to study the materials of the membrane and the electrodes, and their structures changes over time through the operation. The goal is to obtain information to model specific degradation mechanisms, and the effects of catalyst active area reduction over time. A pristine membrane and the membrane after 500 h of operation were tested from both sides, the anode and the cathode.

The membranes were placed on the X-ray diffractometer, which emitted an X-Ray beam onto the sample. The scattered radiation was captured by an X-Ray detector. The crystallinity, structure, and particle size were calculated from the resulting diffraction pattern. Figure 5.11 shows the XRD results for the anode, and Figure 5.12 shows the results for the cathode:

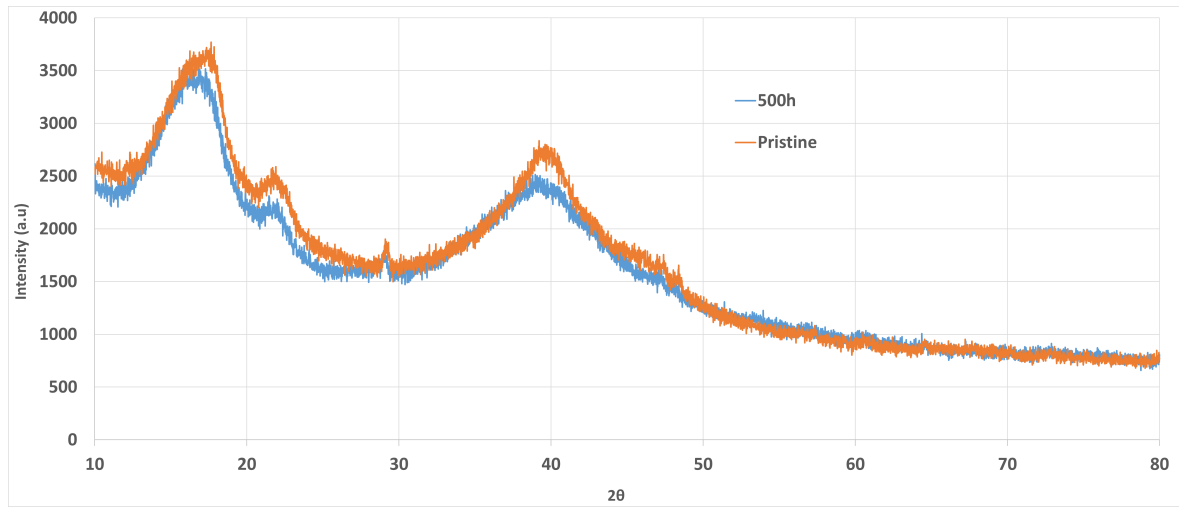


**Figure 5.11.** XRD anode side

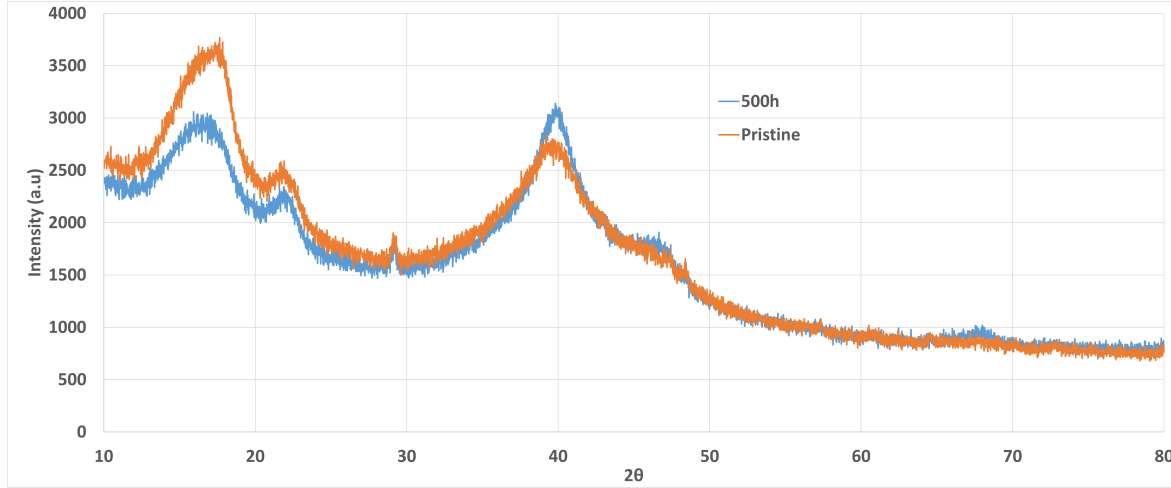


**Figure 5.12.** XRD cathode side

4 peaks can be easily observed, at 17-18 degrees, at 22 degrees, at 29 degrees, and at 39-40 degrees. It looks like the materials from one side affect the test for the other side, since the XRD test for the anode and for the cathode are very similar. When comparing the peaks with references, the compounds and their geometry can be determined.

The first peak, at 18 degrees, corresponds to the membrane material, Nafion 117.[68] The peak at 22 degrees corresponds to Pt/C 002, and the peak at 39-40 degrees represents Pt/C 111. the intensity is higher in the XRD of the cathode because Pt/C is on the cathode side.[69] [70]

The small peak at 29 degrees can be attributed to the crystalline amorphous parts of the membrane. [71]

To simplify the model, only the evolution of the Nafion structure at 18 degrees and the Pt/C 111 at 39 degrees are studied. The Scherrer equation is used to calculate the particle size ( $D_p$ ) at different times of operation:

$$D_p = \frac{Sc \cdot \lambda_{wave}}{\beta_{FWHM} \cdot \cos(\theta)} \quad (5.46)$$

Where Sc is the Scherrer constant that depends on the shape of the crystal, it is assumed that they are spheres, so the value of Sc is 0.9.  $\lambda_{wave}$  is the wavelength of the X-Ray used, which is 0.15406 nm in this case.  $\beta_{FWHM}$  is the Full Width at Half Maximum (FWHM) of the peak in radians, and  $\theta$  is the Bragg angle, which is equal to the x-axis value of the peak divided by 2. [72] [73]

To study the Pt/C evolution, the XRD data for the cathode side were analyzed. The Pt/C peak at 39 degrees is negatively influenced by the Nafion peak, since the Pt/C layer is not thick enough to only reflect the Pt/C data, so Nafion is also represented in this peak, making it wider. However, for the correct analysis, only the final narrow part of the peak or the final half of it is considered. The parameters used to calculate the particle size and the particle size result are presented in Table 5.4. A width of 4 degrees for the pristine data and a width of 2.5 degrees for the 500h data are considered:

| Data     | Angle peak ( $2\theta$ ) | $\beta$ (rad) | $\theta$ ( $^\circ$ ) | D (nm) |
|----------|--------------------------|---------------|-----------------------|--------|
| Pristine | 39.7                     | 0.06981       | 19.85                 | 2.11   |
| 500h     | 39.9                     | 0.04363       | 19.95                 | 3.38   |

**Table 5.4.** XRD parameters for Pt/C peak

A clear increase in the particle size of Pt can be observed, from 2.11 to 3.38 nm. This is due to particle agglomeration and other degradation mechanisms that contribute to the agglomeration of catalyst particles, increasing their size and reducing the total active surface.

To implement these results in the model, it is necessary to calculate a parameter that relates the increase in particle size with time (k). This is done using the Lifshitz-Slyozov-Wagner (LSW) theory [74]:

$$k = \frac{D_p^3 - D_{p,0}^3}{t} \quad (5.47)$$

Where D is the final diameter,  $D_0$  the initial diameter and t the time between measurements, 500h for this case. As a simplification, the agglomeration rate obtained experimentally was considered as a constant, the effects of temperature on the agglomeration rate on the PtC particle size increase are not taken into account. The pressure effects are considered negligible.

The diameter of the particle can be extrapolated and calculated at any time. However, a maximum particle size is set as a boundary condition to avoid making the model calculate unreal scenarios over time with huge particles. The value set as maximum particle size is 6nm. [75]

Then, the particle growth is linked to the loss of the active surface of the catalyst, which will affect the exchange current density, and increase the activation losses. The geometry of the Pt/C particles is assumed to be perfectly spherical, so, assuming no catalyst losses and only catalyst ripening or agglomeration, an increase in the diameter of the particle will proportionally reduce the active surface:

$$A = A_0 \cdot \frac{D_0}{D} \quad (5.48)$$

The new area is used to calculate the exchange effective current density:

$$i_{0,eff,A} = i_0 \cdot \frac{A}{A_0} \quad (5.49)$$

Finally, similarly to the bubbles impact on the activation voltage losses, the activation voltage loss caused by Pt/C active surface loss due to agglomeration is calculated as:

$$V_{act,A} = \frac{R \cdot T}{\alpha \cdot F} \cdot \operatorname{arcsinh}\left(\frac{i}{2 \cdot i_{0,eff,A}}\right) \quad (5.50)$$

$$V_{act,PtC} = V_{act,A} - V_{act,ideal} \quad (5.51)$$

The particle size growth and its impact on the cell overpotential will be discussed in the following chapter.

The membrane structure is also studied by analyzing the peak at 18 degrees, which corresponds to Nafion. The following table presents the parameters used to calculate the particle size from the Scherrer equation:

| Data     | Angle peak ( $2\theta$ ) | $\beta$ (rad) | $\theta$ ( $^\circ$ ) | D (nm) |
|----------|--------------------------|---------------|-----------------------|--------|
| Pristine | 17.5                     | 0.05585       | 8.75                  | 2.51   |
| 500h     | 16.75                    | 0.06370       | 8.38                  | 2.20   |

**Table 5.5.** XRD parameters for Nafion peak

The difference between the angle peak points for the Nafion structure is notable, and it indicates some kind of restructuring of the membrane. The Bragg Law can be applied to demonstrate this statement: [76]

$$d = \frac{\lambda_{wave}}{2 \cdot \sin(\theta)} \quad (5.52)$$

Where d is the distance between the lines where the atoms lie. The value of the pristine membrane is 0.506 nm and the value of the membrane after 500h of operation is 0.529 nm. This indicates a reduction in the degree of crystallinity of the Nafion membrane, which has a negative impact on the membrane performance. [76] [77]

The results obtained for the Nafion membrane XRD test can be used to justify the increase of membrane resistance over time. However, no numerical relation between the XRD results and the degradation parameters was found.

## 5.6 Calibration

To make the model fit the experimental data, it was calibrated using a solver. The I-V curve data points obtained for the PEM electrolyzer at 0h of operation were used as a reference. The values of ohmic resistance, coefficient of charge transferred in the anode ( $\alpha_{an}$ ), and the exchange current density of the anode were optimized to find the calibration values. The activation and ohmic overpotential depend on these parameters, so they will be modified to find the optimal fit.

The values for the coefficient of charge transferred and the exchange current density in the cathode were assumed to be constant, since the impact of the cathode activation overpotential is considerably smaller than the anode activation overpotential. Concentration overpotential was not taken into account for the calibration, since it can cause a solver over parametrization. It was considered that the impact of the concentration overpotential can be neglected for the current density range of the experimental I-V curve used to run the solver.

Figure 5.13 shows the experimental I-V curve data-points (red dots), and the curve obtained with the experimental fit (blue line):

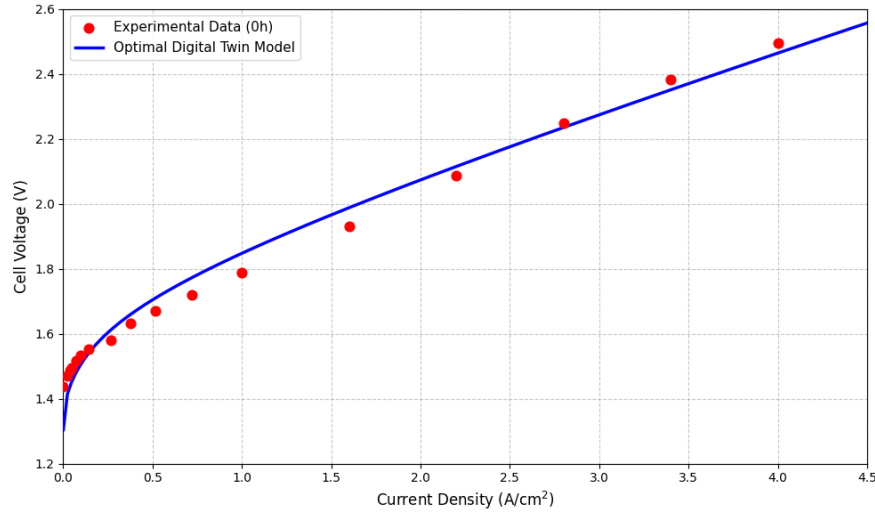


**Figure 5.13.** Maximum alpha 1

The values obtained are presented in Table 5.6. A better fit was obtained for  $\alpha_{an} = 2$ . However, fundamental electrochemistry theory states that  $\alpha_{an}$  must be lower than or equal to 1. Consequently, the solver was limited by a maximum value of  $\alpha_{an}$  of 1. The simplification of the fit model or low quality data are likely the reason of the inconsistency. [29]

**Table 5.6.** Calibrated Parameters for the PEM Electrolyzer at 0h. Maximum alpha 1

| Parameter                          | Symbol        | Value                 | Unit              |
|------------------------------------|---------------|-----------------------|-------------------|
| Anodic Exchange Current Density    | $i_{0,an}$    | $8.03 \times 10^{-5}$ | A/cm <sup>2</sup> |
| Anodic Charge Transfer Coefficient | $\alpha_{an}$ | 1                     | -                 |
| Ohmic Resistance                   | $R_0$         | 0.006580              | $\Omega$          |

## 5.7 Total Overpotential

Finally, the total overpotential that must be administered to the cell ( $V_{loss}$ ) can be calculated as the sum of all overpotentials:

$$V_{loss} = V_{act,bubble} + V_{act,PtC} + V_{act} + V_{ohm} + V_{conc} + V_{Ir} \quad (5.53)$$

The total potential that must be applied to the cell can be calculated as the sum of the reversible potential and the total overpotential:

$$V_{tot} = V_{rev} + V_{loss} \quad (5.54)$$

The reversible potential for the operating conditions is calculated using the Nernst equation. The value obtained was validated against the reversible potential values depending on temperature and pressure presented in the literature: [1]

$$V_{rev} = V_{rev,T}^0 - \frac{R \cdot T}{2 \cdot F} \cdot \ln\left(\frac{1}{\frac{p_{H_2}}{p_{ref}} \cdot \left(\frac{p_{O_2}}{p_{ref}}\right)^{0.5}}}\right) \quad (5.55)$$

Where  $V_{rev,T}^0$  is the reversible voltage corrected for temperature T. Assuming isobaric conditions in the cell, the absence of hydrogen in the anode and the absence of oxygen in the cathode, the partial pressures of oxygen and hydrogen can be calculated as:

$$p_{H_2} = p_{O_2} = P - P_{sat,H_2O} \quad (5.56)$$

Where  $P_{sat,H_2O}$  is the saturation pressure of water.

Additionally, the heat generated during the operation ( $Q_{gen}$ ) can be calculated by knowing the thermoneutral potential and the total potential applied:

$$Q_{gen} = (V_{tot} - V_{th}) \cdot i \quad (5.57)$$

This parameter shows how much heat must be removed from the cell to operate under isothermal conditions. It also helps to estimate the economic viability of the cell operation over time and the end of life of the cell.

## 5.8 End of Life

The end of life of the cell is dictated by the safety criterion described in Section 4.2.2. The operation of the PEM electrolyzer is stopped when the hydrogen content in oxygen ( $x_{H_2}$ ) is equal to 2%, since the lower flammability limit is at 4%. This conservative threshold was selected following literature recommendations about operating at safe limits [78][79]. This parameter is calculated using the following equation:

$$x_{H_2} = \frac{n_{H_2,an}}{n_{O_2,an} + n_{H_2,an}} \quad (5.58)$$

Where  $n_{H_2,an}$  and  $n_{O_2,an}$  are the number of moles of hydrogen and oxygen in the anode, respectively.

## 5.9 Model Framework

This chapter summarizes the development of a dynamic, semi-empirical 1D model for a PEM electrolyzer. Its primary function is to simulate the cell performance and degradation at both short-term and long-term scales for a wide range of operating conditions and cell parameters.

The model consists of three core parts. First, the thermodynamic and physical properties are established. Second, the dynamic flow and mass transfer of species are calculated. Finally, the cell performance and degradation are simulated over time.

Compared to literature, this model provides a coupled approach between mass transport, electrochemical phenomena, and degradation mechanisms. The digital twin developed implements several critical degradation mechanisms simultaneously, such as reversible degradation, catalyst agglomeration, catalyst dissolution, porosity loss, membrane thinning, and ohmic resistance increase. The model parameters can be easily modified to predict the end of life of a PEM electrolyzer, to optimize its performance over time, and to study the phenomena that occur inside the cell.

# Results and Discussion 6

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The results and discussion of the values obtained in the simulation are presented in this section. A study of sensitivity was performed, obtaining results for simulations at different temperatures, pressures, and current densities. The model was also demonstrated to work under symmetric and asymmetric pressures. The impact of fixed values, such as charge transfer coefficients or anode exchange current density, is also studied. All the simulations were performed for a 25 cm<sup>2</sup> PEM electrolyzer with an inlet water flow of 0.25 L/min, following the experimental cell configuration

In addition, interesting phenomena such as mass transport limitations and bubble coverage depending on pressure are discussed.

As mentioned in Model Methodology (Chapter 5), the first part of the simulation is modeled based on experimentally obtained parameters. The reliability of the data must be discussed since the cell did not operate as expected from the very beginning. A break-in procedure was performed on the cell before starting the data recording.

However, the first recorded cell voltage was higher than expected, with a value of 2.15 V when operating at 2 A/cm<sup>2</sup> and 70 °C, and the data obtained show a kind of initial transient degradation, significantly increasing the cell voltage in the first hours of operation. This could be caused by some inefficiencies in the cell assembly or some external problem. The model simulation will be performed with these data to show the adaptability of the model to real data and the processing of the experimental results.

The robustness of the model was successfully tested for a wide range of operating parameters and conditions. Only the most important results will be discussed in this chapter. A total of more than 28 parameters can be plotted over time to study their evolution during PEM electrolyzer operation, influenced by degradation. An example of a case study with all the graphs is attached in the Appendix B.

To better approximate real-world operating conditions, sensitivity analyses were performed at asymmetric pressures. The anode pressure was fixed at 2 bar and the cathode was operated at high pressures. Nevertheless, the recombination of hydrogen gas with oxygen to form water was not implemented in the model, so the maximum cathode pressure is limited to a lower value than the industrial standard due to safety protocols.

The recombination of hydrogen with oxygen to form water consumes the hydrogen and the oxygen that crosses the membrane. Consequently, this phenomenon significantly increases the life expectancy of the cell, potentially extending its lifespan by a factor of 7.4. It also reduces the H<sub>2</sub> content in O<sub>2</sub> by a factor of 4.4, making cell operation safer. [80]

## 6.1 I-V curve

The I-V curve of the cell aging under experimental conditions: 70 °C, 2 A/cm<sup>2</sup>, and isobaric conditions was obtained from the simulation at different times of operation. The evolution of the I-V curve is strongly influenced by the real data extracted from the experiment and their implementation in the model through the calibration at the beginning of operation. Figure 6.1 shows the I-V curves for a current density range of 0–4 A/cm<sup>2</sup>:

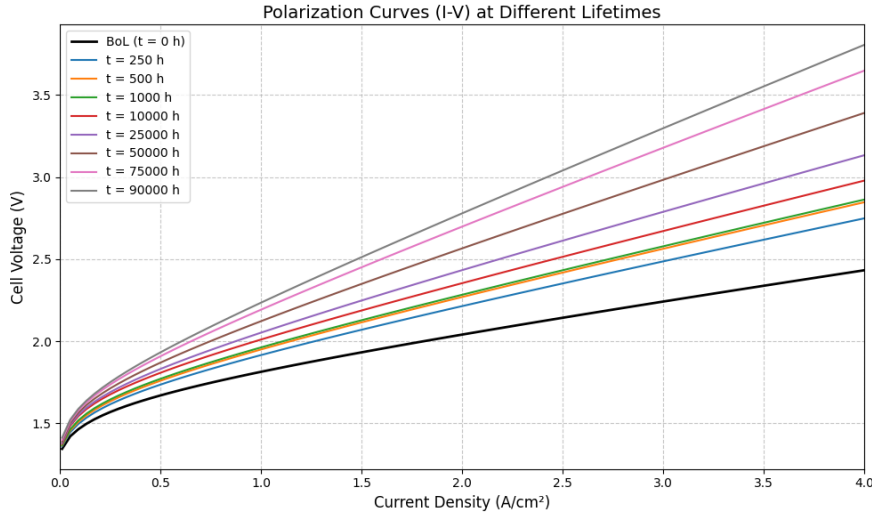


**Figure 6.1.** I-V curve at different times of operation ( $T = 70$  °C,  $i = 2$  A/cm<sup>2</sup>,  $P = 1.5$  bar)

Two zones can be easily identified: the activation region at low current densities and the linear ohmic region after 0.25 A/cm<sup>2</sup>. The large gap between the initial I-V curve and the curve at 250 or 500 h verifies the aforementioned discussion of the validity of the experimental data. This large gap can be caused by the wrong assembly of the cell, cell malfunction, or a measurement mistake.

The model was simulated for a fixed anode and cathode pressure of 1.5 bar. The low pressure contributes to the increase in the longevity of the cell, as there is no convective crossover of gases. The end of life of the cell is determined here by the H<sub>2</sub> content in O<sub>2</sub> and not by the thickness of the membrane.

After the experimental zone (<323 h), the cell reaches a more steady operation and controlled degradation, where the degradation penalty becomes more linear. The system stabilizes, reaching a fixed overpotential for the catalyst agglomeration, a linear and almost constant bubble penalty, an almost constant kinetic rate of membrane degradation caused by the slow gas transport under isobaric conditions, and the stabilization of the catalysts.

The study of the I-V curve of the cell over time is very useful to determine the health of the cell and the economic viability of its operation. The difference in the cell voltage is directly related to the energy that must be supplied. The cell voltage at 2 A/cm<sup>2</sup> at  $t = 25000$  h is 2.42 V and at  $t = 50000$  h is 2.56 V. The voltage increased 5.78% and, consequently, the power supply must deliver 5.78% more power.

## 6.2 Temperature Sensitivity

To simulate the cell at different temperatures, the code was modified based on the experimental data obtained for 70 °C. A correction to the anode exchange current density dependent on temperature was applied, utilizing the experimental reference temperature and the Arrhenius equation:

$$i_{0,an,0} = i_{0,an,ref} \cdot \exp \left[ \frac{-Ea}{R} \cdot \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (6.1)$$

### 6.2.1 Symmetric Pressure

The experiment was performed at a constant current density of 2 A/cm<sup>2</sup> and at isobaric pressure of 10 bar for 60, 70, 80, and 90 °C. The simulation was performed at a fixed and symmetric pressure to isolate the effects of temperature on membrane thinning, since other phenomena, such as mass transport and kinetics limitations, at low or asymmetric pressures strongly influence membrane thinning. Figure 6.2 shows membrane thinning depending on the temperature of operation:

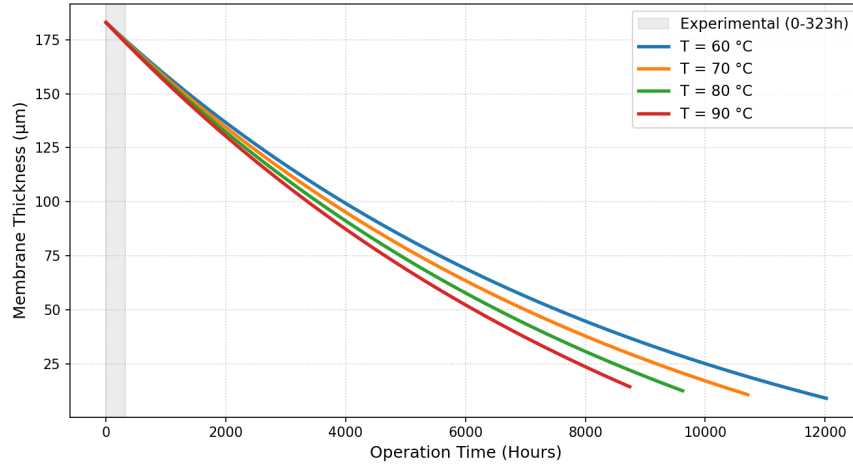


**Figure 6.2.** Membrane thinning dependency on T for  $i = 2$  A/cm<sup>2</sup> and  $P = 10$  bar

The expected behavior of membrane thickness over time is observed. The membrane degrades significantly faster at higher temperatures, following the kinetics and temperature dependency described in Chapter 5.3.5. Even though the membrane thinning also depends on the cathode activation overpotential and the oxygen crossover, the temperature influence dominates these other effects.

#### 6.2.1.1 Total Voltage

To understand the temperature impact on the cell, the total voltage applied is also discussed. The same conditions as in the previous simulation are set. Figure 6.3 shows the evolution of the cell potential over time at different temperatures:

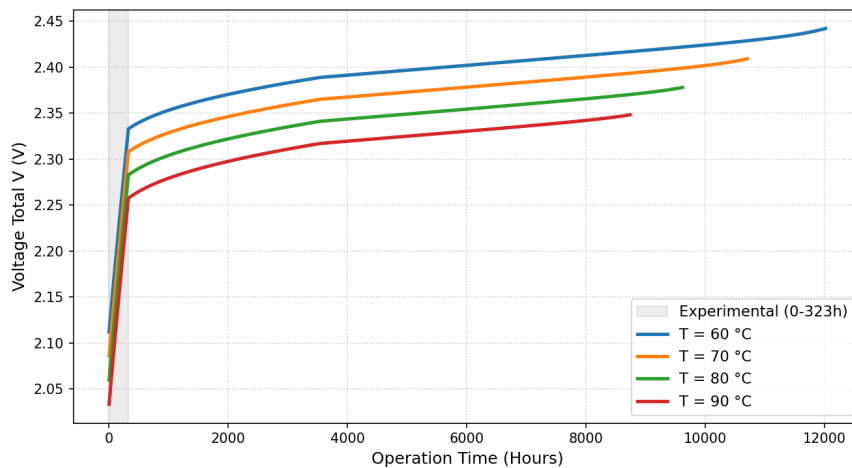


**Figure 6.3.** Total cell potential at different  $T$  for  $i = 2 \text{ A/cm}^2$  and  $P = 10 \text{ bar}$

The initial period ( $< 323 \text{ h}$ ) corresponds to the previously discussed experimental region. At higher temperatures of operation, the potential applied to the cell is lower because activation overpotential is reduced, enhancing the kinetics of the reactions. The ohmic losses are not considerably influenced by temperature. The concentration losses are higher at higher temperatures, following the Nernst equation. However, the activation losses are in the range of  $0.01\text{-}0.1 \text{ V}$  penalty, making them much more significant than the concentration losses impact, in the magnitude of  $1 \cdot 10^{-6} \text{ V}$ . Figure 6.4 shows the difference in the activation overpotential depending on temperature.

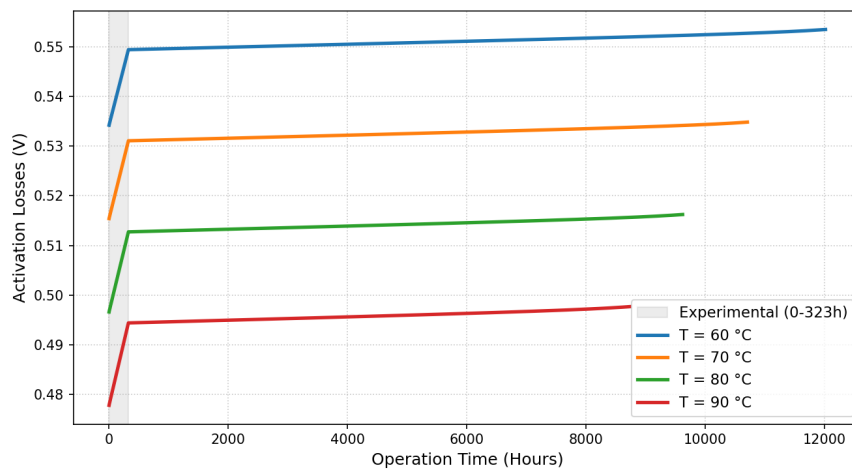


**Figure 6.4.** Activation losses at different  $T$  for  $i = 2 \text{ A/cm}^2$  and  $P = 10 \text{ bar}$

### 6.2.2 Asymmetric Pressures

When operating both the anode and the cathode at the same pressure, considerable amount of oxygen crosses the membrane to the cathode and quickly consumes the membrane.

To reduce the operational expenses of hydrogen compression, the electrolyzer is operated at asymmetric pressures, with a much higher pressure in the cathode. When operating under these conditions, only the oxygen that travels by diffusion and with electro-osmotic water is considered to reach the cathode.

The partial pressure of gases, such as oxygen, decreases considerably at higher temperatures, as there is more water vapor. Consequently, the concentration of oxygen that crosses the membrane with water is lower. There is less oxygen reaching the cathode and reacting to consume the membrane, resulting in a lower thinning rate. Figure 6.5 shows the results of the simulation of the membrane thickness operation at a constant current density of  $2 \text{ A/cm}^2$ , an anode pressure of 1.5 bar, and a cathode pressure of 10 bar, for different temperatures:

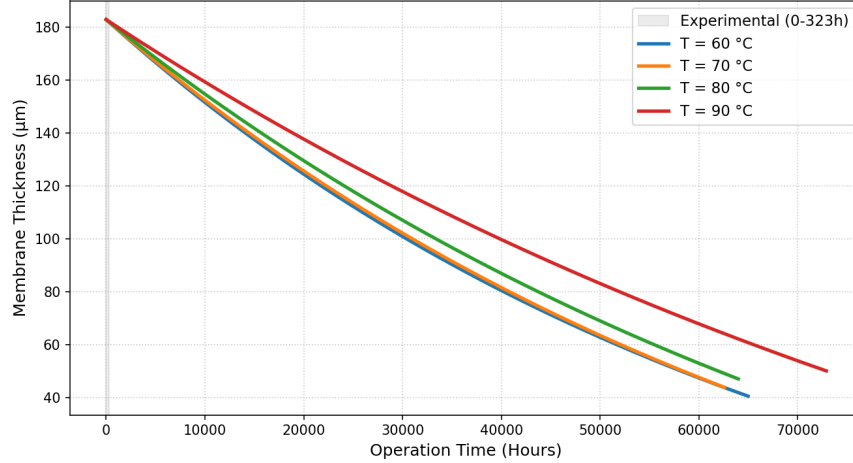


**Figure 6.5.** Membrane thickness at different  $T$  for  $i = 2 \text{ A/cm}^2$ ,  $P_{an}=1.5 \text{ bar}$ , and  $P_{cat}= 10 \text{ bar}$

The life expectancy becomes much longer when operating only the cathode at high pressure than when operating both the cathode and the anode at high pressure, since less oxygen reaches the cathode due to the high pressure difference. However, the hydrogen crossover will be higher and can force the PEM electrolyzer shutdown due to safety concerns.

Counterintuitively, the membrane degrades faster at lower temperatures. Following Chandresis equations, at higher temperatures the membrane consuming reactions occur faster. However, the activation overpotential of the cathode and the concentration of oxygen and protons in the cathode slow the kinetics of the membrane consuming reactions.

It was previously discussed how the membrane degrades faster at higher temperatures when operating at symmetric and considerable high pressures. However, if the anode is operated at low pressure and the cathode at high pressure, the dissolved oxygen available to permeate to reach the cathode is considerably lower. No water with dissolved oxygen reaches the cathode due to the high pressure difference. Figure 6.6 shows the diffusion oxygen rate over time for different temperatures, operating at fixed  $2 \text{ A/cm}^2$ , anode pressure of 1.5 bar, and cathode pressure of 10 bar:

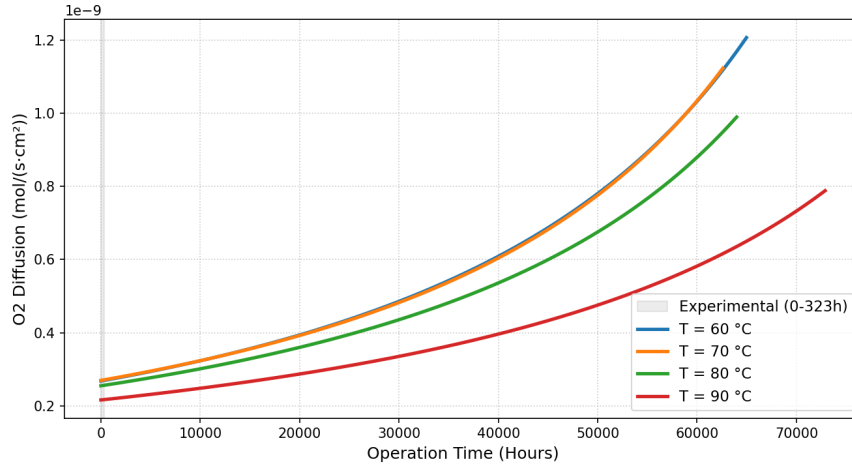


**Figure 6.6.** O<sub>2</sub> diffusion at different T for  $i = 2 \text{ A/cm}^2$ ,  $P_{an}=1.5 \text{ bar}$ , and  $P_{cat}= 10 \text{ bar}$

Figure 6.7 shows the oxygen rate transferred by water EOD over time for different temperatures, operating at fixed  $2 \text{ A/cm}^2$ , anode pressure of 1.5 bar, and cathode pressure of 10 bar:

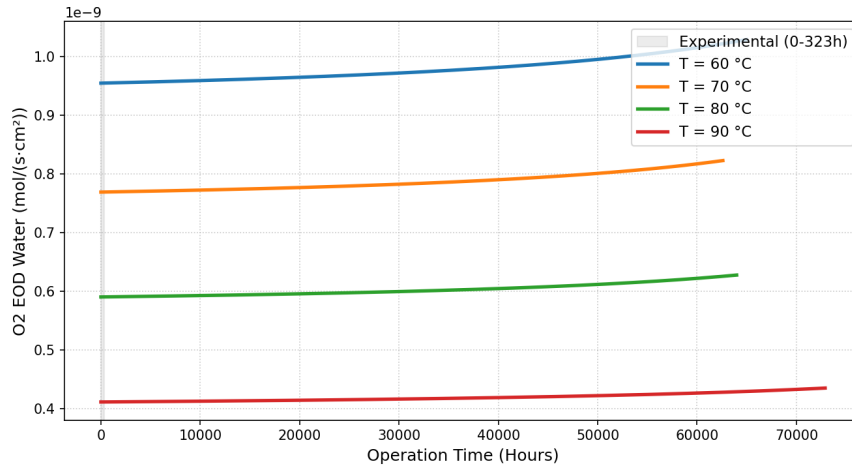


**Figure 6.7.** O<sub>2</sub> in EOD water at different T for  $i = 2 \text{ A/cm}^2$ ,  $P_{an}=1.5 \text{ bar}$ , and  $P_{cat}= 10 \text{ bar}$

It can be observed how there is a significant difference between the oxygen mass transfer fluxes at different temperatures. This occurs due to the the solubility of gases in water decreases significantly when increasing temperature. This difference overcomes the temperature impact on the kinetics, slowing down the membrane thinning at higher temperatures for low pressure operation. The same phenomenon occurs when operating the cell at low isobaric pressure. It will be discussed in the following.

### 6.2.3 Mass Transport Limitations at Low Pressure

Operating under low symmetric pressures significantly extends the life expectancy of a PEM electrolyzer. Results showed the expected lifetime is around 8 times longer when operating at 1.5 bar compared to 10 bar. Because the operation is at isobaric low pressure, the presence of oxygen in the cathode is significantly lower.

When operating under these conditions, the oxygen transport is dictated by diffusion.

Following Henry's and Fick's laws, at lower pressures there is a lower concentration of gases in water, and the concentration difference between the anode and the cathode is smaller, reducing the gas diffusion. Consequently, there is less oxygen crossing the membrane and reacting to consume it.

An interesting non-linear behavior was also observed when the model was simulated at 60, 70, and 80 °C, under a fixed current density of 2 A/cm<sup>2</sup> and low pressure (1.5 bar). Figure 6.8 shows the membrane thickness loss over time at different temperatures of operation:

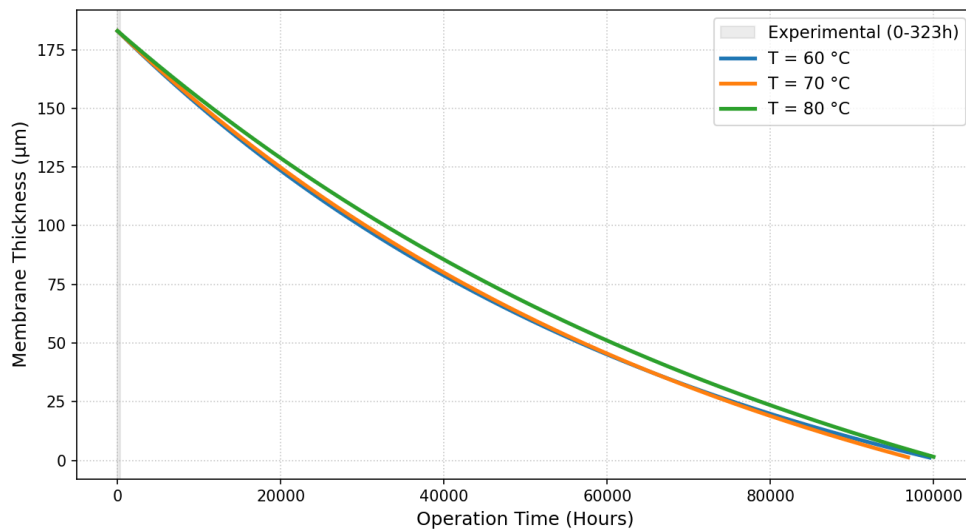


**Figure 6.8.** Membrane thickness at different temperatures (P=1.5 bar, i=2 A/cm<sup>2</sup>)

It can be observed that the membrane degrades faster at 70 °C than at 80 °C. This can seem contradictory, but the same phenomenon as for asymmetric pressures occurs. There is a limitation in the oxygen that reaches the cathode due to the low solubility of gases in water at low pressure.

Conversely, the degradation rate is higher at 70 °C than at 60 °C. At this point, the temperature impact on the kinetics of the reactions dominates over the loss of gas solubility in water and the decrease of oxygen concentration in water. The difference in gas solubility at 60°C and 70°C is much smaller than for 70°C to 80°C.

## 6.3 Pressure Sensitivity

The study of pressure sensitivity is of great importance in order to understand the impact of pressure on the performance of the PEM electrolyzer. The industrial anode pressure is usually fixed at a low value, and the cathode side aims to operate at very high pressures to reduce the costs of hydrogen compression.

Different techniques are applied to reduce gas crossover and membrane thinning, i.e. embedding a single layer of graphene in the middle of the membrane to reduce the hydrogen crossover by a factor of eight, or the coating of membrane with Pt based materials, which enhance the hydrogen and oxygen recombination, reducing the hydrogen and oxygen crossover. [81] [80]

However, no gas crossover mitigation techniques were implemented in the model. The model simulates a Nafion 117 membrane with no mitigation. The simulations were performed at a fixed temperature of 70°C, and current density of 2 A/cm<sup>2</sup>. The anode pressure was fixed at 1.5 bar for all simulations and the cathode pressure was studied at 1.5, 5, 10, 15, and 20 bar. The modeled experimental cell is supposed be able to operate at 30 bar. However, when setting 30 bar for cathode pressure, the simulation stopped at  $t = 0$ h due to the safety protocols. The maximum cathode pressure at which this PEM electrolyzer can operate without H<sub>2</sub> content in O<sub>2</sub> risks was found to be 23.75 bar.

The asymmetric pressure operation drives more hydrogen crossover to the anode, following Darcy's Law. Figure 6.9 shows the convection-driven hydrogen rate over time for the different cathode pressures:

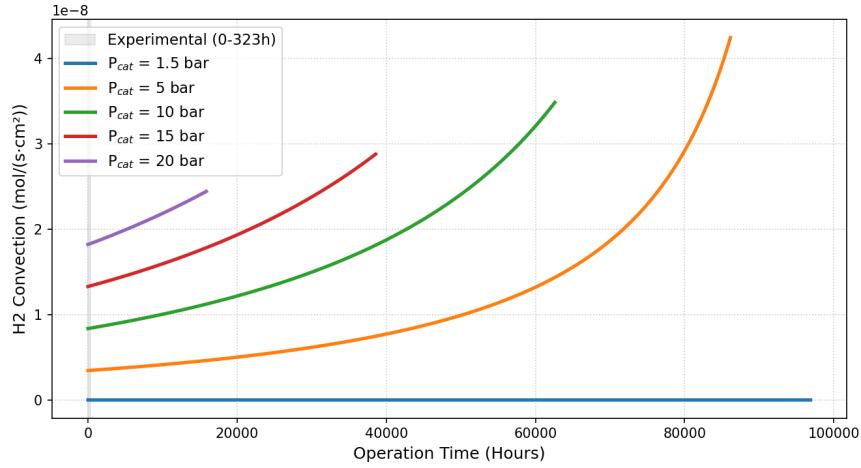


**Figure 6.9.** Convective H<sub>2</sub> rate at different  $P_{cat}$  for  $T = 70^\circ\text{C}$ ,  $P_{an}=1.5$  bar, and  $i = 2$  A/cm<sup>2</sup>

The graph demonstrates the impact of the cathode pressure on the convective-driven hydrogen rate. When operating under isobaric conditions, convection is non-existent. However, at higher cathode pressures, the convective hydrogen starts to move faster, reaching the safety limit of H<sub>2</sub> in O<sub>2</sub> faster and stopping cell operation.

The hydrogen transported by diffusion also plays a role in the shutdown of the PEM electrolyzer. Figure 6.10 shows the hydrogen diffusion rate for different cathode pressures:

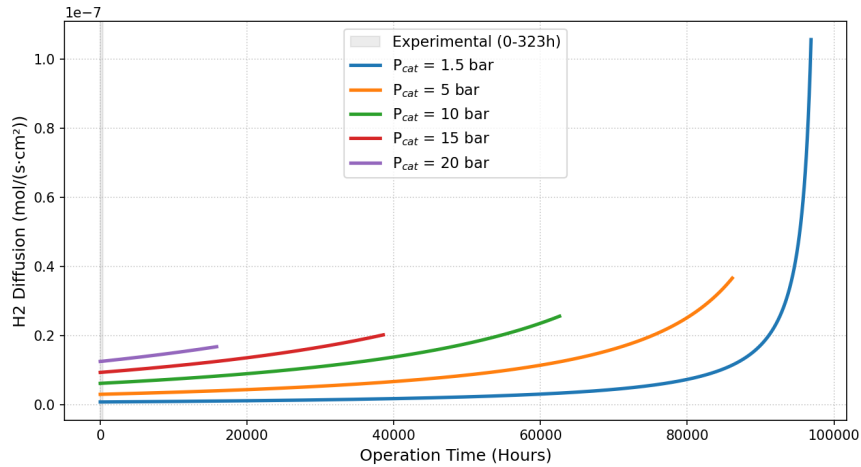


**Figure 6.10.** H<sub>2</sub> diffusion rate at different  $P_{cat}$  for  $T = 70^\circ\text{C}$ ,  $P_{an}=1.5$  bar, and  $i = 2$  A/cm<sup>2</sup>

The diffused hydrogen flow is higher at higher cathode pressures due to the increased solubility and partial pressure of hydrogen at high pressures. The concentration of dissolved hydrogen is directly proportional to the partial pressure of the hydrogen, following Henry's Law.

The membrane thinning rate is practically not dependent on the pressure difference between the anode and the cathode. The most important factor that affects membrane degradation is the oxygen transfer by diffusion, which is independent of the pressure difference. Figure 6.11 shows the evolution of the membrane thickness depending on the cathode pressure:

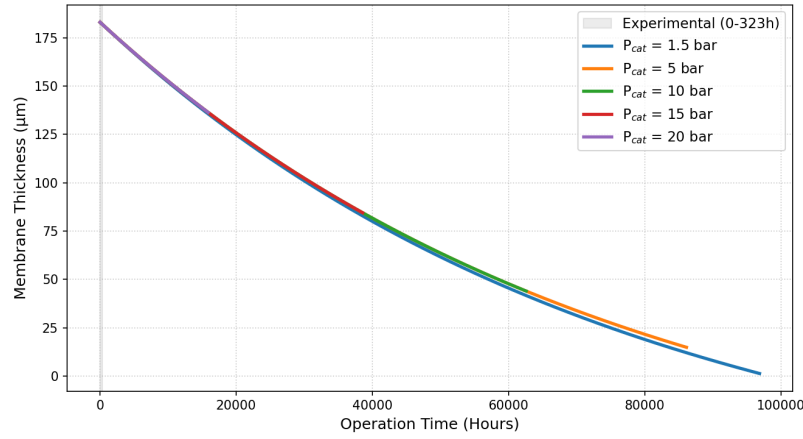


**Figure 6.11.** Membrane thickness at different  $P_{cat}$  for  $T = 70^{\circ}\text{C}$ ,  $P_{an}=1.5$  bar, and  $i= 2 \text{ A/cm}^2$

The graph shows how the membrane thickness evolution is practically the same for the different cathode pressures, indicating that the operation is stopped for safety reasons. There is a small difference between operating under isobaric conditions ( $P_{cat} = 1.5$  bar) and operating with higher pressure in the cathode. Diffusion-driven water is assumed to not reach the cathode when operating with a pressure difference. As a consequence, only under isobaric conditions the oxygen that travels with this water affects membrane degradation.

The Faraday efficiency is significantly affected by the high hydrogen crossover caused by the pressure difference. At higher pressure differences, more hydrogen crosses through the membrane to the anode, resulting in more hydrogen loss and less hydrogen output. Consequently, the Faraday efficiency decreases with greater pressure differences. Figure 6.12 shows the Faraday efficiency over time for the different cathode pressures:

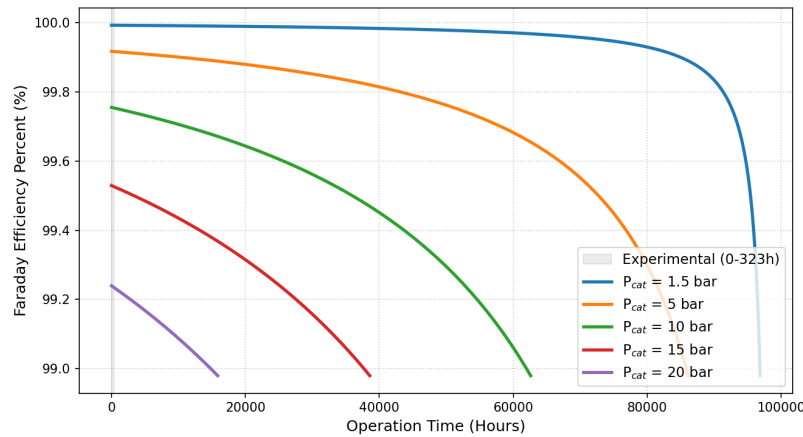


**Figure 6.12.** Faraday efficiency at different  $P_{cat}$  for  $T = 70^{\circ}\text{C}$ ,  $P_{an}=1.5$  bar, and  $i= 2 \text{ A/cm}^2$

It can be observed that the Faraday efficiency is higher at lower pressure differences. It also decreases faster when operating the cathode at high pressure, as a consequence of the increase in hydrogen convection and diffusion. The simulations were terminated at the same Faraday efficiency, just below 98%. This point is where the  $H_2$  content in  $O_2$  is 2% and the PEM electrolyzer operation is stopped.

### 6.3.0.1 Bubble Coverage

The bubble coverage of the electrode surface depends on the pressure of operation. The gas saturation concentration is proportional to its partial pressure. [55]

Following the Ideal Gas Law, the volume occupied by a gas is inversely proportional to the pressure. Since the number of moles produced is independent of the pressure, following Faraday's Law, the same amount of moles will be produced at different pressures. However, they will occupy a smaller volume at higher pressures and will be dissipated faster. Figure 6.13 shows the bubble coverage at different pressures:

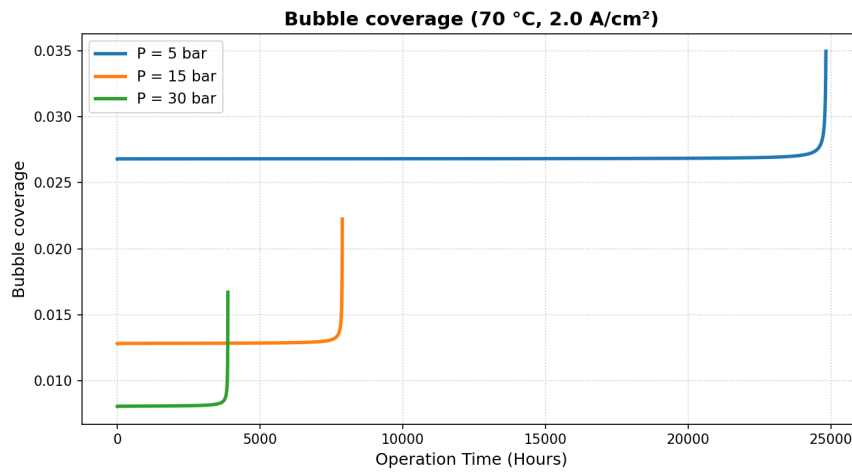


**Figure 6.13.** Bubble coverage at different pressures

This graph shows a significant decrease in bubble coverage depending on pressure, dropping from 27% at 5 bar to 7.5% at 15 bar. The bubble coverage has a direct impact on the cell overpotential, operating at higher pressures would reduce the negative impact of bubbles. However, the negative impacts of operating at high pressures, discussed in the pressure sensitivity section, outweigh the positive impact on bubble overpotential.

## 6.4 Current Density Sensitivity

The current density sensitivity test was performed at a fixed temperature of 70°C, an anode pressure of 1.5 bar, and a cathode pressure of 10 bar. The aim is to study the degradation and hydrogen production at different current densities to obtain the optimal conditions of operation and understand the impact of the current density in the production and degradation rates.

Following Faraday's Law, the hydrogen produced is proportional to the current applied to the cell. Figure 6.14 shows the total hydrogen produced at different current densities, taking into account the hydrogen lost by diffusion and convection. The linear relation to the current can

be observed, producing around 4 times more hydrogen when increasing the current applied by a factor of 4:

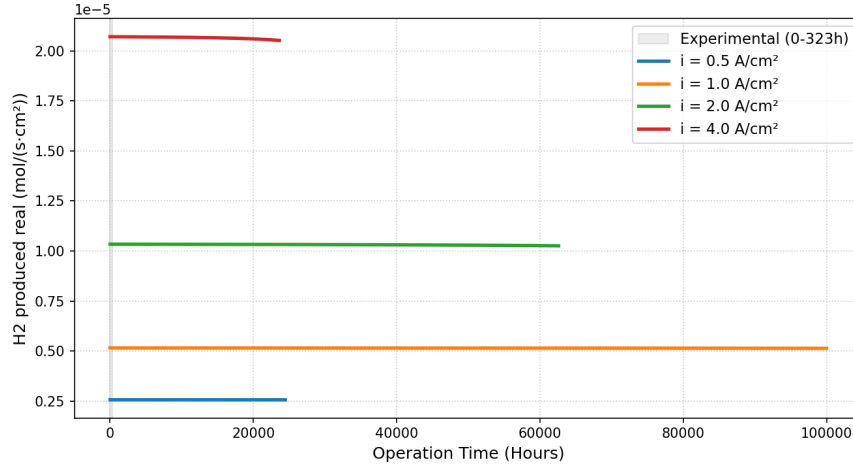


**Figure 6.14.**  $H_2$  produced at different  $i$  for  $T = 70^\circ\text{C}$ ,  $P_{an}=1.5$  bar, and  $P_{cat} = 10$  bar

The simulation also shows how important it is to operate at the optimal current density to optimize the hydrogen production and membrane degradation. Figure 6.15 shows how the membrane thickness over time for the different current densities. It can be observed how the membrane suffers minimal physical degradation when operating at  $0.5\text{ A/cm}^2$ , and how the membrane thinning is accelerated at higher current densities.

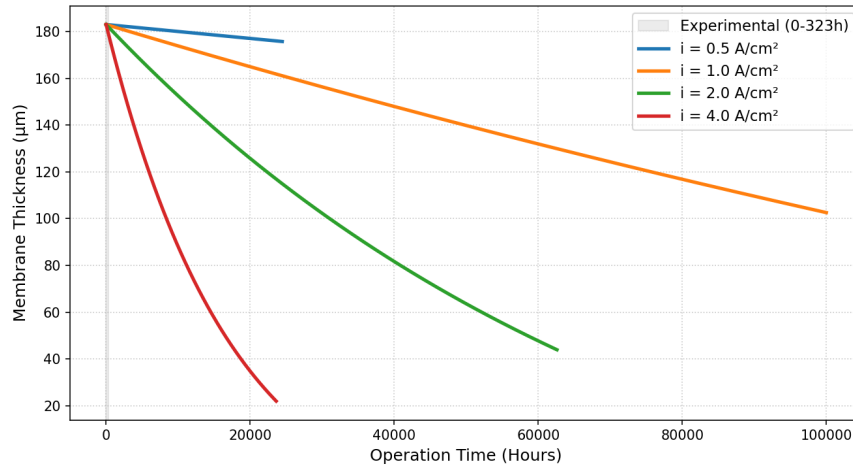


**Figure 6.15.** Membrane thickness evolution at different  $i$  for  $T = 70^\circ\text{C}$ ,  $P_{an}=1.5$  bar, and  $P_{cat}= 10$  bar

More oxygen is produced at higher current densities. Consequently, more oxygen reaches the cathode and consume the membrane. However, the operation is stopped almost at the same time for  $0.5\text{ A/cm}^2$  as for  $4\text{ A/cm}^2$ . This occurs due to the safety shut down due to high  $H_2$  content in  $O_2$ . Figure 6.16 shows the  $H_2$  content in  $O_2$  over time for the different current densities:

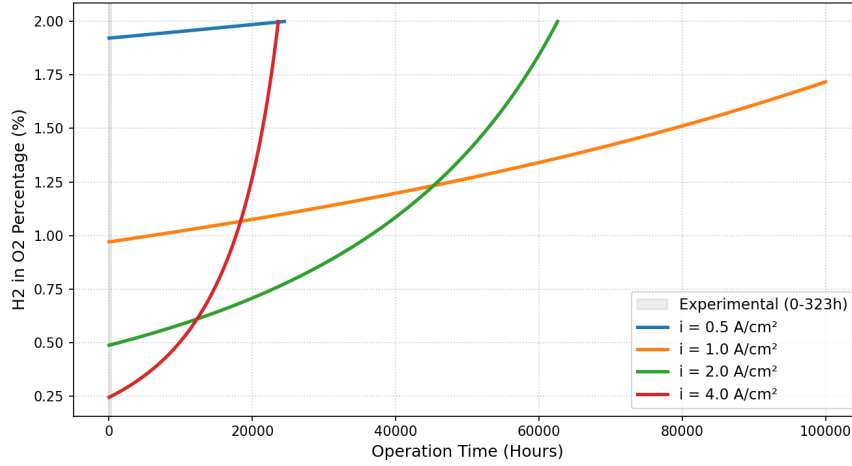


**Figure 6.16.**  $H_2$  in  $O_2$  (%) at different  $i$  for  $T = 70^\circ\text{C}$ ,  $P_{an}=1.5$  bar, and  $P_{cat}= 10$  bar

At low current densities, a very small quantity of oxygen is produced. This causes the hydrogen percentage in oxygen to be very high since the beginning of the operation, as less oxygen is available to dilute the hydrogen. And after a minimal membrane thickness loss, around 3% for the simulation at  $0.5 \text{ A/cm}^2$ , the safety limit is reached.

Contrary, operating at higher current densities reduces the  $H_2$  content in  $O_2$  due to the large amount of oxygen available to dilute hydrogen. However, the membrane thinning rate is higher when operating at higher current densities, which causes more hydrogen crossover and a rapid increase in the  $H_2$  content in  $O_2$ .

The voltage applied must also be studied to determine the economic viability of the PEM electrolyzer operation. Figure 6.17 shows the total applied voltage over time for the different current densities of operation:

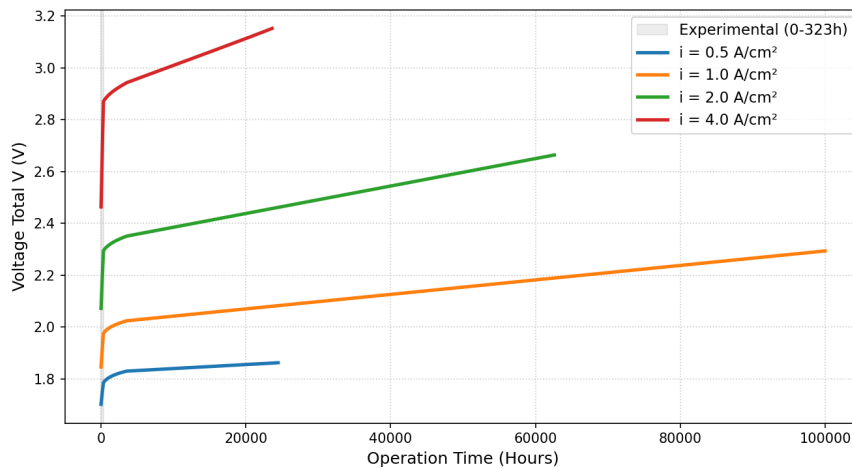


**Figure 6.17.** Total cell voltage at different  $i$  for  $T = 70^\circ\text{C}$ ,  $P_{an}=1.5$  bar, and  $P_{cat}= 10$  bar

It can be observed how the potential applied is higher at higher current densities as a consequence of the higher current applied. The voltage evolution over time is more pronounced at higher current density due to the current impact on the ohmic losses, which follows a proportional relation to the current.

It is of great importance to find the optimal current density of operation to maximize the hydrogen production, minimize the membrane degradation and the operation costs, and assure the safe operation of the PEM electrolysis. The simulation showed that operating at  $1\text{A}/\text{cm}^2$  extends the life expectancy of the cell and reduces the operation costs, but the amount of hydrogen produced is reduced. More hydrogen was produced during the lifetime of the electrolyzer operating at  $2\text{ A}/\text{cm}^2$ .

## 6.5 PtC Particle Size

The particle size evolution of PtC over time was modeled using experimental data derived from the XRD test. Figure 6.18 shows the diameter evolution of the particle, assuming spherical geometry:

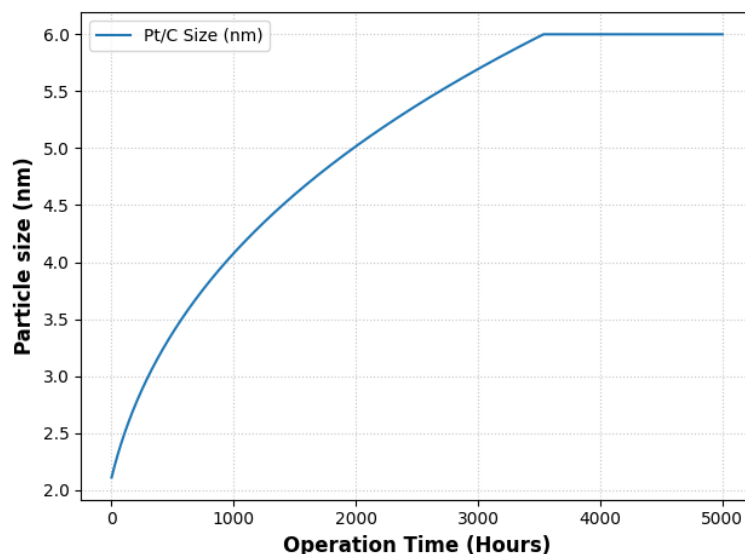


*Figure 6.18.* PtC particle size evolution over time

It can be observed how the particle grows faster in the beginning of the PEM electrolyzer operation, following a logarithmic trajectory until reaching the maximum size of 6nm, determined by literature. [75]

The PtC particles diameter grows due to agglomeration and Ostwald ripening. The particles move and reorganize faster during the first hours of operating due to the high surface energy of the small particles. They are dissolved and reorganize rapidly, increasing the particle diameter and reducing their surface energy. Consequently, the thermodynamic energy is lower, reducing the dissolution rate and the particle diameter growth. The  $\text{Pt}^{+2}$  ions are also dissolved in the water and react with hydrogen to form solid Pt crystal in the cathode/membrane interphase, which negatively contributes to the cell losses. [75]

The overpotential penalty caused by the growth of PtC particles size is presented in Figure 6.19:

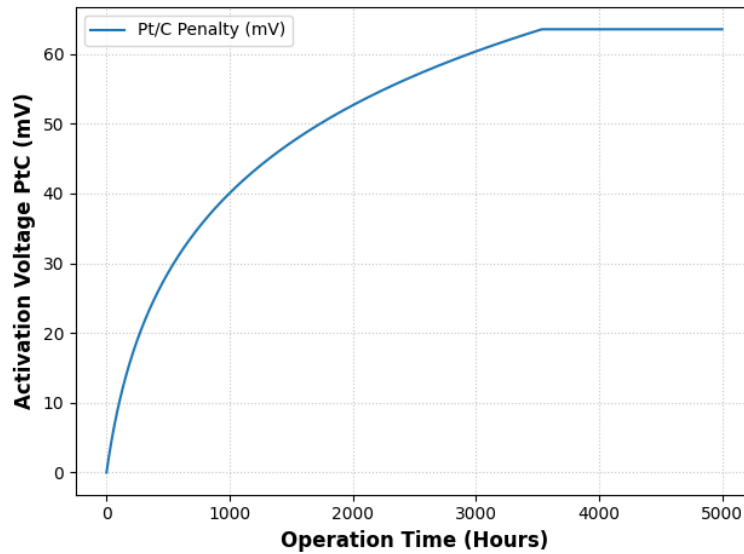


**Figure 6.19.** PtC particle size penalty evolution over time

The overpotential penalty presents a direct correlation with the particle size. As presented in Equation 5.49, the effective current density that must be applied is calculated based on the ratio of current particle size to initial particle size. The simulation presents a maximum voltage penalty of 60mV, which is a significant number that must be taken into account when designing long-term PEM electrolyzers.

## 6.6 Iridium dissolution

Iridium dissolution occurs at high potentials of operation. It does not have a significant effect when operating with a structurally intact membrane. However, when the membrane thickness is reduced and the gas crossover and the potential applied to the anode increase, it can cause catastrophic failure. The PEM electrolysis operation is usually stopped before this happens, following the corresponding safety protocols.

Figure 6.20 shows a comparison between the ohmic losses taking into account the iridium dissolution (blue line) and neglecting the iridium dissolution (red line):

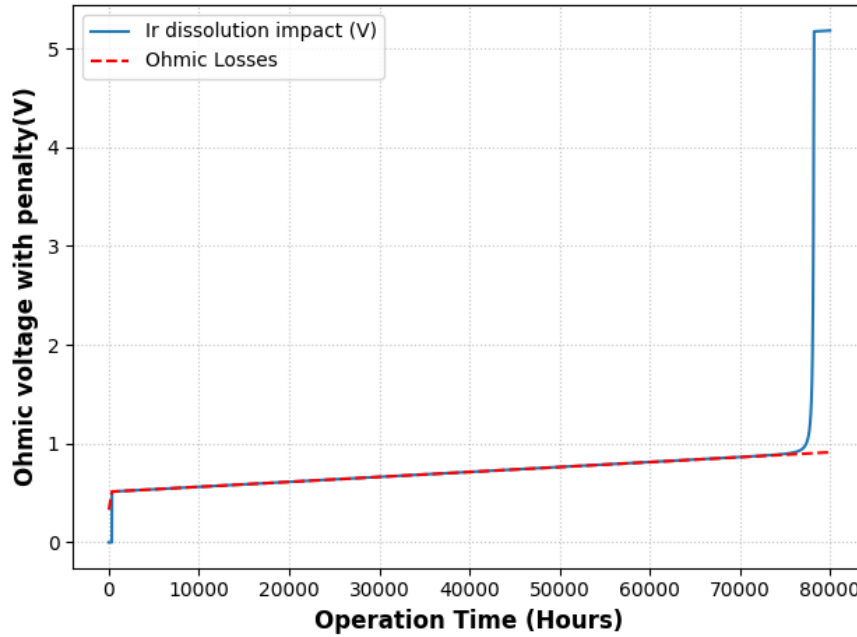


*Figure 6.20.* Ir dissolution impact on  $V_{ohm}$

The ohmic losses were taken as a reference since the impact on the activation overpotential is negligible during operation. The catastrophic failure is attributed to a spike in the ohmic overpotential caused by irreversible catalyst delamination, critical membrane thinning, and loss of contact between components.

There are minimal differences during normal operation. The voltage penalty of iridium during normal operation is of magnitude  $10 \mu\text{V}$ . It becomes more noticeable at high cell potentials, when the PEM electrolyzer starts to reach the end of life and full membrane consumption. At this point, the iridium starts to dissolve quickly due to the high potential, causing an exponential increase in the voltage that must be applied to the cell to maintain a constant current density.

# Conclusion 7

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In this project, a comprehensive model for a single PEM electrolyzer cell was developed. The theoretical equations used to simulate cell performance were coupled with experimentally obtained data, resulting in a robust and flexible semi-empirical model. The experimental PEM electrolyzer was operated for 500 hours at a current density of  $2 \text{ A/cm}^2$ , a temperature of  $70 \text{ }^\circ\text{C}$ , and ambient pressure.

The model successfully links the mass transport phenomena with the thermodynamic and electrochemical principles of the PEM electrolyzer, coupling these domains to different degradation mechanisms.

Electrochemical impedance spectroscopy (EIS) tests were performed at different times of operation to obtain the evolution of the activation and ohmic resistances over time. X-Ray Diffraction (XRD) tests were also performed to study the structural evolution of the catalyst particles.

The data obtained showed a non-ideal behavior of the experimental cell. However, they were used to model the initial stages of cell operation to demonstrate the data treatment procedure and the model's adaptability to real operation data.

The results show the flexibility and robustness of the model. The model was tested for a wide range of operating conditions, varying temperatures, current densities, and both symmetric and asymmetric pressures.

Several critical phenomena affecting the operation and design of a PEM electrolyzer were discussed. It is concluded that mass transport limitations play a pivotal role in the long-term operation of the cell. Counterintuitively, the results showed that membrane thinning can be mitigated when operating at high temperatures by controlling the oxygen crossover. Operating at symmetric low pressure and high temperature limits the solubility of oxygen in water, and consequently, the amount of oxygen that reaches the cathode and degrades the membrane.

Furthermore, operating under asymmetric pressure, with higher pressure in the cathode, considerably reduces the oxygen crossover due to the pressure difference. However, this configuration promotes hydrogen crossover to the anode, which accelerates premature cell shutdown due to safety concerns.

In conclusion, a fully functional 1D semi-empirical model of a PEM electrolyzer was developed. This digital-twin provides a predictive tool to optimize PEM electrolyzer operation, lifetime, and economic viability of green hydrogen production by successfully coupling degradation kinetics and fluid dynamics with industrial safety limits. It can also be used to study specific transport or degradation phenomena under diverse operating conditions.

# Future Work 8

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This chapter outlines the pathways that can be followed to refine and expand the developed model.

## 8.1 Experimental Data Quality and Duration

The available experimental data were implemented into the model, despite the aforementioned constraints on the quality of the data. Future work should focus on obtaining long-term high-quality data. This would enable a deeper understanding of the degradation kinetics and their long-term impact on the PEM electrolyzer.

## 8.2 Experimental Conditions and Parameters of Operation

The experimental data were obtained for a specific cell under fixed operating conditions. To validate the robustness and flexibility of the model, experiments could be performed under a different set of operating conditions for different cell parameters. The implementation of these results in the digital-twin and their validation would expand the scope of the model.

## 8.3 Stack of Cells Modeling

In industrial applications, PEM electrolyzers are assembled in stacks, rather than as single-cell units. The model only simulates an individual PEM electrolyzer. Future work would be to couple the dynamics between individual cells to simulate a stack.

## 8.4 Dynamic Loading and Intermittency

The model operates at a constant current density. However, PEM electrolyzers operate under dynamic current densities in reality, when powered by renewable sources. Although dynamic current inputs can be configured to run the model, the degradation triggered by the dynamic operation was not integrated into the model. Future work would be to implement dynamic load degradation to obtain a high-fidelity model for real operating scenarios.

## 8.5 Degradation Mechanisms

The current model only accounts for the dominant degradation mechanisms. Additional degradation mechanisms, such as corrosion or titanium passivation, could be implemented to obtain a more accurate model. The analysis of the impact of each individual mechanism and the coupling between them is of great importance for the lifetime modeling of the electrolyzer.

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# Appendix A

Tables A.1, A.2, and A.3 summarize the list of parameters used to run the model.

The libraries needed to run the model in Python are listed in table A.4.

## Tables of Parameters

**Table A.1.** Operating Conditions and Thermodynamic Parameters

| Symbol          | Parameter                                   | Value                | Unit              |
|-----------------|---------------------------------------------|----------------------|-------------------|
| $T$             | Operating temperature                       | 343.15               | K                 |
| $P$             | Operating pressure                          | 1.5                  | bar               |
| $I$             | Nominal current                             | 50                   | A                 |
| $i$             | Nominal current density                     | 2.0                  | A/cm <sup>2</sup> |
| $V_{rev}^0$     | Reversible cell voltage                     | 1.23                 | V                 |
| $V_{th}^0$      | Thermoneutral voltage                       | 1.48                 | V                 |
| $\Delta G^0$    | Gibbs free energy of reaction               | -237.13              | kJ/mol            |
| $\Delta H^0$    | Enthalpy of reaction                        | -285.83              | kJ/mol            |
| $F$             | Faraday constant                            | 96485                | C/mol             |
| $R$             | Universal gas constant                      | 8.314                | J/(mol·K)         |
| $\alpha_{an}$   | Anodic charge transfer coefficient          | 1.0                  | -                 |
| $\alpha_{cat}$  | Cathodic charge transfer coefficient        | 0.5                  | -                 |
| $i_{0,ref,an}$  | Reference anodic exchange current density   | $5.0 \times 10^{-9}$ | A/cm <sup>2</sup> |
| $i_{0,ref,cat}$ | Reference cathodic exchange current density | $2.0 \times 10^{-2}$ | A/cm <sup>2</sup> |
| $E_{a,an}$      | Anodic activation energy                    | 76.0                 | kJ/mol            |
| $E_{a,cat}$     | Cathodic activation energy                  | 18.0                 | kJ/mol            |

**Table A.2.** Geometry and Mass Transport Parameters

| Symbol           | Parameter                        | Value                  | Unit               |
|------------------|----------------------------------|------------------------|--------------------|
| $A_{cell}$       | Active surface area              | 25                     | cm <sup>2</sup>    |
| $\delta_{mem}$   | Membrane thickness (Nafion 117)  | 0.0183                 | cm                 |
| $\delta_{an}$    | Anode catalyst layer thickness   | 0.001                  | cm                 |
| $\delta_{cat}$   | Cathode catalyst layer thickness | 0.0015                 | cm                 |
| $EW$             | Equivalent weight of Nafion      | 1100                   | g/mol              |
| $\rho_{mem,dry}$ | Dry membrane density             | 1.967                  | g/cm <sup>3</sup>  |
| $\lambda_{mem}$  | Membrane hydration level         | 22                     | -                  |
| $\epsilon_0$     | Initial PTL dry porosity         | 0.56                   | -                  |
| $n_d$            | Electro-osmotic drag coefficient | 2.5                    | -                  |
| $D_{H_2O,mem}$   | Water diffusivity in membrane    | $1.28 \times 10^{-6}$  | cm <sup>2</sup> /s |
| $P_{H_2}$        | Hydrogen permeability            | $1.8 \times 10^{-14}$  | mol/(m·s·Pa)       |
| $k_{m2}$         | Hydraulic membrane permeability  | $1.58 \times 10^{-18}$ | m <sup>2</sup>     |
| $I_{su}$         | Bubble coverage shape factor     | 30                     | A/cm <sup>2</sup>  |

**Table A.3.** Degradation Constants

| Symbol            | Parameter                                     | Value                 | Unit                   |
|-------------------|-----------------------------------------------|-----------------------|------------------------|
| $R_{0,initial}$   | Initial ohmic resistance fit                  | 0.00658               | $\Omega$               |
| $k_{ohm}$         | Break-in ohmic growth rate                    | $1.14 \times 10^{-5}$ | $\Omega/h$             |
| $i_{0,initial}$   | Initial exchange current density fit          | $8.03 \times 10^{-5}$ | $A/cm^2$               |
| $k_{decay}$       | Break-in kinetic decay rate                   | $1.63 \times 10^{-3}$ | $h^{-1}$               |
| $E_{a,deg}$       | Activation energy for membrane thinning       | 42.45                 | $kJ/mol$               |
| $k_{1,0,ref}$     | Reference thinning rate constant              | $2.56 \times 10^{-5}$ | $cm^7/(mol^2 \cdot s)$ |
| $\alpha_{H_2O_2}$ | Transfer coefficient for $H_2O_2$ generation  | 0.5                   | -                      |
| $E_{H_2O_2}^0$    | Equilibrium potential for $H_2O_2$ generation | 0.695                 | V                      |
| $D_0$             | Initial Pt/C particle diameter                | 2.11                  | nm                     |
| $D_{500}$         | Pt/C particle diameter at 500 h               | 3.38                  | nm                     |
| $D_{max}$         | Maximum Pt/C particle size boundary           | 6.0                   | nm                     |

**Table A.4.** Primary Python libraries utilized in the simulation model.

| Package    | Version | Description                                           |
|------------|---------|-------------------------------------------------------|
| altair     | 6.0.0   | Declarative statistical visualization                 |
| cantera    | 3.2.0   | Chemical kinetics and thermodynamics                  |
| chemicals  | 1.5.1   | Chemical properties compilation                       |
| CoolProp   | 7.2.0   | Thermophysical properties of fluids                   |
| fluids     | 1.3.0   | Fluid dynamics calculations                           |
| iapws      | 1.5.4   | Properties of water and steam                         |
| impedance  | 1.7.1   | Electrochemical impedance spectroscopy (EIS) analysis |
| matplotlib | 3.10.8  | Primary plotting and data visualization               |
| mendeleev  | 1.1.0   | Periodic table of elements properties                 |
| numpy      | 2.4.2   | Core numerical computing and matrix operations        |
| openpyxl   | 3.1.5   | Reading and writing Excel data files                  |
| pandas     | 3.0.0   | Data manipulation and analysis                        |
| Pint       | 0.25.2  | Dimensional analysis and unit conversions             |
| scipy      | 1.17.0  | Scientific computing and equation solving             |
| thermo     | 0.6.0   | Thermodynamics and phase behavior                     |

# Appendix B

This appendix shows the complete set of graphs obtained for the case study of temperature sensitivity at a symmetric pressure of 1.5 bar and a current density of 2 A/cm<sup>2</sup>. These figures are provided as supplementary material to show parameters not discussed in chapter 6:

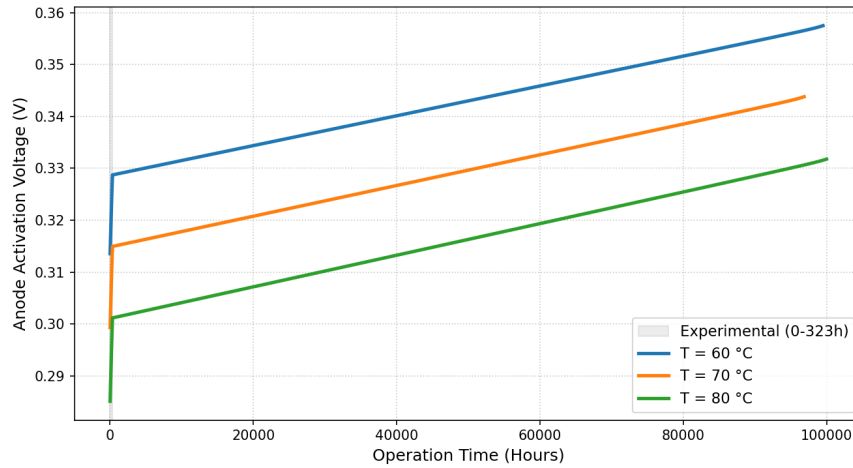


*Figure B.1.* Anode activation losses

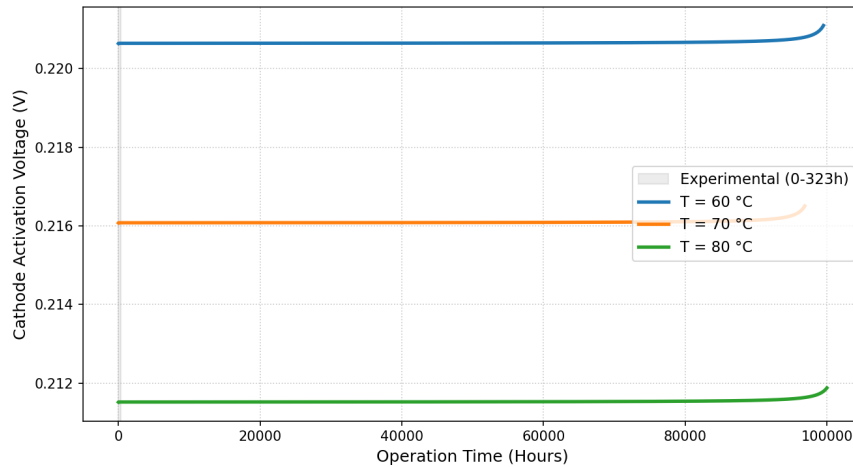


*Figure B.2.* Cathode activation losses

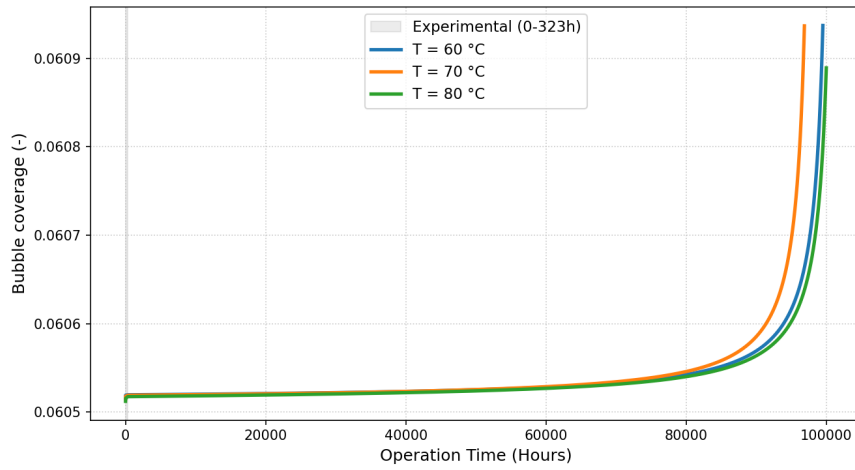


*Figure B.3.* Bubble coverage

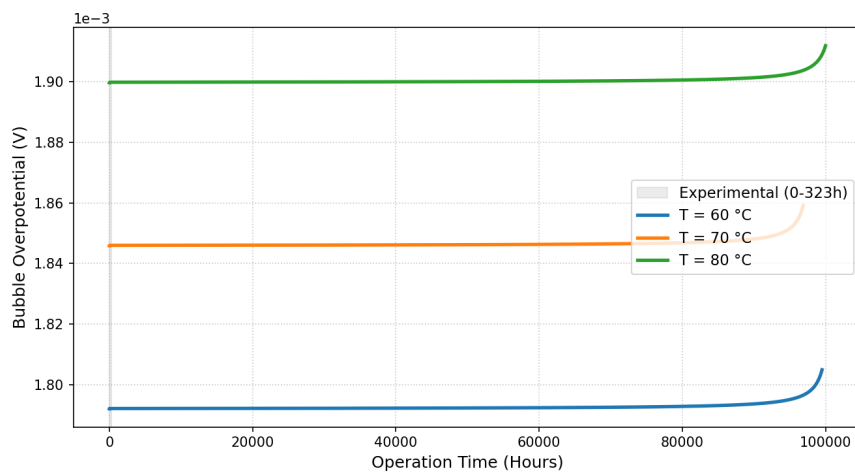


*Figure B.4.* Bubble overpotential

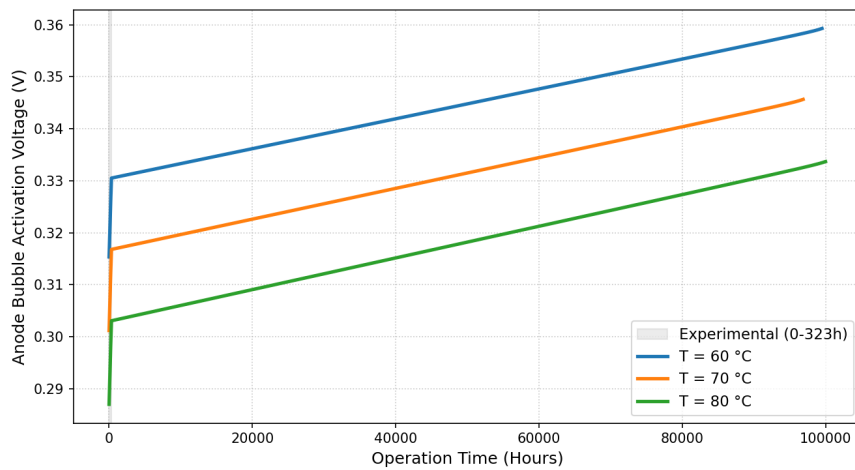


*Figure B.5.* Bubble activation losses

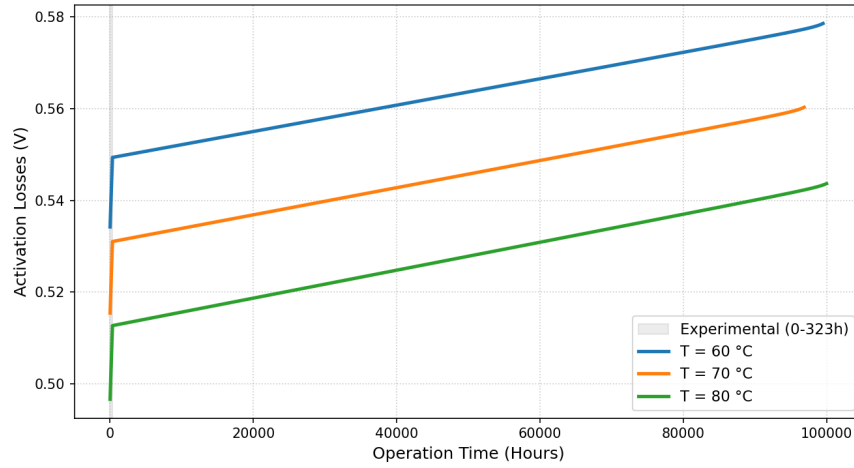


**Figure B.6.** Total activation losses

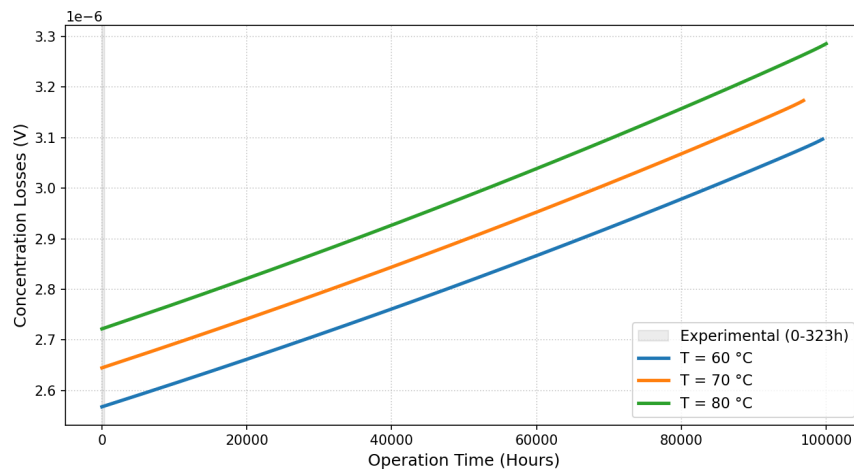


**Figure B.7.** Concentration losses

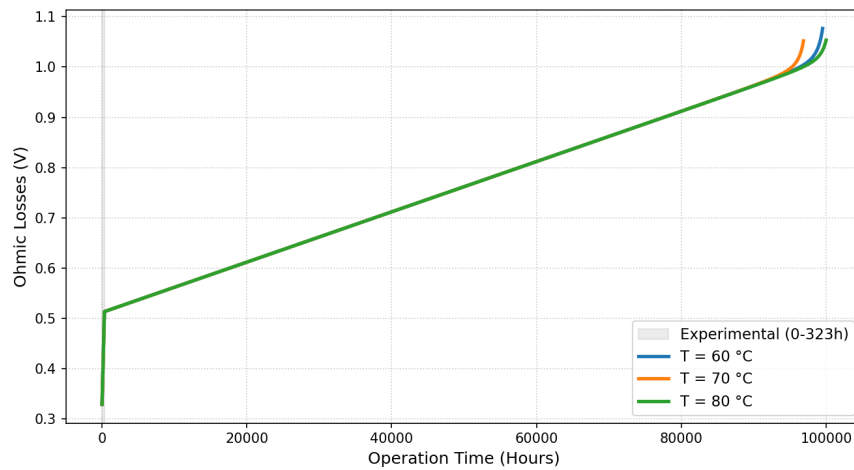


**Figure B.8.** Ohmic losses

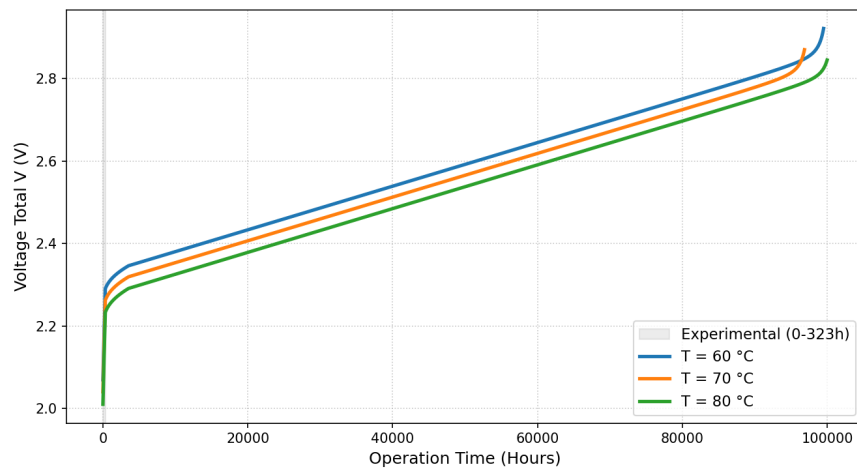


*Figure B.9.* Total voltage

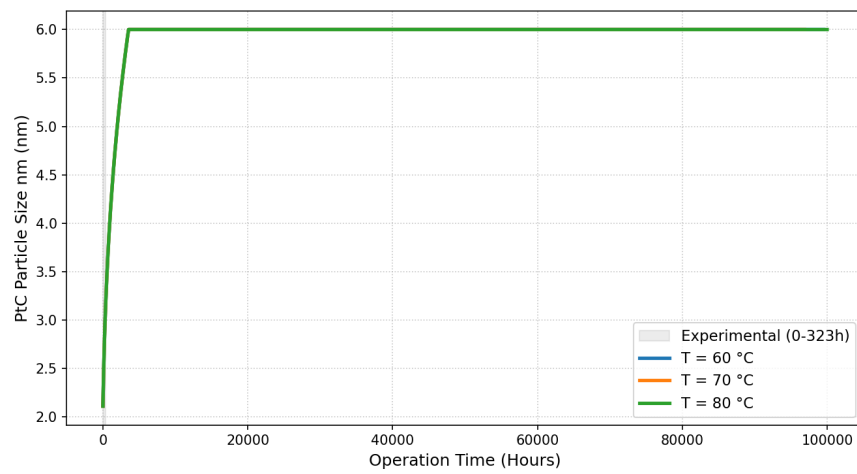


*Figure B.10.* PtC particle size

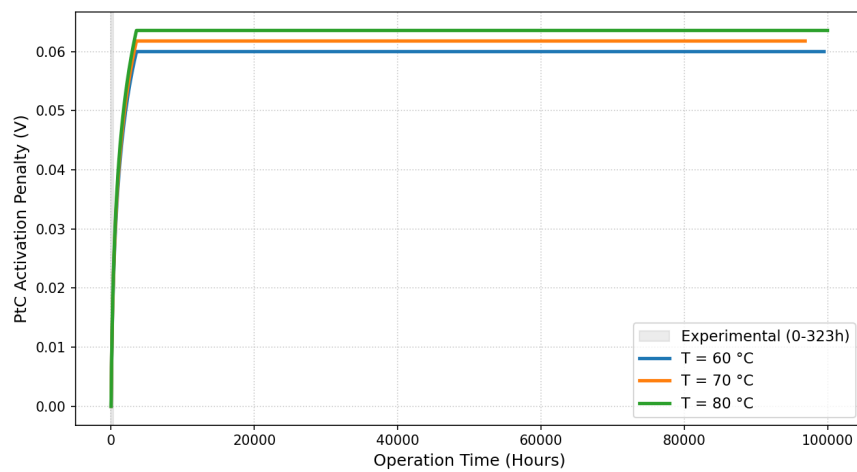


*Figure B.11.* PtC particle size penalty

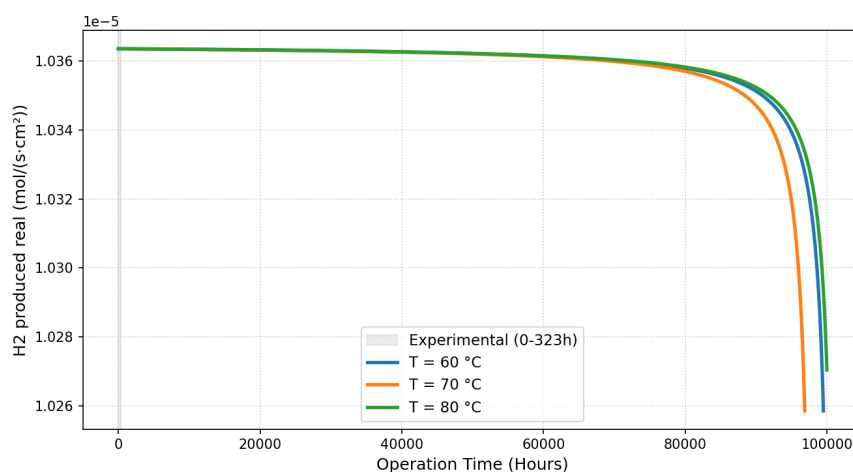


*Figure B.12.* Hydrogen produced

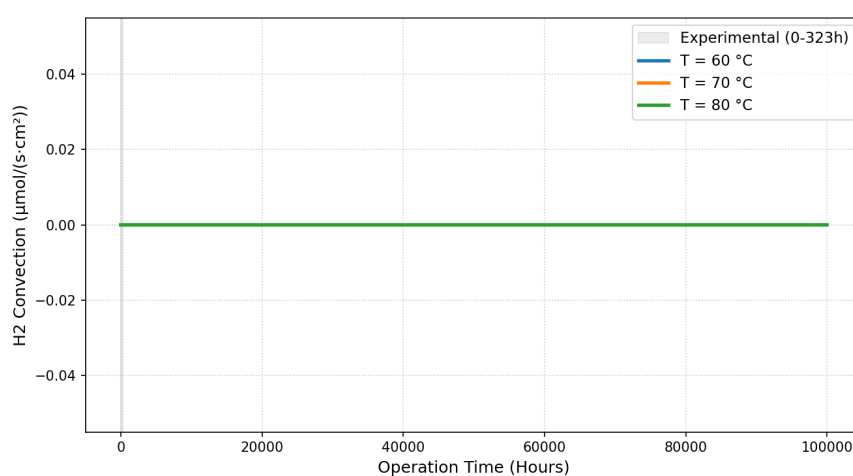


*Figure B.13.* hydrogen convection flow

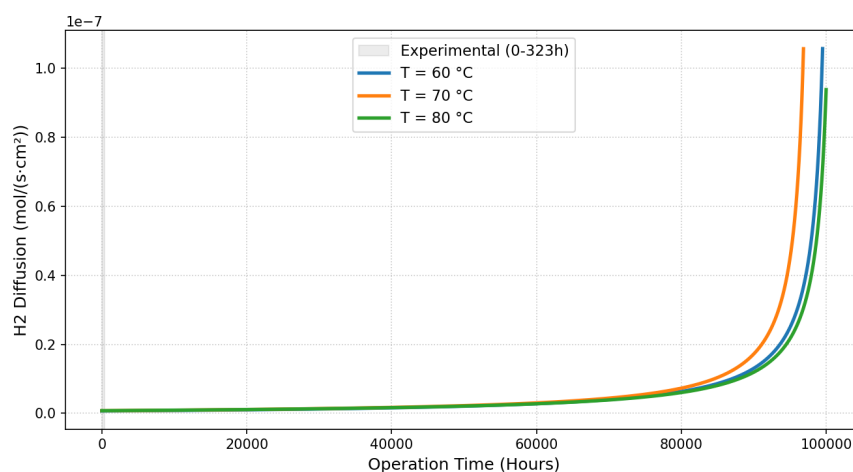


*Figure B.14.* Hydrogen diffusion flow

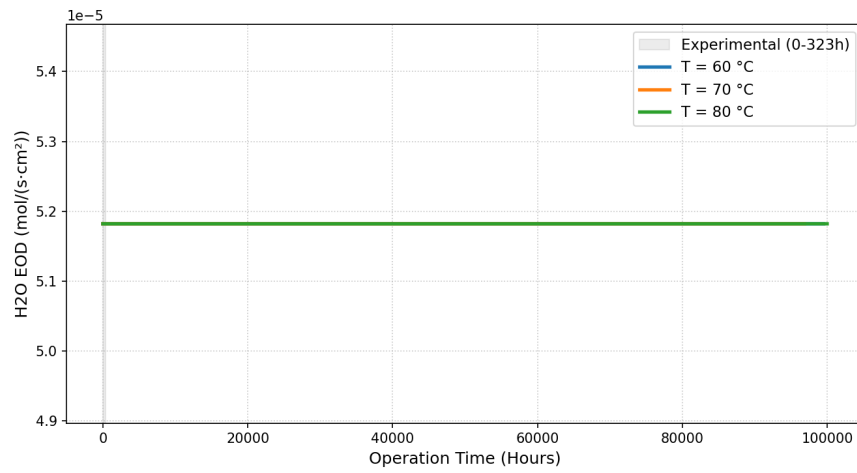


*Figure B.15.* Electro-osmotic drag water

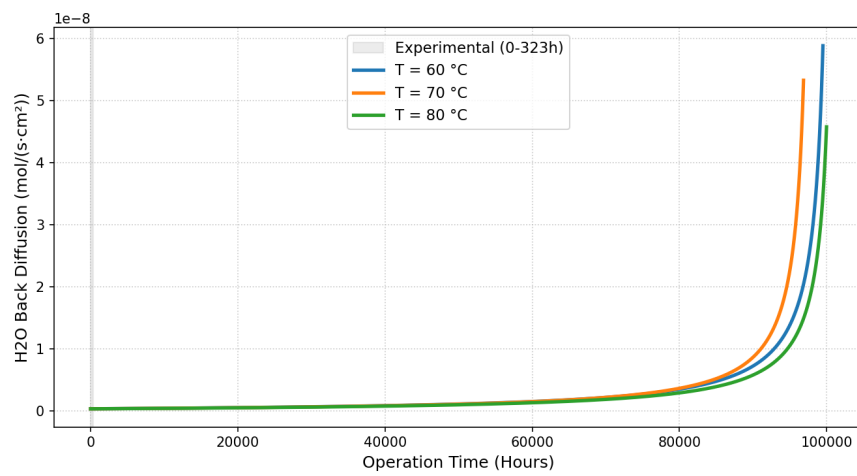


*Figure B.16.* Back diffusion water flow

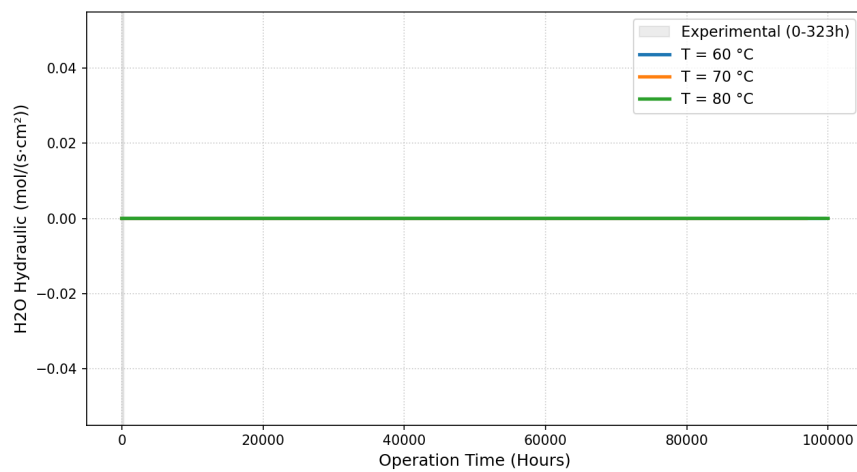


*Figure B.17.* Hydraulic permeation water flow

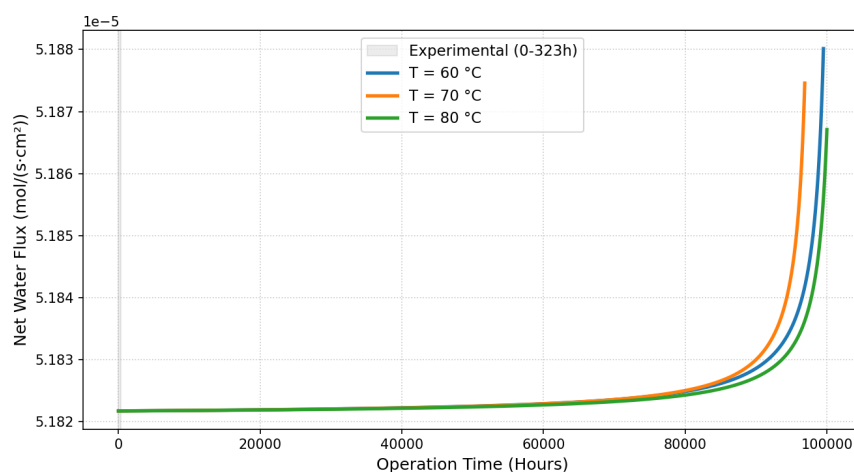


*Figure B.18.* Net water flow

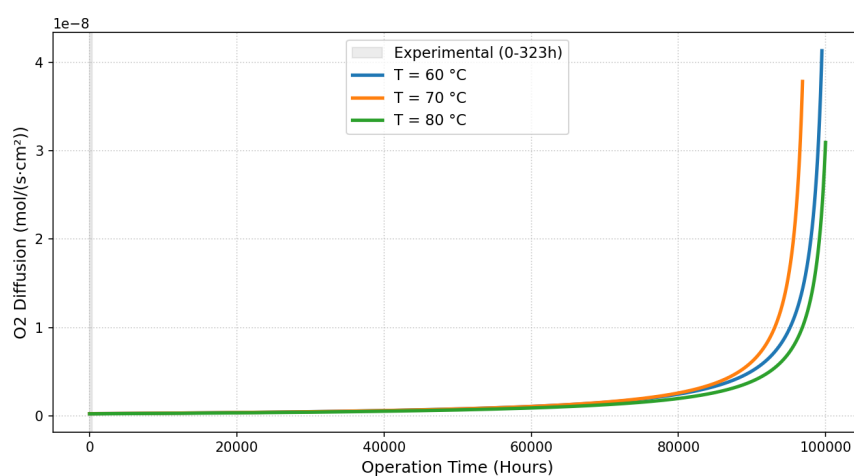


*Figure B.19.* Oxygen diffusion flow

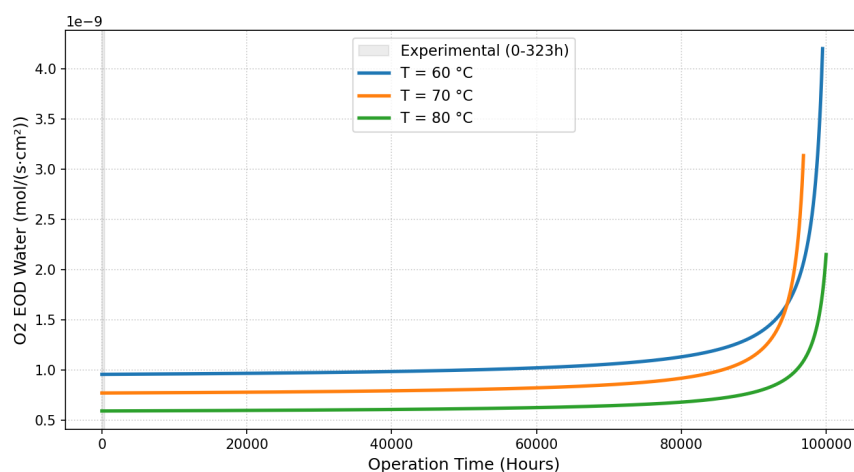


*Figure B.20.* Oxygen with eod water flow

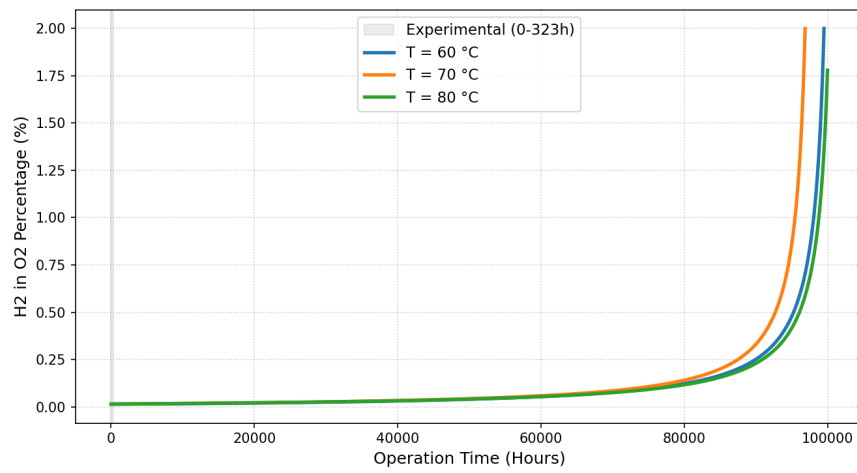


*Figure B.21.* H<sub>2</sub> content in O<sub>2</sub>

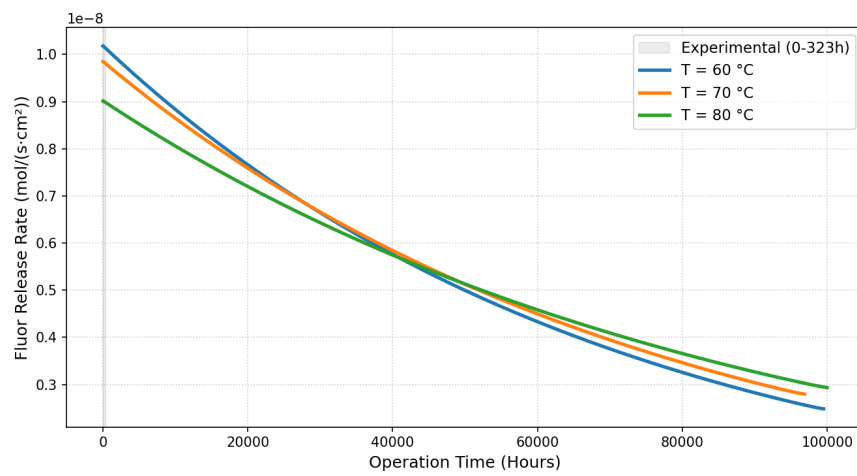


*Figure B.22.* Fluoride released

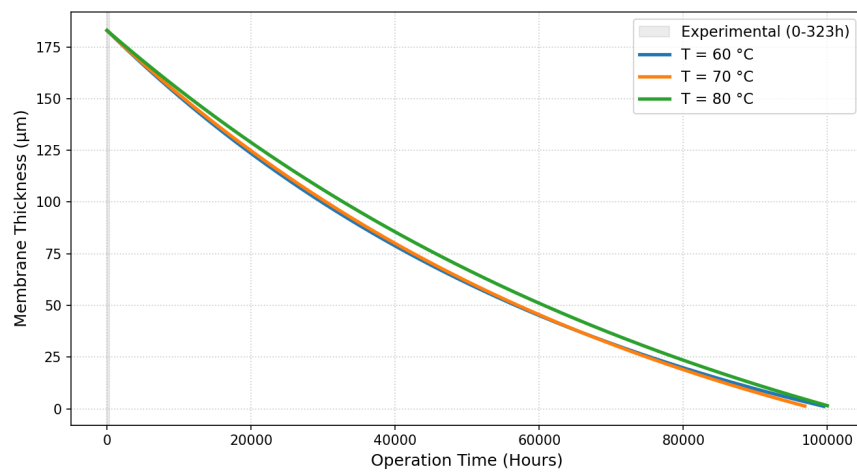


*Figure B.23.* Membrane thickness

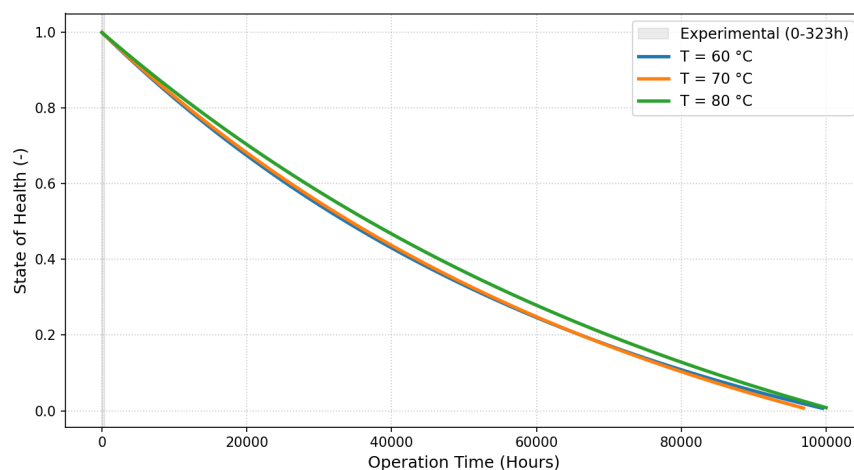


*Figure B.24.* State of health

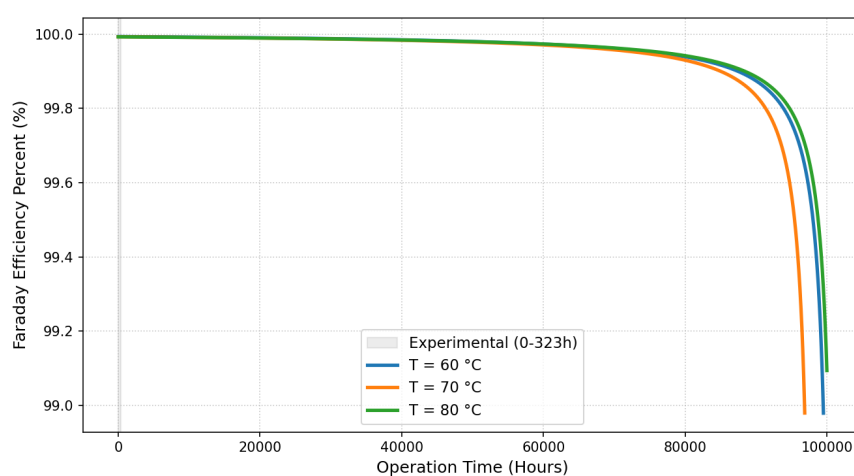


*Figure B.25.* Faraday efficiency

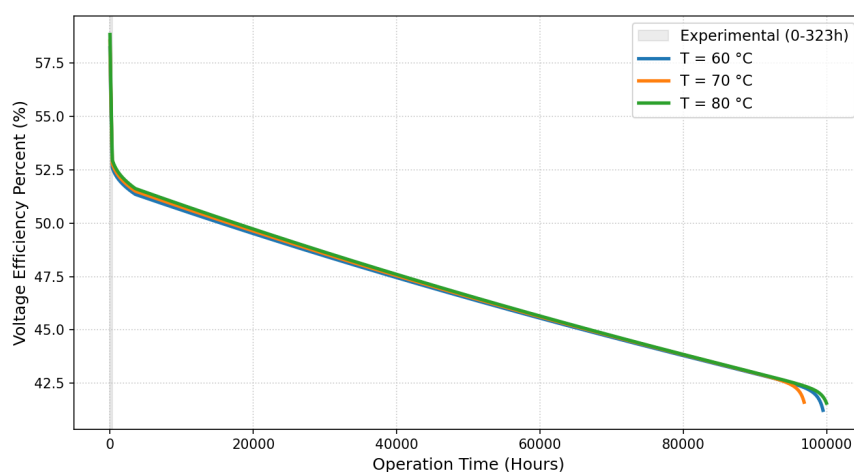


*Figure B.26.* Voltage efficiency

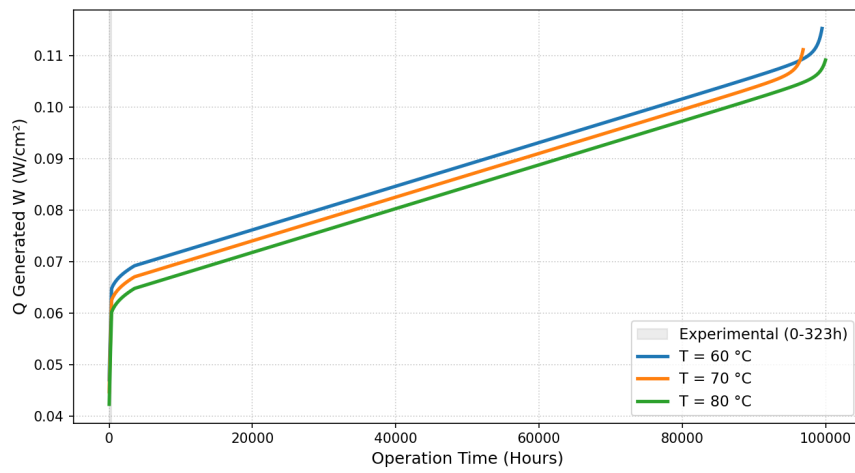


*Figure B.27.* Heat generated

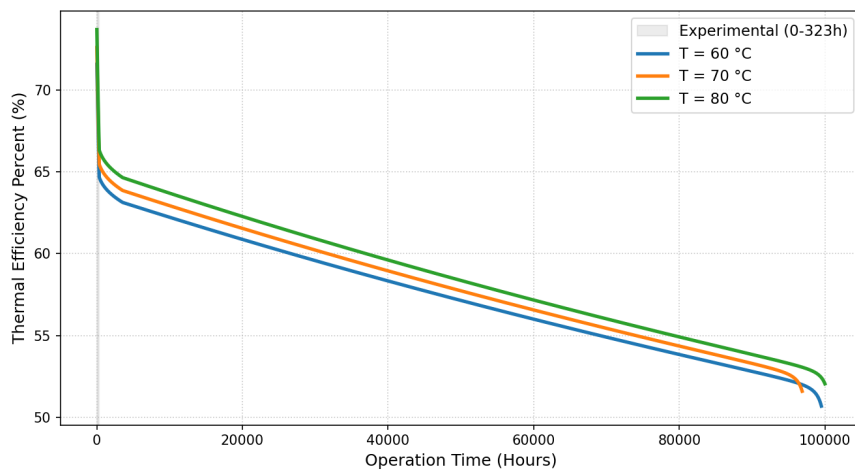


*Figure B.28.* Thermal efficiency