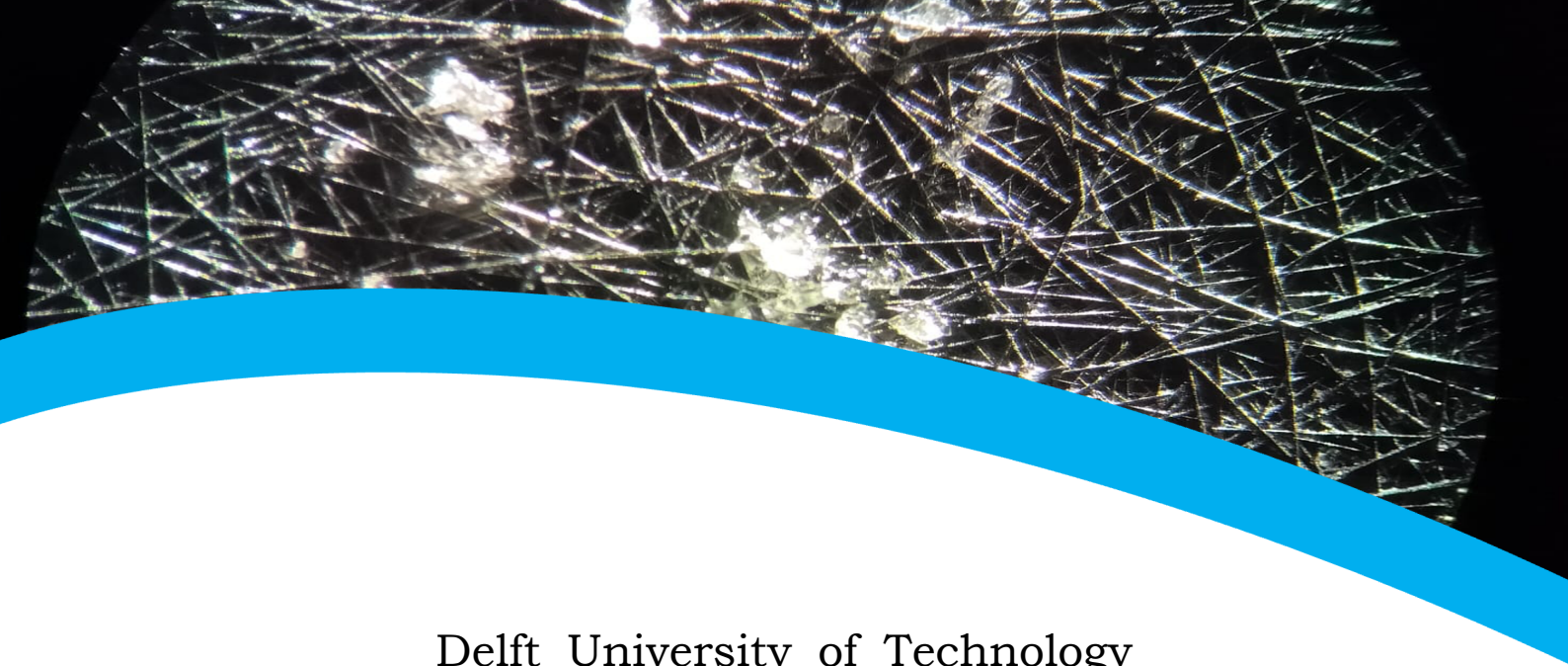




Delft University of Technology
Department of Chemical Engineering
Transport Phenomena

Master Thesis

Asymmetrically varying BPM layer thickness
for use in CO₂-to-CO electrolyzers

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Abstract

Electrochemical reduction of carbon dioxide (CO_2) to carbon monoxide (CO) offers a promising pathway for sustainable chemical production, but its large-scale implementation is limited by challenges related to energy efficiency, selectivity, and membrane-mediated ion transport. Bipolar membrane (BPM) CO_2 electrolyzers have emerged as an attractive architecture, as they enable independent control of cathodic and anodic pH environments, therefore allowing the use of earth-abundant anode materials. However, BPM operation in CO_2 electrolysis is governed by complex transport phenomena and inherent trade-offs between performance metrics like cell voltage, faradaic efficiency (FE), water dissociation efficiency, and co-ion crossover.

In this thesis, the effect of asymmetric bipolar membrane design on CO_2 -to-CO electrolysis performance is investigated. A series of Nafion/PiperION-based BPMs with systematically varied AEL and CEL thicknesses were fabricated and evaluated in a zero-gap membrane-electrode assembly CO_2 electrolyzer. Key performance metrics including cell voltage, faradaic efficiency toward CO, crossover of species through the membrane and water dissociation efficiency (WDE), were quantified under relevant operating conditions. Additionally, results were compared to the commercially available state-of-the-art Fumasep bipolar membranes.

The results demonstrate that membrane layer thickness strongly influences ion transport and charge-carrier distribution across the BPM. Increasing AEL thickness effectively suppresses co-ion crossover and improves WDE, but can limit cation transport to the cathode and thereby reduce FE toward CO. In contrast, variations in CEL thickness have a smaller impact on crossover and selectivity for the membrane chemistries studied. Co-ion fluxes across the membrane were shown to be dominated by K^+ transport for the Nafion/PiperION membranes, which contrasted with the HCO_3^- dominant behaviour found for the Fumasep membranes. This indicates that co-ion transport is also largely dependent on layer chemistry, rather than thickness alone, and the optimization strategy will differ with layer identity. Additionally, the first limiting current density was shown to correlate with co-ion transport behavior, specifically K^+ crossover, indicating its potential as a diagnostic tool for evaluating asymmetric BPM performance. Along with these findings, important tradeoffs in BPM CO_2 electrolysis were evaluated. Although layer thicknesses were found to enable decoupled control over ion fluxes, important tradeoffs between conductivity and FE to CO remain for Ag based configurations, regardless of layer asymmetry.

Overall, this work elucidates how asymmetric BPM layer thicknesses shape transport phenomena and performance trade-offs in CO_2 electrolysis. The insights obtained provide guidance for the rational design of bipolar membranes optimized for selective, energy-efficient CO_2 conversion and highlight BPM layer thickness as a practical design lever for mitigating key challenges in BPM CO_2 electrolyzers.

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List of Abbreviations

- AEL** anion exchange layer.
- AEM** anion exchange membrane.
- BPM** bipolar membrane.
- CEL** cation exchange layer.
- CEM** cation exchange membrane.
- CO₂RR** CO₂ reduction reaction.
- DI** Deionized.
- EIS** Electrical Impedance Spectroscopy.
- FE** Faradaic efficiency.
- GC** Gas Chromatograph.
- GDE** Gas Diffusion Electrode.
- HER** Hydrogen Evolution Reaction.
- IEC** Ion Exchange Capacity.
- IEM** Ion Exchange Membrane.
- IL** Intermediate Layer.
- LSV** Linear Sweep Voltammetry.
- MEA** membrane electrode assembly.
- MFM** Mass Flow Meter.
- OER** Oxygen Evolution Reaction.
- PEM** Proton Exchange Membrane.
- PGM** Platinum group metals.
- SEM** Scanning Electron Microscopy.
- WD** Water Dissociation.
- WDE** Water Dissociation Efficiency.

Introduction

1.1. Background

1.1.1. CO₂ electrolysis

The chemical industry is a major contributor to global greenhouse gas emissions, making up about 10% of the total yearly emissions [8]. As concerns about increasing CO₂ emissions and the resulting climate change rise, there is a growing demand for sustainable ways of generating carbon-based fuels and chemicals. One technology that has garnered a lot of attention in recent years is CO₂-electrolysis [9], which provides a way to utilize CO₂ captured from industrial processes and the transport sector to make valuable new products, as illustrated in Figure 1.1.

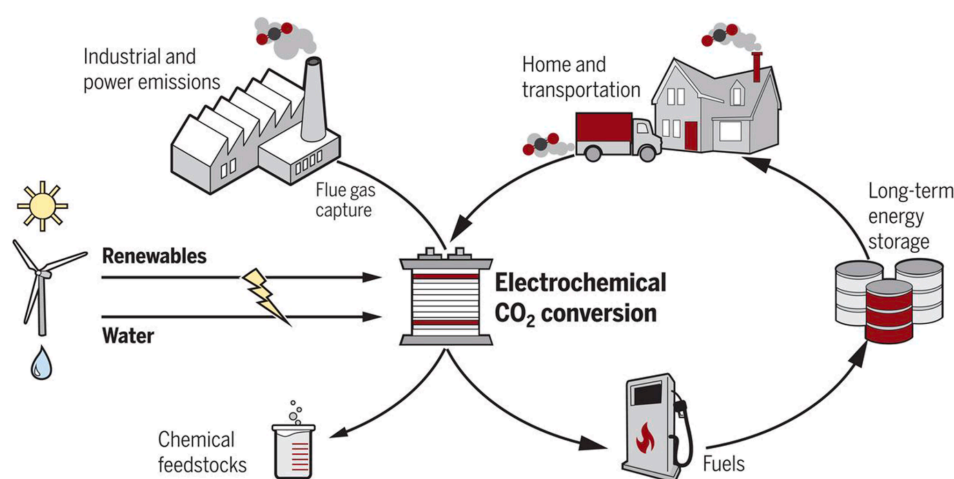


Figure 1.1: The general idea of CO₂ electrolysis, reproduced from [1].

1.1.2. MEA assemblies for CO₂ electrolyzers

CO₂-electrolyzers are electrochemical cells, consisting of two electrodes separated by an ion-conducting membrane. CO₂ is fed to the cathode, where it is reduced to other carbon-based products like CO or methanol, the exact product depending on the catalyst and operating conditions. CO is the simplest molecule to form through CO₂ reduction, and for that reason is often chosen as desired product [10]. At the anode, in most configurations oxygen evolution takes place. Different electrolyzer configurations are possible, but for ambient temperature operation a zero-gap configuration or membrane electrode assembly (MEA) has proven most promising. In this configuration, the membrane is directly pressed against the electrodes, minimizing internal resistances due mass transport limitations and ohmic losses [11].

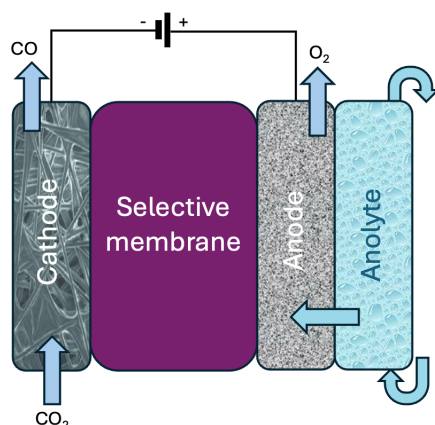


Figure 1.2: Basic configuration of a zero-gap CO₂-to-CO electrolyzer

1.1.3. Performance metrics

In order for CO₂ electrolysis to become a commercially viable technology, there are several performance metrics that should be optimized. To utilize the energy fed into the system efficiently, a high **Faradaic efficiency (FE) towards CO** at the cathode is desired, and therefore the occurrence of side reactions, like hydrogen evolution, should be minimized. Additionally, the internal resistance of the cell should be reduced to be able to run the cell at **low voltages**, and crossover of reaction products of CO₂ should be limited to ensure a high **CO₂ utilization efficiency** [12, 13].

Two important aspects of the technology to optimize these performance metrics are the electrode material and the separating membrane. The material at the electrodes should be chosen in such a way that the CO₂ reduction reaction (CO₂RR) is preferred at the cathode, and the Oxygen Evolution Reaction (OER) at the anode, at low overpotentials to keep cell voltages as low as possible. For selectivity towards CO, at the cathode various relatively earth-abundant metals like Ag and Au can be used [10]. At the anode however, in most configurations only Platinum Group Metals (PGM), like Iridiumoxide allow for stable performance. As Iridium is a rare metal with only 7 tonnes being produced per year [10] [14], serious concerns are raised for the viability of usage in CO₂-electrolyzers upon scale-up. An alternative is to use Nickel-based anodes. Nickel is an earth-abundant, cheap metal, but the drawback here is the limited stability of Nickel-based anodes: they require an alkaline environment, which is difficult to maintain in many CO₂ electrolyzer configurations due to cross-over of ions through the membrane.

The separating membrane inside of the electrolyzer has a big impact on the local electrode environment, as they can be chosen in such a way to selectively block certain ions and molecules from crossing over to the other side. Much early work on CO₂ electrolyzers focused on either anion exchange membrane (AEM) CO₂ electrolysis, or cation exchange membrane (CEM) CO₂ electrolysis, but those configurations come with important inherent limitations [14–16]. In CEM CO₂ electrolysis, FE to CO is limited due to the acidic conditions at the cathode. Additionally, Platinum group metals (PGM) materials are essential due to the low anodic pH. On the other hand, AEM CO₂ electrolyzers suffer from poor CO₂ utilization and salt formation due to carbonate formation and crossover [17][18].

1.1.4. BPM CO₂ electrolysis

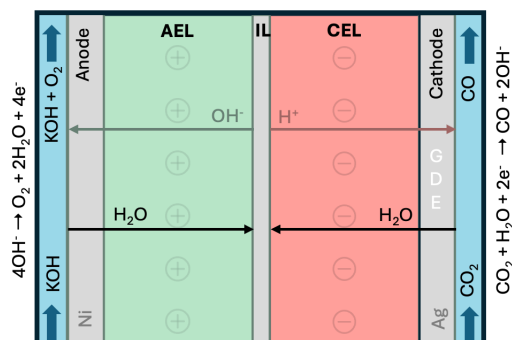


Figure 1.3: Illustration of an ideal reverse bias BPM CO₂ electrolyzer.

More recently, researchers have therefore looked at the possibility of using bipolar membranes (BPMs) in CO₂ electrolyzers, as BPMs allow independent control of cathodic and anodic pH [12, 19]. BPMs are made up out of a cation exchange layer (CEL) that selectively transports cations, and an anion exchange layer (AEL) that is conductive to anions. BPM-based electrolyzers can be run either in forward or reverse bias. In forward bias, the AEL faces the cathode and the CEL the anode, in reverse bias it is the other way around. Although forward-bias BPM configurations have received considerable attention in literature due to their lower achievable voltages and omission of sluggish water dissociation reaction kinetics [20, 21], reverse-bias operation does have the benefit that it allows for the use of non-PGM anode materials. In a reverse-bias BPM CO₂ electrolyzer, water is split at the junction of the AEL and the CEL to form H⁺ and OH⁻. In order to maintain an alkaline anode environment, the OH⁻ generated from water splitting should completely offset the OH⁻ consumed by the OER. An ideal BPM in reverse-bias operation blocks H⁺ and carbonates from reaching the anode, allowing for alkaline operation at the anode with high single-pass CO₂ conversion. This corresponds to a **Water Dissociation Efficiency (WDE)** of 100%, which means that all current in the cell is carried by ions generated by water splitting. Deviations from this ideal behavior arise from parasitic ion transport through the membrane [14]. This means that, specifically in BPM CO₂ electrolysis, the WDE can be considered another important performance metric.

1.2. Problem Definition

1.2.1. Challenges and tradeoffs in BPM CO₂ electrolysis

While in theory reverse-bias BPM CO₂ electrolysis is a promising technology, in practice it remains limited by several challenges [12]. Voltages are generally higher in BPM CO₂ electrolysis, due to the added water dissociation overpotential. Additionally, FE to CO using traditional silver catalysts remains limited [22], and WDEs have been shown to be insufficient for commercial application [14]. Additionally, the technology appears to be plagued by trade-offs: improving one aspect of its performance often comes at the expense of another [12, 14, 15]. For example, increasing cation availability at the cathode has been shown to enhance the FE toward CO [22], but simultaneously increased cation crossover through the membrane reduces the WDE [14]. Similarly, highly conductive membranes can reduce ohmic losses and lower cell voltages, but often exhibit increased ion and carbon crossover, leading to anolyte acidification and reduced CO₂ utilization [14, 15]. Figure 1.5 illustrates the way these tradeoffs are presented in literature. The limited experimental studies exploring these trade-offs have predominantly relied on commercially available Fumasep bipolar membranes [13, 14]. As a result, much of the current understanding of transport-performance relationships in BPM CO₂ electrolysis is based on membranes that were not specifically designed for this application. While Fumasep membranes provide a

valuable benchmark, their fixed material composition and layer thicknesses offer limited flexibility for independently tuning transport properties and systematically probing the origin of observed trade-offs [15].

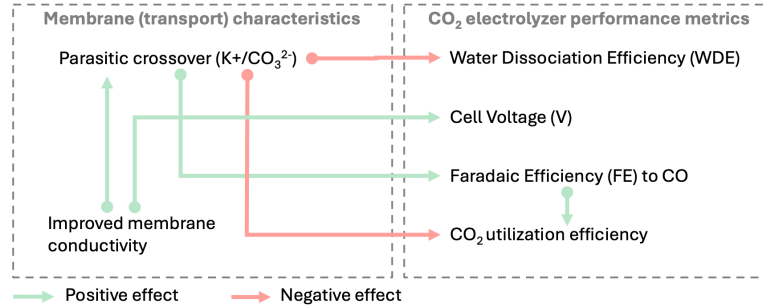


Figure 1.4: Illustration of trade-offs in BPM CO₂ electrolysis

1.2.2. Asymmetric bipolar membranes

Recently, researchers have proposed the use of asymmetric BPMs as a strategy to leverage selective control over pH gradients and ion fluxes [12, 15, 23]. The idea here is that the AEL mainly dictates cation crossover, while the AEL mainly dictates parasitic carbon crossover. By varying them independently, improved electrolyzer performance might be achieved.

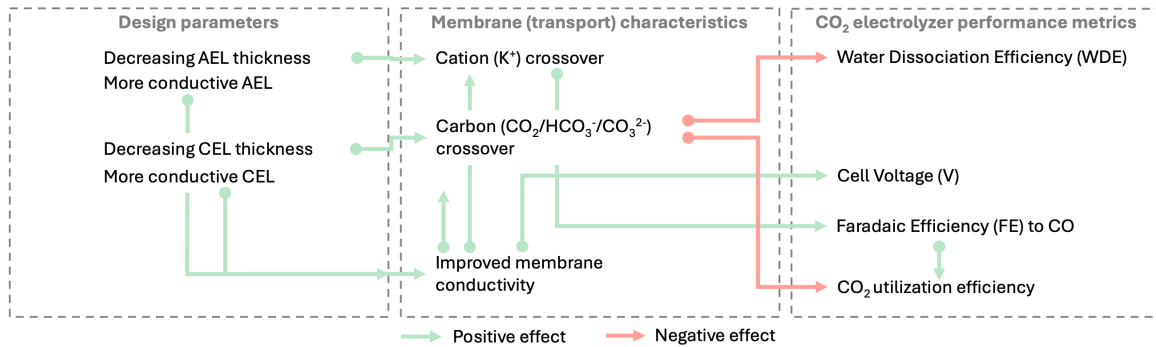


Figure 1.5: Illustration of the hypothetical potential of asymmetric membranes: if layer thicknesses or chemistry can be varied independently, trade-offs in optimizing CO₂ electrolyzer performance metrics may be subverted.

Asymmetric bipolar membranes have been discussed as a solution in different applications, such as electrodialysis [24, 25], where they were employed to improve product purity. Additionally, they have recently been explored in forward-bias BPM CO₂ electrolysis [21], to selectively block carbon transport through the membrane. To add to that, both experimental and modeling studies have demonstrated that changing the thickness of individual ion-exchange layers can significantly influence transport behavior in bipolar membranes [23, 26]. In modeling studies that vary both the anion- and cation exchange layers, the *first limiting current density* often emerges as a key feature [23]. This limiting current has been linked to the depletion of co-ions in the membrane and the onset of water dissociation. Therefore, it could give an indication for the way co-ions on both sides of the bipolar membranes influence transport through the membrane, and affect the WDE. However, these modeling studies typically assume liquid electrolytes on both sides of the membrane, which results in different conditions than those seen in state-of-the-art BPM CO₂ electrolyzers, that use a dry cathode. Therefore, the applicability of this potentially useful relationship in a CO₂ electrolysis context remains yet to be explored.

Furthermore, experimental studies into varying BPM layer thicknesses in different applications often only vary one layer [26], or investigate a single asymmetric configuration

[27]. The limited research into the application of asymmetric bipolar membranes in the context of reverse-bias CO_2 electrolysis does not investigate the specific effects of varying different layer thicknesses [16]. In CO_2 electrolysis, employing asymmetrical membranes could allow for the selective transport of species through the membrane, therefore potentially omitting certain trade-offs. Nevertheless, to the best of our knowledge, the implications of selectively varying anion- and cation-exchange layer thicknesses in reverse-bias bipolar membrane CO_2 electrolyzers have not yet been systematically investigated.

Therefore, this thesis investigates the effect of anion- and cation-exchange layer thickness on key performance metrics in reverse-bias BPM CO_2 electrolysis, including cell voltage, faradaic efficiency toward CO, co-ion crossover, and limiting current density. By systematically studying a series of asymmetric bipolar membranes made out of state-of-the-art AEL and CEL materials, this work aims to elucidate how individual layer thicknesses shape electrochemical performance and to assess the potential of limiting current density as a diagnostic tool for asymmetric bipolar membrane behavior. The insights obtained are intended to better understand the transport phenomena apparent in BPM CO_2 electrolysis, and inform the rational design of bipolar membranes optimized for efficient and selective electrochemical CO_2 conversion.

1.3. Thesis objectives and research questions

The main objective of this thesis is to investigate how varying AEL and CEL thickness of bipolar membranes influences ion transport and key performance metrics in BPM CO_2 electrolyzers, specifically configurations without a catholyte, operated under reverse bias. The corresponding **research question** is therefore:

How does varying AEL and CEL thickness influence ion transport and performance metrics in dry-cathode reverse bias bipolar membrane CO_2 electrolyzers?

Specifically, this work pursues the following **interconnected objectives**:

- (i) **Transport and performance mapping.** To evaluate the electrochemical performance of bipolar membranes composed of state-of-the-art AEL and CEL materials (Nafion and PiperION) in a CO_2 electrolysis context, with a focus on how individual layer thicknesses influence membrane-mediated transport and performance metrics. The WDE is treated as an integrative metric reflecting the extent to which charge is carried by water dissociation rather than parasitic ion transport. To interpret variations in water dissociation efficiency, ion transport is resolved into cation (K^+) transport, due to its influence on the FE toward CO, and carbon-containing species transport, due to its relevance for reactant losses and CO_2 utilization. Carbon-containing species transport is evaluated instead of the CO_2 utilization efficiency, as it can be quantified independently of the cathodic product distribution and therefore decoupled from the FE toward CO. In parallel, the FE toward CO and the cell voltage are evaluated directly as key performance metrics. Within this framework, the potential of asymmetric membrane architectures to achieve water dissociation efficiencies approaching values required for commercial operation is assessed.
- (ii) **Trade-off analysis.** To assess whether asymmetric bipolar membrane architectures enable partial decoupling of the inherent trade-offs between cation (specifically K^+) transport, carbon crossover, FE to CO, and WDE that have been reported for bipolar membrane CO_2 electrolysis, and to identify which transport processes fundamentally limit simultaneous optimization of these metrics.
- (iii) **Benchmarking against a commercial standard.** To compare the performance and transport behavior of Nafion/PiperION-based asymmetric bipolar membranes with

that of commercially available state-of-the-art Fumasep bipolar membranes, in order to contextualize observed improvements and to distinguish the role of membrane chemistry in governing performance.

- (iv) Diagnostic evaluation.** To investigate the relationship between the first limiting current density and ion transport behavior in bipolar membranes in a CO₂ electrolyzer context, and to assess whether it can serve as a diagnostic tool for membrane performance.

Based on these objectives, the following **sub-questions** are formulated:

1. What is the effect of the CEL thickness on (i) carbon and cation crossover through the membrane, (ii) cell voltage, and (iii) faradaic efficiency?
2. What is the effect of the AEL thickness on (i) carbon and cation crossover through the membrane, (ii) cell voltage, and (iii) faradaic efficiency?
3. How does the crossover of species through the membrane, WDE, Voltage, and FE change with current density?
4. What trade-offs become apparent from applying asymmetrical bipolar membranes in CO₂ electrolysis?
5. How do Nafion/PiperION-based asymmetric bipolar membranes compare to commercially available Fumasep bipolar membranes in terms of transport behavior and performance metrics?
6. What is the relationship between the limiting current density and co-ion transport through the membrane?

1.4. Thesis outline

The next chapter (Chapter 2), the theoretical background, will give more context on the phenomena needed to understand the tradeoffs and relationships between performance metrics in BPM CO₂ electrolysis. The chapter is divided into three parts: fundamentals of CO₂ electrolysis, (transport) properties of BPMs, and specifics of BPM CO₂ electrolysis. After this, Chapter 3 will dive into the experimental procedures and data analysis methods used for this thesis research. Chapter 4 presents and discusses the most important findings. In Chapter 5, the research questions will be answered, and suggestions for further research are presented.

2

Theoretical background

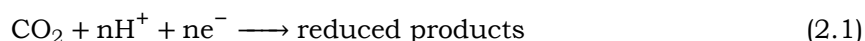
This section aims to provide sufficient information for understanding BPM CO₂ electrolysis. Section 2.1 provides fundamental information on the basics of CO₂ electrolysis: it explores thermodynamics, kinetics, and reaction mechanisms. Section 2.2 explores different electrolyzer configurations and performance metrics. Section 2.3 explores the chemistry and physics of bipolar membranes, including transport mechanisms and morphology, thereby providing a basis for understanding ion transport through bipolar membranes. Section 2.4 builds on the concepts explained in the previous sections and presents the state-of-the-art of bipolar membrane CO₂ electrolysis, as well as highlighting the fundamental challenges and trade-offs in the field.

2.1. Fundamentals of CO₂ electrolysis

Before diving into the specifics of CO₂ electrolyzers, it is useful to first establish a basic understanding of the key electrochemical reactions governing CO₂ reduction. In particular, this thesis focuses on the reduction of CO₂ to CO, a pathway whose selectivity and efficiency are strongly influenced by the local reaction environment. Understanding the fundamental reactions and their dependence on conditions such as pH and cation availability provides essential context for interpreting the challenges observed in CO₂ electrolyzers.

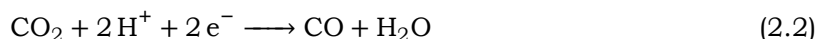
2.1.1. Important reactions in electrochemical reduction of CO₂ to CO

The electrochemical reduction of CO₂ can be described using the following general reaction equation.



This reaction is known as the CO₂ Reduction Reaction (CO₂RR). The desired reduction product varies. Carbon monoxide (CO) is frequently selected as a target product due to its relatively simple two-electron reaction pathway and comparatively low energy input compared to more complicated products [10].

In practice, the true reaction equation of reduction of CO₂ to CO depends on the local pH at the cathode. Depending on this, the equation can be written in either of two forms:



CO₂ reduction takes place in electrochemical cells. The anodic counter reaction varies, but in many cell configurations the Oxygen Evolution Reaction (OER) is used:

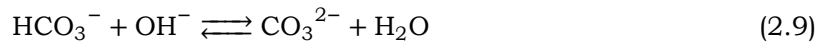




In many low-temperature CO₂ electrolyzer configurations, two main parasitic reactions take place: Formation of carbonates and bicarbonates (CO₃²⁻ and HCO₃⁻) and the competing Hydrogen Evolution Reaction (HER) at the cathode.



(Bi)carbonates are generated by subsequent reaction of the OH⁻ formed either by CO₂ reduction or Hydrogen evolution [17]:



2.1.2. Thermodynamics of CO₂ reduction

The thermodynamic requirements of an electrochemical reaction can be expressed in terms of the change in Gibbs free energy associated with the transfer of electrical charge. For a redox reaction involving the transfer of n electrons, the Gibbs free energy change ΔG is related to the equilibrium electrode potential E according to [28]:

$$\Delta G = -nFE \quad (2.10)$$

where F is Faraday's constant. A negative Gibbs free energy change corresponds to a positive equilibrium potential, indicating that the reaction is thermodynamically favorable under the specified conditions.

The equilibrium potential of an electrochemical half-reaction depends not only on its standard potential E° , but also on the activities of reactants and products. This dependence is described by the Nernst equation [28]:

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad (2.11)$$

where R is the universal gas constant, T is the temperature, and Q is the reaction quotient. For reactions involving protons or hydroxide ions, the equilibrium potential therefore depends explicitly on the local pH, shifting by approximately 59 mV per pH unit at room temperature.

The reversible cell voltage is defined as the difference between the equilibrium potentials of the anodic and cathodic half-reactions. Using standard equilibrium potentials versus the standard hydrogen electrode, the equilibrium potential of the CO₂/CO redox couple is approximately $E^\circ = -0.11$ V, while the equilibrium potential for the oxygen evolution reaction is $E^\circ = +1.23$ V. This yields a minimum reversible cell voltage for the CO₂ electrolysis cell with the OER as an anode reaction of approximately:

$$E_{\text{cell}}^{\text{rev}} = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \approx -0.11 \text{ V} - 1.23 \text{ V} = -1.34 \text{ V} \quad (2.12)$$

This value represents the thermodynamic lower bound for the electrical energy input required to drive electrochemical CO₂ reduction to CO under standard conditions.

While thermodynamics defines the minimum energy requirement, practical CO₂ electrolyzers operate at substantially higher cell voltages. This will be further explored in Section 2.2.2.

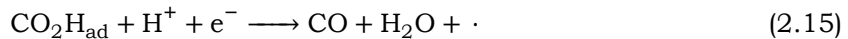
2.1.3. Kinetics and reaction mechanism of CO₂ electrolysis

While the intrinsic reaction mechanism of CO₂ reduction determines the possible product pathways and their kinetic barriers, the local reaction environment controlling these kinetics is strongly influenced by membrane-mediated ion transport. In this work, reaction mechanisms are therefore discussed only to the extent necessary to interpret changes in selectivity arising from transport phenomena.

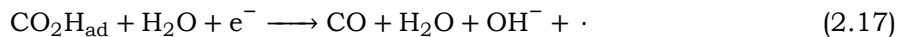
The exact mechanism for CO formation depends on the catalyst used. Silver is commonly used in CO₂-to-CO electrolyzers, owing to its selectivity towards CO over other carbon-based products. Therefore, this part will briefly explore the relevant kinetics of CO₂ to CO on Ag.

Proposed mechanism for CO formation

The reduction of CO through the CO₂RR is commonly proposed to happen according to a simple two-step pathway, with the following intermediates [29]:



Or, in the presence of water rather than protons [30]:



In both pathways, the key adsorbed intermediate is a surface-bound carboxyl species (CO₂H_{ad}). Although denoted as CO₂H_{ad}, this intermediate is expected to be largely deprotonated under alkaline conditions, existing in a carboxylate-like state at the electrode surface. In the proton-mediated mechanism, formation of this intermediate is preceded by a short-lived CO₂^{•−} radical that is weakly stabilized near the electrode surface. Subsequent proton–electron transfer steps reduce the carboxyl intermediate to CO, which desorbs from the catalyst surface.

Cation effects

Research has shown that metal cations play a crucial role in the reduction of CO₂ to CO, by forming a complex with CO₂, which promotes the formation of the CO₂^{•−} intermediate. Without any metal cations, no CO can be formed on gold, copper or silver electrodes [29].

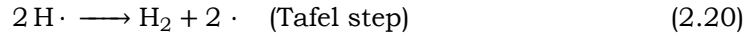
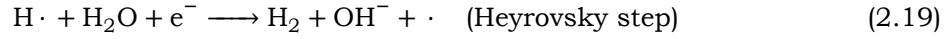
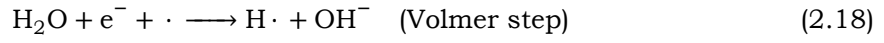
The presence of metal cations (Na⁺, K⁺, Cs⁺) stabilizes the adsorption of CO₂ primarily through the M⁺-O(CO₂) electrostatic interaction. Additionally, coordinating metal cations decrease the O-C-O angle from 180° to 140°, enhance the electron transfer and give rise to high electric fields in the vicinity of the ion [29]. The nature of the metal cation also affects the reaction rate. Under weakly acidic or alkaline conditions, weakly hydrated nonacidic cations like K⁺ and Cs⁺ lead to the highest CO₂ to CO activity [29]. These species can coordinate better with the CO₂ molecule, due to their soft solvation shell, and are able to accumulate readily at the interface.

It is important to note here that the presence of metal cations can also promote the HER. Although reduction of protons to H₂ (acidic mechanism, Equation 2.7) is independent of presence of cations, water reduction (Equation 2.6) is promoted by alkali metal cations, although likely to a lesser extent than the CO₂RR [29].

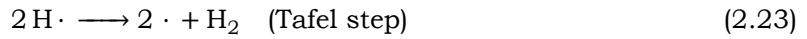
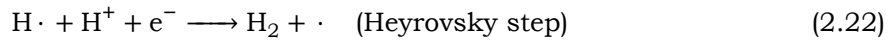
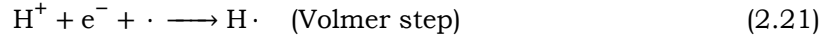
HER vs CO₂RR competition

As discussed in Section 2.1.1, the CO₂RR competes with the HER at the cathode. The nature of this competition makes sense when we dive into the micro-environment at the cathode.

Just like the CO₂RR, the HER mechanism can take either of two forms [31]. Under near neutral or alkaline conditions, water dissociates to form hydrogen:



In the presence of protons, protons are reduced through a similar mechanism:



The CO₂RR competes with the HER for electrons and active catalyst surface sites, although proton reduction is not considered a surface-limited process [32]. Owing to fewer elementary steps and lower activation barriers, the HER exhibits higher exchange current densities and is therefore favored under conditions of high proton availability or when mass-transport and interfacial conditions are unfavorable for CO₂ reduction. Although CO₂ reduction can proceed via proton-coupled pathways, experimental evidence indicates that water is the dominant hydrogen donor under typical operating conditions, and that excessive proton availability preferentially enhances HER [32]. Consequently, alkaline environments—where proton availability is suppressed and water-mediated pathways dominate—favor CO₂ reduction relative to hydrogen evolution.

2.2. Fundamentals of CO₂ electrolyzers

While the previous section focused on the fundamental electrochemical reactions governing CO₂ reduction, the practical performance of CO₂ electrolysis is determined by the design and operation of the electrolyzer system as a whole. This section therefore introduces the main components and configurations of CO₂ electrolyzers and defines the key performance metrics used to evaluate and compare their operation.

2.2.1. MEA configurations for CO₂ electrolyzers

The core components of any electrolyzer system are an external power source, a CO₂ feedstock, an electrolyte, and anode and cathode materials, particularly optimized for specific anode or cathode reactions [33]. Within these basic requirements, various variations are possible, depending on factors like operating temperature, pressure, and choice of electrolyte.

Membrane Electrode Assemblies, also known as zero-gap electrolyzers, are commonly used for CO₂ electrolysis. A MEA electrochemical cell typically consists of at least seven layers, in the following order:

1. Metal backplate (current collector)
2. Gasket
3. anode catalyst
4. membrane
5. cathode catalyst
6. gasket
7. Metal back plate (current collector)

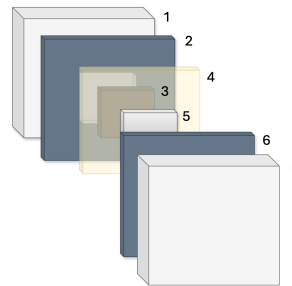


Figure 2.1: Illustration of the layers of the simplest MEA configuration.

Because the membrane is directly pressed against the anode and cathode catalyst, the configuration exhibits low ohmic resistance, and is able to run at high current densities. This makes it promising for use in industrial applications [33]. As the cathode inlet is often a gaseous stream of CO₂, in many configurations the cathode catalyst is attached to a Gas Diffusion Electrode (GDE). In other configurations, a liquid catholyte is recirculated. At the anode side, often an aqueous anolyte is used to provide hydration for the membrane, cool the cel, and provide specific reaction conditions.

The choice of membrane is an important factor in MEA cell design. Generally, four different configurations are possible: Anion Exchange Membrane (AEM), Cation Exchange Membrane (CEM), forward bias Bipolar membrane (f-BPM) and reverse bias bipolar membrane (r-BPM). The difference between the latter two, as shown in Figure 2.2, is the orientation of the membrane.

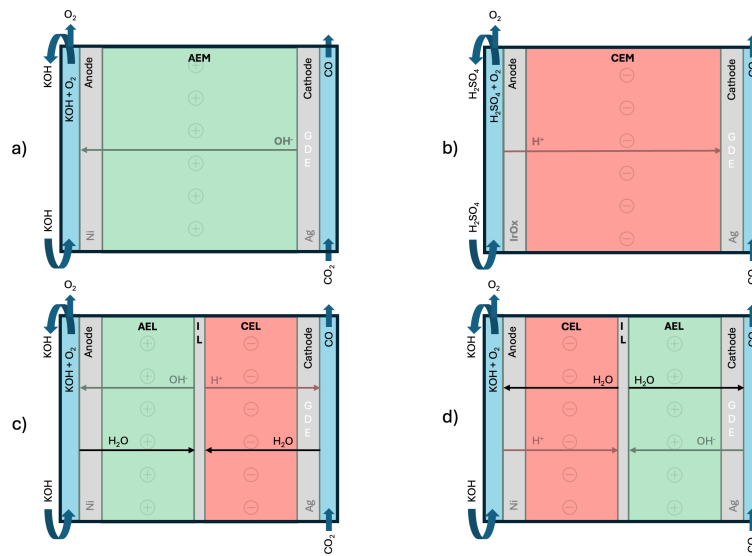


Figure 2.2: Simplified illustration of different CO₂-electrolyzer membrane configurations, showing only major charge carriers and main reaction products: (a) AEM, (b) CEM, (c) reverse bias BPM, (d) forward bias BPM

Depending on the type of membrane used, the charge carriers across the membrane, and the mode of operation (alkaline or acidic), differs. As the local pH also affects the reactions taking place at the electrodes, this has a significant effect on the way the cell works. Section 2.4.1 will further explore this.

2.2.2. Performance metrics for CO₂ electrolyzers

There are various important performance metrics in CO₂ electrolyzer design. The exact metrics differ across literature sources, but operational stability, Faradaic Efficiency (FE), operating cell voltage and current density, and carbon/CO₂ utilization efficiency are often repeated as important figures of merit [10, 22, 34].

Operational stability

In order to be able to be used for industrial applications, operation should remain constant for longer timeframes. A commonly cited benchmark here is about 10.000 hours of continuous operation [14]. This requires stability of the materials used in the electrolyzer design. This can be a challenge for membranes, as will be discussed in Section 2.3.5. Additionally, Nickel anodes are only stable under sufficiently alkaline conditions, and can also pose a challenge for long-term operational stability [14].

Faradaic Efficiency

the FE of an electrochemical cell is a metric to describe how efficiently electrical energy is used to create the desired product. It is therefore a measure of *selectivity* of the system. It can be described with the following formula:

$$FE_i = \frac{n_i F N_i}{Q} \quad (2.24)$$

Here, FE_i is the Faradaic Efficiency, n_i is the number of electrons required to form one molecule of product i , F is Faradays constant, defined at 96485 C/mol, N_i is the number of moles of product i formed, and Q is the total charge passed through the cell.

Cell voltage (and current density)

The cell voltage, usually denoted as E_{cell} or V_{cell} is an important performance metric, as it is directly related to the energy input required to drive the electrolyzer.

$$P = I V_{cell} \quad (2.25)$$

The cell voltage is related to the current and the resistance according to Ohm's law:

$$V = IR \quad (2.26)$$

Therefore, for galvanostatic operation, the electrical power required to operate an electrolyzer scales with the square of the applied current and linearly with the total cell resistance:

$$P = I_{cell}^2 R \quad (2.27)$$

In an electrolyzer context, usually the *current density* ($j = I/A$), is used. For industrial applications, it is desirable to run the cell at high current densities, as it reflects the rate of reaction, and therefore the contribution of capital cost in the production of chemicals [35]. However, this also leads to higher voltages, and a higher power consumption. In order to keep energy costs low, it is therefore important to reduce cell resistances, and therefore minimize the cell voltage. The measured cell voltage is made up out of several components, and can be broken down in multiple ways. Often, a distinction is made between the thermodynamic minimum, losses due to overpotentials and ohmic losses, or a distinction is made between losses in the membrane and losses at the electrode [15, 36]. In this thesis, we break it down as follows:

1. The thermodynamic minimum E_{rev}
2. Overpotentials at the cathode and anode η_{an} and η_{cat} (thermodynamic and kinetic)
3. ohmic losses of the membrane and electrolyte iR_{Ω}
4. mass transport limitations η_{mt}
5. System specific losses, for example due to water dissociation in r-BPM systems.

For a typical electrolyzer, that means the operating voltage can be described by:

$$V_{cell} = V_{rev} + \eta_{an} + \eta_{cat} + \eta_{\Omega} + \eta_{mt} (+ \eta_{WD}) \quad (2.28)$$

Thermodynamic minimum

As discussed in Section 2.1.2, the thermodynamic minimum voltage depends on the electrode reactions. The OER at the anode and CO₂RR at the cathode give rise to a total minimum cell potential of $E_{rev} = -1.33$ V vs SHE. In electrolyzer analysis, it is customary to report the required operating cell voltage as a positive quantity. Therefore, $V_{rev} = 1.33$ V.

Electrode overpotentials

Another factor increasing the overall cell voltage are the overpotentials at the electrodes. The overpotential is the additional potential required to drive an electrochemical reaction:

$$\eta = E - E_{\text{eq}} \quad (2.29)$$

Electrode potentials consist of a Nernstian equilibrium contribution determined by local pH and activities, and a kinetic (activation) overpotential associated with finite-rate charge transfer, which depends on the catalyst.

Ohmic losses

Ohmic losses arise from ionic resistance in all parts of the cell: the membrane, the electrolyte, the electrodes, current collectors and contacts. The ohmic losses can be described by:

$$\eta_{\Omega} = IR_{\Omega} \quad (2.30)$$

As becomes clear, ohmic losses increase linearly with the applied current.

Mass transport overpotentials

Mass transport overpotentials arise when the reaction at the electrode surface becomes mass transport limited; which means that the rate at which reactants are supplied to, or products are removed from the electrode surface is insufficient to sustain the electrochemical reaction imposed by the current.

$$\eta_{\text{mt}} \equiv E_{\text{eq,bulk}} - E_{\text{eq,surf}} \quad (2.31)$$

Mass transport limitations typically become significant at high current densities, when the electrolyte and membrane cannot keep up with the consumption of reactants or formation of products at the electrodes [37]. This will more readily happen at low ion concentrations and poorly conductive membranes. In BPM CO₂ electrolysis, overpotentials may also arise from water transport limitations to the membrane junction.

System specific losses

Lastly, system specific losses can contribute to the cell voltage. Notably, in BPM systems, an extra voltage penalty occurs due to water dissociation to OH⁻ and H⁺ in the membrane. The thermodynamic minimum potential for this reaction is 0.83V [38], which is referenced to pH 0 vs pH 14, and therefore may change under different pH conditions.

CO₂ utilization efficiency

The *CO₂ utilization efficiency* is a metric used to denote the efficiency with which the available CO₂ is actually converted to the desired product, in this case CO [22].

$$\text{CO}_2 \text{ utilization efficiency} = \frac{\text{CO}_2 \text{ converted to CO}}{\text{CO}_2 \text{ consumed}}$$

As described in section 2.1.1, CO₂ can also be converted into (bi)carbonates. Sequentially, it can leave the system by precipitating as a salt with crossed-over K⁺, or cross over to the anode.

2.3. Ion transport through bipolar membranes

In electrochemical systems, the membrane functions as a solid *electrolyte*, that selectively transports ionic species between electrodes, thereby closing the electric circuit. From this function, a few desirable properties emerge. An ion exchange membrane should have high *ionic conductivity*, to reduce ohmic losses in the cell. Additionally, it should have a high *permselectivity*, meaning that it selectively transports certain ions, so the reaction environments are effectively separated. This section explores the morphology of ion exchange membranes, desired properties of ion exchange membranes, ionic transport mechanisms through membranes, and in particular, bipolar membranes.

2.3.1. Morphology of Ion Exchange Membranes

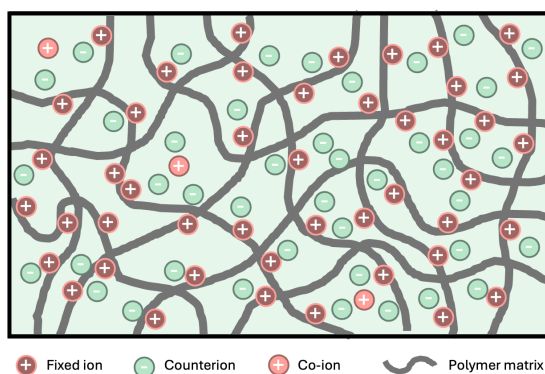


Figure 2.3: Illustration of the structure of an ion exchange membrane, particularly an anion exchange membrane, adapted from [2].

Ion Exchange Membranes (IEMs) typically consist of a polymer backbone, which acts as a hydrophobic matrix giving mechanical stability. This base is often either made of hydrocarbons, or perfluorinated carbons [39]. Attached to this base are covalently linked functional groups [2]. CEMs have negatively charged (acidic) fixed groups, while AEMs have positively charged (basic) fixed groups.

The hydrophilic charged groups form clusters that absorb water from the environment. This results in a network of pores and channels filled with water inside the IEMs [3]. These groups give rise to a channeled structure, as shown in Figure 2.4. Ion transport occurs through these hydrated domains. The morphology of IEMs dictates their properties, which will be discussed in Section 2.3.3

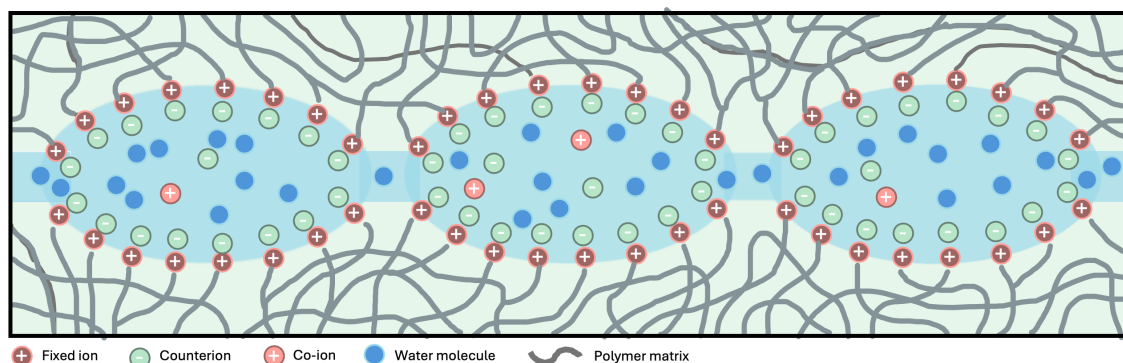


Figure 2.4: Illustration of the channeled structure within an ion exchange membrane, particularly an anion exchange membrane, adapted from [3].

2.3.2. Ionic transport mechanisms in ion-exchange membranes

In ion exchange membranes, ionic flux is almost never driven by a single force. Instead, transport arises from a combination of multiple mechanisms:

$$\text{Total ion flux} = \text{migration} + \text{diffusion} + \text{convection} \quad (2.32)$$

The driving force for **migration** is an *electric potential gradient*. In applications such as CO₂ electrolysis, where an electric potential is applied over the membrane, this is the dominant transport mechanism [4]. Migration force acts on mobile ions inside the membrane, with the direction depending on ion charge. The migration term of the total flux is commonly expressed as [40]:

$$\mathbf{J}_i^{\text{mig}} = -\frac{D_i z_i F}{RT} c_i \nabla \phi \quad (2.33)$$

where D_i is the diffusion coefficient of ion species i , z_i is the ionic valence, c_i is the ion concentration, F is the Faraday constant, R is the universal gas constant, T is the absolute temperature, and $\nabla \phi$ is the electric potential gradient. The diffusion coefficient D_i depends on both membrane properties and ion-specific interactions within the membrane. Furthermore, D_i is directly related to the ionic mobility through the Einstein relation, $u_i = D_i F / (RT)$, where u_i denotes the ionic mobility.

Contrary to migration, **diffusion** takes place even when there is no applied current. The driving force for diffusion through an ion exchange membrane is a *concentration gradient*. The diffusion force affects both ions and uncharged particles. The diffusion force is commonly expressed as [40]:

$$\mathbf{J}_i = -D_i \nabla c_i \quad (2.34)$$

where D_i is the diffusion coefficient of the migrating species, and ∇c_i is the concentration gradient.

Lastly, **electro-osmosis** may play a role in ion transport in membranes. This is a convective drag force, that causes water molecules to be dragged along with migrating ions. This force is especially relevant for highly hydrated membranes. In bipolar membranes, migrating ions away from the junction may cause an electro-osmotic drag for other water molecules away from the junction, limiting water dissociation at higher current densities. The convective force can be expressed as [40]:

$$\mathbf{J}_i = c_i \mathbf{v} \quad (2.35)$$

where c_i is the concentration of the ion species and $\mathbf{v}$ is the convective flow inside the membrane.

Together, these contributions form the extended **Nernst-Planck equation**[40]:

$$\mathbf{J}_i = c_i \mathbf{v} - D_i \nabla c_i - \frac{D_i z_i F}{RT} c_i \nabla \phi \quad (2.36)$$

An additional mechanism that is thought to play a role in membrane transport through IEMs is **surface site "hopping"** of counter-ions [4]. This type of transport is not included in the traditional extended Nernst-Planck equation, and the degree to which it contributes to the full flux is likely small. Figure 2.5 shows the different contributions to ion transport.

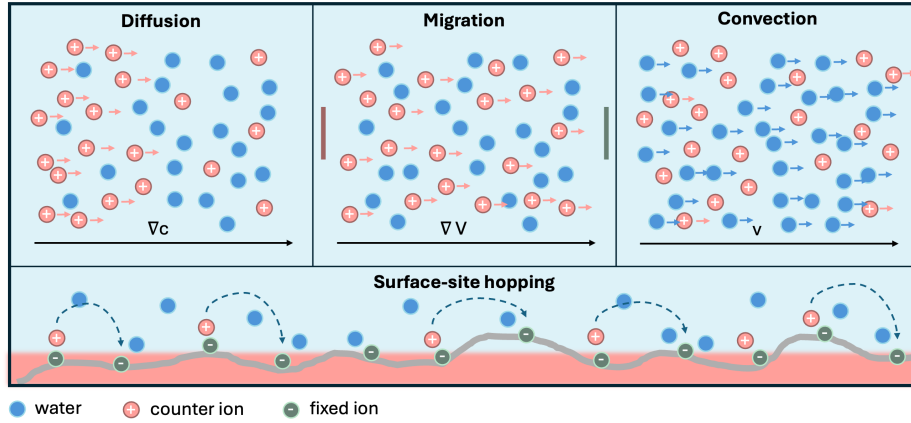


Figure 2.5: Transport mechanisms through ion exchange membranes: Diffusion, Migration, Convection and surface site hopping, adapted from [4].

Besides the mechanisms illustrated in Figure 2.5, H^+ and OH^- exhibit specific transport behavior that differs fundamentally from other ions. In aqueous environments, protons are transported via structural diffusion through reorganization of the hydrogen-bond network (Grotthuss mechanism)[41]. In IEMs with sufficiently high hydration, this mechanism can contribute significantly to proton transport and results in an exceptionally high effective proton mobility. A similar, but slower, transport mechanism exists for OH^- ions.

2.3.3. Co-ion and counter-ion transport in anion and cation exchange layers

Co-counter and ion-specific selectivity

Ions transported through the membrane with the same charge as the fixed-charge groups are referred to as *co-ions*, while ions with an opposite charge are known as *counter ions* [2]. In IEMs, co-ions are rejected from the membrane because of their electrical charge. This type of exclusion is known as **Donnan exclusion**. Because it affects a selectivity of co-ions vs counter-ions, it is also known as **co-ion counter-ion selectivity**. This selectivity is often meant when discussing the **permselectivity** of IEMs. The origin of this effect is an electric potential at the membrane-solution interface [4], as illustrated in Figure 2.6.

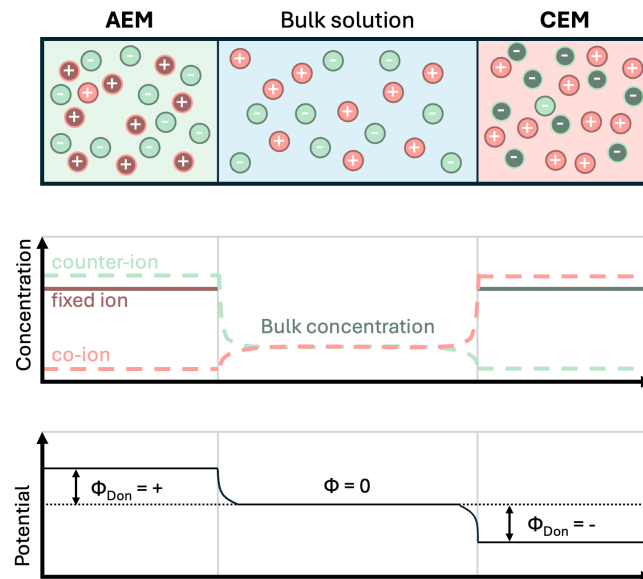


Figure 2.6: The origin of Donnan potentials for a solution in contact with an AEM or a CEM, adapted from [4].

In ideal IEMs, all co-ions are excluded from passing through the membrane. The ideal CEM would therefore allow only cations through, effectively blocking all anions through Donnan exclusion. In reality, there is always a *co-ion leakage current*, which is further explained in Section 2.3.3. Beyond co-ion/counter-ion selectivity, ion exchange membranes exhibit **ion-specific selectivity**, whereby ions of the same charge sign are transported or excluded to different extents depending on their physicochemical properties, like valence and hydrated radius [4].

Factors governing ion transport and selectivity

Building on the previously discussed transport mechanisms (diffusion, migration, and electro-osmotic convection) and the origin of counter-ion and co-ion selectivity, ion transport through ion-exchange membranes can be understood in terms of both intrinsic *ion properties* and *membrane-specific characteristics*. These parameters influence ion transport either by affecting the diffusion coefficient (and thus ionic mobility) or by modifying other terms in the transport equations, such as concentration gradients and effective transport length.

Ion properties. Key ion-specific parameters governing transport include ionic valence and hydrated radius. Ion valence directly affects electrostatic interactions with the fixed charges in the membrane and therefore the magnitude of Donnan exclusion, with multivalent co-ions experiencing stronger exclusion than monovalent species [38]. In addition, ions with smaller hydrated radii generally exhibit higher mobility and diffuse more readily through ion-exchange membranes due to reduced steric hindrance and weaker ion-polymer interactions, leading to higher effective diffusion coefficients [38].

Membrane properties. Ion transport is further governed by several membrane-specific parameters, including membrane thickness, fixed charge density/ion-exchange capacity (IEC) and ionomer self-assembled micromorphology [42].

Membrane thickness affects both the electric potential gradient and the concentration gradient across the membrane. For a membrane of thickness L , these gradients can be approximated as

$$\frac{d\phi}{dx} \approx \frac{\Delta\phi}{L}, \quad (2.37)$$

and

$$\frac{dc_i}{dx} \approx \frac{\Delta c_i}{L}. \quad (2.38)$$

In electrolyzer systems operated at fixed current density, the migrative ion flux is constrained by the imposed current and therefore does not change with membrane thickness; instead, the potential drop across the membrane increases with increasing L . In contrast, the diffusive flux scales inversely with thickness,

$$J_i^{\text{diff}} = -D_i \frac{\Delta c_i}{L}, \quad (2.39)$$

such that increasing membrane thickness suppresses diffusion-driven co-ion transport. As a result, membrane thickness primarily influences selectivity through its effect on diffusive fluxes rather than migrative transport. For migrative transport, reducing the thickness can actually reduce the number of mass transfer paths [42].

The effect of *fixed charge density* on selectivity can be understood through the Donnan potential at the membrane-solution interface,

$$\varphi_{\text{Don}} = \varphi^m - \varphi^s = \frac{RT}{z_i F} \ln \left(\frac{a_i^s}{a_i^m} \right), \quad (2.40)$$

where φ^m and φ^s are the electric potentials in the membrane and solution phases, respectively, and a_i^m and a_i^s are the corresponding ionic activities. A higher fixed charge density increases the Donnan potential, thereby reducing co-ion partitioning into the membrane phase and suppressing co-ion leakage currents. Conversely, increasing the external electrolyte concentration raises the co-ion activity in the membrane phase and increases co-ion transport [4]. The Ion Exchange Capacity (IEC), defined as the millimoles of fixed charge per gram of dry membrane, is commonly used as a quantitative measure of membrane charge density [43]. Membranes with a higher IEC also provide more transport sites for transport through the hopping mechanism, improving conductivity for counter-ions. A downside of a higher IEC is that it may incur excessive water absorption, which can then lead to a decrease in mechanical strength and ionic selectivity [42]. Therefore, *water uptake* plays a dual role in determining membrane conductivity and selectivity. Increased hydration enhances ionic mobility and conductivity by facilitating ion transport through hydrated domains, but excessive water uptake can lead to membrane swelling, diluting the fixed charge density and weakening Donnan exclusion. Optimal membrane performance is therefore achieved by balancing sufficient hydration with controlled swelling, for example through polymer backbone rigidity or cross-linking, which allows high conductivity without excessive loss of selectivity [44].

The *self-assembly* of membrane layers affects the formation of the transport channels within the membrane. Micromorphology can be improved by designing ionomers with precisely spaced functional groups [42].

2.3.4. State-of-the-art AEM and CEM materials for CO₂ electrolysis application

CEMs Nafion[®] is widely considered the state-of-the-art CEM, also known as a Proton Exchange Membrane (PEM) because of its high proton selectivity. It is the membrane commercially used in PEM hydrogen electrolyzers and fuel cells [45]. Nafion is a random copolymer of tetrafluorethylene and sulfonyl fluoride vinyl ether. The tetrafluorethylene makes up the hydrophobic perfluorinated backbone, while the sulfonyl fluoride vinyl ether molecules form side chains with sulfonic acid (-SO₃H) groups [3]. This structure is illustrated in Figure 2.7. Nafion has excellent chemical and thermal stability and efficient ion transport, making it the preferred membrane choice despite research into alternative proton exchange membranes. Although significant efforts have been made to develop new PEMs, no alternatives have lived up to the performance of Nafion [45].

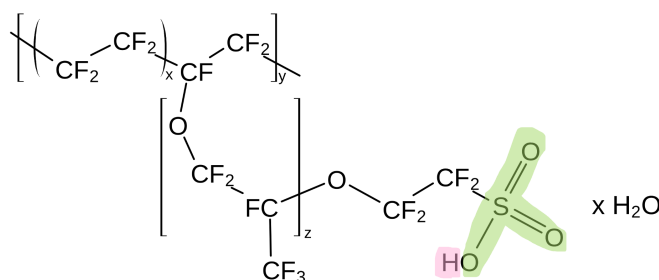


Figure 2.7: Chemical structure of Nafion membranes, illustrated in its non dissociated form. The SO₃⁻ functional group is highlighted in green, the attached counter-ion (proton) in in pink.

AEMs Contrary to CEMs, there is no single "state-of-the-art" AEM, as several options are available and under development. AEMs are inherently less conductive than CEMs due to the larger size, and therefore reduced mobility of the hydroxide ion (OH⁻) compared to the proton (H⁺). Furthermore, AEMs are susceptible to OH⁻ attack. Many of the state-of-the-art AEMs feature ether-free backbones to mitigate this issue [44]. However, functional groups such as quaternary ammonium and imidazolium, which are commonly used in AEMs, are

also vulnerable to alkaline degradation, presenting a challenge in the alkaline conditions typical for many AEM applications [46, 47]. Additionally, AEMs are generally developed for applications like electrodialysis and water electrolysis rather than specifically for CO₂ electrolysis [46].

Several AEMs have been extensively compared in reviews, to evaluate their usefulness in applications such as CO₂ capture, hydrogen electrolysis, and CO₂ reduction [44, 48, 49]. Notable options, their structures illustrated in Figure 2.8 include:

- Sustainion® (Dioxide Materials): A polystyrene-based membrane functionalized with imidazolium groups.
- PiperION® (Versogen): A poly(aryl piperidinium) based AEM, available in thicknesses ranging from 20 to 80 µm.
- Aemion® (Ionomr Innovations): Based on methylated polybenzimidazoles.
- Fumasep® FAA-3 series (Fumatech): Known for a good balance between price and performance, with a polysulfone backbone and quaternary ammonium groups in the side chain. Available in thicknesses from 20 to 130 µm. Its exact structure remains somewhat undefined, although a proposed structure is presented by Giovanelli et al. [5].

Of these, PiperION has shown great promise, particularly in AEM-based CO₂ electrolysis applications. Unlike many other AEMs, PiperION maintains high conductivity even when interacting with carbonate species, which typically reduces the conductivity of most AEMs [50]. PiperION has also demonstrated superior cation barrier properties when compared to Sustainion and Fumasep in AEM CO₂ electrolysis applications [49, 51]. Additionally, it boasts excellent OH⁻ conductivity, good water uptake with a low swelling ratio, and superior mechanical stability [44]. Notably, it has demonstrated stable ion exchange capacity (IEC) and swelling behavior in 1M KOH for over 1000 hours [48]. For these reasons, PiperION is widely regarded as the state-of-the-art AEM material for CO₂ electrolysis [47].

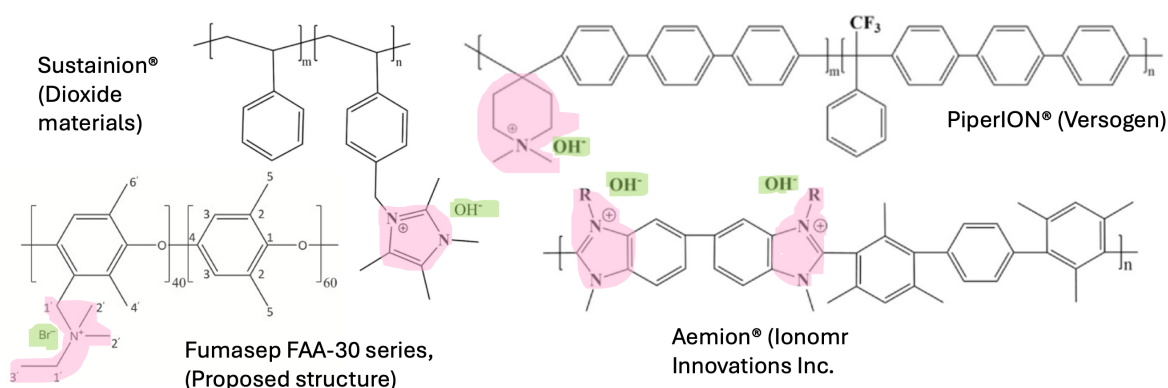


Figure 2.8: Chemical structure of state-of-the-art anion exchange membranes. Structures for Nafion, Sustainion and PiperION as described by the producer, proposed structure of Fumasep FAA-3 reproduced from [5]. Functional groups are highlighted in pink, attached counter-ions in green.

2.3.5. Structure and working principle of bipolar membranes

Now we have an idea of how transport through regular IEMs works, we can take a look at bipolar membranes. The special morphology of BPMs changes the way ion transport takes place: in contrast to single layer IEMs, BPM operation under reverse bias is characterized by ion depletion at the CEL-AEL junction, leading to water dissociation as the dominant charge-transfer mechanism. As the experiments in this thesis were performed under reverse bias, this is the membrane orientation that will be implicitly assumed in this subsection.

Morphology of (commercial) BPMs

A bipolar membrane consists of a cation-exchange layer (CEL) pressed against an anion-exchange layer (AEL). At their intersection, a junction layer forms, also called the Intermediate Layer (IL). A simplified structure is illustrated in Figure 2.9. For reverse bias, often a (thin) catalyst layer is added between the CEL and the AEL to promote water dissociation. Commercial BPMs generally have different layer materials than commercially available AEMs and CEMs. Whereas Nafion is usually used for CEM applications, various CEL materials exist, usually containing sulfonic acid groups, based on crosslinked polystyrenes [52]. Most commercial BPMs have AELs with quaternary ammonium groups, again using a polystyrene matrix.

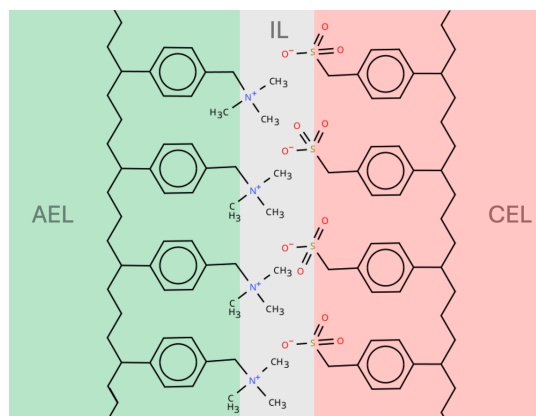


Figure 2.9: Simplified illustration of the morphology of a BPM.

There are a few commercially available BPMs. However, they are not optimized for CO_2 electrolysis application, as they are commercially mainly used for production and recovery of inorganic acid-base through electrodialysis. This is mainly problematic for their use in electrolysis applications, as current densities in these applications are much lower- no higher than $100\text{mA}/\text{cm}^2$ - whereas higher current densities are favourable for electrolysis [15, 42, 52]. Research using commercial bipolar membranes in CO_2 electrolysis in reverse bias has mainly employed Fumasep FBMs [1]. Although the exact structure of this BPM is proprietary, it is reported to consist of a CEL of sulfonated crosslinked poly-ether ether ketone and an AEL made of polysulfone with quaternary ammonium groups [14].

Preparing BPMs from individual AEMs and CEMs

It is also possible to create BPMs using commercially available or specially designed AEMs and CEMs, which allows for a greater freedom over individual layer properties, like thickness, chemistry and modifications [1]. However, not all CELs and AELs are suited to be combined into a BPM. There are two important factors here: the membranes should have *matching swelling behaviour* and *good interfacial adhesion*. Matching swelling behaviour is important because IEMs expand when taking up water. In the aqueous circumstances of many BPM applications, mismatched swelling will cause the two layers to delaminate. Interfacial adhesion is important for the same reason [15]. In literature, various different assembled BPMs have been reported, mainly using a variety of Nafion as the CEL, and various options for the AEL, like Aemion/Nafion212, PiperION/Nafion212, PPO/Nafion117 [1], using various production methods, as shown in Figure 2.10.

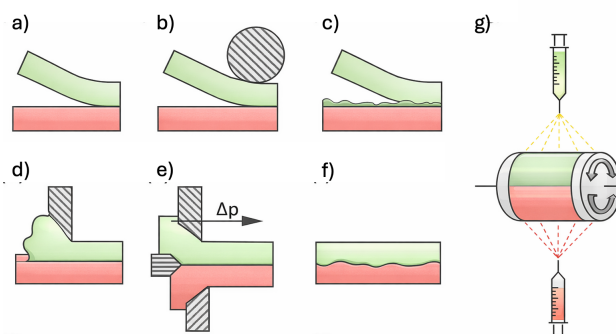


Figure 2.10: BPM production methods, reproduced from [1]. **a)** loose lamination, **b)** (hot) pressing, **c)** lamination with a binder, **d)** casting, **e)** co-extruding, **f)** modifying the opposite sides of a basis membrane, **g)** electrospinning.

Operating regions and water dissociation

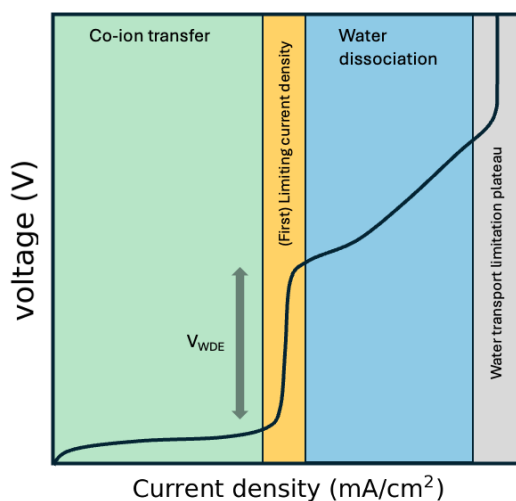


Figure 2.11: Current regimes in a BPM, based on [6]

Upon applying a current to a BPM, a few distinct stages can be identified. Figure 2.11 illustrates the different regions seen in the polarization curve of a typical BPM under reverse bias. In the first region, current is predominantly carried by co-ions from the electrolytes on either side of the membrane. At a relatively low voltage, a plateau arises from mobile ion depletion, giving rise to the first limiting current density. At current densities above the (first) limiting current density, the water dissociation rate dramatically increases. This is due to a combined effect of electric field enhancement and the catalytic mechanism. At this stage, known as the water dissociation region, total current is dominated by outward transport of OH^- and H^+ , through the AEL and CEL, respectively. Efficient transport of water to the membrane junction is essential to ensure good performance in this region. The second limiting current arises due to water transport limitations. This region is characterized by a rapid increase in voltage and interface failure [53]. The exact shape of the curve depends on the pH on both sides of the membrane [38]. Additionally, the current in the co-ion transfer region is likely not completely dominated by co-ions. Vermaas et al. mention that at current densities of $0.5\text{mA}/\text{cm}^2$, already 70-90% of the current is carried by water dissociation [38]. However, this number could be different in different configurations.

Although the exact mechanism of water dissociation in BPMs is not fully understood yet, high rates of Water Dissociation (WD) are commonly explained by electric-field enhancement at the AEL-CEL interface via the second Wien effect, the increase in the dissociation rate of weak electrolytes under a strong electric field, augmented by a proton-transfer mechanism [54]. At the junction of a bipolar membrane, the fixed positive charges in the AEL and the fixed negative charges in the CEL create an extremely strong electric field, that accelerates water dissociation. A better WD catalyst lowers the kinetic barrier, and therefore reduces the WD overpotential required (it lowers V_{WDE} in Figure 2.11). Additionally, better WD catalysts decrease the slope of the increase of the cell voltage with current density.

2.4. Bipolar membrane CO₂ electrolysis

Bipolar membranes introduce a fundamentally different operating principle in CO₂ electrolysis compared to single-layer ion-exchange membranes, owing to the formation of a junction region where water dissociation enables decoupled pH environments. While this architecture offers clear advantages with respect to carbon utilization and anode catalyst possibilities, it also introduces additional transport phenomena, voltage penalties, and

coupled trade-offs that are specific to bipolar membrane operation. This section reviews the motivation for using bipolar membranes in CO₂ electrolysis, outlines the key challenges associated with their operation, and discusses the dominant trade-offs and design considerations that motivate the focus on membrane thickness in this work.

2.4.1. Why use BPMs for CO₂ electrolysis?

BPMs have been attracting a lot of attention in recent years for application in CO₂ electrolysis, because of their inherent advantages towards CEM and AEM configurations [14, 16]. In AEM CO₂ electrolysis, carbonate formation and crossover leads to a cap in CO₂ utilization efficiency at 50% [17, 22], and significant salt formation limiting stable long-time performance [18]. CEM CO₂ electrolysis is not limited by the carbonate problem, but rather by hydrogen evolution being favoured over CO₂ reduction at the acidic system conditions [55]. Additionally, operation at this low pH makes the use of non PGM anodes impossible. In an ideal BPM CO₂ electrolyzer, the CEL suppresses carbonate crossover while water dissociation at the membrane junction supplies H⁺ and OH⁻ to maintain decoupled pH environments. This enables carbonate reconversion to CO₂ on the cathode side and sustains alkaline anodic conditions compatible with non-precious metal catalysts, while mitigating hydrogen evolution. This way, a configuration with high FE to CO and carbon utilization efficiency, using non PGM materials becomes possible. Figure 2.12 shows a comparison between the three types of CO₂ electrolysis configurations, highlighting the unwanted side reactions limiting AEM and CEM electrolysis.

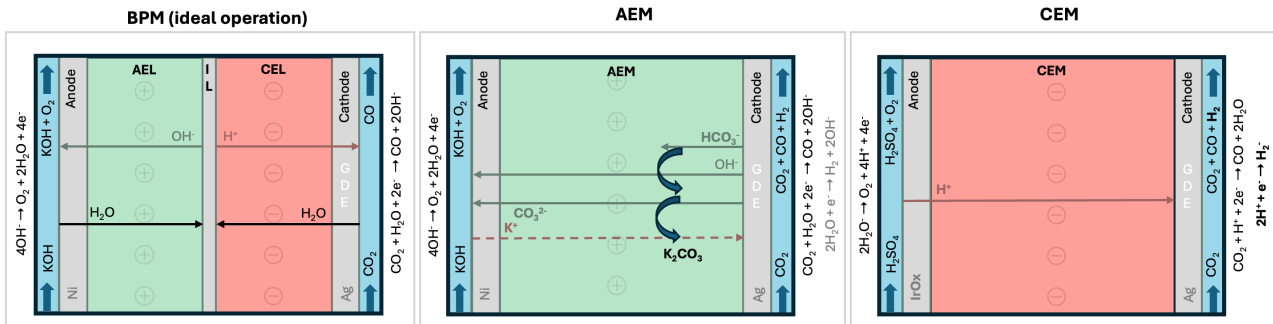


Figure 2.12: Comparison of CO₂ electrolysis with an ideal bipolar membrane, an anion exchange membrane and a cation exchange membrane.

In reality, BPM systems are not perfect yet, and are characterized by side reactions and species crossover, as shown in Figure 2.13. Section 2.4.3 will highlight the challenges this gives rise to.

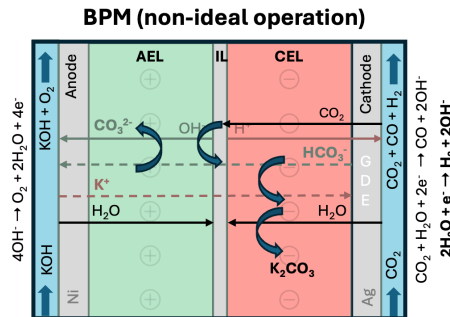


Figure 2.13: Illustration of non-ideal behaviour in BPM CO₂ electrolysis, highlighting unwanted crossover, salt formation and hydrogen evolution.

2.4.2. Design considerations for BPM CO₂ electrolysis

Designing effective bipolar membranes for CO₂ electrolysis requires balancing *efficient water dissociation* with *low ionic resistance* and *suppression of undesired crossover* [12, 15]. *High water permeability* and *junction activity* are required to sustain water dissociation at practical current densities, while *sufficient permselectivity* is needed to limit transport of alkali metal cations and carbonate species. At the same time, *membrane conductivity* must remain high to avoid excessive voltage penalties. *Mechanical compatibility* between the anion- and cation-exchange layers is also critical, particularly in asymmetric designs, as mismatched swelling behavior can compromise membrane integrity [56]. Finally, *electrode and electrolyte choices* interact with membrane transport by shaping local reaction environments and influencing crossover-driven degradation mechanisms.

2.4.3. Specific challenges of BPM CO₂ electrolysis

Despite these design requirements, bipolar membrane CO₂ electrolyzers remain limited by a set of interrelated challenges that arise from imperfect selectivity, finite water dissociation rates, and transport-driven side reactions. These challenges are summarized below.

Crossover-related challenges

Crossover of species through the membrane remains one of the dominant challenges in bipolar membrane CO₂ electrolysis, as it directly affects *carbon utilization*, *electrolyte stability*, and *long-term device performance*.

Salt formation. Species crossover can lead to the formation of insoluble salts within the electrolyzer, which poses a major operational challenge [13]. At the cathode, CO₂ reacts with locally generated OH[−] to form bicarbonate and carbonate species. When alkali metal cations such as K⁺ cross over through the membrane, these species can combine to form sparingly soluble salts that precipitate in the gas diffusion layer or gas channels, as illustrated in Figure 2.14. Such salt precipitation can block CO₂ transport to active sites, reducing the FE toward CO, and negatively impact electrolyzer longevity. Although bipolar membranes mitigate salt formation compared to anion-exchange membrane systems by suppressing cation crossover and enabling carbonate reconversion to CO₂ in the cation-exchange layer, salt precipitation remains a relevant concern, especially on longer time scales.

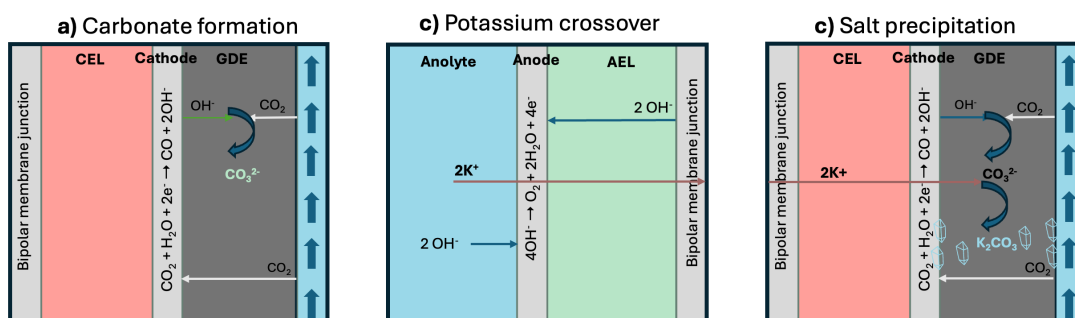


Figure 2.14: Salt precipitation in BPM CO₂ electrolysis. a) shows the mechanism of carbonate formation at the cathode. b) Potassium crossover to the cathode. c) Formation of insoluble H₂CO₃ at the cathode, forming crystals.

Electrolyte acidification due to insufficient water dissociation efficiency. Another critical consequence of species crossover is the acidification of the anolyte, which can occur when the WDE of the bipolar membrane is insufficient [13, 14]. In an ideal system, all OH[−] consumed by the oxygen evolution reaction at the anode is replenished by OH[−] generated at the bipolar junction. However, when charge is instead carried by co-ions such as K⁺ or carbonate species, this balance is disrupted, leading to net consumption of OH[−] and a gradual decrease in anolyte pH, as illustrated in Figure 2.15. Anolyte acidification has been identified as a key barrier to scaling bipolar membrane CO₂ electrolyzers, as it compromises the stability of non-precious metal anode catalysts such as nickel. In the literature,

carbonate crossover from the cathode is frequently identified as a dominant contributor to this phenomenon [13, 14].

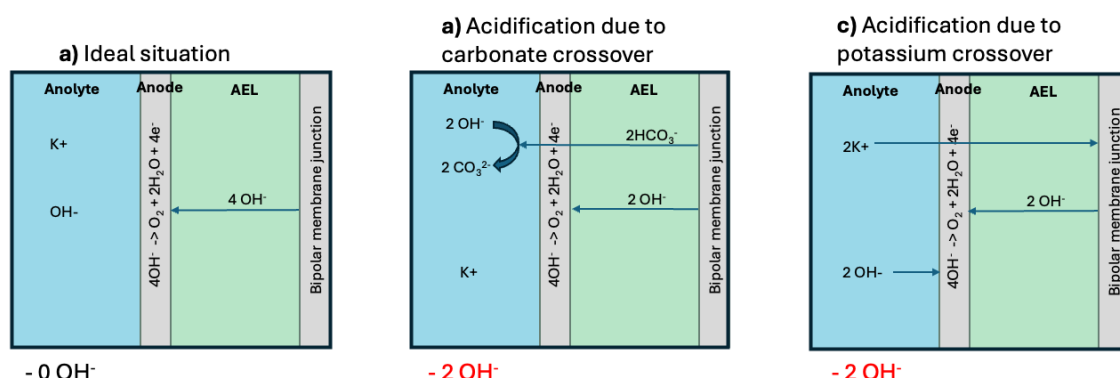


Figure 2.15: Acidification of the anolyte in BPM CO₂ electrolysis. a) ideal situation: all OH⁻ that is consumed by the OER is replenished by OH⁻ generated by water dissociation. b) Acidification due to carbonate crossover: OH⁻ reacts with HCO₃⁻ crossing over from the cathode, acidifying the anolyte. c) Acidification due to potassium crossover: Instead of OH⁻ generated by water dissociation carrying current across the membrane, K⁺ crosses over. Anolyte acidifies because the reacted OH⁻ is not replenished.

Reduced CO₂ utilization efficiency. Although BPM architectures offer a significant improvement over the approximately 50% maximum CO₂ utilization efficiency associated with AEM systems, carbon crossover (as CO₂(aq)/HCO₃⁻/CO₃²⁻) and salt precipitation still result in a reduced CO₂ utilization [22].

Challenges inherent to bipolar membrane operation

In addition to challenges arising from crossover, bipolar membrane operation is subject to limitations that are intrinsic to the membrane architecture and operating principle.

Voltage penalties associated with water dissociation. A fundamental challenge inherent to bipolar membranes is the additional voltage required to drive water dissociation at the membrane junction. Even under ideal conditions, the thermodynamic overpotential associated with water splitting at the junction is approximately 0.83 V [38]. In practice, this voltage penalty is often larger and depends strongly on water transport to the junction, membrane hydration, and the presence and activity of water dissociation catalysts. Insufficient water availability or suboptimal junction catalysis or architecture can therefore lead to elevated cell voltages, particularly at high current densities.

Mechanical and chemical stability of membrane layers. Long-term operation of bipolar membranes requires stable adhesion between the anion- and cation-exchange layers. Delamination can occur when swelling behavior or mechanical properties of the individual layers are poorly matched [15]. In addition, the chemical stability of the individual layers remains a concern, particularly for anion-exchange layers operating under highly alkaline conditions.

Challenges specific to BPM CO₂ electrolysis

Finally, some challenges are specific to the application of bipolar membranes in CO₂ electrolysis and arise from the interaction between membrane transport, catalyst selectivity, and local reaction environments.

Limited faradaic efficiency toward CO. Despite significant progress, faradaic efficiencies toward CO of 100% have not yet been consistently achieved in bipolar membrane CO₂

electrolyzers employing silver-based cathode catalysts [22]. Competing hydrogen evolution, insufficient cation availability, and unfavorable local reaction environments can all contribute to reduced selectivity.

2.4.4. Emergent trade-offs in BPM CO₂ electrolysis

The challenges discussed in the previous section do not occur independently, but instead give rise to a number of coupled trade-offs that fundamentally constrain the performance of bipolar membrane CO₂ electrolyzers. These trade-offs originate from the interplay between membrane conductivity, selectivity, hydration, and water dissociation behavior, and must be carefully balanced when designing membranes for efficient and stable operation.

Conductivity/Voltage vs crossover

A central trade-off in bipolar membrane CO₂ electrolysis arises between low ionic resistance and suppression of undesired ionic crossover. Membranes with high ionic conductivity—often achieved through high water uptake and enlarged hydrophilic domains—reduce ohmic losses and enable operation at lower cell voltages [57]. However, these same features weaken electrostatic exclusion and facilitate transport of alkali metal cations and carbon-containing species across the membrane. Conversely, thicker or less hydrated membranes suppress diffusive and migrational crossover by increasing transport path length, but incur higher ohmic resistance and voltage penalties. This conductivity–selectivity trade-off has been identified as a fundamental limitation in bipolar membrane operation [14, 15] and directly motivates the investigation of membrane thickness in this work.

FE to CO vs WDE and long-term stability

Ionic crossover plays a dual role in bipolar membrane CO₂ electrolysis. Transport of alkali metal cations such as K⁺ to the cathode can enhance the local reaction environment for CO₂ reduction by stabilizing key intermediates and suppressing hydrogen evolution, thereby increasing the FE toward CO [38]. At the same time, ionic crossover reduces the fraction of current carried by H⁺ and OH[−] generated through water dissociation, lowering the WDE. Over longer time scales, cation transport combined with carbonate formation promotes salt precipitation, obstructing CO₂ transport and leading to gradual performance degradation. As a result, membrane designs or operating conditions that enhance instantaneous FE through increased ionic crossover may compromise WDE and long-term stability [13, 16, 22]. The relative importance of these effects depends on the dominant transported species and membrane chemistry, highlighting the system-specific nature of this trade-off [14].

Water uptake, selectivity, and operation at high current density

Operation at high current densities introduces an additional trade-off between water transport and ionic selectivity. Sufficient water uptake is required to sustain water dissociation at the bipolar junction and avoid steep voltage increases at elevated current densities. However, increased membrane hydration is commonly associated with charge dilution and reduced permselectivity, leading to enhanced ionic crossover. Membranes with low water uptake may provide improved selectivity, but can become water-limited at the junction, resulting in reduced WDE and rapidly increasing voltage penalties. Commercial bipolar membranes have frequently been reported to perform suboptimally under high-current operation, and membrane thickness has been identified as one of the most accessible parameters to tune water permeance while managing resistance and selectivity [15, 23].

Collectively, these trade-offs demonstrate that improvements in one performance metric often come at the expense of others. Understanding how membrane properties, particularly ion-exchange layer thickness and asymmetry, govern these competing effects is therefore essential for the rational design of bipolar membranes optimized for CO₂ electrolysis.

2.4.5. Membrane-focused design levers in BPM CO₂ electrolysis

The trade-offs described above originate primarily from transport phenomena within the bipolar membrane itself. Accordingly, this section focuses on membrane-focused design levers in bipolar membrane CO₂ electrolysis. While electrode materials and operating conditions also influence overall electrolyzer performance, they are treated as boundary conditions rather than primary design variables in this thesis.

Ion-exchange layer chemistry. The chemistry of the anion- and cation-exchange layers determines hydration, ionic conductivity, permselectivity, and chemical stability. Fixed-charge identity, ion-exchange capacity, and crosslinking density influence water uptake and ionic crossover and therefore set the baseline transport behavior of the membrane [3, 43].

Membrane architecture (layer selection, asymmetry, and thickness). Beyond material chemistry, simply using existing membranes and using them to vary the BPM composition is an easy to use and potentially promising design lever. Selecting different AEL and CEL materials changes individual layer conductivity and permselectivity, while asymmetry can decouple transport constraints in the two layers. In particular, membrane thickness controls the diffusion length for co-ions (such as K⁺ or HCO₃⁻, thereby suppressing their diffusive crossover) but increases ohmic losses and required voltage at fixed current. Layer-thickness asymmetry has been explicitly proposed as a lever to tune the balance between conductance, water permeance, and ion crossover in BPM-based CO₂ electrolysis and related electrochemical processes [7, 12, 23, 25].

Bipolar junction engineering (water dissociation catalyst and junction morphology). Because water dissociation at the bipolar junction introduces a fundamental voltage penalty, targeted junction engineering is a direct lever to reduce cell voltage and improve water dissociation efficiency. Strategies include incorporation of metal-oxide or carbon-based water dissociation catalysts at the interface and modifying junction morphology (e.g., interpenetrating/entangled interfaces) to increase active interfacial area and facilitate water access. [20, 54]

Electrode-membrane interface engineering. The local reaction environment is strongly influenced by the electrode-membrane interface, including ionomer content, catalyst-layer wetting, and interfacial contact resistance. Interface engineering can therefore impact faradaic efficiency toward CO (via local pH and cation availability) as well as voltage losses associated with contact resistances and mass transport limitations. [22]

Among these levers, **membrane thickness** is particularly well-suited for systematic investigation because it can be tuned in a controlled manner without changing the underlying membrane chemistry. Moreover, selectively varying the thicknesses of the AEL and CEL provides a practical route to explore asymmetric BPM designs and to identify how individual layer thicknesses shape key performance metrics. Therefore, membrane thickness is employed as the primary design lever explored in this thesis.

3

Materials and Methods

This section describes the experimental procedure and data analysis approach used for this study. Section 3.1 shows an overview of the experimental setups used. Section 3.2 describes the choice of materials and gives an overview of experiments performed, along with the corresponding objectives. Section 3.3 details the experimental procedure used, along with details on specific materials and instruments. Finally, Section 3.4 provides clarity on the methodology used to process the collected data, and analyse measurement errors.

3.1. Experimental setup

The experiments for this thesis were performed using a CO₂ electrolysis setup connected to a Gas Chromatograph. The analyte was analysed using a titration setup. A schematic displaying all setups used is shown in Figure 3.1. Further sections will go into the specifics of the setups.

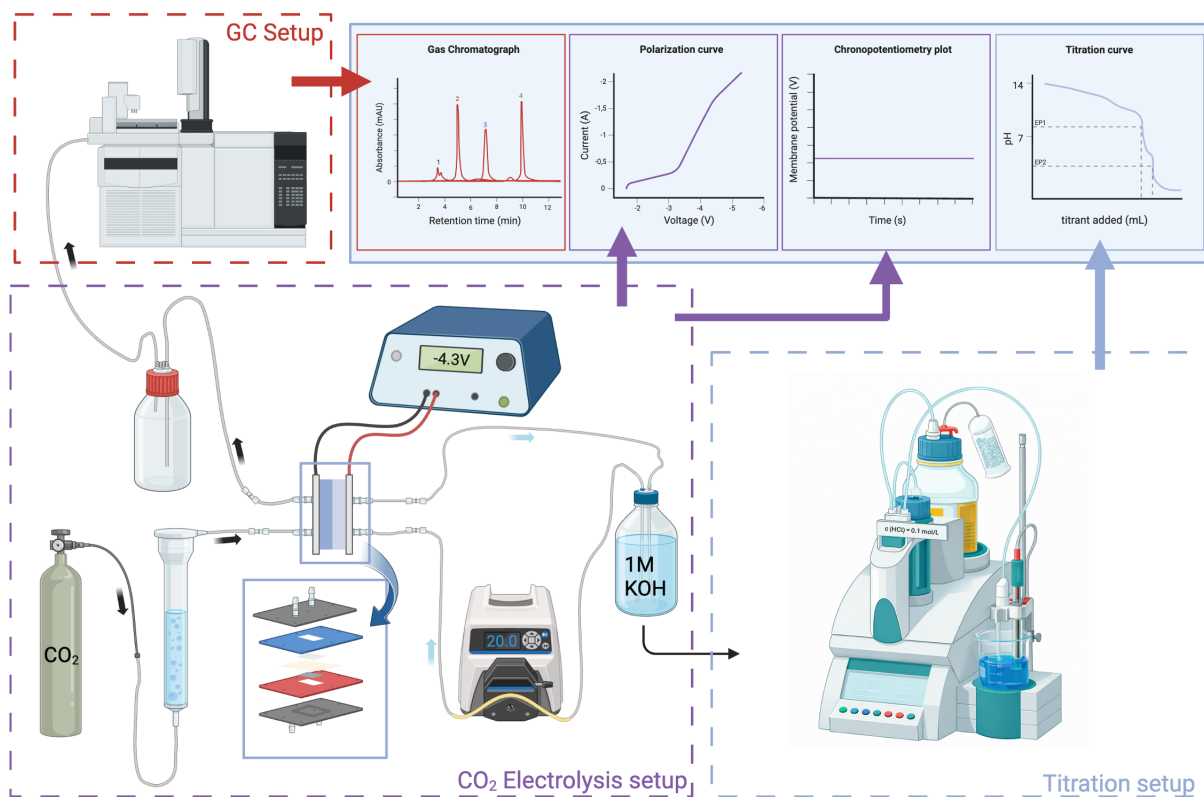


Figure 3.1: Schematic of the CO₂ electrolysis setup used for this setup

3.2. Experimental matrix and materials choice

3.2.1. Materials choice

Bipolar membrane choice. In order to be able to analyse the effect of AEL and CEL thicknesses on FE, cell voltages and co-ion crossover, asymmetric bipolar membranes were prepared using different membrane thicknesses. The asymmetric bipolar membranes were made by combining various thicknesses of Nafion® as CEL and PiperION® as AEL, with a Graphene Oxide catalyst in between (As shown in Figure 3.2). The thicknesses used were PiperION 20, 40 and 80 (Versogen), and Nafion 211 (25µm), Nafion 211 (50µm) and Nafion 211 (175µm) (Fuel Cell Store). An effort was made to make the increase in thickness similar for both membranes, but the thickest available membrane for PiperION at our lab was 80µm. Therefore, the range of thicknesses for Nafion slightly exceeds the one for Piperion. Interfacial adhesion is not ideal due to the different polymer backbones, but this combination of AEL and CEL, with a thin catalyst layer in between, has been shown to provide an efficient catalytic junction for water splitting in previous work [27, 56]. Furthermore, Nafion exhibits high proton conductivity and strong permselectivity towards H^+ over other ionic species, making it a suitable CEL for applications requiring efficient proton transport and carbonate recombination, like CO_2 electrolysis. PiperION-based AELs have also been shown to exhibit relatively high water permeability, enabling operation at higher current densities compared to some commercial bipolar membranes, for which water transport can become rate-limiting for water dissociation [27]. Graphene oxide serves as an effective water dissociation catalyst due to its low WD overpotential and the presence of multiple ionizable functional groups [27].

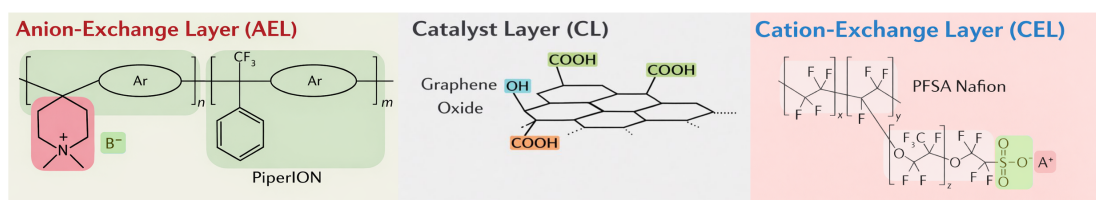


Figure 3.2: Schematic representation of the structure of the Nafion/PiperION membranes tested for this thesis, adapted from [7]

The Fumasep FBM (FM-FBM-PK, QuinTech) was chosen as a commercial standard to compare results to, due to its frequent use in literature and status as 'state-of-the-art' bipolar membrane [14]. This BPM consists of a CEL of sulfonated crosslinked poly-ether ether ketone and an AEL made of polysulfone with quaternary ammonium groups [14].

Electrode choice. The electrode materials employed in this work were selected based on their widespread use and proven performance in bipolar membrane CO_2 electrolysis. A nickel foam anode was chosen due to its earth abundance, mechanical robustness, and stability under alkaline conditions, while exhibiting reasonable OER overpotentials [14]. At the cathode, silver was selected as a benchmark catalyst due to its well-known selectivity toward CO over other CO_2 reduction products, and its frequent use in membrane-electrode assembly configurations for CO_2 electrolysis [14].

Electrolyte choice. An alkaline anolyte was employed to enable stable operation of the nickel anode. Following the work of [14], potassium hydroxide (KOH) and cesium hydroxide (CsOH) were considered as candidate electrolytes. Higher electrolyte concentrations have been shown to increase co-ion crossover, whereas lower concentrations can lead to more rapid anolyte acidification due to insufficient buffering capacity. Although CsOH has been reported to enhance faradaic efficiency toward CO, it also promotes increased co-ion crossover. As the primary objective of this thesis is to investigate strategies for reducing co-ion crossover, a 1 M KOH anolyte was selected over CsOH.

Additionally, the use of this anode, cathode, and electrolyte combination facilitates direct comparison with the results reported by Prats Vergel *et al.* [14], enabling meaningful assessment of the performance of commercial Fumasep membranes relative to asymmetric bipolar membranes with a different layer identity in CO₂ electrolysis.

3.2.2. Experimental matrix

Each membrane was prepared and tested multiple times using the same AEL and CEL batches. In the rest of the report, composite membrane names will use the format 'N[Nafion thickness]P[Piperion thickness]'. Table 3.1 shows an overview of the experiments performed on composite membranes. Table 3.2 shows the experimental matrix used for the results of this study. The 1 h chronopotentiometry measurements, LSV experiments and 15 min chronopotentiometry measurement were also performed twice on a commercial Fumasep membrane. The next sections will further describe experimental procedure.

Table 3.1: Overview of experiments and their corresponding goals.

#	Experiment	Goal
1	4× 1h chronopotentiometry at 25, 50, 100 & 200 mA/cm ² , using 25 mL 1 M KOH anolyte, taking samples and switching anolyte after each run.	• Determine V at different current densities. • Determine crossover of co-ions (CO₃²⁻ and K⁺) at different current densities. • Determine FE at different current densities.
2	Linear sweep voltammetry 0–10 mA/cm ²	• Determine location of the first limiting current (and potential relation to crossover).
3	3× 15 min chronopotentiometry at 300, 400 & 500 mA/cm ²	• Determine current–potential behaviour at higher current densities.
4	15 h chronopotentiometry experiment at 100 mA/cm ² using 100 mL 1 M KOH anolyte, taking an anolyte sample before and after the experiment.	• Obtain crossover data with smaller error margins. • Observe differences with 1 h experiments. • Observe stability of FE and V over longer time spans.

Table 3.2: Experimental matrix for investigated bipolar membranes. Numbers indicate the amount of repetitions per experiment (see Table 3.1).

	Nafion 211 (25 μm)				Nafion 212 (50 μm)				Nafion 117 (175 μm)			
Piperion	E1	E2	E3	E4	E1	E2	E3	E4	E1	E2	E3	E4
20	2x	2x	2x	2x	3x	3x	3x	2x	3x	3x	3x	2x
40	2x	2x	2x	2x	2x	2x	2x		2x	2x	2x	
80	2x	2x	2x	2x								

3.3. Experimental procedure

3.3.1. Membrane preparation

The assembly approach for the bipolar membranes was based on a common approach in literature [27, 56]. PiperION membranes were supplied in the carbonate form and were therefore cut into 4 x 4 pieces and pretreated by storage in 1 M KOH to exchange carbonate ions with hydroxide prior to use. Prior to assembly, the Nafion membranes were spraycoated with a catalyst ink containing graphene oxide and Nafion. To prepare this ink,

Graphene oxide paste (Graphene Supermarket) was first diluted with deionized water from 30 to 10 g L^{-1} and sonicated in an ultrasonic bath for 10 min to obtain a homogeneous suspension. The catalyst ink was then prepared by combining 2 mL of the graphene oxide suspension (10 g L^{-1}) with 17 mL of a 1:1 (v/v) water/isopropyl alcohol mixture and 1 mL of Nafion D520 dispersion. The resulting mixture was sonicated for an additional 10 min prior to membrane coating. The spraycoating was performed using a custom-built spray-coating setup (Details shown in [58]). For the spraycoating, a piece of Nafion was taped to a heating plate (130°C), and the catalyst was spraycoated using two passes of a serpentine pattern. Afterwards, the coated CEL was placed in an oven for 10 min at 100°C to allow solvents to evaporate completely. To prepare the bipolar membrane from the two layers, first the non-spraycoated side of the Nafion membrane was wetted from the back using Deionized (DI) water. The PiperION membrane was removed from the KOH solution, dried off using lint-free tissue paper, and pressed on top of the Nafion. The two layers were manually pressed together using gloved hands. Any bubbles and remaining liquid was gently pressed out of the resulting composite film. After preparation, the membranes were directly used in the cell. For the tests on the commercially available BPM, the Fumasep BPM was soaked in 0.5 NaCl overnight prior to the experiments.

3.3.2. Electrochemical experiments

All electrochemical experiments were performed using the same conditions, using the setup displayed in Figure 3.3 in more detail. As a gas feed, 99.9997% pure CO_2 was humidified by bubbling through a column with water, and led to the cell at a constant flow rate of 50 s.c.c.m. On the anode side, an 1M KOH anolyte was circulated at 20 mL/min. The KOH for the anolyte was prepared by diluting a 45 wt% solution of KOH (Sigma-Aldrich) in water by using a scale to weigh 124.7 g and using a 1L volumetric flask to fill with DI water to 1L. The voltage was applied using a Potentiostat (Ivium Technologies), using IviumSoft XP2313 software. A liquid trap was used after the cell to prevent any water from reaching the gas chromatograph.

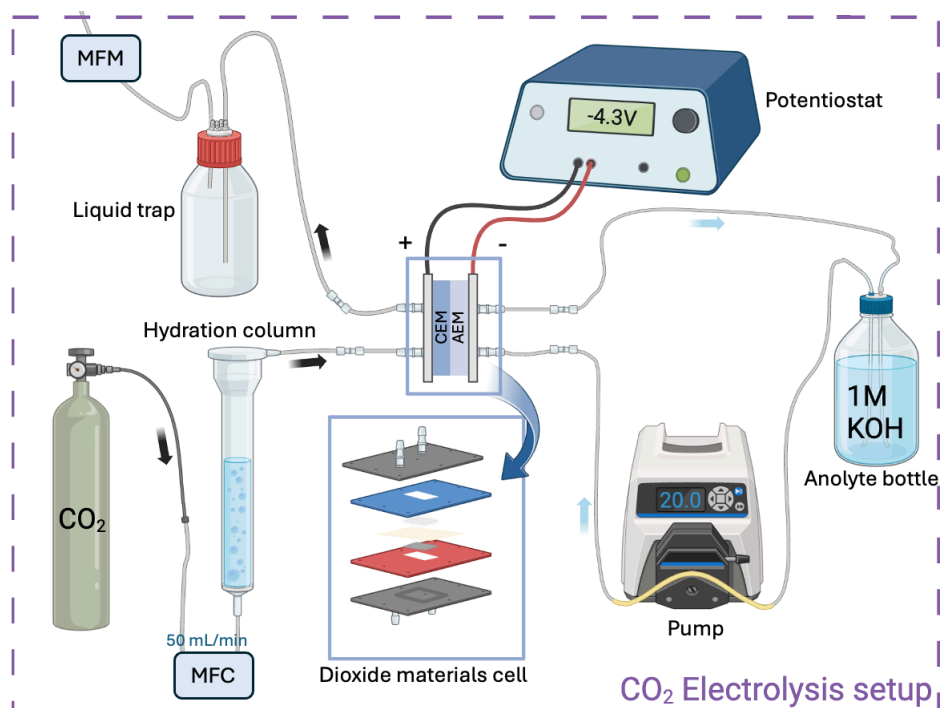


Figure 3.3: More detailed schematic of the CO₂ electrolysis setup used for this setup

Cell assembly

For all experiments, a 5cm² MEA cell with a serpentine flow field from Dioxide Materials were used, with Titanium and steel back plates. As a cathode, spraycoated carbon paper with a loading of 1.1 mg/cm² Ag nanoparticles was used. Nickel foam (Ni-4753.005 from Recemat BV) was used as an anode. The cathode and anode were cut into square 5cm² pieces using a scalpel. The orientation of these layers is displayed in Figure 3.4. 2 gaskets were used to prevent overcompression of the electrodes.

The cell was assembled by placing the first gasket on the titanium back plate, positioning the nickel anode in the hole of the gasket. Consequently, the freshly prepared asymmetric membrane was placed on the anode, with the AEL facing the anode. Then, the cathode gasket and cathode were placed on top, with the AEL facing the anode. Finally the steel back plate was placed on top, and the cell was compressed using a cross-pattern bolt-tightening sequence with a torque of 2.5 Nm to ensure an uniform pressure distribution.

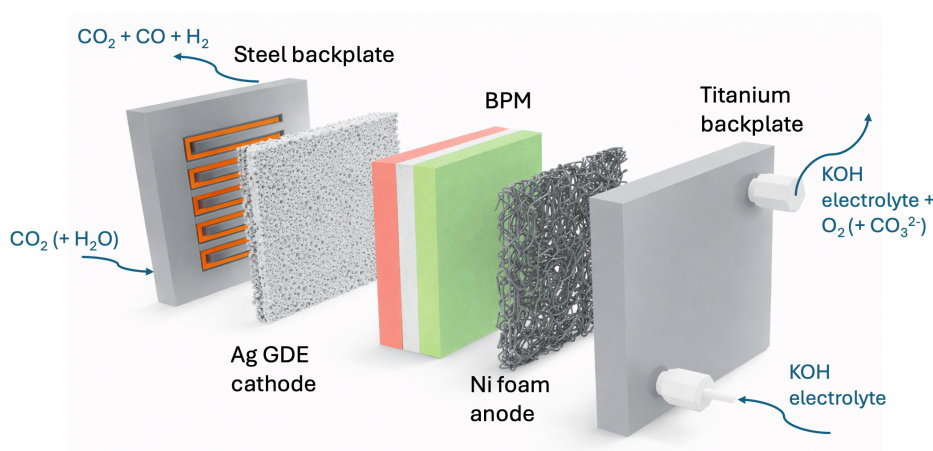


Figure 3.4: Illustration of orientation of layers in the CO₂ electrolysis cell, zoomed in on the flow field, therefore leaving out gaskets.

1 h Chronopotentiometry runs (25, 50, 100, 200 mA/cm²)

For each membrane, 1 hour chronopotentiometry tests were performed in order to determine ion crossover and cell voltages at different current densities. Each membrane was tested at current densities of 25, 50, 100 and 200 mA/cm². The outlet volumetric flow rate at the cathode was quantified with a Mass Flow Meter (MFM) (Bronckhorst), and its composition was analysed by a Gas Chromatograph (GAS compact 4.0) in order to determine the FE, as described in Section 3.4.4. Each experiment used 25 mL 1 M KOH anolyte in a partially closed bottle, allowing formed oxygen to escape. Two samples were taken, one just before and one directly after each chronopotentiometry experiment. The 'before' samples were taken directly from the bottle after connecting it to the setup. After each 1 h run, the anolyte was refreshed. After this, a new run at a new current density commenced. In between runs, DI water was pumped through the tubing for a few minutes, in order to rinse the piping of any anolyte from the previous experiment. Experiments were consistently performed in the same order, starting at 25mA/cm², followed by 50, 100 and finally 200.

Linear Sweep Voltammetry

In order to determine the position of the first limiting current, Linear Sweep Voltammetry (LSV) measurements were performed immediately after the last 1 h chronopotentiometry measurement. For the linear sweeps, 100 mL 1M KOH was used as anolyte. The sweep was performed by increasing the current from 0 to 10 mA/cm² with a step size of 0.1mA and a scan rate of 0.040 mA/cm², ensuring clear visibility of the first limiting current.

15 min chronopotentiometry runs (300, 400, 500 mA/cm²)

After the linear sweep, high current density runs were performed in order to establish current-potential behaviour at higher current densities, to see if the behaviour became water transport or WD kinetics limited at industrially relevant current densities. In order to do so, chronopotentiometry measurements of 15 minutes were performed at 300, 400 and 500 mA/cm². These measurements were always performed directly after the LSV sweep, and therefore also employed 100 mL KOH as anolyte.

15 h chronopotentiometry experiments

15 h chronopotentiometry experiments were performed to gain additional crossover data with less uncertainty in concentration differences, and to assess the performance of the membranes during longer operation times. The procedure for the 15h chronopotentiometry was identical to the 1 h chronopotentiometry experiments, except all 15 h chronopotentiometry experiments were performed using an applied potential of 100mA/cm², and an anolyte volume of 100 mL. Additionally, for these experiments, anolyte volume was measured after each run, to account for differences in concentration due to evaporation.

3.4. Characterization and data processing

3.4.1. Crossover analysis through titration

Titration setup and methodology

The concentrations of hydroxide (OH⁻), carbonate (CO₃²⁻), and potassium (K⁺) ions in the anolyte samples were determined by conductivity acid-base titration using 0.100(3) mol/L HCl (Titripur, Merck) as titrant. For each titration, 1 (1.000(8) mL) of the sample was taken using a LIG Labware automatic pipette with a nominal volume of 1000 µL. Titrations were performed with a Metrohm 848 Titrino Plus equipped with a conductivity probe. This setup is illustrated in Figure 3.5.

For each titration, the sample was diluted with ultra-pure DI water (MilliQ) to ensure the head of the conductivity probe and the buret tip were submerged in the sample. During titrations the sample was continuously stirred using a stirrer and a magnetic stirring pad, and the stirring rate was manually adjusted in case of large vortexes forming. Each sample was titrated three times. The beaker was rinsed with DI water between titrations, and pipette tips were replaced between samples.

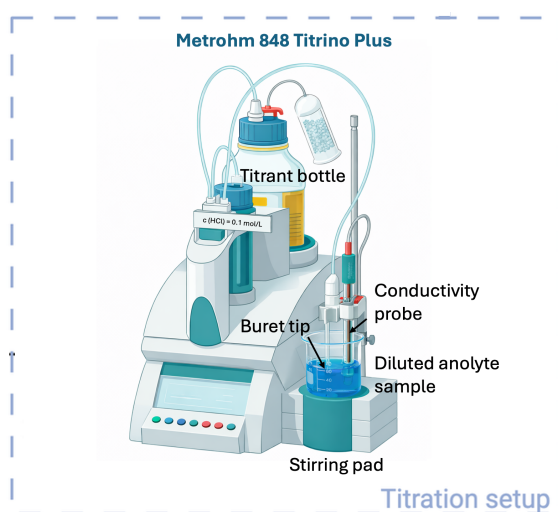


Figure 3.5: Illustration of the titration setup.

Membrane fluxes determination

Determination of ion concentrations

The ion concentrations were determined using the equivalence points from the conductivity curve. The curves generally contained 2 clear equivalence points. As the pH is highly alkaline due to the high analyte KOH concentration, initially only CO_3^{2-} is assumed to be present. Therefore, the first equivalence point (V_1 , around pH 8.4) corresponds to the neutralization of carbonate (CO_3^{2-}) to bicarbonate (HCO_3^-), while the second equivalence point (V_2 , around pH 4.7) corresponds to the subsequent neutralization of bicarbonate to carbonic acid (H_2CO_3). In some cases a third equivalence point can be observed around pH 10, likely due to the neutralization of OH^- . This equivalence point often showed a less steep curve, as illustrated in Figure 3.6b, and was ignored in the analysis.

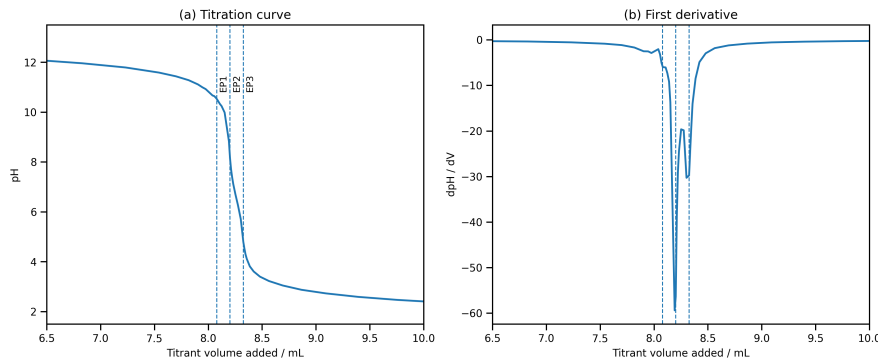


Figure 3.6: Titration curve from one of the measurements. **a)** shows the curve and **b)** shows the derivative of the curve. EP2 and EP3 showed the strongest curve and were used for the analysis as the first and second equivalence point.

The concentrations of carbonate and hydroxide were determined according to the following relationships:

$$[\text{CO}_3^{2-}] = \frac{(V_2 - V_1)C_{\text{HCl}}}{V_s} \quad (3.1)$$

$$[\text{OH}^-] = \frac{(2V_1 - V_2)C_{\text{HCl}}}{V_s} \quad (3.2)$$

where C_{HCl} is the titrant concentration (mol/L), V_1 and V_2 are the titrant volumes (mL) at the first and second equivalence points, and V_s is the sample volume (mL).

The potassium concentration was then calculated using the principle of electroneutrality:

$$[\text{K}^+] = 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (3.3)$$

Which simplifies to:

$$[\text{K}^+] = \frac{V_2 C_{\text{HCl}}}{V_s} \quad (3.4)$$

Three titrations were performed per sample, and the reported concentration represents the arithmetic mean of the three replicates.

Error propagation for concentration determination

Uncertainties in the calculated concentrations were estimated using a two-step approach that separates random titration variability from systematic volumetric and concentration uncertainties.

For each sample, three replicate titrations were performed and the relevant effective titrant volume (dV) was determined for each species based on the corresponding equivalence point

relations. The mean effective volume $\overline{dV}$ was calculated for each analyte (OH^- , CO_3^{2-} , and K^+). The uncertainty in the mean effective volume, denoted $\sigma_{\overline{dV}}$, was estimated as the standard error of the mean, calculated from the standard deviation of the replicate dV values divided by $\sqrt{n}$, where $n = 3$. This uncertainty reflects random errors associated with endpoint determination, pH response, and burette handling.

Concentrations were calculated from the mean effective volume according to:

$$c = \frac{\overline{dV} C_{\text{HCl}}}{V_s} \quad (3.5)$$

The combined standard uncertainty in the concentration was obtained by propagating the uncertainties in $\overline{dV}$, the titrant concentration C_{HCl} , and the sample volume V_s , assuming independent errors:

$$\sigma_c = c \sqrt{\left(\frac{\sigma_{\overline{dV}}}{\overline{dV}}\right)^2 + \left(\frac{\sigma_{C_{\text{HCl}}}}{C_{\text{HCl}}}\right)^2 + \left(\frac{\sigma_{V_s}}{V_s}\right)^2} \quad (3.6)$$

The uncertainty in $\overline{dV}$ represents the random variability of the titration procedure, while uncertainties in C_{HCl} and V_s originate from titrant standardization and pipette calibration, respectively, and were treated as systematic contributions that are not reduced by averaging.

Computation of membrane fluxes and water dissociation efficiency

Species fluxes were obtained from the change in anolyte concentration over time and area. For a species with concentration C (in mmol/L), the molar flux J (in mol/(m² s)) was calculated as

$$J = 10 \cdot \frac{(C_{\text{after}} - C_{\text{before}}) V_{\text{anolyte}}}{A t},$$

where V_{anolyte} is the anolyte volume (in L), A is the electrode area (in cm²), and t is the duration (in s). The numerical factor $10 = 10000/1000$ converts mmol/L $\times$ L $\times$ 1/(cm² s) to mol/(m² s).

The fluxes of K^+ and carbonate were computed analogously from their concentration changes, assuming that all carbonate species cross the membrane as bicarbonate (HCO_3^-) rather than carbonate (CO_3^{2-}). This approach corresponds with the slightly alkaline expected pH in the CEL, and follows the approach taken in literature [14].

The hydroxide flux was obtained by difference as

$$J_{\text{OH}} = J_{\text{tot}} - J_{\text{K}} - J_{\text{HCO}_3},$$

where the total ionic flux J_{tot} was derived from the applied current density according to

$$J_{\text{tot}} = \frac{I}{A} \cdot \frac{10}{F},$$

with I the applied current (in mA), A the electrode area (in cm²), F the Faraday constant (96485 C/mol), and the factor 10 converting from mA/cm² to A/m².

Uncertainty propagation for fluxes

Uncertainties were propagated assuming that all input quantities are independent. For flux

obtained from concentration change,

$$\sigma_J = \left[\left(\frac{10 V_{\text{anolyte}}}{A t} \sigma_{C_{\text{after}}} \right)^2 + \left(\frac{10 V_{\text{anolyte}}}{A t} \sigma_{C_{\text{before}}} \right)^2 + \left(\frac{10 (C_{\text{after}} - C_{\text{before}})}{A t} \sigma_{V_{\text{anolyte}}} \right)^2 + \left(\frac{10 (C_{\text{after}} - C_{\text{before}}) V_{\text{anolyte}}}{A^2 t} \sigma_A \right)^2 + \left(\frac{10 (C_{\text{after}} - C_{\text{before}}) V_{\text{anolyte}}}{A t^2} \sigma_t \right)^2 \right]^{1/2}.$$

For the total flux computed from current density,

$$\sigma_{J_{\text{tot}}} = \sqrt{\left(\frac{10}{A F} \sigma_I \right)^2 + \left(\frac{10 I}{A^2 F} \sigma_A \right)^2}.$$

The hydroxide-flux uncertainty (by difference) was evaluated as

$$\sigma_{J_{\text{OH}}} = \sqrt{\sigma_{J_{\text{tot}}}^2 + \sigma_{J_{\text{K}}}^2 + \sigma_{J_{\text{HCO}_3}}^2}.$$

When multiple independent repeats of an experiment were performed, fluxes were averaged to obtain representative values. For a given flux J_x ($x = \text{K}^+, \text{HCO}_3^-, \text{OH}^-$), the average flux was calculated as

$$\bar{J}_x = \frac{1}{N} \sum_{i=1}^N J_{x,i},$$

where N is the number of experimental repeats. The uncertainty associated with the averaged flux was calculated as the combined uncertainty, considering both the repeatability error and the propagated uncertainty from the measurements, and was given by the standard error of the mean:

$$\sigma_{\bar{J}_x} = \sqrt{\frac{\sum_{i=1}^N \sigma_{J_{x,i}}^2}{N^2} + \frac{\sigma_{\text{repeat}}^2}{N}},$$

where:

- $\sigma_{J_{x,i}}$ is the uncertainty associated with the flux measurement for each repeat i .
- σ_{repeat} is the standard deviation of the flux values across the repeated experiments.
- N is the number of experimental repeats.

This equation accounts for both the individual measurement uncertainty and the variability between repeat measurements (i.e., the repeatability error), assuming statistical independence between experimental repeats.

Water dissociation efficiency determination

The water dissociation efficiency was defined as

$$\text{WDE}(\%) = 100 \times \frac{J_{\text{OH}}}{J_{\text{tot}}} = 100 \left(1 - \frac{J_{\text{K}} + J_{\text{HCO}_3}}{J_{\text{tot}}} \right),$$

with $J_{\text{OH}} = J_{\text{tot}} - J_{\text{K}} - J_{\text{HCO}_3}$. Because J_{OH} depends on J_{tot} , these two quantities are not independent. The standard uncertainty was therefore propagated in terms of the independent inputs J_{tot} , J_{K} , and J_{HCO_3} :

$$\sigma_{\text{WDE}} = \sqrt{\left(100 \frac{J_{\text{K}} + J_{\text{HCO}_3}}{J_{\text{tot}}^2} \sigma_{J_{\text{tot}}} \right)^2 + \left(\frac{100}{J_{\text{tot}}} \sigma_{J_{\text{K}}} \right)^2 + \left(\frac{100}{J_{\text{tot}}} \sigma_{J_{\text{HCO}_3}} \right)^2}.$$

All fluxes and uncertainties are reported in mol/(m² s), and efficiencies in percent. The water dissociation efficiency was evaluated separately for each experimental repeat. For a given repeat i , the efficiency $\eta_{WD,i}$ and its associated uncertainty $\sigma_{\eta,i}$ were calculated using the expressions above. When multiple independent repeats were available, the reported water dissociation efficiency was obtained as the arithmetic mean:

$$\overline{WDE}(\%) = \frac{1}{N} \sum_{i=1}^N WDE_i$$

where N is the number of experimental repeats. The uncertainty associated with the averaged efficiency was calculated as the standard error of the mean:

$$\sigma_{WDE} = \sqrt{\frac{\sum_{i=1}^N \sigma_{WDE}^2}{N^2} + \frac{\sigma_{repeat}^2}{N}},$$

assuming statistical independence between experimental repeats.

3.4.2. Cell voltage determination

The cell voltages over the entire cell were obtained using the potentiostat. To get the values for the voltages at 25, 50, 100 and 200 mA/cm², the average value of the last 10 minutes of the 1 h chronopotentiometry measurements were used, to ensure the system has equilibrated. For the voltages at 300, 400 and 500 mA/cm², the average of the last 10 minutes of the 15 minute chronopotentiometry measurements were used. For the 15 h experiments, the average voltage of the second hour and the last hour were used, in order to identify changes over the course of the experiment.

3.4.3. Limiting current determination

The position of the first limiting current was determined from LSV measurements. The LSV data were analyzed using a custom Python script to identify the current density region corresponding to the first limiting-current plateau. The midpoint of this plateau was defined as the limiting current position. For each membrane, this procedure was applied independently, and the reported limiting current density represents the average value obtained from the individual membrane measurements.

3.4.4. Faradaic Efficiency Determination

The FE for gaseous products was determined from gas chromatography and MFM data obtained during the experiments. The Gas Chromatograph (GC) sampled the outlet stream at the cathode side every 4 minutes. For the 1 h experiments, 11 injections were selected after both the gas flow rate and GC signals had stabilized. For the 15 h experiments, 11 injections from the first hour after stabilization and 11 injections from the final hour were selected in order to assess long-term stability.

For each gas component, the composition reported by the GC was averaged over the selected 11 injections. The standard deviation of these measurements was used to represent the uncertainty associated with the GC analysis.

The total cathode outlet gas flow rate was measured using a MFM. Since GC injection temporarily disturbs the flow, the flow rate corresponding to each GC injection was determined by averaging the MFM signal over a time window from 20 s to 10 s prior to the injection. For each injection, both the mean flow rate and its standard deviation were extracted from this time window.

The MFM measures a volumetric flow rate that depends on the gas composition due to gas-dependent thermal and physical properties. Consequently, the measured volumetric flow rate

must be corrected to obtain the true volumetric flow of the gas mixture. To correct the MFM signal, component-specific conversion factors provided by the manufacturer (Bronkhorst) were used. For a gas mixture containing components i , the mixture correction factor K_{mix} was calculated as:

$$\frac{1}{K_{\text{mix}}} = \sum_i \frac{y_i}{k_i} \quad (3.7)$$

where y_i is the mole fraction of component i obtained from GC analysis, and k_i is the corresponding conversion factor.

The measured volumetric flow rate $\dot{V}_{\text{meas}}$ was then corrected according to:

$$\dot{V}_{\text{corr}} = \dot{V}_{\text{meas}} \cdot K_{\text{mix}} \quad (3.8)$$

The conversion factors provided by the manufacturer are reported relative to nitrogen, while the mass flow meter was calibrated using CO_2 as the reference gas. Therefore, the corrected flow rate was normalized by the CO_2 conversion factor ($k_{\text{CO}_2} = 0.74$):

$$\dot{V}_{\text{real}} = \frac{\dot{V}_{\text{corr}}}{k_{\text{CO}_2}} \quad (3.9)$$

This procedure yields the true volumetric gas flow rate of the outlet stream. The uncertainty of the MFM measurement was propagated through all correction steps to obtain the standard deviation of the corrected flow rate.

The molar flow rate $\dot{n}_i$ of a gaseous product i was calculated from the corrected volumetric flow using the ideal gas law:

$$\dot{n}_i = y_i \cdot \left(\frac{\dot{V}_{\text{real}}}{60} \right) \cdot \frac{P}{RT} \quad (3.10)$$

where y_i is the mole fraction of component i (derived from the GC), $\dot{V}_{\text{real}}$ is expressed in L min^{-1} , $P = 1.01325 \times 10^5 \text{ Pa}$ is the pressure, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the universal gas constant, and $T = 273.15 \text{ K}$.

The partial current density j_i for gaseous product i was calculated as:

$$j_i = n_{e,i} F \dot{n}_i \quad (3.11)$$

where $n_{e,i}$ is the number of electrons involved in the formation of product i and $F = 96485.3 \text{ C mol}^{-1}$ is the Faraday constant.

The FE for component i was calculated by dividing the partial current density by the total applied current density j_{tot} :

$$\text{FE}_i = \frac{j_i}{j_{\text{tot}}} \quad (3.12)$$

This calculation was performed for each of the 11 GC injections. To compute the uncertainty of the mean FE from the 11 measurements, both the propagated uncertainty of the individual measurements and the statistical variability between measurements were taken into account. The total uncertainty of the mean is given by:

$$\sigma_{\bar{j}} = \sqrt{\frac{\sigma_{\text{indiv}}^2}{N^2} + \frac{\sigma_{\text{std}}^2}{N}} \quad (3.13)$$

where σ_{indiv} is the combined uncertainty from individual propagated errors, calculated as

$\sigma_{\text{indiv}} = \sqrt{\sum_{i=1}^N \sigma_{\text{indiv},i}^2}$, σ_{std} is the standard deviation of the measured values, and N is the number of injections.

Results & Discussion

4.1. General observations, stability and reproducibility

Before discussing individual performance metrics in detail, general experimental behavior, stability, and reproducibility are addressed, as these aspects are relevant for the interpretation of the results. These observations apply to all performed experiments, unless otherwise indicated.

Visual inspection after electrochemical operation indicated minor changes in membrane and electrode appearance. Membranes generally showed slight discoloration following experiments, while cathodes appeared marginally lighter in color and nickel foam current collectors occasionally appeared darker (Figure B.2). In addition, limited salt formation was observed for most experiments. For the 15 h experiments, visibly increased salt formation was present compared to the 1 h experiments. Furthermore, experiments performed with Fumasep membranes consistently exhibited more pronounced salt formation than those using the Nafion/PiperION membranes, although the extent of salt formation was not quantified. A picture of salt formation in the GDE and cathode flow field can be found in Appendix B.1.

For the 1h experiments, voltage stayed generally constant over time, with only minor increases observed during some experiments, and a short equilibration period observed at the start, as illustrated in Figure 4.1.

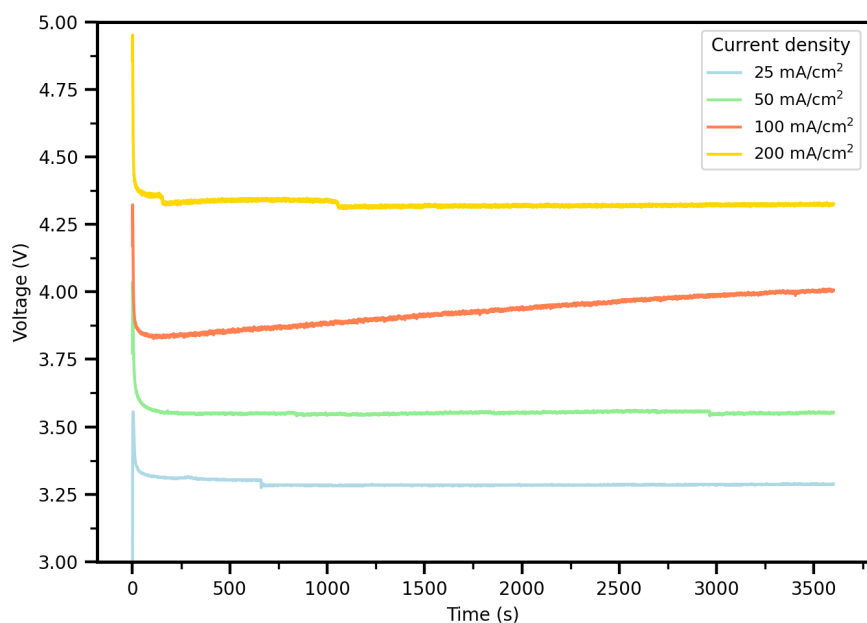


Figure 4.1: Voltage stability over time for a 1 h experiment (Data from N25P80).

For the 15 h experiments, an increasing trend in voltage, accompanied by a decreasing trend in FE was observed over time, as shown in Figure 4.2. The decrease in FE to CO with time is also commonly observed in AEM systems, where it is commonly attributed to salt formation blocking active catalyst sites [59]. Work on reverse-bias CO₂ electrolyzers employing a different catalyst and a Fumasep membrane also shows this effect for BPM CO₂ electrolysis, and attributes it to salt formation [60]. In their system, the salt formation eventually led to system failure around 17h at 200 mA/cm². In earlier work in BPM systems by Li et al, a similar decrease of FE with time was noted[13]. They suggested either an increase of the contact area between the catalyst and H⁺, or possible deactivation of the catalyst layer in the acidic environment due to the lack of sufficient K⁺, and concluded based on IES data that it was likely a result of increased H⁺ availability for the HER. They also observed an increase of V wwith time, although the degradation rate was limited to 0.086% per hour, whereas the increase of about 0.4% per hour observed in our experiments exceeds this rate. Although their increase of potential could be attributed to the increase of polarization resistance over either the anode or cathode, rather than deterioration of the BPM, the higher rate in our system suggests that some deterioration did play a role here. This could possibly be attributed to the long-term storage (40+ days) of the PiperION AEMs in 1M KOH, as the increase was less severe for the second round of experiments with PiperION that had soaked for shorter times. Nevertheless, further experiments and tests should be performed to ensure the potential for long-term performance of these membranes.

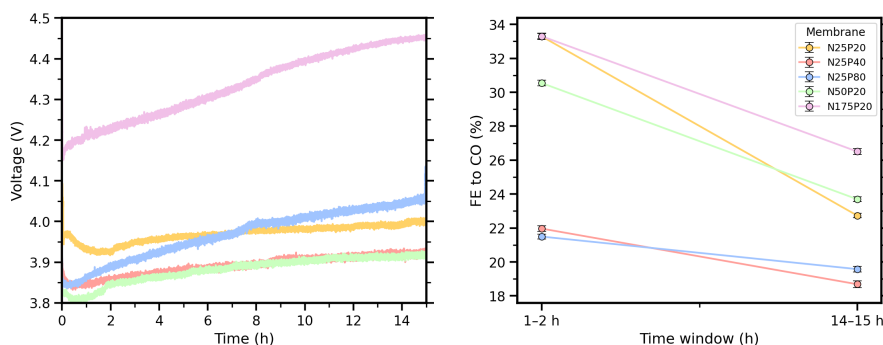


Figure 4.2: Increase in cell voltage and decrease in FE to CO during 15h operation

Gas production increased with increasing applied current density, as expected due to increased product generation. During individual experiments, gas flow rates remained relatively constant over time. It was later identified that the mass flow controller calibration deviated from the nominal value of 50 mL min⁻¹, resulting in a systematic offset in the absolute flow rate. However, this deviation was not expected to significantly influence the observed trends or comparative conclusions presented in this work.

Reproducibility between repeated experiments varied and was strongly dependent on membrane type. Variations can be attributed to several factors, including the use of different spray-coated cathode pieces, small differences in electrode alignment and effective active area, minor variations in catalyst loading, and differences in bipolar membrane assembly. These variations explain the considerably large error bars observed in many of the results. Beyond these expected sources of variability, a pronounced difference was observed between two batches of overnight experiments. In the first batch (tested over the span of 2 weeks), PiperION membranes that had been stored in 1 M KOH for 20–30 days prior to use were employed, whereas in the second batch (tested over the span of 2 weeks, but later) membranes stored for only 2–14 days were used. It is likely that prolonged exposure to hydroxide ions led to partial membrane degradation, resulting in reduced conductivity and lower co-ion crossover compared to the fresher membranes, as also proposed by [7]. Consequently, significant differences in cell voltage (As shown in Appendix

Figure B.3), FE and crossover were observed between the two batches.

Despite these differences, the overall trends in the key variables of interest remained consistent across both batches, and averaged values were therefore retained for further analysis. The increased variability observed for the overnight experiments is reflected in larger error bars and should be taken into account when interpreting these results and when designing future experiments.

4.2. AEL and CEL thickness effects

This section presents the effect of AEL and CEL thickness on (i) K^+ and carbon transport through the membrane, (ii) WDE, (iii) cell voltage, and (iv) FE toward CO for all investigated current densities.

4.2.1. Effect on species crossover through the membrane

Figures 4.3, 4.4, and 4.6 show the effect of BPM layer thickness on K^+ flux, carbon flux, and WDE, respectively, at different applied current densities. Carbon was assumed to cross the CEL as HCO_3^- , and therefore denoted as such in the following section.

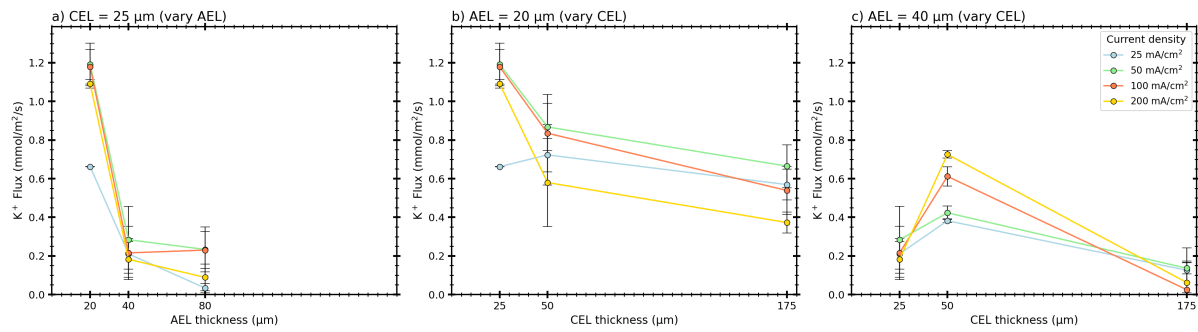


Figure 4.3: Figure showing the effect of BPM layer thickness on K^+ flux through the membrane. x and y-axes are kept constant for visual comparison. Error bars represent the combined uncertainty arising from the propagated uncertainty of individual measurements and the standard deviation obtained from replicate experiments. a) The effect of AEL thickness on K^+ flux through the membrane. AEL varied from 20, to 40, to 80 µm, CEL kept constant at 25 µm. b) The effect of CEL thickness on K^+ flux through the membrane. CEL varied from 25, to 50, to 175 µm, AEL kept constant at 20 µm. c) Same plot as b, with AEL now constant at 40 µm

For the K^+ flux (Figure 4.3), increasing the AEL thickness at constant CEL thickness results in a pronounced decrease in cation crossover, while increasing the CEL thickness at constant AEL thickness also leads to a reduction, albeit significantly less pronounced. These effects are strongest for the more asymmetric membrane configurations with an AEL thickness of 20 µm, compared to configurations with a 40 µm AEL. Across all membrane configurations, the magnitude of the K^+ flux remains of comparable order for different applied current densities, with consistent trends observed at each current density (Figure B.4 in the Appendix).

Importantly, the reduction in K^+ crossover with increasing AEL thickness appears to be strongly non-linear. Increasing the AEL thickness from 20 to 40 µm reduces the K^+ flux from approximately 1.2 to 0.2 mol m⁻² h⁻¹, corresponding to a decrease of roughly 4.2% per µm. In contrast, a further increase from 40 to 80 µm yields a more modest reduction, from approximately 0.3 to 0.1 mol m⁻² h⁻¹ (about 1.6% per µm). This indicates diminishing returns with increasing AEL thickness. A similar but weaker diminishing-return behavior is observed for changes in CEL thickness. Increasing the CEL thickness from 25 to 50 µm reduces the K^+ flux from approximately 1.2 to 0.8 mol m⁻² h⁻¹ (a 1.3% decrease per µm), while a further increase to 175 µm reduces the flux to roughly 0.5 mol m⁻² h⁻¹ (a 0.3% decrease per µm), with the exact magnitude depending on the applied current density. This confirms that K^+ crossover is primarily governed by transport resistance in the AEL, with the CEL exerting a secondary influence.

The strong sensitivity of K^+ crossover to AEL thickness is consistent with previous reports in the literature [23]. This behavior can be rationalized by considering Donnan exclusion within the anion exchange layer. The weaker, yet still observable, dependence of K^+ flux on CEL thickness suggests that ion transport in BPMs cannot be described as strictly layer-isolated. This may be related to intrinsic membrane properties. Nafion exhibits exceptionally high selectivity for proton transport compared to other cations due to the fundamentally different transport mechanisms involved. Protons are conducted primarily via structural diffusion through a Grotthuss-type hopping mechanism between water molecules and sulfonic acid groups (as described in Section 2.3.2), whereas alkali metal cations such as K^+ are transported by slower vehicular diffusion as fully hydrated species. This difference is reinforced by the strong acidity of Nafion's sulfonic acid groups and the nanoscale morphology of its hydrated ionic domains, which are optimized for proton hopping but impose steric and frictional barriers to larger hydrated cations. As a result, Nafion-based membranes exhibit proton conductivities that are orders of magnitude higher than their conductivities toward other cations.

Interestingly, literature on single-layer anion exchange membranes suggests that above a critical thickness—typically reported to lie between 20 and 40 μm , depending on the AEM identity—further increases in membrane thickness do not significantly enhance selectivity [57, 59]. While the present results show a clear reduction in K^+ crossover when increasing the AEL thickness beyond this range, the magnitude of the effect decreases substantially from 40 to 80 μm compared to the change from 20 to 40 μm . This behavior is consistent with the onset of a plateau in selectivity, even though a fully thickness-independent regime is not yet reached within the investigated range. The absence of a sharp selectivity plateau in the present BPM system likely reflects the fundamentally different transport mechanisms compared to single-layer membranes. In bipolar membranes, ion transport is coupled to water dissociation at the junction and influenced by interactions between the anion- and cation-exchange layers, rather than being governed solely by Donnan exclusion within a single layer. As a result, the characteristic thickness at which selectivity saturates may be shifted to higher values or depend on additional parameters such as junction activity, hydration, and layer asymmetry. Further increases in AEL thickness, or a denser sampling of intermediate thicknesses, would be required to determine whether a true selectivity plateau exists for BPM-based CO_2 electrolysis systems and to identify the thickness regime beyond which additional material yields negligible benefit.

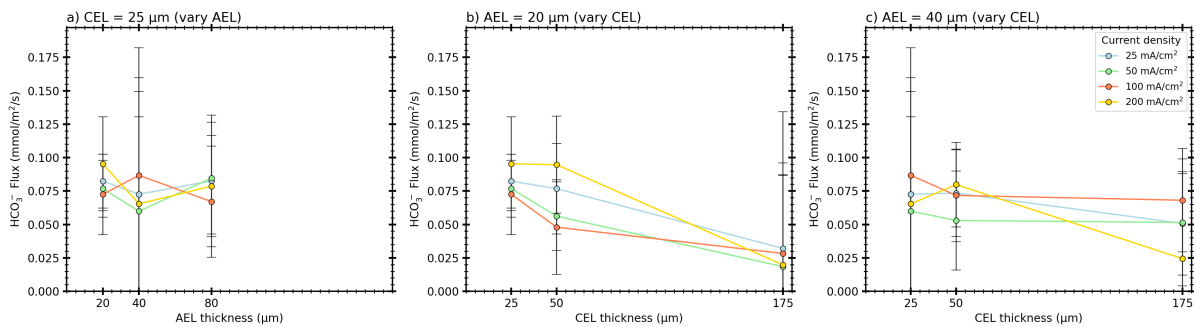


Figure 4.4: Figure showing the effect of BPM layer thickness on HCO_3^- flux through the membrane. x and y-axes are kept constant for visual comparison. Error bars represent the combined uncertainty arising from the propagated uncertainty of individual measurements and the standard deviation obtained from replicate experiments. a) The effect of AEL thickness on HCO_3^- flux through the membrane. AEL varied from 20, to 40, to 80 μm , CEL kept constant at 25 μm . b) The effect of CEL thickness on HCO_3^- flux through the membrane. CEL varied from 25, to 50, to 175 μm , AEL kept constant at 20 μm . c) Same plot as b, with AEL now constant at 40 μm

For the HCO_3^- flux (Figure 4.4), changes in AEL thickness at constant CEL thickness result in relatively small variations in the measured flux. In contrast, increasing the CEL thickness leads to more noticeable changes in the HCO_3^- flux for both investigated AEL thicknesses. Similar to the K^+ flux, these trends are more pronounced for the more asymmetric membrane configurations with an AEL thickness of 20 μm than for those with

an AEL thickness of 40 μm . The HCO_3^- flux remains of comparable magnitude across the different applied current densities, with consistent trends observed for each current density (Figure B.4). Additionally, the magnitude of the HCO_3^- flux in this system is consistently about 2-10 times as small as the K^+ flux. Quantitatively, increasing the CEL thickness from 25 to 50 μm reduces the carbon flux from approximately 0.08 to 0.06 $\text{mol m}^{-2} \text{h}^{-1}$ (1% decrease per μm), while a further increase to 175 μm yields a reduction to approximately 0.03 $\text{mol m}^{-2} \text{h}^{-1}$ (0.4% decrease per μm). Similar to K^+ crossover, this behavior appears to exhibit diminishing returns with increasing layer thickness. Additionally, the K^+ flux appears to be more sensitive to layer thickness than the HCO_3^- flux.

Overall, the observed dependence of both K^+ and carbon fluxes on membrane layer thickness suggests that crossover in this BPM system is dominated by diffusion rather than migration. If migration were the dominant transport mechanism, increasing layer thickness would not substantially reduce net counter-ion fluxes, as the increased ohmic drop would enhance the migrational driving force. Instead, the measured fluxes decrease with increasing thickness, consistent with a reduction in concentration gradients and therefore a diminished diffusive driving force (Figure 4.5). This interpretation is further supported by literature comparisons. In AEM-based CO_2 electrolysis operated in concentrated KOH electrolytes, increased K^+ crossover with membrane thickness has been reported and attributed to migration-dominated transport driven by larger voltage drops [49]. In contrast, the decreasing K^+ flux with thickness observed here is consistent with diffusion-controlled transport, in agreement with findings by Hendershot *et al.* [51] for diffusive cation transport through PiperION membranes.

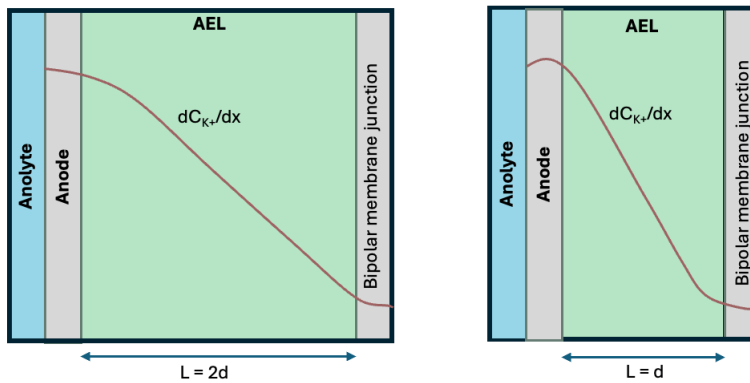


Figure 4.5: Decrease of driving force for diffusion with membrane layer thickness, demonstrated through the effect of AEL thickness on K^+ flux. As diffusion is driven by a concentration gradient, a larger slope means a larger driving force.

Figure 4.6 presents the effect of BPM layer thickness on the water dissociation efficiency (WDE) of the system. Variations in AEL thickness result in clear differences in WDE for all current densities, while an increase in CEL thickness also improves WDE, but to a lesser extent. As observed for the ion fluxes, differences in WDE are more pronounced for the more asymmetric membranes with an AEL thickness of 20 μm than for membranes with an AEL thickness of 40 μm . These results indicate that by adjusting the thickness of the BPM layer that predominantly governs co-ion crossover—here, the AEL for K^+ —water dissociation efficiency can be systematically optimized. As K^+ crossover substantially exceeds HCO_3^- crossover, it constitutes the dominant contribution to WDE losses. Consequently, reducing K^+ transport through increased AEL thickness directly translates into improved WDE.

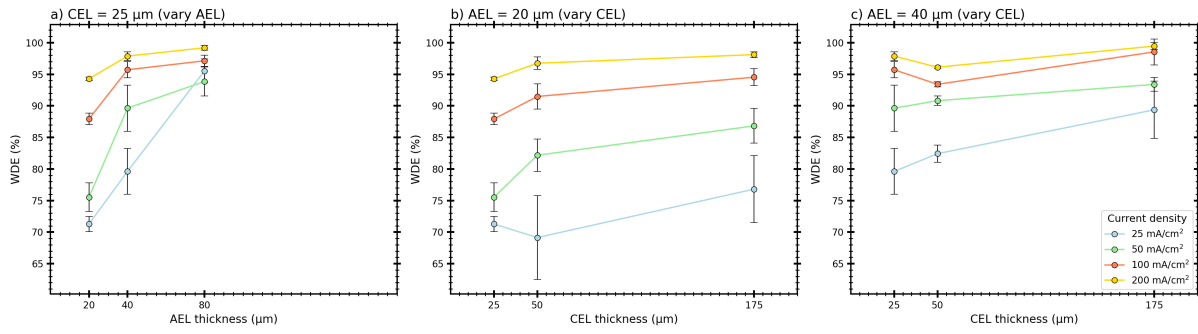


Figure 4.6: Figure showing the effect of BPM layer thickness on WDE of the CO₂ electrolysis system. x and y-axes are kept constant for visual comparison. a) The effect of AEL thickness on WDE (in %) of the system. AEL varied from 20, to 40, to 80 μm, CEL kept constant at 25 μm. b) The effect of CEL thickness on WDE (in %) of the system. CEL varied from 25, to 50, to 175 μm, AEL kept constant at 20 μm. c) Same plot as b, with AEL now constant at 40 μm

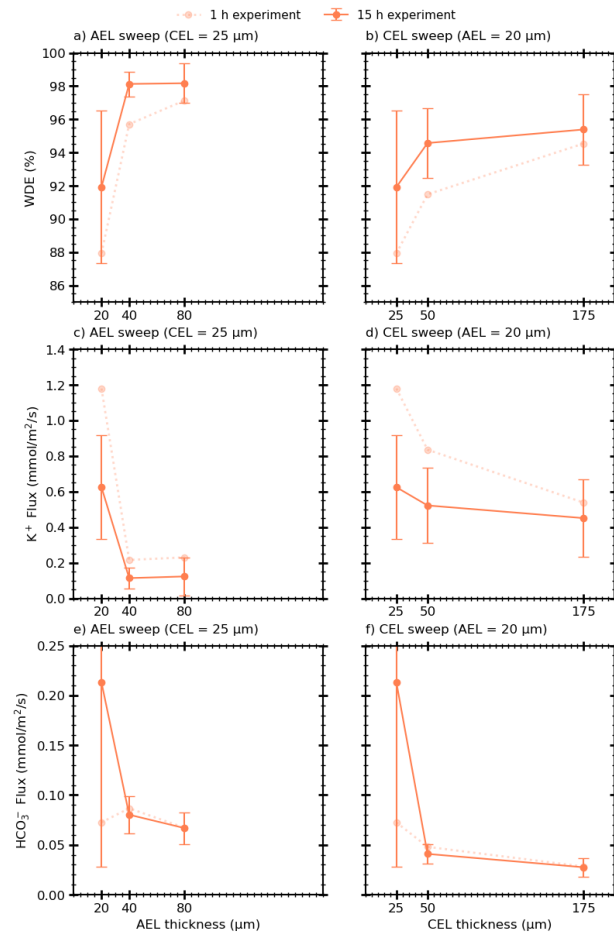


Figure 4.7: Effect of AEL and CEL thickness on WDE, K⁺ flux, and HCO₃⁻ flux for 1 h and 15 h experiments at 100 mA cm⁻².

Figure 4.7 compares WDE, K⁺ flux, and HCO₃⁻ flux for short (1 h) and extended (15 h) operation at 100 mA cm⁻². While the relative dependence of K⁺ and carbon crossover on AEL and CEL thickness remains unchanged, extended operation consistently results in lower net K⁺ fluxes and correspondingly higher WDE values across all membrane configurations. This indicates that BPM performance in suppressing cation crossover improves with time. The improvement in WDE during prolonged operation can be attributed primarily to a reduction in net K⁺ transport toward the cathode. As K⁺ crossover substantially exceeds carbon crossover, it dominates WDE losses; consequently, even a modest reduction in K⁺ flux leads to a noticeable increase in WDE. One plausible explanation is enhanced cation back-diffusion during extended operation. Visual observation of increased salt formation after long-term experiments suggests accumulation of K⁺ near or within the membrane, which would reduce the concentration gradient across the CEL and thereby diminish the diffusive driving force for further K⁺ transport (Figure 4.8).

Such behavior is consistent with earlier observations by Yang *et al.*, who reported that stable long-term operation of BPM-based CO₂ electrolyzers is associated with the establishment of an equilibrium K⁺ concentration below the precipitation threshold of K₂CO₃ [22]. Once this quasi-equilibrium is reached, net cation crossover decreases, while

carbonate species may continue to cross the membrane, potentially shifting the dominant contributor to anolyte acidification over longer timescales. An important implication of these findings is that the WDE values reported here—measured after relatively short stabilization times—may represent conservative estimates. If net K^+ crossover continues to decrease with time, higher WDE values may be attainable at elevated current densities than those observed in the present study. However, further experiments over longer durations are required to determine whether this trend persists, stabilizes, or reverses due to competing degradation or transport phenomena.

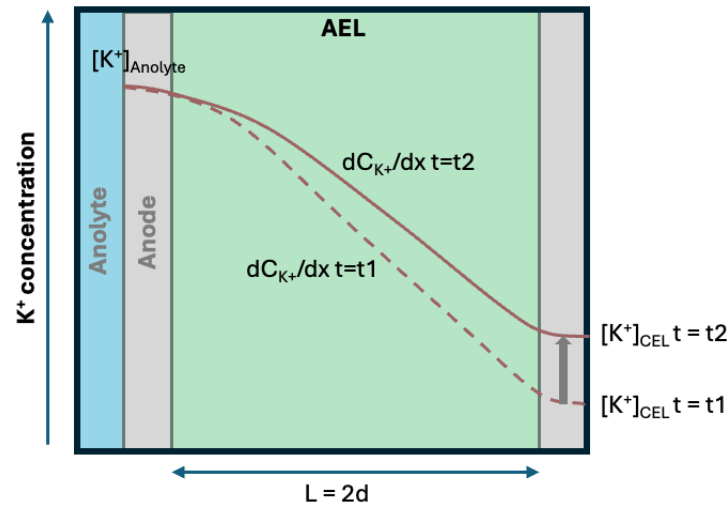


Figure 4.8: Decrease in driving force for K^+ diffusion with time

4.2.2. Effect on cell voltages

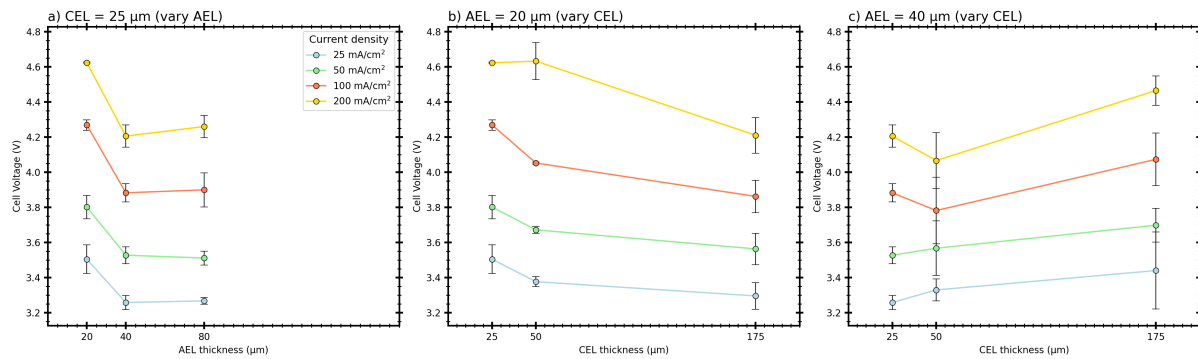


Figure 4.9: Figure showing the effect of BPM layer thickness on cell voltage of the CO_2 electrolysis system. x and y-axes are kept constant for visual comparison. Error bars represent the combined uncertainty arising from the standard deviation of the voltage over the last 15 minutes of the experiment, and the standard deviation obtained from replicate experiments. Measurements at different current densities are indicated with different colours. a) The effect of AEL thickness on cell voltage of the system. AEL varied from 20, to 40, to 80 μm , CEL kept constant at 25 μm . b) The effect of CEL thickness on cell voltage of the system. CEL varied from 25, to 50, to 175 μm , AEL kept constant at 20 μm . c) Same plot as b, with AEL now constant at 40 μm

Figure 4.9 shows the effect of the AEL and CEL thickness on the cell voltage at different current densities. Across all conditions, the cell voltage varies by approximately 0.4 V between the lowest and highest values observed, with reported uncertainties of up to ± 0.2 V.

For the short-duration (1 h) experiments, the cell voltage appears to decrease with increasing AEL and CEL thickness, although this effect is more pronounced for variations in CEL thickness. However, when keeping the AEL thickness constant at $40\ \mu\text{m}$, this trend appears to reverse, with thicker CELs exhibiting slightly higher voltages at higher current densities.

Based on theory and prior literature, an increase in membrane layer thickness is generally expected to result in higher cell voltages due to increased ohmic resistance of the membrane [15]. The absence of a consistent thickness–voltage relationship in the 1 h experiments therefore suggests that factors other than intrinsic membrane resistance may be influencing the measured voltages. One plausible explanation lies in the practical limitations of membrane assembly. Thinner membranes proved more challenging to handle and laminate, and were more prone to incomplete layer adhesion or mechanical defects. Such imperfections may introduce additional interfacial resistances that are not directly related to intrinsic membrane thickness, thereby obscuring the expected trend.

This interpretation is supported by the observation that when the anion-exchange layer thickness was fixed at $40\ \mu\text{m}$ —thereby avoiding the use of very thin AELs—the voltage trend with increasing total membrane thickness became more consistent. Under these conditions, membrane lamination was more reproducible and layer adhesion was visually uniform across samples, suggesting that fabrication-induced resistances rather than fundamental transport limitations dominated the voltage response in the thinnest membranes.

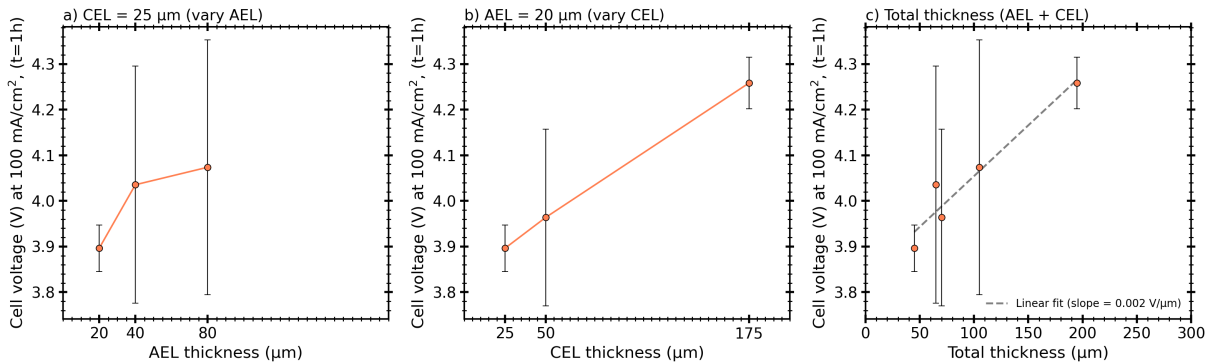


Figure 4.10: Figure showing the effect of BPM layer thickness on V of the CO_2 electrolysis system for 15 h experiments at $100\ \text{mA}/\text{cm}^2$. Voltages shown correspond to the average voltage between $t=1\text{h}$ and $t=2\text{h}$. x and y-axes are kept constant for visual comparison. Error bars represent the combined uncertainty arising from the propagated uncertainty of individual measurements and the standard deviation obtained from two replicate experiments. a) The effect of AEL thickness on V of the system. AEL varied from 20, to 40, to $80\ \mu\text{m}$, CEL kept constant at $25\ \mu\text{m}$. b) The effect of CEL thickness on V of the system. CEL varied from 25, to 50, to $175\ \mu\text{m}$, AEL kept constant at $20\ \mu\text{m}$. c) Same plot as b, with AEL now constant at $40\ \mu\text{m}$

Figure 4.10 presents the voltage trends observed during the longer (15 h) experiments between $t = 1\text{ h}$ and $t = 2\text{ h}$ at $100\ \text{mA}/\text{cm}^2$. In contrast to the short-duration experiments, a clearer trend is observed here, with the cell voltage increasing with both AEL and CEL thickness, effectively scaling linearly with the overall membrane thickness. This behaviour is consistent with theoretical expectations of increased Ohmic resistance for thicker membranes.

Additionally, the 15 h results suggest that variations in AEL thickness have a larger influence on cell voltage than comparable changes in CEL thickness. This observation is consistent with literature reports indicating that AELs generally exhibit lower ionic conductivity than CELs [15], causing changes in AEL thickness to have a disproportionately large effect on overall membrane resistance. The improved results may be due to improved

membrane assembly in later experiments.

Despite the trends observed, the present data do not allow for definitive conclusions regarding the quantitative voltage penalty associated with increasing membrane thickness. The relatively large experimental scatter, combined with a limited number of replicates, makes it difficult to unambiguously separate intrinsic ohmic losses from assembly-related and interfacial contributions. A larger experimental dataset would be required to reduce statistical uncertainty and establish robust thickness–voltage relationships. Further insight could be obtained by decoupling the membrane voltage from the total cell voltage. Measurements in a six-compartment cell configuration, combined with Electrical Impedance Spectroscopy (EIS) in the CO₂ electrolysis setup, would enable decomposition of the total voltage into ohmic, interfacial, and water dissociation contributions. Such an approach would provide direct information on how AEL and CEL thickness individually affect membrane resistance and junction-related losses in a CO₂ electrolysis application. Ultimately, establishing a quantitative relationship between voltage penalties and selectivity gains as a function of membrane thickness is essential for rational BPM design. The present results highlight the importance of membrane thickness as a tuning parameter, but also demonstrate that additional targeted experiments are required to fully resolve the trade-off between increased resistance and improved suppression of co-ion crossover.

4.2.3. Effect on faradaic efficiency to CO

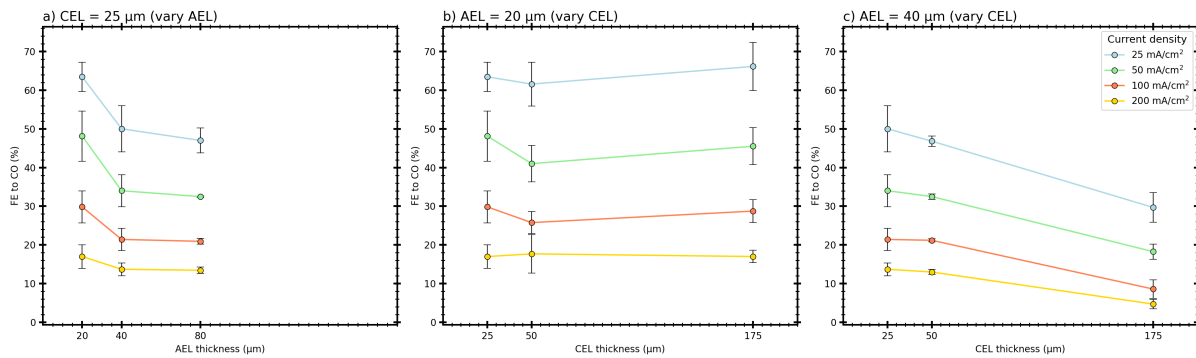


Figure 4.11: Figure showing the effect of BPM layer thickness on Faradaic Efficiency to CO of the CO₂ electrolysis system. x and y-axes are kept constant for visual comparison. a) The effect of AEL thickness on FE to CO (in %) of the system. AEL varied from 20, to 40, to 80 μm, CEL kept constant at 25 μm. b) The effect of CEL thickness on FE to CO (in %) of the system. CEL varied from 25, to 50, to 175 μm, AEL kept constant at 20 μm. c) Same plot as b, with AEL now constant at 40 μm

Figure 4.11 shows the effect of AEL thickness (with the CEL kept constant at 25 μm) and CEL thickness (with the AEL kept constant at 20 or 40 μm) on the FE to CO at different current densities. In the first subplot, a clear trend is visible showing a decrease in FE to CO with increasing AEL thickness. When keeping the AEL constant at 20 μm, no clear trend is observed with increasing CEL thickness, whereas for an AEL thickness of 40 μm, the FE to CO decreases with increasing CEL thickness.

Although the FE to CO decreases with current density for all current densities, the decrease becomes less pronounced at higher current densities, with the curves essentially flattening at 200 mA cm⁻². This behavior suggests that membrane-related effects on FE to CO become less dominant as the system transitions to a regime where other limitations increasingly govern product selectivity.

The decrease in FE to CO with increasing AEL thickness can be rationalized by considering the concurrent reduction in K⁺ flux with increasing AEL thickness, as discussed in the previous section. To further explore this relationship, Figures 4.12 and 4.14 show the

correlation between K^+ flux and FE to CO for different current densities and for the 15 h experiments, respectively. In both cases, a positive correlation is observed, indicating that higher K^+ fluxes are generally associated with higher FE to CO. However, the slope of this correlation decreases with increasing current density, consistent with the observed flattening of the FE trends at higher current densities.

This behavior is consistent with literature reports that attribute reductions in FE to CO to increased H^+ availability at the cathode, resulting from enhanced water dissociation and proton transport, which promote hydrogen evolution over CO formation [22]. As the K^+ flux remains approximately constant with current density, its relative influence on the local cathode environment diminishes at higher current densities, where proton transport and water availability increasingly dictate selectivity. It should be noted that the observed correlation between K^+ flux and FE to CO, although present, is not particularly strong. This is likely due to the presence of multiple competing effects influencing FE to CO simultaneously. For instance, a thinner CEL may promote K^+ transport toward the cathode, but it can also enhance H^+ and water transport, lowering the local pH and increasing the likelihood of cathode flooding—both of which are known to favor hydrogen evolution at the expense of CO formation.

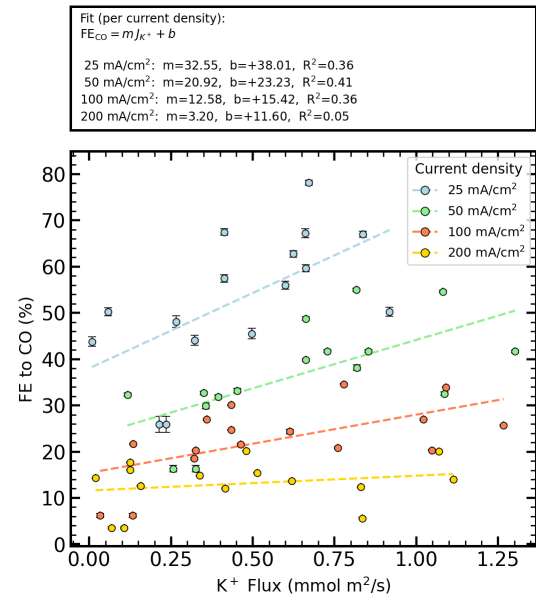


Figure 4.12: Correlation between K^+ flux and FE to CO at different current densities.

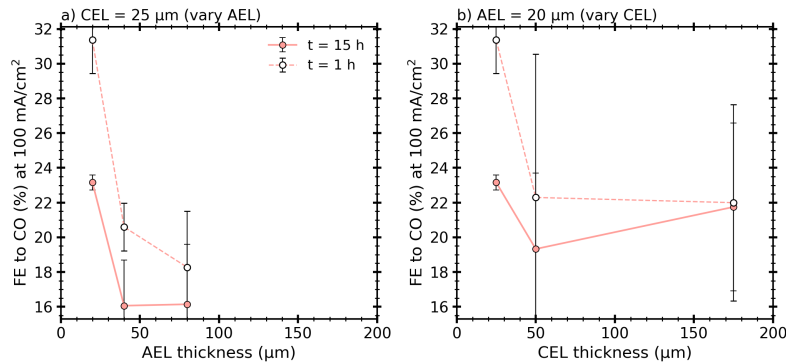


Figure 4.13: Figure showing the effect of BPM layer thickness on Faradaic Efficiency to CO of the CO_2 electrolysis system for the 15 h experiments. The FE to CO was calculated between 1–2 h (dotted line) and between 14–15 h (solid line). Error bars represent the combined uncertainty arising from the propagated uncertainty of individual measurements and the standard deviation obtained from two replicate experiments. All experiments were performed at 100 mA cm^{-2} . x and y-axes are kept constant for visual comparison.

The results from the 15 h experiments, shown in Figure 4.13, follow the same qualitative trends as the short-duration experiments, even if the total FE to CO lowered over time, as noted in Section 4.1. This suggests that the observed relationship between membrane layer thickness, K^+ transport, and FE to CO persists during extended operation, despite the additional complexities introduced by time-dependent effects such as cation accumulation and back-diffusion. However, we only have average values for the K^+ flux over these 15 h, so we do not know if the K^+ flux differed at 1 h of operation and 15 h of operation, and if that may potentially cause the lower FE to CO over time. Experiments explicitly comparing

species crossover at multiple operation timescales would therefore be required to clarify whether evolving ion transport contributes to FE degradation, or whether electrode-related effects dominate. Moreover, longer-term operation may reveal whether FE continues to deteriorate or instead reaches a steady state. Acquiring FE and crossover data at additional time points would enable more quantitative insight into the rate and origin of FE losses, as well as the extent to which improved membrane selectivity can offset these effects.

Overall, these findings indicate that while K^+ transport plays a measurable role in governing FE to CO through its influence on the local cathode environment, it is not the sole determining factor. The diminishing sensitivity of FE to CO to membrane thickness at higher current densities highlights the increasing dominance of proton availability, water management, and mass transport limitations in controlling product selectivity under industrially relevant operating conditions.

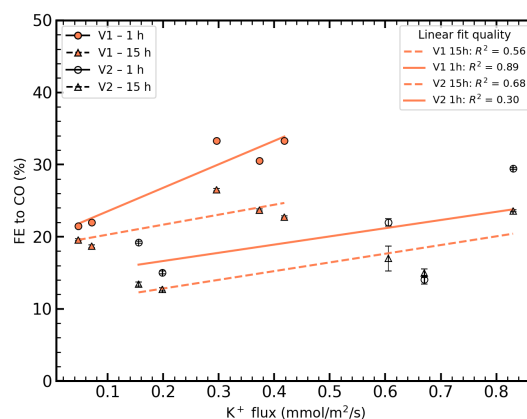


Figure 4.14: Correlation between K^+ flux and FE to CO for the 15 h experiments.

Finally, the observed coupling between K^+ transport and the FE underscores an inherent trade-off in BPM-based CO_2 electrolysis. However, this trade-off is likely governed more by the overall electrolyzer system — particularly the catalyst — than by the membrane thickness or chemistry alone. Consequently, future studies should focus on catalyst designs that exhibit a reduced dependence on alkali metal cations for achieving high CO selectivity. Promising examples include single-atom nickel-based catalysts, which have recently been shown to deliver high FEs in BPM-based CO_2 electrolysis [13, 16]. Integrating such catalysts with the membranes investigated in this thesis may enable electrolyzer systems that simultaneously achieve high FE to CO and high WDE, thereby mitigating — or potentially eliminating — the apparent trade-off between membrane selectivity and CO formation efficiency.

4.3. Changes in performance with current density

For industrial application of BPMs in CO_2 electrolysis, efficient operation at higher current densities. This section will therefore present the change in voltage, FE and charge carriers through the membrane with current density. Again, carbon is assumed to cross over as HCO_3^- , and is therefore denoted as such. 'Co-ion transport' in this section refers to transport of both K^+ and HCO_3^- .

4.3.1. Current density effects on crossover and WDE

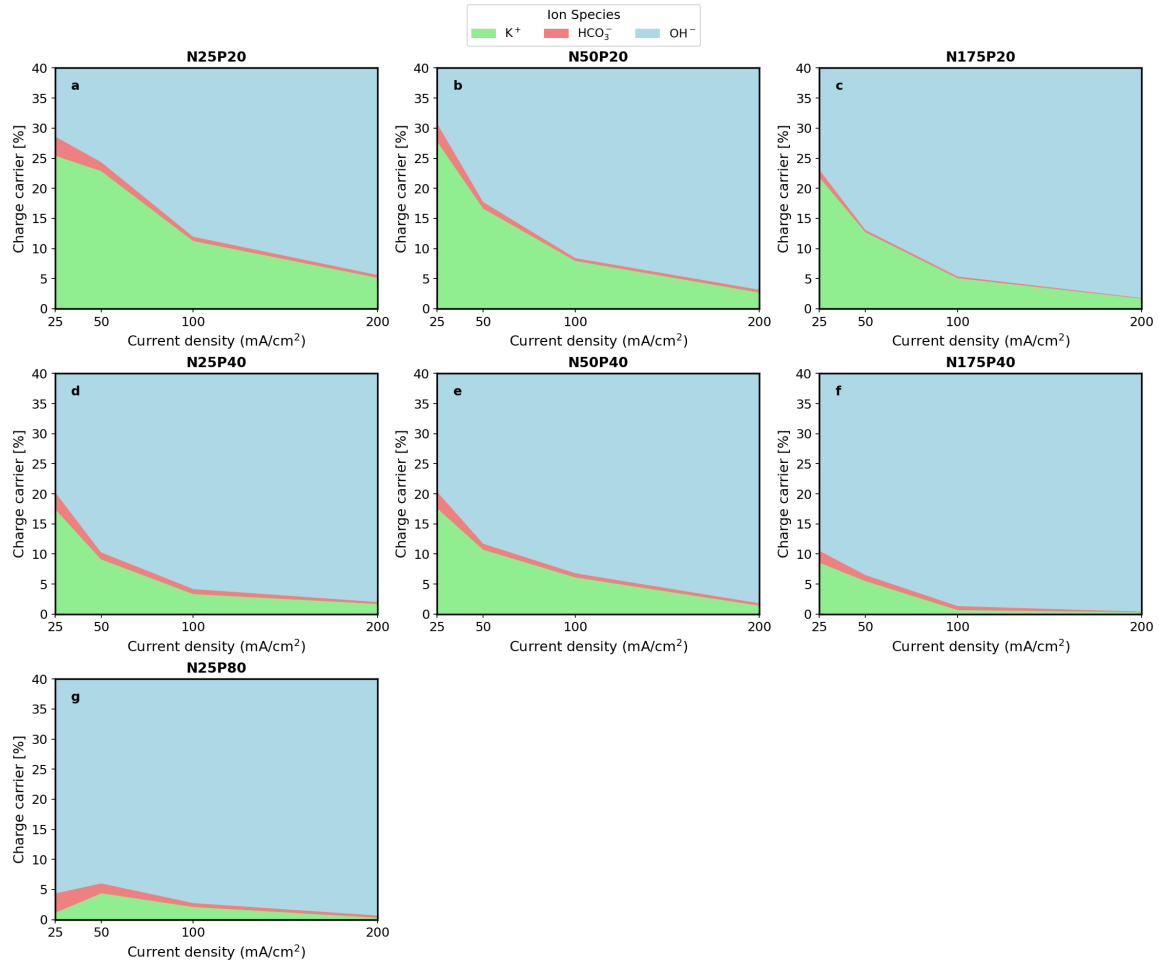


Figure 4.15: Figure showing how the relative charge carriers progress with current density for the different membranes. Along the x-axis a change with CEL thickness can be observed, along the y-axis a change with AEL thickness. Plot h shows the progression for a commercial Fumasep membrane for comparison. All plots were based on 1 h crossover experiments. The figure shows the bottom 40% of the total distribution. Error bars were omitted for clarity.

Figure 4.15 shows the relative distribution of charge carrier fluxes the membrane as a function of current density for the different synthesized asymmetric bipolar membranes. For all synthesized membranes, OH^- is the dominant charge carrier at all current densities, with its contribution becoming increasingly pronounced at higher current densities. As noted before, but now more clearly visible, K^+ is the dominant co-ion contributing to charge transport across the membrane for all membranes, except for N25P80 at lower current densities. Ratios of HCO_3^- to K^+ differ per membrane, and do not exhibit clear trends with current density.

To further elucidate the effect of current density on net ion fluxes through the membrane, Figure 4.16 shows the absolute K^+ and HCO_3^- fluxes as a function of current density. The HCO_3^- flux remains relatively constant across the investigated current density range for all membranes. In contrast, the K^+ flux generally decreases slightly between 50 and 200 mA cm^{-2} , while the value at 25 mA cm^{-2} is often lower than the values at higher current densities. The deviation observed at 25 mA cm^{-2} is likely related to the fact that this measurement is typically the first experiment performed on a given membrane, for which no prior accumulation of co-ions within the membrane has occurred. Subsequent

measurements are conducted after partial ion uptake, which may affect the observed fluxes. This effect should therefore be considered a limitation of the experimental methodology.

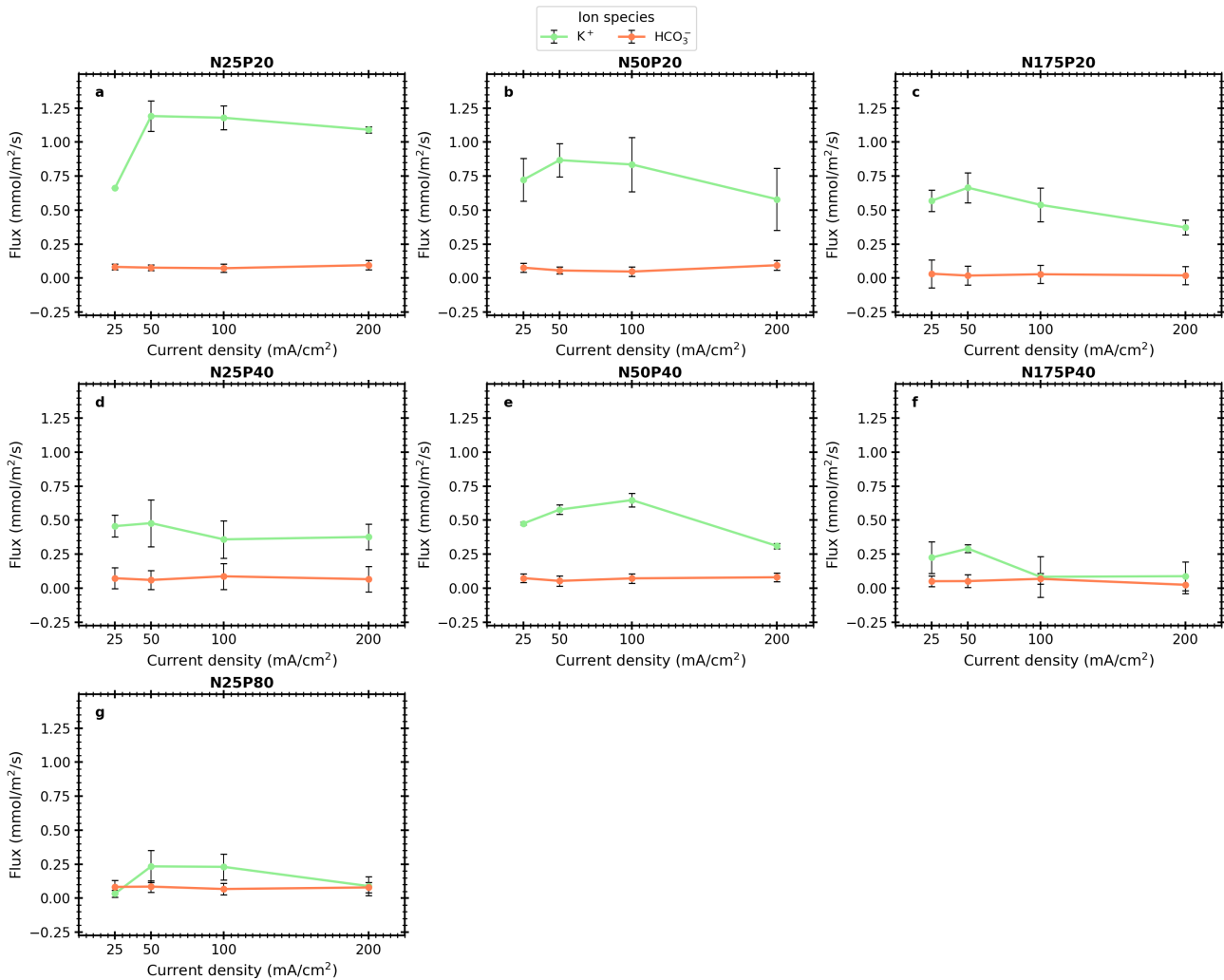


Figure 4.16: Absolute K^+ and HCO_3^- fluxes as a function of current density for different bipolar membrane configurations. Data points correspond to mean values of two replicate measurements. Error bars represent the combined uncertainty, accounting for both the standard deviation between replicates and measurement uncertainty.

A decrease in the *relative* contribution of co-ion transport with increasing current density has previously been reported by Prats Vergel *et al.* and Blommaert *et al.* [14, 61], and is commonly attributed to the increasing dominance of water dissociation at higher current densities. While this explanation is consistent for relative fluxes, reported trends for *absolute* co-ion fluxes differ between studies. Prats Vergel *et al.* observed a decrease in absolute co-ion flux with increasing current density, whereas Blommaert *et al.* reported an increase.

These discrepancies can likely be explained by fundamental differences in system configuration and operating conditions. Prats Vergel *et al.* studied a CO_2 electrolysis system employing a KOH anolyte, a Fumasep BPM and no liquid catholyte, whereas Blommaert *et al.* used a configuration with liquid electrolytes on both sides of the membrane and investigated crossover of Na^+ and H_2PO_4^- rather than K^+ and HCO_3^- . The presence of liquid electrolytes on both sides is expected to reduce concentration gradients and thus diminish diffusive transport, altering the balance between diffusion- and migration-driven co-ion crossover [14]. In membrane-electrode assembly (MEA)

configurations, such as those employed here, steeper concentration gradients may cause diffusive transport to dominate, potentially obscuring migration-driven contributions to co-ion transport at higher current densities.

The slight decrease in co-ion transport with increasing current density may further be explained by enhanced outward migration of OH^- and H^+ ions generated by water dissociation. In the AEL, increased OH^- transport may counteract K^+ crossover through electrostatic drag or coupled ion transport effects, while in the CEL increased H^+ transport may suppress HCO_3^- crossover and promote its conversion back to CO_2 . A similar mechanism was proposed by Prats Vergel *et al.* [14]. The diversity of reported trends across different studies suggests that multiple transport mechanisms—diffusion, migration, and coupled ion transport—compete, with the dominant mechanism depending sensitively on membrane chemistry and structure.

The absence of a dependence of carbon crossover on current density in these results could also be due to the nature of the carbon species that crosses over. In this thesis, the underlying assumption has been that carbon crosses the CEL as HCO_3^- , consistent with the methodology of Prats Vergel *et al.* [14], and often assumed in literature [13]. However, modelling work by Bui *et al.* [62] suggests that carbon crosses the CEL as dissolved CO_2 , rather than HCO_3^- . Under the very alkaline conditions at the AEL, this CO_2 is then converted to CO_3^{2-} . Even though the modeled system is not completely representative for the system considered here, as it employs a liquid HCO_3^- catholyte and a HCO_3^- anolyte, it is possible that the transport of CO_2 through the membrane happens in a similar fashion in our system. This hypothesis is still in line with the earlier findings on carbon transport being dictated by CEL thickness, as diffusive transport of dissolved CO_2 would also decrease with layer thickness due to a decreased concentration gradient.

Finally, the identity of the dominant co-ion charge carrier has important implications for water dissociation efficiency. While previous studies have often attributed anolyte acidification primarily to carbonate crossover [13, 14], the present results indicate that in systems where K^+ transport dominates crossover through the membrane, carbon transport plays a comparatively minor role. This distinction underscores the importance of membrane chemistry and architecture in determining both the nature of co-ion transport and its impact on overall electrolyzer performance.

An increase in WDE with current density is consistently observed across all membrane configurations, as shown in Figure 4.17. These findings are a direct result of the increasing dominance of water dissociation with current density noted in the previous section. As the applied current density increases, a larger fraction of the total current is carried by H^+ and OH^- generated at the bipolar junction, while the relative contribution of co-ion transport diminishes, resulting in higher WDE values.

The highest WDE values are obtained at 200 mA/cm^2 for membranes with thicker AELs, with a maximum measured value of $99.5 \pm 0.2\%$ for the N175P40 membrane. This approaches the $\sim 99.8\%$ WDE cited as a target for industrially viable BPM operation [14], suggesting that this threshold may be attainable either at higher current densities or through further membrane optimization. One obvious strategy would be to further increase the thickness of the AEL, or to use a more permselective layer. However, it should be noted that improvements in WDE at elevated current densities coincide with declines in other performance metrics, such as FE to CO and membrane conductivity, highlighting the importance of evaluating WDE within a broader performance trade-off framework.

Further experiments at higher current densities and employing thicker membrane layers, combined with direct measurements of species crossover under these conditions, are therefore required to assess whether WDE can be further improved without exacerbating losses in selectivity or energy efficiency, in order to surpass the 99.8% required for industrial operation.

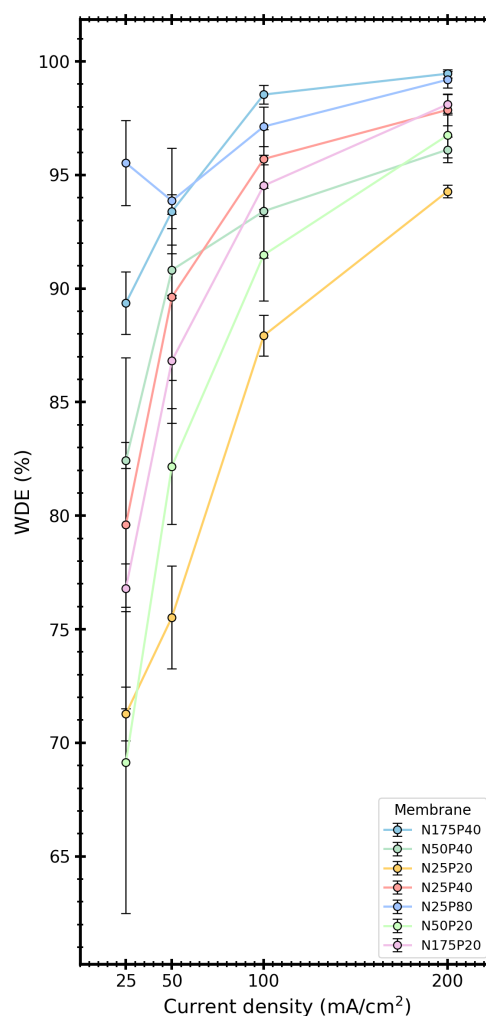


Figure 4.17: Increase in WDE for the different membranes with current density. Error bars represent the combined uncertainty arising from individual measurements and the standard deviation obtained from replicate experiments.

4.3.2. Current density effects on FE to CO

Figure 4.18 shows the faradaic efficiency composition of the tested Nafion/PiperION membranes as a function of current density. For all experiments, the combined FE toward CO and H_2 amounted to approximately 100%, and no additional gaseous products were detected by GC. It can therefore be assumed that CO and H_2 were the only cathodic products formed under the investigated conditions.

For all membranes, increasing current density leads to a decrease in the FE to CO and a concurrent increase in the FE to H_2 . This trend indicates a systematic shift in cathodic selectivity and suggests that the relative rates of CO_2RR and the HER are altered with increasing current density. A central factor underlying this shift is the asymmetric generation, transport, and local consumption of ionic species produced by water dissociation at the bipolar junction and by the CO_2RR at the cathode. Although H^+ and OH^- are generated simultaneously at the bipolar interface and at the cathode, respectively, only protons that successfully traverse the CEL can directly participate in cathodic reactions.

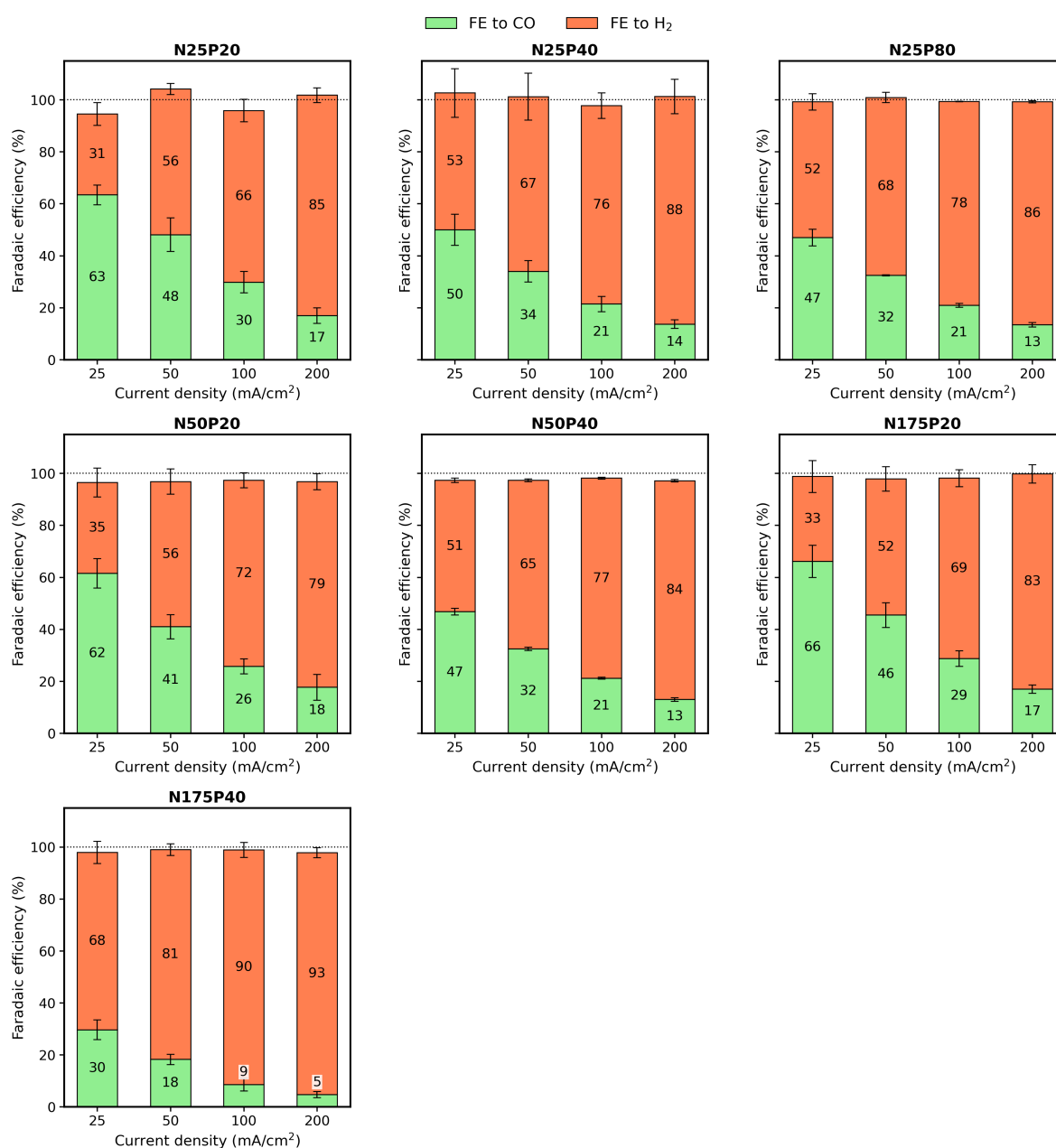


Figure 4.18: Progression in faradaic efficiency to CO and H₂ with current density for the different membranes. Error bars represent the combined error from individual measurements and the standard deviation from repeat measurements. The dotted line indicates the theoretical maximum of 100% total FE.

First, an increase in current density enhances the rate of proton transport to the cathode relative to the rate of OH⁻ generation by the CO₂RR. Proton transport through Nafion-based CELs occurs predominantly via a Grotthuss-type hopping mechanism, resulting in an exceptionally high effective proton mobility. While all ionic species experience a migrational driving force in the electric field across the membrane, the high proton mobility causes proton flux to increase more strongly with increasing cell voltage than that of other ions (see Section ??). As current density increases, the higher operating voltage therefore enhances both the rate of proton generation at the bipolar junction and the driving force for proton transport toward the cathode. At low current densities, the proton flux reaching the catalyst surface may remain sufficiently low for the OH⁻ generated by CO₂RR to neutralize incoming protons, thereby suppressing the HER. At higher current densities, however,

proton transport can outpace OH^- generation, leading to excess protons at the catalyst surface and favoring hydrogen evolution. This interpretation is consistent with the findings of Bondue *et al.*, who demonstrated that in acidic CO_2 electrolysis hydrogen evolution is governed not solely by proton availability, but by the balance between proton transport to the electrode surface and their neutralization by OH^- generated during CO_2 reduction [32]. When the rate of CO_2 reduction is sufficiently high, proton reduction can be suppressed despite acidic conditions; conversely, when proton transport exceeds the neutralization capacity of OH^- , the HER becomes dominant, lowering the FE to CO.

Second, increasing current density alters the absolute proton concentration in the CEL due to a relative increase in H^+ transport compared to alkali cation crossover. While K^+ crossover remains relatively constant with current density, the generation and transport of protons increase with cell voltage. As a result, the CEL becomes progressively more acidic at higher current densities. This effect is further amplified by the different transport mechanisms of protons and alkali cations in the CEL. Protons exhibit significantly higher mobility due to their ability to undergo hopping transport, whereas alkali cations are limited to vehicular transport. Consequently, increases in cell voltage disproportionately enhance proton flux relative to K^+ flux. While this mechanism alone does not fully explain the overall decrease in FE to CO, it provides a plausible explanation for the steeper decline observed at lower current densities compared to the more gradual decrease at higher current densities. A schematic illustration of this effect is shown in Figure 4.19. Similar behavior was reported by Li *et al.* in their modeling study of a BPM-based membrane electrode assembly, where increasing the H^+ transference number was found to suppress K^+ crossover, while the HER was identified as a potential unintended consequence [13].

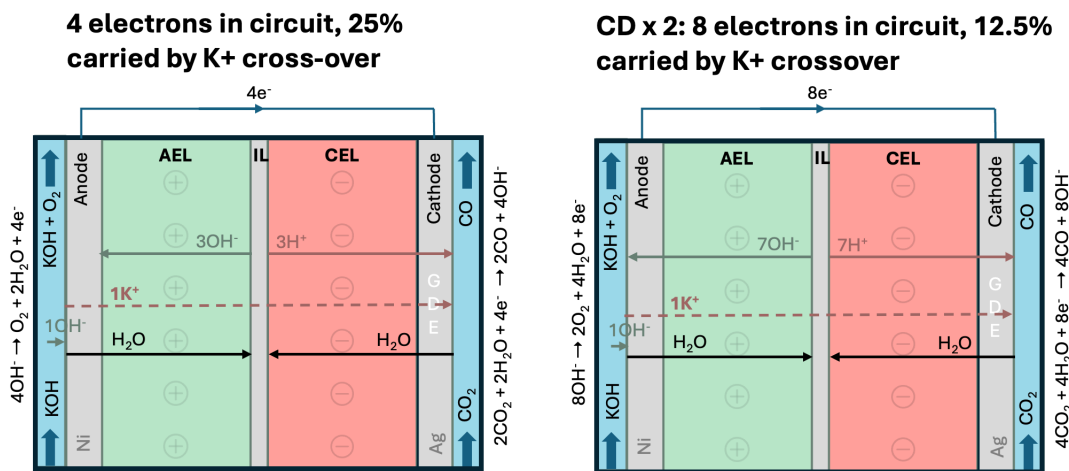


Figure 4.19: Illustration of the proposed effect of higher current density on acidity: at lower current density, a percentually larger amount of current is carried by K^+ . While the K^+ flux does not change much with current density, but the H^+ flux does, the CEL gets more acidic with current density.

Third, mass-transport limitations of CO_2 may further contribute to the loss of CO selectivity at high current densities. A decrease in FE to CO with increasing current density has also been reported for AEM-based CO_2 electrolysis systems, despite the absence of a proton-generating CEL [49]. In those systems, Zhao *et al.* attributed the shift in selectivity to a local buildup of OH^- at high current densities, which reacts with CO_2 to form HCO_3^- , thereby reducing the local availability of CO_2 at the cathode. Under such conditions, water reduction becomes kinetically favored, allowing the HER to dominate. A similar limitation of CO_2 availability, driven by local OH^- accumulation, may also play a role in the present BPM-based system. In summary, the observed decrease in FE to CO with increasing current density is most likely the result of an interplay between multiple coupled phenomena: (i) an increased rate

of proton transport relative to OH^- generation, (ii) a rising proton concentration in the CEL due to disproportionate enhancement of H^+ transport compared to alkali cation crossover, and (iii) transport limitations of CO_2 at the cathode arising from local OH^- accumulation. The relative dominance of CO_2 RR and the HER therefore depends on a delicate balance between transport processes and reaction kinetics. While high current densities are essential for industrially relevant CO_2 electrolysis, these findings highlight an important trade-off in the current state of the technology: increased throughput is accompanied by a significant penalty in energy efficiency for CO production.

As noted previously in the context of mitigating the trade-off between FE to CO and membrane layer thickness, the observed current density effects are also likely to be catalyst dependent. Consequently, the earlier recommendation to further explore alternative catalyst materials for BPM-based CO_2 electrolysis—particularly in combination with the Nafion/PiperION membranes studied here—applies equally to the mitigation of current-density-induced losses in CO selectivity.

4.3.3. Current density effects on cell voltage

All PiperION/Nafion membranes exhibited similar current-voltage behaviours for current densities up to 500 mA/cm^2 , as shown in Figure 4.20.

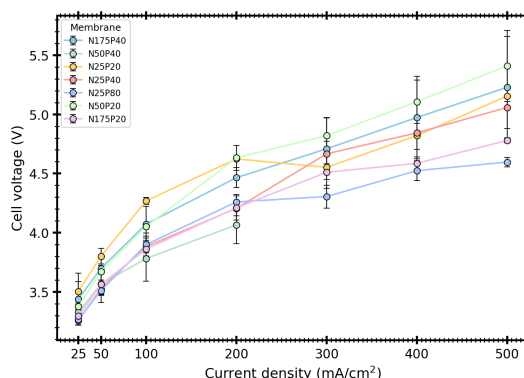


Figure 4.20: Current-voltage behaviour of the Nafion/PiperION membranes at current densities ranging from 25–500 mA/cm^2

At lower current densities, the voltage increases more steeply with current density, which can be attributed to the activation of water dissociation at the bipolar junction and associated interfacial overpotentials. At higher current densities, the voltage increases more linearly with current density, indicating a transition to an ohmic-dominated regime in which water dissociation is sufficiently efficient and the voltage response is primarily governed by ionic resistances. A second limiting current plateau was not observed within this range. This absence can be explained either due to either the use of a high-quality WDE catalyst layer, or the conductive nature of the Nafion/PiperION materials, which enhances water transport and delays the onset of mass-transport limitations. In any case, this current-voltage behaviour is promising for operation at higher current densities. Further research could focus on identifying the current density at which water dissociation becomes mass transport limited.

While the current-voltage behavior observed here is favorable for operation at higher current densities, it must be considered in the broader context of overall system performance. As discussed in the previous section, increasing current density is accompanied not only by higher cell voltages, but also by a decrease in the FE to CO. In contrast, the WDE improves with increasing current density. Together, these trends highlight an inherent trade-off in BPM-based CO_2 electrolysis: operation at higher current densities enhances water dissociation efficiency and throughput, but comes at the cost of increased electrical losses and reduced CO selectivity.

This suggests that an optimal operating window likely exists in which the combined effects of cell voltage, faradaic efficiency, and water dissociation efficiency are balanced. Identifying this optimum requires a system-level perspective that extends beyond electrochemical performance alone. Future work should therefore focus on evaluating the economic implications of operating at different current densities, for example by quantifying the cost trade-offs associated with higher voltages and lower FE to CO versus improved WDE and higher production rates. Such analyses could provide guidance on selecting operating conditions that minimize overall energy and production costs while maintaining industrially relevant performance.

4.4. Performance metrics comparison to Fumasep

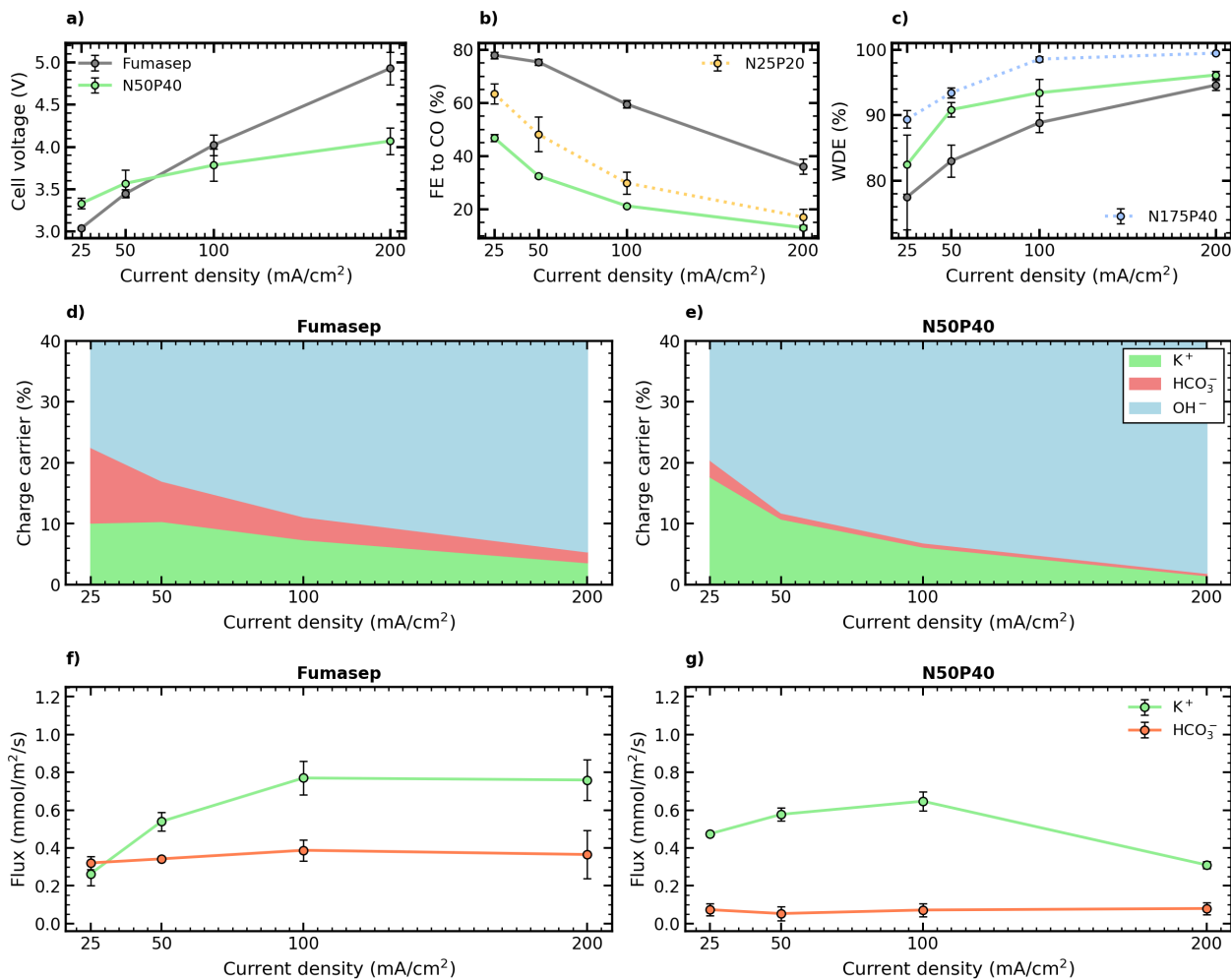


Figure 4.21: Comparison of performance metrics for the Fumasep FMB membrane and the Nafion/PiperION membranes. N50P40 is used as main comparing membrane due to its similar thickness and symmetry. Dotted lines are used to indicate the best performing Nafion/PiperION membranes for each performance metric. **a)** Comparison of cell voltage behaviour with current density. **b)** Comparison of FE to CO with current density. **c)** Comparison of WDE with current density. **d-e)** Comparison of relative charge carrier fluxes across the membrane with current density. **f-g)** comparison of absolute charge carrier fluxes across the membrane with current density

Figure 4.21 shows a comparison of the voltage, FE, and co-ion crossover behaviour of Fumasep compared to one of the Nafion/PiperION membranes. The used Fumasep membrane was determined by Scanning Electron Microscopy (SEM) to be approximately 100 μm thick (As shown in Appendix Figure B.5), with generally symmetrical AEL and CEL. Therefore, for this comparison N50P40 was used. Figure B.6 and Figure B.7 in the

Appendix show a comparison of the relative and absolute charge carriers of Fumasep to all other membranes.

As is visible in Figure 4.21a, At lower current densities the Fumasep membrane outperforms N50P40. At higher current densities, the voltage starts to strongly increase with current density. Figure 4.22 shows Fumasep's current behaviour compared to N25P40 (no higher current density tests were performed for N50P40). This suggests that the performance of Fumasep BPMs quickly becomes significantly limited by either water transport or WD kinetics at higher current densities. This observation was also noted in literature by Lucas et al [27], when comparing Nafion/PiperION membranes to Fumasep BPMs in electrodialysis. This makes sense when keeping in mind that Fumasep was developed for applications that only require current densities up until 100 mA/cm². For application in CO₂ electrolyzers on an industrial scale, performance at higher current densities is necessary. Therefore, these results show that Fumasep's potential for this is limited. For many of the Nafion/Piperion membranes, voltages only slowly increased up until 500mA/cm², as shown earlier in Figure 4.20. This means that in terms of conductivity and WD catalyst the membranes synthesized in this work show good promise.

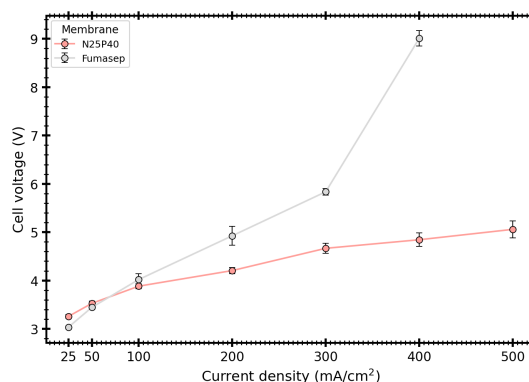


Figure 4.22: Changing current-voltage behaviour with current density for Fumasep and N25P40.

Figure 4.21b shows a comparison of Faradaic Efficiency for Fumasep and N50P40. This is where Fumasep greatly outperforms the membranes studied in this work. Faradaic Efficiencies for Fumasep were consistently 30-40% above FEs reported for the other membranes. An explanation for this likely has to do with the different chemical composition of the two membranes. It could be that Fumasep's CEL is less conductive to protons than Nafion. If protons can diffuse less quickly through the CEL, as discussed in Section 4.3.2, the CO₂RR is preferred over the HER, resulting in better FEs to CO. Additionally, the higher carbon crossover in the Fumasep membrane could also mean that the CEL is less acidic, as less HCO₃⁻ is converted back to CO₂ by H⁺, and more crosses over. Interesting to note here is that Fumasep membranes do have a very good conductivity at low current densities, before the voltage becomes limited by wd behaviour. This suggests a possibility of making a membrane that is very conductive, yet does not transport protons so quickly they infer with the FE to CO.

Figure 4.21c shows a comparison of the WDE of N50P40 and Fumasep. In terms of WDE, the Nafion/Piperion membranes outperform Fumasep, although the effect is more pronounced at lower current densities. This makes sense when we look at the crossover behaviour (Figure 4.21d-g), as for both membranes a decreasing fraction of the current is carried by co-ions with current density. The WDE values obtained for the thicker BPM configurations in this work also exceed those reported for Fumasep membranes in literature under comparable conditions [14]. These results demonstrate that BPM performance can be systematically tuned to achieve water dissociation efficiencies

approaching industrially relevant values.

Aside from a higher overall crossover, leading to a worse WDE compared to the Nafion/PiperION membranes, The Fumasep membrane also shows a different distribution in current carried by co-ions. In the Nafion/Piperion membranes, a large fraction of the current is carried by K^+ , whereas for Fumasep, a significantly larger portion can be attributed to carbonate crossover, with $/K^+$ ratios of about 1 compared to 0.1. In literature this ratio was reported to be even higher, with Prats Vergel et al consistently reporting $/$ ratios of about 2 [14]. The difference of their Fumasep results with ours can likely be attributed to differences between Fumasep batches. The difference in the relative importance of HCO_3^- and K^+ as charge carriers through the membrane can likely, again, be attributed to membrane layer chemistry. A higher co-counter selectivity of Nafion, engineered to mainly conduct protons, could explain the lower HCO_3^- transport. In case, as proposed in Section 4.3.1, CO_2 actually crosses the bipolar membrane junction in dissolved state rather than as an ion, it could mean that Nafion has a lower water uptake than the Fumasep CEL, therefore allowing less CO_2 to dissolve and cross over. Importantly, these results make it clear that layer chemistry can significantly affect both the magnitude of crossover fluxes through the membrane and the nature of the species crossing over. Further research should be conducted to unravel the exact origin of the difference, so it can be used to tune membranes for specific properties. Modelling studies could provide more insight into the nature of the ion fluxes through the membrane, and specific membrane parameters affecting this transport, which could be used to select membranes for further experiments.

4.5. First limiting current

LSV measurements revealed a clear first limiting current plateau for all investigated membranes. A representative LSV curve illustrating the identification of the first limiting current plateau is shown in Figure 4.23.

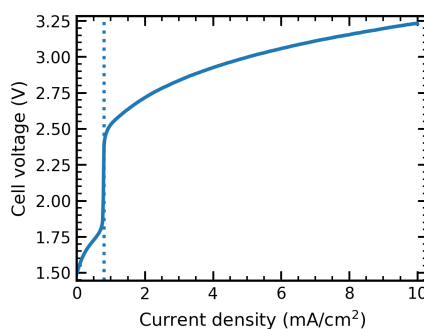


Figure 4.23: LSV curve showing the appearance of a transport-limited plateau, indicated with a curved line. Data shown is from N25P80.

Figure 4.24 shows the correlation between the first limiting current density and the K^+ and HCO_3^- fluxes for all synthesized membranes. The K^+ flux values at 25 mA cm^{-2} were taken as an approximation of the K^+ flux at the limiting current density, as K^+ flux was shown to be approximately independent of current density and no direct measurements were performed at the limiting current densities.

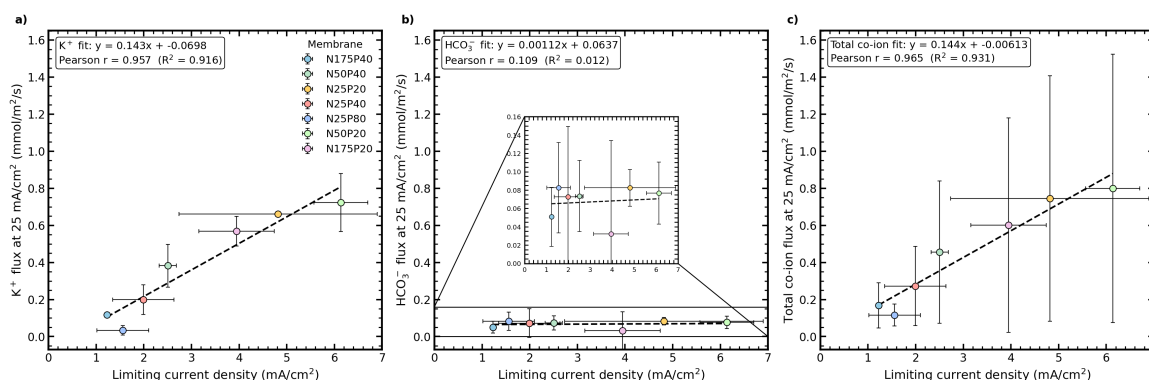


Figure 4.24: Limiting current density versus co-ion fluxes through the membrane including trend lines. The flux values at 25 mA/cm² were taken as an approximation of the flux at the limiting current density, as the co-ion fluxes were shown to be approximately independent of current density and no direct measurements were performed at the limiting current densities. Error bars represent the standard deviation of the limiting current density per membrane and the uncertainty of the average co-ion fluxes. **a)** K⁺ flux vs current density. **b)** HCO₃⁻ flux vs current density. The axes were made to match the axes of plot b&c, so the zoom-in was added for extra clarity. **c)** Total co-ion flux vs current density.

A strong correlation is observed between the K⁺ flux and the first limiting current density, with an R^2 value of 0.916. Membranes exhibiting higher K⁺ fluxes consistently show higher limiting current densities. In contrast, no clear correlation is observed between the limiting current density and the HCO₃⁻ flux, as shown in the right-hand panel of Figure 4.24.

This behavior can be rationalized based on established understanding of bipolar membrane operation. Below the first limiting current density, charge transport is reported to be dominated by co-ion migration rather than by water dissociation [23, 53]. As the co-ion flux in the present system is largely diffusion-controlled and therefore relatively insensitive to current density, it follows that the magnitude of the co-ion flux sets the current density at which the transition to water dissociation occurs.

The strong correlation between limiting current density and K⁺ flux indicates that K⁺ is the primary co-ion governing the onset of the limiting current in the synthesized membranes. This conclusion is consistent with earlier observations in this work (Figure 4.15), which showed that K⁺ is the dominant co-ion charge carrier across these membranes. It is also in agreement with findings by Bui *et al.* [23], who demonstrated that the position of the limiting current in bipolar membranes is primarily governed by properties of the anion exchange layer. In the present study, the K⁺ flux was shown to be mainly dictated by AEL thickness, providing a direct mechanistic link between AEL properties, K⁺ transport, and the first limiting current density.

These results suggest that the first limiting current density can serve as a practical indicator for K⁺ crossover in asymmetric BPMs. Given the strong relationship between K⁺ flux and water dissociation efficiency, the limiting current density may therefore be used as a rapid screening parameter to assess membrane performance when optimizing WDE. Linear sweep voltammetry measurements required to determine the limiting current density are comparatively fast, whereas direct crossover measurements relying on titrations are more time-consuming. As such, the limiting current density provides a useful proxy for evaluating co-ion transport behavior during membrane development. However, the absence of a correlation between the limiting current density and HCO₃⁻ flux indicates that this approach is not suitable for assessing carbonate rejection, which may be a critical parameter in specific CO₂ electrolysis applications. This further emphasizes that the relevance of the limiting current density as a diagnostic tool depends on which co-ion dominates charge transport, which in turn is governed by membrane chemistry and structure.

5

Conclusion

This thesis investigated how independent variation of the anion-exchange layer (AEL) and cation-exchange layer (CEL) thickness in asymmetric bipolar membranes influences ion transport, key performance metrics and trade-offs in dry-cathode, reverse-bias BPM CO₂ electrolysis. By systematically studying Nafion/PiperION-based membranes with different layer thicknesses, this work aimed to clarify how membrane architecture shapes crossover behaviour, water dissociation efficiency, Faradaic efficiency toward CO, cell voltage, and limiting current density.

5.1. Key findings and implications for BPM electrolyzer design

This work demonstrated that asymmetric bipolar membrane design provides a practical means to selectively influence transport pathways in CO₂ electrolysis. Increasing AEL thickness strongly suppressed K⁺ crossover, while increasing CEL thickness effectively reduced the transport of carbon-containing species across the membrane. These effects could be tuned largely independently, confirming that cation and carbon crossover respond differently to membrane architecture. However, complete decoupling was not achieved, as K⁺ transport also exhibited a weaker dependence on CEL thickness, indicating intrinsically coupled transport behavior in the present system. These transport trends translated directly into performance metrics. Water dissociation efficiency improved with increasing membrane thickness, particularly with thicker AELs, demonstrating that in the Nafion/PiperION system studied here, WDE is primarily governed by K⁺ crossover. Thicker membranes allowed for near industrially relevant WDE's to be reached, indicating that the WDE can actually be effectively improved by asymmetrically varying layer thicknesses, especially the AEL. At the same time, the faradaic efficiency toward CO decreased with increasing AEL thickness, consistent with reduced alkali cation availability at the cathode. This establishes a clear trade-off between water dissociation efficiency and CO selectivity. Carbon crossover, by contrast, could be mitigated through increased CEL thickness, with a comparatively smaller impact on voltage and CO selectivity within the experimental uncertainty. Together, these results show that asymmetric thickness variation enables prioritization of specific performance objectives, but does not allow simultaneous optimization of all metrics.

Current density emerged as an additional system-defining parameter. Increasing current density reduced overall crossover and improved water dissociation efficiency, yielding values approaching those required for industrially relevant operation. However, higher current densities were also accompanied by increased cell voltages and a pronounced decrease in the faradaic efficiency toward CO. As CO selectivity directly affects both energy efficiency and CO₂ utilization, this decline represents a critical limitation of high-current-density operation in the present system. These observations reveal a fundamental trade-off between throughput, selectivity, and energy efficiency that cannot be resolved through membrane thickness variation alone.

The interdependence of membrane architecture, transport behavior, and performance metrics is summarized schematically in Figure 5.1. Asymmetric variation of CEL and AEL thickness allows partial rebalancing of trade-offs between cation crossover, carbon

crossover, water dissociation efficiency, voltage, and CO selectivity. However, these trade-offs are shifted rather than eliminated. In particular, improvements in WDE and suppression of crossover are accompanied by penalties in voltage or faradaic efficiency, highlighting intrinsic constraints at the system level.

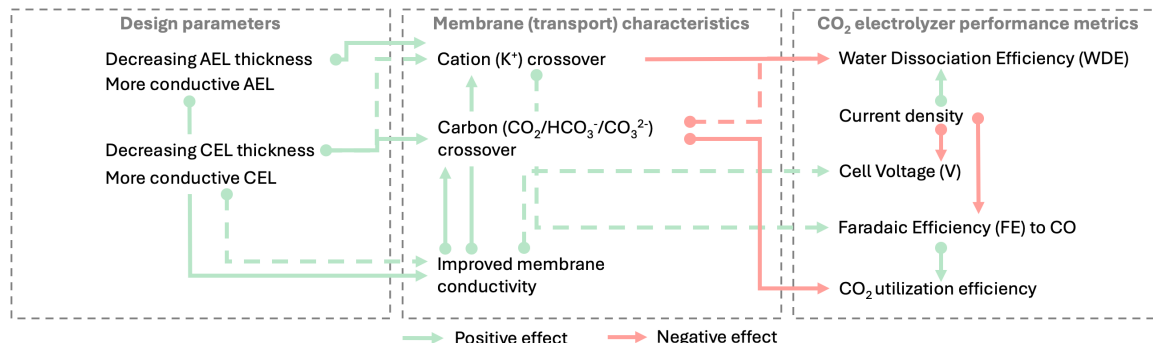


Figure 5.1: Schematic overview of the interdependent relationships between membrane design parameters, transport characteristics, and CO₂ electrolyzer performance metrics identified in this work. Green arrows indicate effects leading to an increase, while red arrows denote effects leading to a decrease. Independent variation of AEL and CEL thickness enables partial decoupling of K⁺ and carbon crossover, but complete decoupling remains limited by coupled transport phenomena. Increasing current density improves water dissociation efficiency but simultaneously increases cell voltage and reduces the faradaic efficiency toward CO.

Comparison with commercially available Fumasep bipolar membranes demonstrated that membrane chemistry plays a decisive role in transport behavior and electrolyzer performance. Nafion/PiperION-based membranes exhibited lower overall crossover and superior water dissociation efficiency at high current densities, resulting in improved anolyte stability. However, this performance advantage came at the cost of lower faradaic efficiency toward CO. In contrast, Fumasep membranes showed substantially different crossover behavior, with a larger contribution from carbon-containing species. These differences confirm that membrane chemistry, not thickness alone, determines which species dominate charge transport and how performance metrics are coupled.

The first limiting current density was found to correlate strongly with co-ion transport through the membrane. In the Nafion/PiperION system studied here, this behavior was primarily governed by K⁺ transport, indicating that the first limiting current density can serve as a diagnostic indicator for overall co-ion transport and water dissociation efficiency. However, the comparison with Fumasep membranes showed that the dominant contributors to co-ion transport depend on membrane chemistry. As a result, the limiting current density cannot be used to infer individual species fluxes or be directly generalized across different bipolar membrane systems without additional characterization.

5.2. Limitations and outlook

While this work establishes clear qualitative relationships between membrane architecture, ion transport, and electrolyzer performance, it also identifies several directions for future research.

To begin with, the results obtained are recognized as being valid solely for the particular configuration examined in this thesis. Notably, this study focused only on membrane characteristics, particularly layer thickness. Therefore, operating conditions like temperature, electrolyte composition and concentration were not investigated. A broader study, varying multiple operating conditions should be conducted to further identify an optimal configuration for CO₂ electrolysis employing the Nafion/PiperION BPMs studied in this thesis. To build on this, the observed trends in thicknesses, transport behaviour and

performance metrics cannot be readily extrapolated to systems with different membrane chemistry. This also applies to the findings on the limiting current density: while limiting current density was shown to correlate strongly with K^+ crossover in this system, its general applicability as a diagnostic metric depends on membrane chemistry and dominant co-ion species. Further research could provide more insight into how different layer chemistries behave and whether they demonstrate the same trends and performance. Notably, our research was constrained by our assembly method, using only commercially available membranes. Different preparation methods, such as spraycoating or casting could be used to make membranes with a wider range of thicknesses and different layer identities. This may also help uncover a more quantitative trend of membrane thickness with voltage, as the observed assembly-related voltage penalties could possibly be omitted.

Additionally, the progression of anolyte acidification should be studied over longer time spans. The results of the longer duration experiments presented in this thesis indicated an improved WDE performance, potentially even breaching the lower limit for industrial operation. Experiments with even longer durations, during which both crossover of species and anolyte pH are periodically evaluated, should be conducted in order to determine the true stability of the system. On the topic of improved WDE performance, the present study should also be expanded to higher current density operation. Higher current densities were shown to improve the WDE. At higher current densities, the lower limit for WDE required for industrial application may be in reach, employing the thickest Nafion/PiperION combination investigated in this thesis.

Another important limitation is that the present study gives little insight into the actual origin of observed transport phenomena within the membrane, and the effect of relative species transport on the performance metrics, beyond mere hypotheses. This calls for the development of improved models of dry-cathode CO_2 electrolyzer systems. Such models may provide a more pointed direction for further optimization of the membrane layer thicknesses and chemistries. Likewise, this study did not focus on uncovering specific contributions to the voltage and therefore does not have very specific insights on that. It is therefore yet unclear which parts of the membrane or of the overall system have the largest contribution to the observed overpotentials. Further research and characterization of individual membrane resistances using EIS in a CO_2 electrolysis setup, or membrane-only studies could break down individual components' contribution to the overall cell voltage, to identify further targets for optimization.

Finally, further research should focus on establishing quantitative relationships between tradeoffs, rather than the mere uncovering of qualitative trends as done in this thesis. More data points are needed to identify the exact relationship between layer thickness and performance metrics, and to find possible plateaus after which extra thickness does not add to more selectivity, but only adds to the voltage. To add on to this, the economical implications of the tradeoffs should be explored through techno-economic modeling, in order to determine acceptable ranges for performance metrics within the broader framework of trade-offs.

Acknowledgements

First of all, I would like to thank my daily supervisor, Max, for all the enthusiastic discussions and the replies to my texts with ideas at 12 on a Friday night. I hope this thesis provides you with ample input for your paper, and I'm very curious to hear what the future has in store - almost disappointed I won't be there to see it happen. I also want to thank David Vermaas for supervising my project and the valuable input, discussions, and occasionally funny dad jokes throughout. My gratitude also goes out to the TP research group, in particular the EFS group. I would like to thank my fellow EFS master's students, especially the ones also working at E1.090, for making the long lab days just a bit more bearable and making the failed experiments sting just a little less. I also want to thank the PhD students at EFS: Ai-Yu, Christel, Maartje, Sten & Vojtech for their valuable suggestions and discussions throughout my research, and for making me feel instantly welcome in the group. Extra gratitude goes out to Pasha, for being on my committee, and for always being there to answer my lab related questions in Max's absence. My gratitude also goes to Tom Burdyny, not only for agreeing to serve on my committee, but especially for allowing me to use the titrator in the MECS lab, which was integral for obtaining the main results of this thesis. Building on that, I would like to express my gratitude to Gerard, for showing me all necessary titrator tips and tricks and for sparring with me, and to the people at the MECS lab for making titrating just a tad bit less boring. Lastly I want to thank my dear roommates for always being there when I get home, and for making sure I still retained somewhat of a social life during my locked-in writing and experimenting days.

Ethical use of AI

For the writing of this thesis, ChatGPT 5.2 was used to improve grammar and wording of certain sentences. The generated sentences were critically evaluated to ensure they retained their intended meaning. Additionally, ChatGPT was used to find literature sources to defend or explain statements made in the research. The subsequent interpretation and analysis of these sources was done without the help of AI. ChatGPT was also used to aid in generating the plots for the results section of this thesis, by improving and generating Python code for use in a Jupyter notebook, after manual data preparation. This function proved very useful, as it allowed me to quickly generate plots and solve coding errors, in a thesis that did not have coding as an objective. Lastly, ChatGPT's imaging functions were used to alter some colours in the thesis, to keep a coherent colour scheme, and to turn some pictures into illustrations, namely in the Methods chapter. This saved me some time in improving the overall layout of the thesis.

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Appendices Contents

A	Appendix A	1
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A

Appendix A

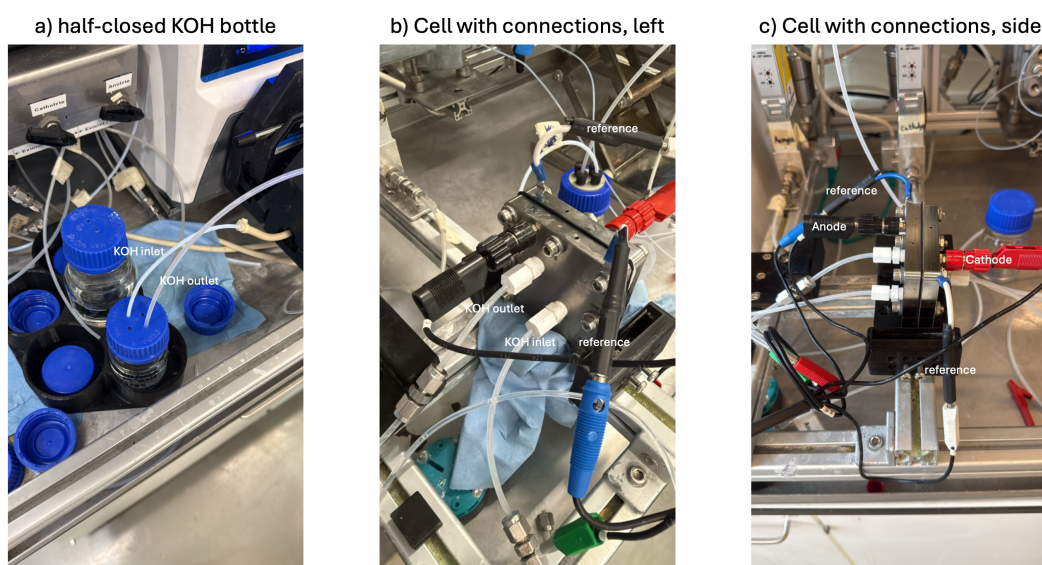


Figure A.1: Pictures showing how the setup was connected. a) illustrates the 'half-opened' anolyte bottle that allowed formed oxygen gas to escape, while b) & c) show two perspectives of the cell with connections in the setup.

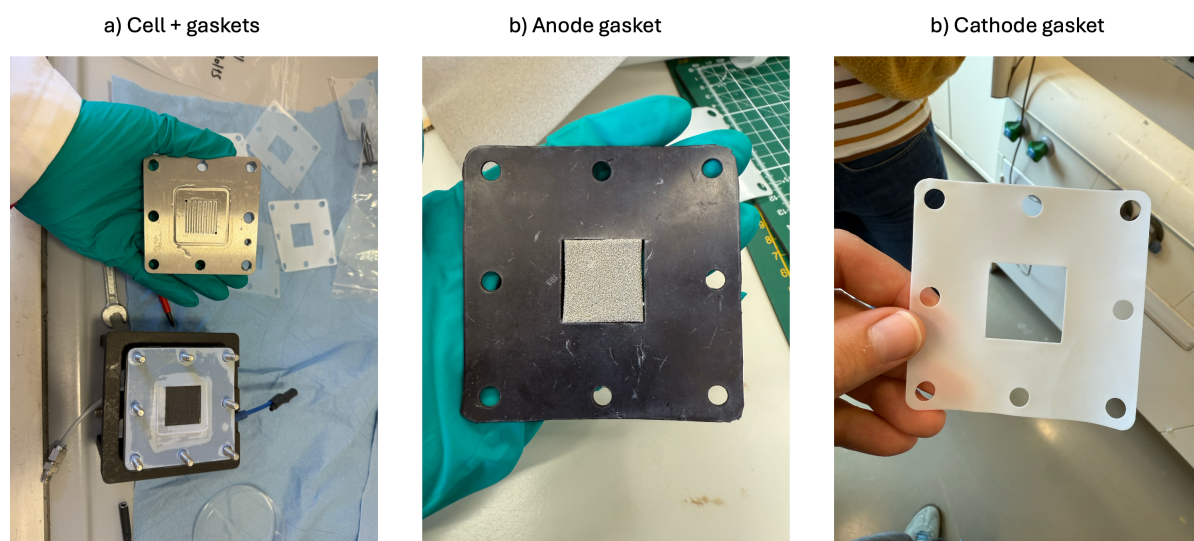


Figure A.2: Pictures showing gaskets used in cell assembly.

B

Appendix B



Figure B.1: Salt formation in flow field and on GDE cathode after running the Fumasep membrane chronopotentiometry tests.

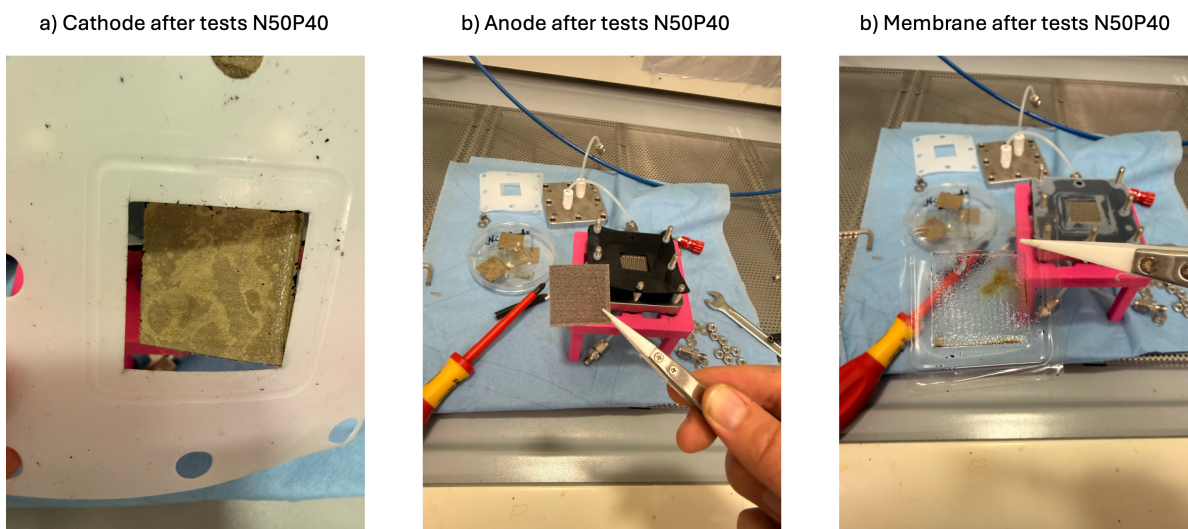


Figure B.2: Pictures showing slight discolouration of **a)** the cathode, **b)** the anode, and **c)** the membrane, after performing the complete set of experiments on N50P40.

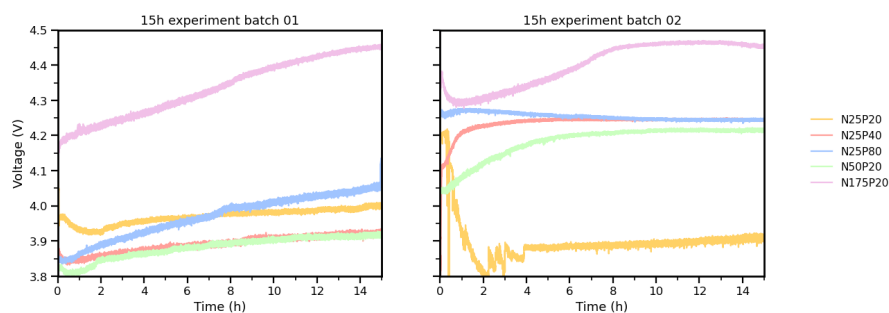


Figure B.3: Comparison of cell voltages for the different batches of 15h experiments

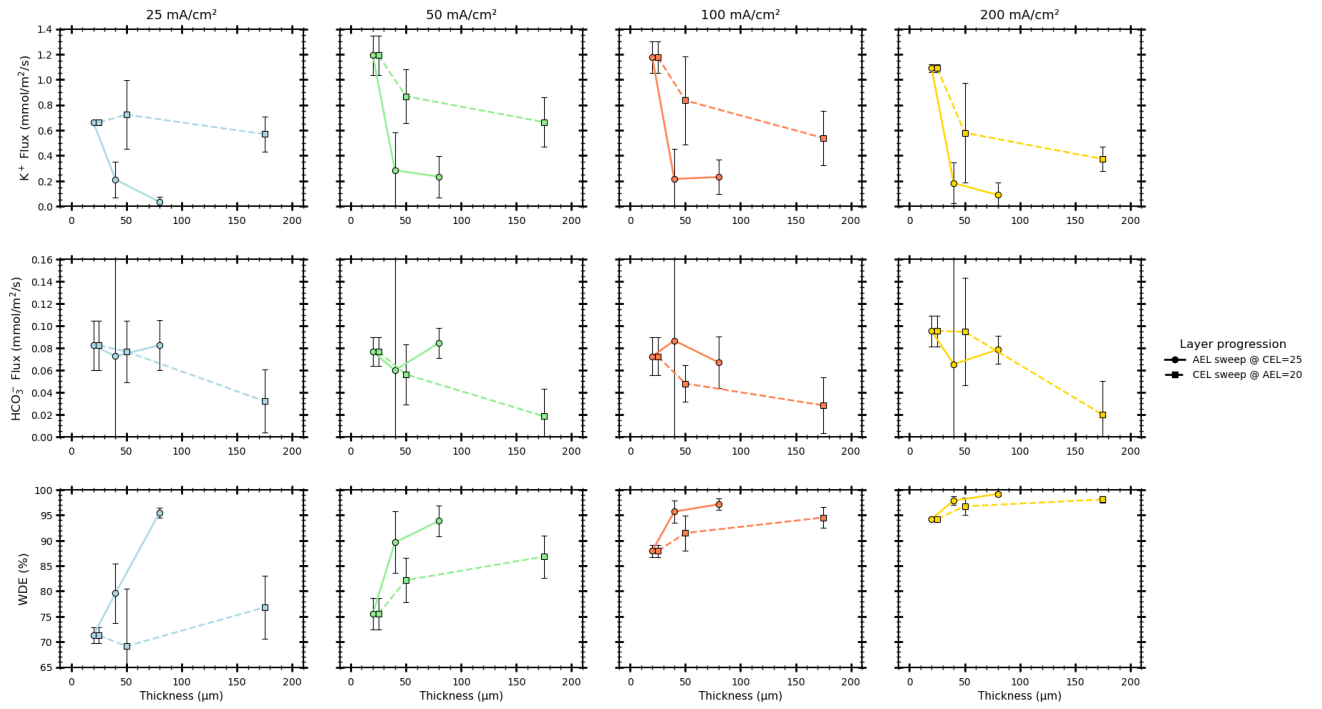


Figure B.4: Figure showing the effect of membrane layer thickness on K^+ flux through the membrane (top row), HCO_3^- flux through the membrane (middle row), and water dissociation efficiency (bottom row). Plots are shown for different current densities. The filled lines with circular markers show the progression with AEL thickness (varying between 20, 40 and 80 μm), dashed lines with square markers show the progression with CEL thickness (varying between 25, 50 and 175 μm)



Figure B.5: SEM image of the tested Fumasep BPM. The picture shows an almost symmetrical BPM, with a thickness of about 100 μm .

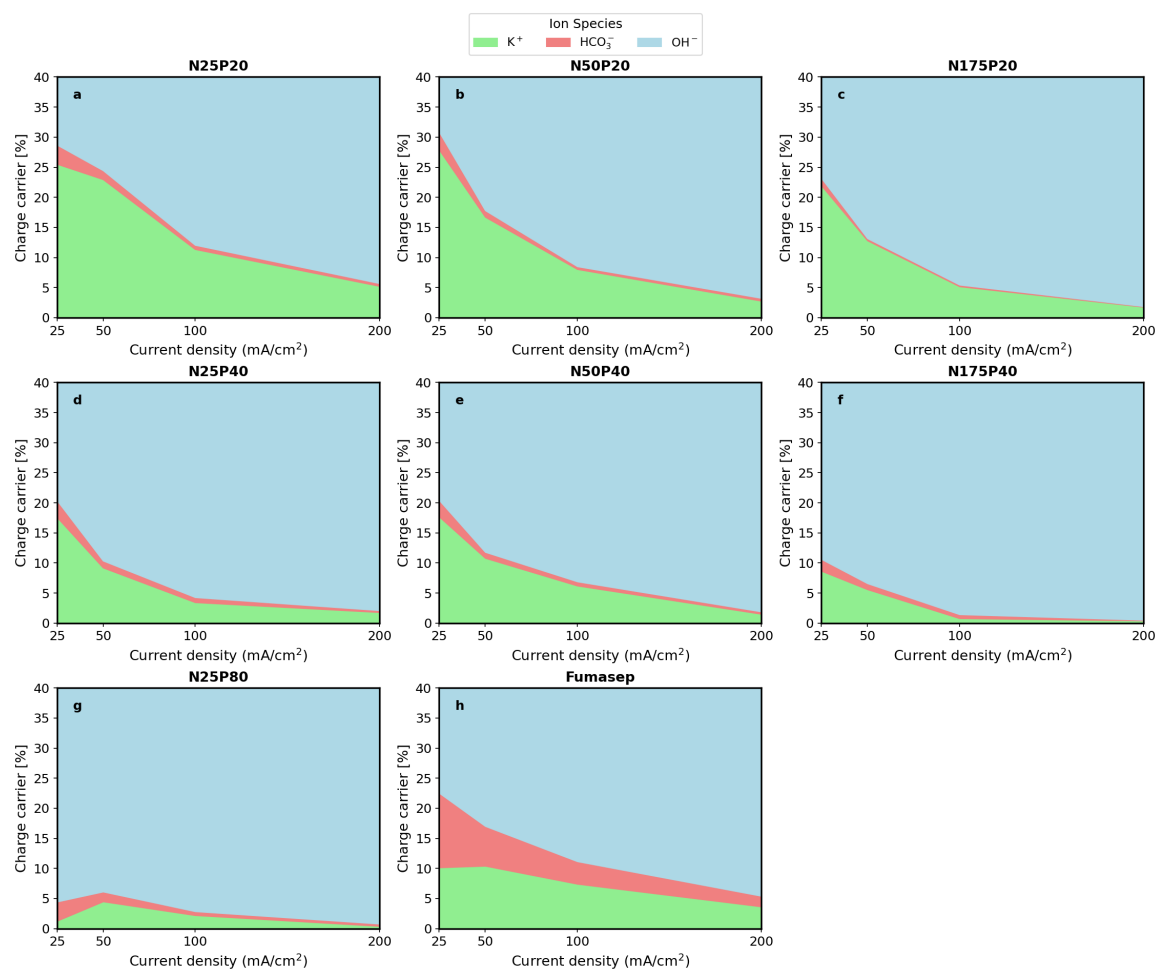


Figure B.6: Figure showing how the relative charge carriers progress with current density for the different membranes. Along the x-axis a change with CEL thickness can be observed, along the y-axis a change with AEL thickness. Plot h shows the progression for a commercial Fumasep membrane for comparison. All plots were based on 1 h crossover experiments. The figure shows the bottom 40% of the total distribution. Error bars were omitted for clarity.

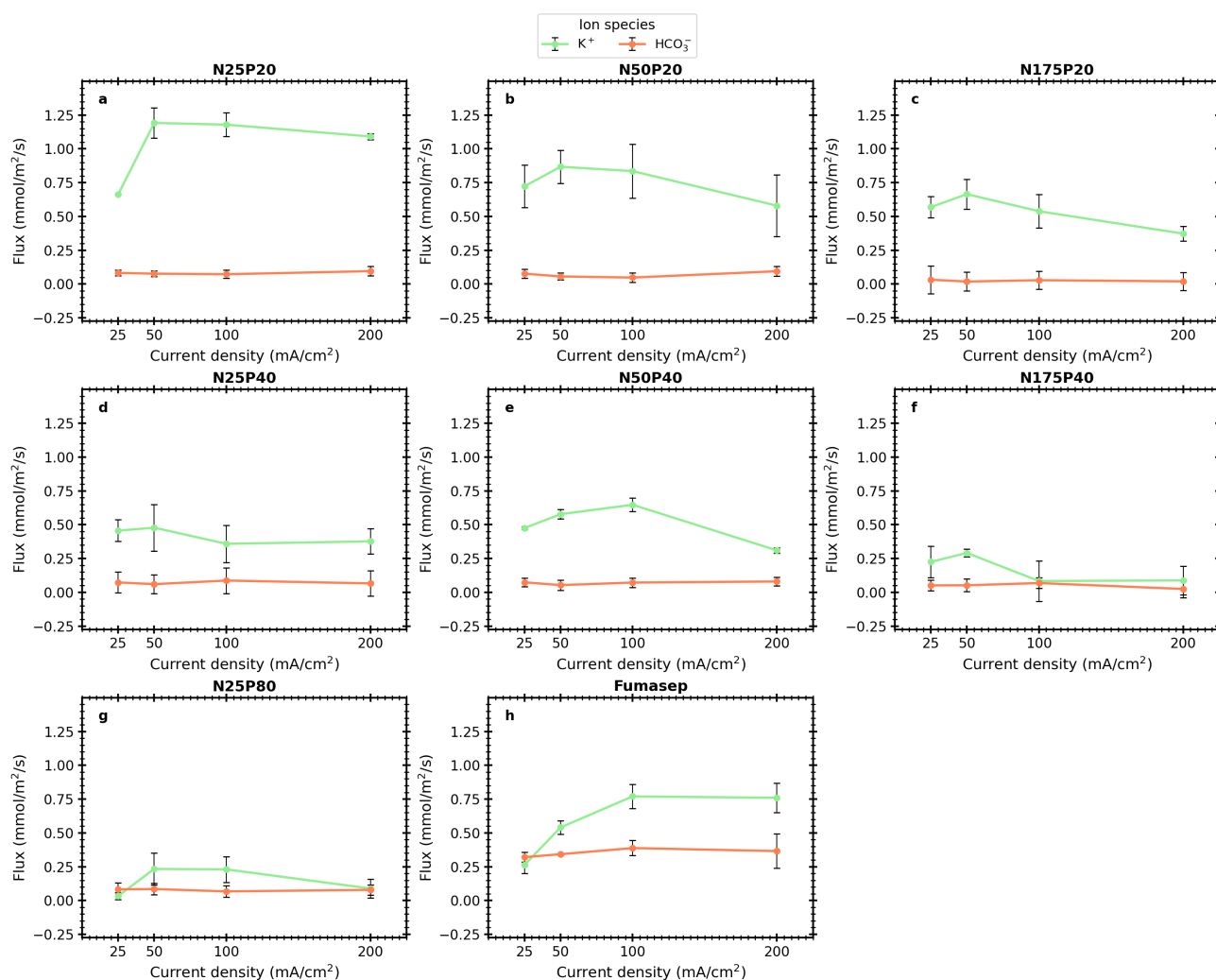


Figure B.7: Absolute K^+ and HCO_3^- fluxes as a function of current density for different bipolar membrane configurations. Data points correspond to mean values of two replicate measurements. Plot h shows the progression for a commercial Fumasep membrane for comparison. Error bars represent the combined uncertainty, accounting for both the standard deviation between replicates and measurement uncertainty.