

Co-ions Transport Phenomenon Cross Reverse-bias Bipolar Membrane in Low-temperature Zero-gap CO₂ Electrolyser

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Preface

The seven-month research project has come to an end. Time flew by during this period of intense and fulfilling work. I am delighted to have had the opportunity to engage with CO_2 electroreduction and ion exchange membranes (especially bipolar membranes), both of which are key topics in energy electrochemistry. Additionally, I am proud to have used a straightforward technique—titration—to study the fundamental topic of co-ions transport behavior across membranes.

First, I would like to express my sincere gratitude to my supervisor, **Tom** Burdyny. Thank you for offering me the opportunity to work in the Materials for Energy Conversion and Storage (MECS) group within the Department of Chemical Engineering. The people here are passionate, creative, thoughtful and possess sharp analytical minds, making it an excellent incubator for innovation.

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I also want to extend my gratitude to the committee (Dr. **David** Vermass and Dr. **Alina** Rwei). Thank you for being a part of this MSc defense and assessing my work. I look forward to obtaining further inspiration at the final stage of this project—the defense—and deepening my understanding of this topic through our Q & A session. In addition, Prof. **Fokko** Mulder give me a lot of helps, very grateful to him.

Last but not least, thanks to my family for your constantly great support—our love for each other has always been the driving force behind my journey forward.

*MU Huan
Delft, March 2025*

Abstract

The widespread use of fossil fuels since the Industrial Revolution has caused CO_2 concentrations in the atmosphere to rise exponentially, leading to severe ecological and social challenges. Large-scale renewable energy adoption is key to reducing carbon emissions, while sources like solar and wind are intermittent and variable. As a result, they require large-scale, long-duration energy storage systems. The low-temperature CO_2 electrolyser addresses this issue by using renewable electricity to convert CO_2 into fuels and chemicals, enabling both energy storage and CO_2 valorization, and closing the loop on anthropogenic CO_2 emissions.

Low-temperature CO_2 electroreduction is typically coupled with water oxidation (oxygen evolution reaction, OER) in electrolyser cells. However, the acidic nature of CO_2 triggers carbonation reactions and carbonate crossover, gradually lowering the electrolyte pH. As a result, earth-abundant catalysts like nickel (commonly used in alkaline water electrolysis) corrode when the pH drops below 12, necessitating the use of rare platinum-group metals such as iridium for OER. This reliance on scarce materials significantly limits the industrialization of low-temperature CO_2 electrolyzers.

A reverse-bias bipolar membrane (r-BPM) can theoretically mitigate electrolyte pH decline caused by carbonation reactions. Its structure, composed of a cation exchange layer (CEL) and an anion exchange layer (AEL), prevents co-ion crossover through Donnan exclusion. Under bias, water dissociates at the AEL-CEL junction (inter layer, IL), generating OH^- ions that replenish those consumed by the oxygen evolution reaction (OER), while H^+ ions convert (bi)carbonate back into CO_2 . Therefore, water dissociation can stabilize the electrolyte pH, allowing the use of earth-abundant OER catalysts. However, co-ions crossover cannot be entirely eliminated in practice. This thesis, therefore, investigates co-ions transport behavior (co-ions leakage) across the reverse-bias bipolar membrane.

This study investigates co-ions transport flux in a membrane electrode assembly (MEA) cell using chronopotentiometry (CP) electrolysis, target products are CO and O_2 , parasitic products are H_2 and carbonate ions. Titration is employed to measure the concentrations of cations and carbonate ions in the anolyte before and after electrolysis. Four variables are controlled: current density, anolyte concentration, operation duration, and cation identity. Co-ion transport and water dissociation collectively sustain the set current value, highlighting a trade-off between the two processes.

This study demonstrates that a high current density enhances the perm-selectivity of r-BPM, whereas an elevated anolyte concentration diminishes it. Cesium ions exert a stronger perm-selectivity reduction impact on r-BPM compared to potassium ions. Co-ion transport is governed by both diffusion and migration jointly. Furthermore, this study elucidates how four key variables influence the effective fixed charge density and perm-selectivity of r-BPM, shedding light on the intrinsic characteristic of co-ions transport across r-BPM, specifically, ion role shifting and its consequential effects.

Keywords: CO_2 electrolysis, membrane electrode assembly, reverse-bias bipolar membrane, co-ions counter-ions, water dissociation, fixed charge

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Nomenclature

Abbreviations

Abbreviation	Definition
(r-/f-) BPM	(Reverse-bias/Forward-bias) Bipolar Membrane
AEM (L)	Anion Exchange Membrane (Layer)
BPMED	Bipolar membrane electrodialysis
BPR	Back Pressure Regulator
(P)CD	(Partial) Current Density
CEM (L)	Cation Exchange Membrane (Layer)
CFL/MPL/CL	Carbon Fiber Layer/Micro-porous Layer/Catalyst Layer
CP	Chronopotentiometry
eCO ₂ RR	CO ₂ Electroreduction Reaction
EFE	Electric Field Enhancement (Effect)
EP	Equivalent Point
EOD	Electro-osmosis Drag
FE	Faradic Efficiency
GC	Gas Chromatography
GDL (E)	Gas Diffusion Layer (Electrode)
HER	Hydrogen Evolution Reaction
IEM (C)	Ion-exchange Membrane (Capacity)
IL	Inter-layer
MEA	Membrane Electrode Assembly
MFM	Mass Flow Meter
OER	Oxygen Evolution Reaction
PCET	Proton-coupled Electron Transfer
PGM	Platinum Group Metal
ppm	Part per Million
sccm	Standard Cubic Centimeters per Minute
SCR	Space Charge Region
SHE	Standard Hydrogen Electrode
SPC	Single Pass Conversion
VRE	Variable Renewable Electricity
WDR(E)	Water Dissociation Reaction (Efficiency)
WP	Working Package
WU	Water Uptake

Symbols

Symbol	Definition	Unit
A	Area	$[m^2]$
$C(c)$	Concentration	$[ppm]$ or $[mol/L]$
D	Diffusion Coefficient	$[m^2.s^{-1}]$
E & V	Electric Potential	$[V]$
F	Faradic Constant	$[C/mol]$

Symbol	Definition	Unit
J	Flux	$[\mu\text{mol.s}^{-1}.\text{m}^{-2}]$
K & K_a	Reaction Equilibrium Constant & Acid Dissociation Constant	[-]
$N(n)$	Amount of Substance	$[\text{mol}]$
P	Pressure	$[\text{Pa}]$
Q	Electric Charge	$[\text{Coulomb}]$
R	Gas Constant	$[\text{J}/(\text{mol.K})]$
T	Temperature	$[\text{K}]$
X	Fixed Charge Concentration	$[\text{mol}/\text{L}]$
$\dot{V}$	Gas Flow Rate	$[\text{sccm}]$
V	Liquid Volume	$[\text{L}]$
a	Ion Activity	$[\text{mol}/\text{L}]$
i	Current	$[\text{A}]$
j	Current Density	$[\text{mA}/\text{cm}^2]$
k	Reaction Kinetic Rate Constant	$[\text{s}^{-1}]$
k_B	Boltzmann Constant	$[\text{J}/\text{K}]$
t	Transference Number	[-]
u	Ion Mobility	$[\text{m}^2/(\text{V.s})]$
v	Ion Migration Velocity	$[\text{m}/\text{s}]$
x	Mole Fraction	[-]
z	Ion Valence	[-]
Π	Osmosis Pressure	$[\text{Pa}]$
α	Carbonation Species Fraction	[-]
δ	Diffusion Layer Thickness	$[\mu\text{m}]$
ϵ_r	Relative Permittivity	[-]
η	Solvent Dynamic Viscosity	$[\text{Pa.s}]$
λ	Thickness of Space Charge Region	$[\mu\text{m}]$
μ ($\bar{\mu}$)	(Electro) Chemical Potential	$[\text{J}/\text{mol}]$
ϕ	Potential of Electrode, Membrane and Solution	$[\text{V}]$

Introduction

1.1. Broader Contexts

Anthropogenic (human-caused) CO_2 emissions is a globally severe problem. Based on the annual report from NOAA's (National Oceanic and Atmospheric Administration of US) global monitoring lab, global average atmospheric carbon dioxide was 419.3 parts per million ("ppm" for short) in 2023, setting a new record high. The increase between 2022 and 2023 was 2.8 ppm—the 12th year in a row where the amount of carbon dioxide in the atmosphere increased by more than 2 ppm [19].

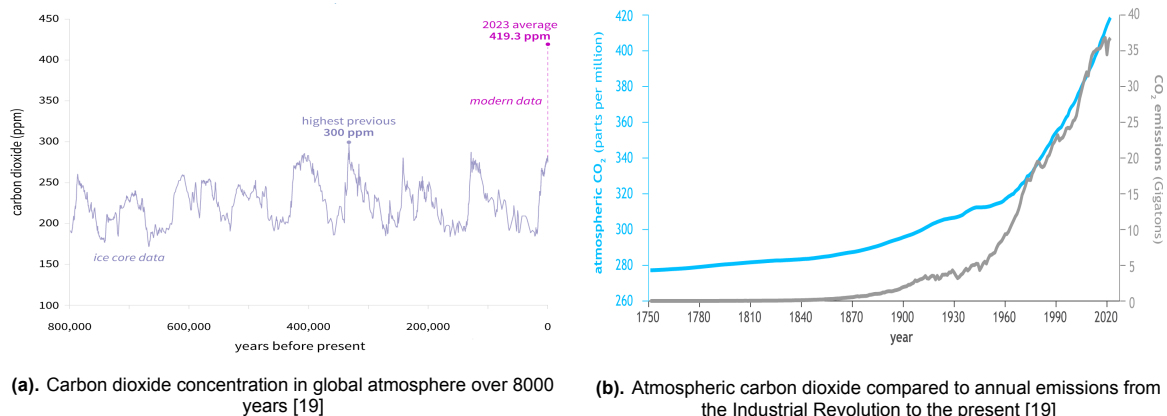


Figure 1.1: The Anthropogenic carbon emission

Figure 1.1 illustrates how human industrial civilization has released vast amounts of CO_2 into the atmosphere, exerting a profound impact on Earth's ecosystems through its own actions. The social costs of excessive carbon dioxide emissions ($SC-CO_2$) are extraordinarily high, representing the monetized value of societal damages caused by the emission of an additional metric ton of CO_2 .

As illustrated in Figure 1.2, the mean $SC-CO_2$ estimate is \$185 per tonne of CO_2 (\$44–\$413 per tCO_2 : 5%–95% range, 2020 US dollars) at a near-term risk-free discount rate of 2% [1]. As the discount rate decreases, the distribution of $SC-CO_2$ shifts to the right, with both the mean and median increasing, and the tail (95th percentile) extending further. This indicates that the severity of future climate change damages receives greater weight in the estimation.

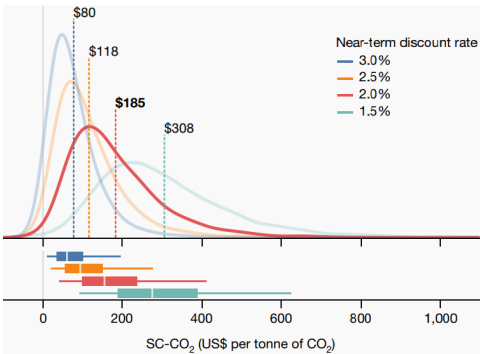
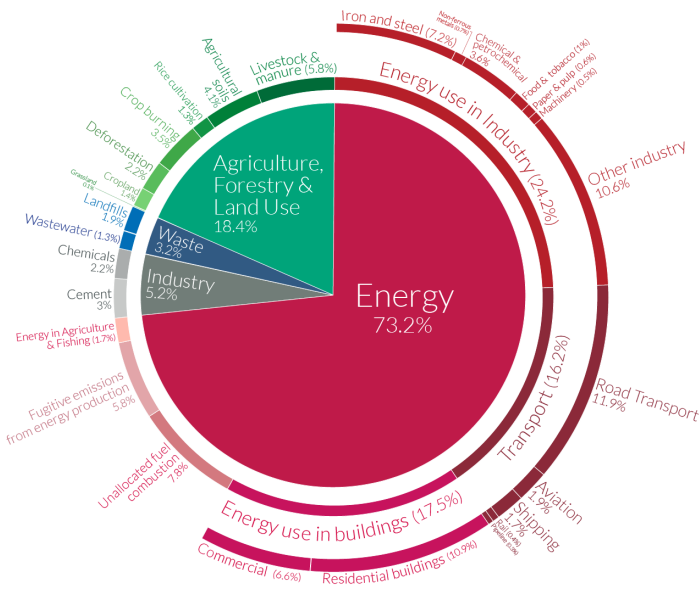
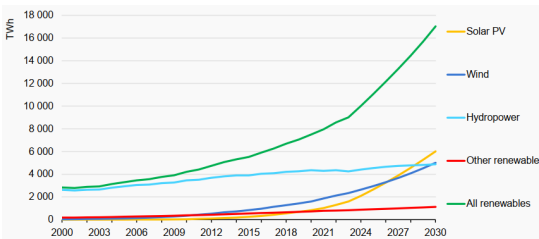


Figure 1.2: SC-CO2 distributions vary with the choice of near-term discount rates [1]

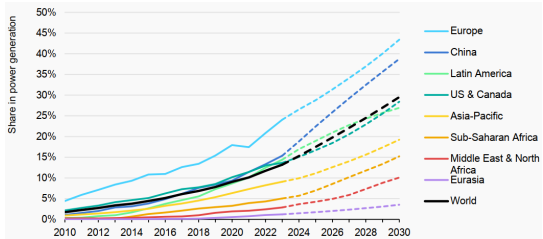
Figure 1.3a highlights that energy consumption is the dominant contributor to carbon emissions. Thus, transitioning to green energy is imperative to reduce the human carbon footprint.



(a). Global greenhouse gas emission by sectors in 2016, total emission is 49.4 billion tonnes CO2eq [20]



(b). Global electricity generation by technology, 2000-2030 [21]



(c). Annual variable renewable electricity (VRE = solar + wind) shares in power generation by region, 2010-2030, 2024-2030 values are based on the main-case capacity forecast [21]

Figure 1.3: Renewable electricity penetration for CO2 emission reduction

Figure 1.3b illustrates that, compared to hydropower, photovoltaics and wind energy possess significantly greater growth potential. Meanwhile, Figure 1.3c projects that by 2030, the share of variable

renewable electricity (VRE) in total power generation will reach nearly 45% in Europe and 40% in China, respectively.

With the rapid surge in VRE supply, its core issue—intermittency—has become increasingly apparent. The direct consequence is significant electricity price volatility, posing substantial challenges to both power generation and consumption enterprises. Low electricity prices undermine the incentive for generation companies to invest in new capacity to ensure supply, while high prices lead to soaring costs for electricity consumers, eroding their market competitiveness.

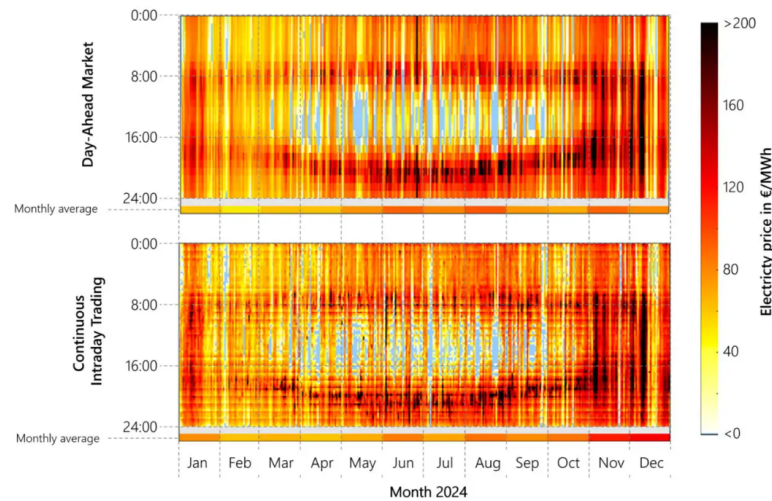


Figure 1.4: German electricity prices on the day-ahead market and in continuous intra-day trading in 2024 based on EPEX SPOT data [2]

Figure 1.4 presents the electricity prices in Germany throughout 2024 on the European Power Exchange Spot Market (EPEX SPOT) for both day-ahead and intra-day trading. With nearly 460 hours of negative prices, the historical record set last year has been broken once again [2]. While EPEX SPOT has enhanced the overall inter-connectivity of Europe's power grid, extreme price volatility remains unavoidable. Therefore, in principle, only energy storage can effectively mitigate such dramatic fluctuations in electricity prices.

With the increasing penetration of VRE, long-term and large-scale energy storage technologies have become indispensable for the grid. Currently, only chemical storage and flow batteries within electro-chemical storage are considered promising solutions. Power-to-X (P2X) is a collective term for conversion technologies that transform green electricity into carbon-neutral fuels and chemicals, thereby meeting energy storage demands, especially by effectively addressing negative electricity prices and curtailment issues. More importantly, it offers a pathway to decarbonize hard-to-abate sectors.

Green hydrogen is undoubtedly the primary product of P2X, but fuels and chemicals synthesized from carbon dioxide as a raw material (CO_2 electro-valorization) hold irreplaceable significance, primarily reflected in the following aspects:

- Liquid fuels, compared to hydrogen, are easier to store and transport globally, making it easier to effectively connect regions with abundant VRE supply to areas with high energy demand.
- Internal combustion engines remain essential for powering aviation and maritime sectors, as well as long-haul heavy-duty trucks. CO_2 -based synthetic fuels (e-fuels) serve as a key enabler for decarbonizing these sectors and can be blended with biofuels for combined use.
- CO_2 -based chemicals (e.g., ethylene) enable carbon sequestration, embodying the principles of carbon circular economy (CCE).
- E-fuels also have unique applications in the passenger car sector, despite the rapid rise of battery electric vehicles. To preserve the brand heritage and competitive edge of luxury cars, the German Automobile Industry Association (VDA) and Porsche aim to make internal combustion engine

passenger cars sustainable through e-fuels. Additionally, Geely Auto, in collaboration with Saudi Aramco, is actively promoting methanol (CO₂ based)-powered vehicles.

1.2. Cell Configurations of Low Temperature CO₂ Electrolyser

Figure 1.5 illustrates three configurations of CO₂ electrolyser cells: the H-cell (a), the flow cell (b), and the zero-gap membrane electrode assembly (MEA) cell (c). The standard H-cell, relying on CO₂ dissolved in the electrolyte without a gas diffusion electrode (GDE), operates at low current density and is primarily used for catalyst performance screening.

The flow cell consists of three chambers: a gas chamber, a catholyte chamber, and an anolyte chamber. By employing a GDE, it shortens the CO₂ mass transfer distance, significantly enhances current density, creates a more realistic local pH environment at the cathode, and facilitates the tuning of electrolyte-related factors while enabling liquid product collection for analysis. Building on the flow cell design, the MEA cell features a zero-gap configuration between the electrode and the ion exchange membrane, consisting of only two chambers: a gas chamber and an anolyte chamber. This design effectively minimizes ohmic resistance, reduces stack size, and represents the configuration commonly adopted in industrial-scale cells.

It is worth noting that, compared to the MEA cell, both the H-cell and flow cell are more suitable for implementing a three-electrode system, allowing for the acquisition of more detailed electrochemical information. Furthermore, flow cells are highly susceptible to flooding due to the GDE being soaked in catholyte, necessitating the use of hydrophobic GDE. On the other hand, MEA cells are less resistant to catholyte salt precipitation because there is almost no solvent in the zero-gap interface; however, MEA cells also face a significant risk of flooding.

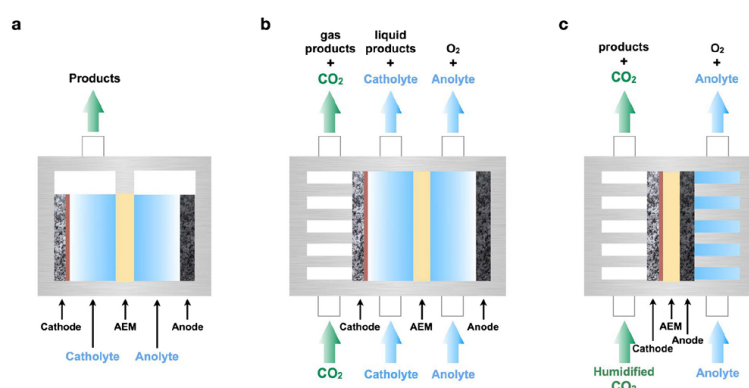


Figure 1.5: (a) Schematics for a conventional H-cell electrolyser: a cathode and an anode are separated by an anion exchange membrane (AEM) in a CO₂ saturated electrolyte. (b) A flow-cell electrolyser with a cathode (the gas diffusion electrode) and an anode, separated by an AEM. CO₂, catholyte, and anolyte are continuously flowing in separated chambers. The gas chamber uses a flow channel. (c) A membrane-electrode-assembly (MEA) electrolyser with a cathode (the gas diffusion electrode) and an anode, assembled with the AEM. Humidified CO₂ flows in the cathode chamber while anolyte flows in the anode chamber. Both chambers use flow channels [3]

1.3. Purpose and Research Questions

Nowadays, in low-temperature CO₂ electrolyzers, the anodic reaction primarily involves the oxygen evolution reaction (OER), which can occur in both acidic and alkaline environments. PGM such as iridium (Ir) and ruthenium (Ru)-based materials, have been extensively studied as benchmarks in acidic conditions due to their exceptional activity. However, their limited natural abundance significantly hinders their scalability for large-scale applications, as illustrated in Figure 1.6.

For instance, transitioning the predominant hydrogen production from hydrocarbons (currently exceeding 70 million tonnes annually) to electrochemical water splitting would require over 90 tonnes of Ir for

OER catalysis. Moreover, replacing global fossil fuel energy with hydrogen produced via water splitting would demand more than 900 tonnes of Ir. In contrast, the current global annual production of Ir is approximately 4 tonnes [22].

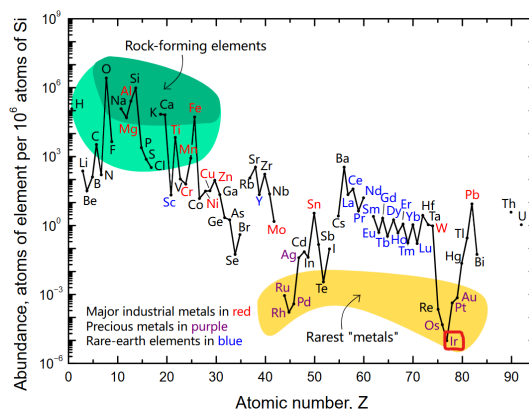


Figure 1.6: Elements abundance on earth (Wikipedia)

To unlock the potential of electrolyzers, developing earth-abundant OER catalysts is crucial. Over the past decade, significant progress has been made in PGM-free catalysts for OER in alkaline environments. For example, transition metal oxides, hydroxides, and oxyhydroxides (e.g., NiFeOOH) have become benchmarks for high-performance OER in alkaline water electrolysis.

Nickel-based OER catalysts are susceptible to corrosion when the pH falls below 12, making it crucial to maintain the alkaline electrolyte's pH above this threshold to ensure their stability—an essential factor for the viability of PGM-free catalysts. However, the key difference between CO_2 electrolysis and alkaline water electrolysis is that CO_2 is an acidic substance, which gradually lowers the electrolyte pH over time during operation, due to carbonation and (bi)carbonate membrane crossover.

In this project, a reverse-bias bipolar membrane (r-BPM) is employed to counteract the pH drop in the electrolyte. By utilizing its unique water dissociation reaction (WDR), it independently regulates the pH levels at the cathode and anode. The protons generated through WDR can revert (bi)carbonate to CO_2 in situ, while the hydroxide ions produced by WDR replenish those consumed during the anodic OER process.

A bipolar membrane consists of a cation exchange membrane (CEM) and an anion exchange membrane (AEM), which ideally allow only counter-ions to pass through while completely blocking co-ions. Co-ions are ions with the same charge as the functional groups in the ion exchange material, and as a result, they are repelled by the membrane rather than attracted to it. The same principle applies to counter-ions. This phenomenon is known as Donnan exclusion. In practice, however, there is always some membrane crossover of co-ions, which leads to a reduction in the electrolyte pH, as dictated by the principle of charge neutrality in the electrolyte.

Potassium ions, as co-ions in the AEL, cross over from the anode to the cathode, while (bi)carbonate ions, as co-ions in the CEL, cross over from the cathode to the anode. This results in a decrease in the hydroxide ion concentration in the KOH electrolyte, thereby lowering the pH. Therefore, studying the co-ions crossover behavior through r-BPM is crucial to guide the r-BPM design.

Visionary Purpose is

to realize PGM-free catalyst feasibility in low temperature CO_2 electrolyzers via r-BPM

Research Question is

to study the co-ions transport behavior cross r-BPM

The main research question can be divided into six sub-questions:

- How diffusion (driven by concentration gradients) and migration (influenced by current density) contribute to co-ions transport?
- Is there a relationship between (bi)carbonate co-ion transport and cation co-ion transport?
- How does the co-ion transport behavior vary with cumulative duration?
- How does the identity of the cation influence co-ion transport?
- What is the essential theory (key essence) of co-ions transport cross r-BPM?
- How is the CO_2 electrolyser system reliability influenced by co-ions transport?

2

Theory and Literature Review

This chapter is divided into three main parts: Part A: **Reaction**. This section encompasses Sections 2.1 to 2.3 and Section 2.9, covering topics such as eCO₂RR over silver catalysts, cation effect; acid base equilibrium, carbonation, precipitation; Faradic efficiency, hydrogen evolution reaction; and alkaline oxygen evolution reaction. Part B: **Transport**. This part focuses on Sections 2.4 and 2.5, discussing gas diffusion electrodes; the transport of ions and water, as well as flooding. Part C: **Membrane**. This section includes Sections 2.6 to 2.8, addressing topics such as fundamental electrochemistry; ion exchange membranes, Donnan potential; bipolar membranes and water dissociation reaction.

2.1. CO₂ Electroreduction Mechanism Over Ag Film and Cation Effect

2.1.1. Mechanism of CO Conversion via eCO₂RR on Ag Film Catalysts

The electrocatalytic reduction of CO₂ to CO is the most well-established one in the CO₂ electroreduction family (eCO₂RR).

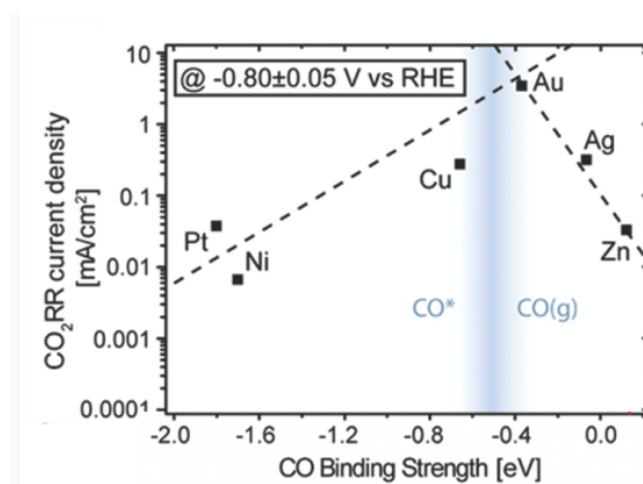
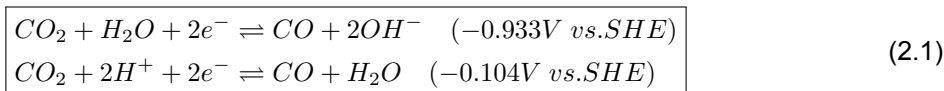
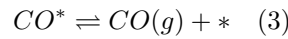
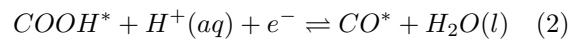
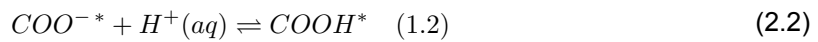
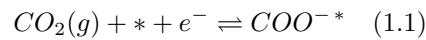
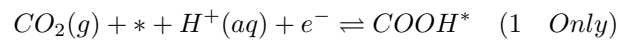


Figure 2.1: Volcano plot of partial current density for eCO₂RR vs CO binding strength [4]

A useful figure of merit to compare eCO₂RR activity among catalysts is by means of their partial current density for the eCO₂RR (to any product) at a common potential, as shown in Figure 2.1, plotting the partial current densities for the eCO₂RR at this potential versus CO binding energy, where a volcano-shaped trend emerges [4].

Figure 2.1 illustrates that gold exhibits the highest catalytic activity, attributed to its optimal CO binding strength. If the binding strength is too strong, as in the case of Pt, active sites on the catalyst surface can become occupied, leading to catalyst poisoning. Conversely, if the binding strength is too weak, as with Zn, CO cannot adsorb firmly and desorb prematurely, hindering subsequent reactions. Considering cost-effectiveness, Ag is the most commonly used catalyst for eCO₂RR conversion to CO. Meanwhile, Cu, with a stronger CO binding strength than Ag, is frequently employed for C-C coupling reactions and the production of C₂ products.

The reaction pathway of the electrochemical reduction of CO₂ to CO on silver electrodes has been proposed to consist of either three or four elementary reaction steps [5]:



In literature, two types of path mechanisms are proposed: the proton-coupled electron transfer (PCET), represented by formula (1 only), and the sequential electron-proton transfer (SEPT), represented by formulas (1.1) and (1.2). Regardless if the initial step occurs in one PCET or two uncoupled steps, a COOH* intermediate is formed and reacts with another proton and electron to form CO* and H₂O (formula 2). The final step is the desorption of CO from the catalyst surface (formula 3). Fiet and Smith utilized in situ attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) to clearly elucidate the mechanism [5].

Fiet conducted experiments at potentials of -1.40 V, -1.45 V, -1.50 V, -1.55 V, and -1.60 V vs Ag/AgCl, as these values are reported in the literature to yield favorable CO production. The conclusion is that in the potential range of -1.40 V to -1.55 V vs. Ag/AgCl, COOH* is the only reaction intermediate observed. At a potential of -1.60 V vs. Ag/AgCl, COO⁻* is also detected. Specifically, at -1.60 V, the silver catalyst becomes so negatively charged that CO₂ binds directly to the surface without requiring proton coupling in the initial reaction step. In contrast, at less negative potentials, the energy barrier for CO₂ binding to the catalyst is relatively high, requiring protons to remain close to the surface and favor the formation of COOH*.

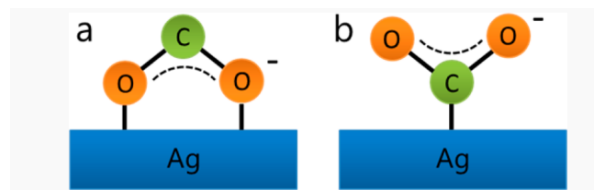


Figure 2.2: Two possible configurations of a COO⁻ intermediate bound to an Ag catalyst are depicted: bound to the surface through (a) the oxygen atoms or (b) the carbon atom [5]

Meanwhile, using the ATR-FTIR method, the adsorption configuration of the COO⁻ intermediate on the silver surface has been clarified and confirmed. As shown in Fig. 2.2, the orientation where oxygen bonds to the Ag catalyst surface is ruled out. In configuration (a), the COO⁻ intermediate cannot form COOH* and can only produce formic acid. Thus, the carbon atom is directly bonded to the Ag surface, as shown in (b).

2.1.2. The Effect of Cation on eCO₂RR

The effect of cations on eCO₂RR has become a highly active and widely studied research topic. Koper et al. confirmed that without the involvement of cations in the electrolyte, eCO₂RR cannot proceed on Ag or Au catalysts [23]. Malkani et al [24]. and Chandrashekar et al [25]. used crown ether to chelate potassium ions, effectively shielding their cationic effects, which led to a significant reduction in Faradic efficiency. Mi et al. [26] discovered that the positive fixed charges in the ionomer (QAPPT) can similarly induce cationic effects, promoting eCO₂RR. Furthermore, research has shown that as the atomic number of alkali metals in Group I increases, the cation effect becomes more pronounced. Specifically, the enhancement of Faradic efficiency follows the trend: $Cs^+ > K^+ > Na^+ > Li^+$ [27].

The mechanism underlying the cation effect can be explained through several key aspects. Firstly, cations play a crucial role in stabilizing the intermediate species ($COOH^*$) [23]. Secondly, it has been observed that repulsive interactions among hydrated cations in the Helmholtz layer significantly alter the surface charge density and the associated electric field. Among alkali cations, Cs^+ , with the smallest hydrated ionic radius, exhibits the weakest repulsion near the electrode. This leads to higher cation concentrations at the interface, resulting in a greater surface charge density and a stronger interfacial electric field, which promotes the adsorption of CO_2 [27], as shown in Figure 2.3a. Furthermore, Qin et al. [28] proposed that the presence of cations enhances the electric field within the Stern layer as the potential becomes more negative, thereby accelerating CO_2 reduction at higher overpotentials, as illustrated in Figure 2.3b. In contrast, Figure 2.3b also shows that in cation-free solutions, ϕ_M and ϕ_{OHP} shift equally, keeping the electric field (ϵ) constant, which prevents larger overpotentials from facilitating eCO₂RR.

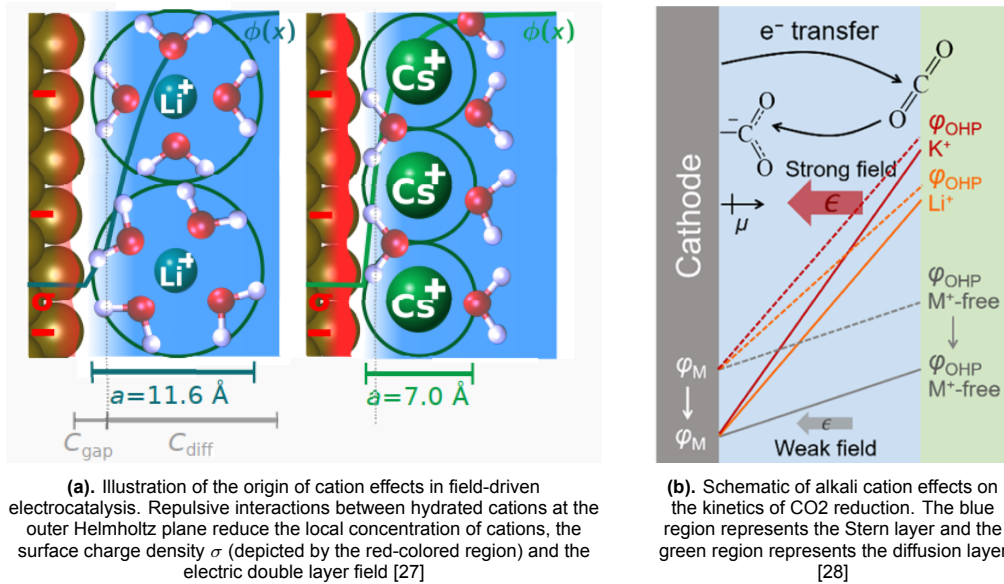
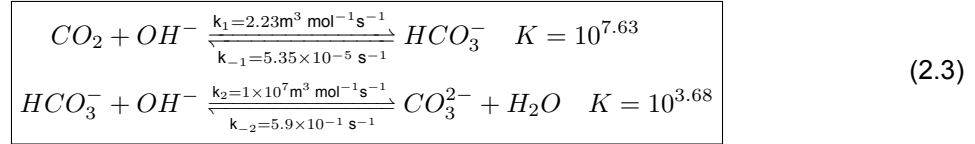


Figure 2.3: Cation Effect at Outer Helmholtz Plane

2.2. Acid-Base Equilibrium, Carbonation and Precipitation

2.2.1. Acid-Base Equilibrium of Carbonation System

Carbonation (parasitic carbon loss) represents a significant and persistent challenge in CO_2 electrochemical reduction, leading to reduced carbon efficiency and subsequent precipitation. The acid-base equilibrium theory provides an effective framework for understanding and describing carbonation. Carbonation refers to the homogeneous reaction between CO_2 and hydroxide anion, represented by the following equations [29] [30]:



Acid dissociation constant (K_a) is a fundamental concept in monoprotic acid-base equilibrium, defined as:

$$HA \xrightleftharpoons{K_a} H^+ + A^- \Rightarrow K_a = \frac{[H^+][A^-]}{[HA]} \quad \& \quad pK_a = -\log K_a \tag{2.4}$$

Where HA means a generic weak acid that is not completely dissociated, and A^- denotes the conjugated base of HA. The spices in square brackets indicates their concentration. The pK_a values at 298 K in water for formic acid (HCOOH), carbonic acid (H_2CO_3) and bicarbonate ion are 3.75, 6.35, and 10.33, respectively [31]. From formula (2.4), the Henderson-Hasselbalch equation can be derived as follows:

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \tag{2.5}$$

For the carbonation system at 298 K, this equation can be rewritten as:

$$pH = 6.35 + \log \frac{[HCO_3^-]}{[H_2CO_3]} = 10.33 + \log \frac{[CO_3^{2-}]}{[HCO_3^-]} \tag{2.6}$$

Considering mass balance constraint equation (2.7) and combining equation(2.6), the concentrations of carbonate speciation and fractional compositions (dissociation fraction, α) at any pH value can be determined (298K).

$$Sum = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad \& \quad \alpha = \frac{[specific\ carbonate\ speciation]}{Sum} \tag{2.7}$$

The fractional composition as a function of pH (commonly known as a Bjerrum plot) can be constructed using the following set of equations.

$$\begin{aligned}
 \alpha_{H_2CO_3} &= \frac{[H_2CO_3]}{Sum} = \frac{10^{-2*pH}}{10^{-2*pH} + 10^{-pH-6.35} + 10^{-6.35-10.33}} \\
 \alpha_{HCO_3^-} &= \frac{[HCO_3^-]}{Sum} = \frac{10^{-pH-6.35}}{10^{-2*pH} + 10^{-pH-6.35} + 10^{-6.35-10.33}} \\
 \alpha_{CO_3^{2-}} &= \frac{[CO_3^{2-}]}{Sum} = \frac{10^{-6.35-10.33}}{10^{-2*pH} + 10^{-pH-6.35} + 10^{-6.35-10.33}}
 \end{aligned} \tag{2.8}$$

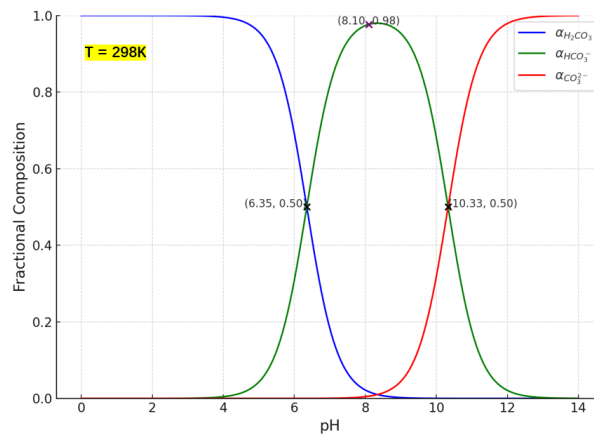


Figure 2.4: Bjerrum Plot of Carbonate System, fractional composition vs. pH, T = 298 K. The intersection points of the curves correspond to the pK_a values, while bicarbonate ion reaches its maximum fractional composition at $pH = \sqrt{6.35 * 10.33} = 8.1$

2.2.2. Carbonation Reduces Energy Efficiency of Low-Temperature CO₂ Electrolyser Indirectly

Single pass conversion (SPC) of CO₂ feedstock significantly influences the overall operational costs of electrolyzers, including both upstream (carbon capture) and downstream processes (anolyte regeneration). A low SPC renders the CO₂ electrolyser less fuel-efficient and more wasteful. When anion exchange membrane (AEM) is employed in the electrolyser, CO₂ conversion efficiency is limited to 50% in the production of CO [32]. For eCO₂RR involving multi-electron transfers to produce C₂ products, more OH⁻ is generated, leading to a lower SPC.

The following equation combines eCO₂RR and carbonation, assuming the anolyte is KOH and main product is CO only,

$$(1 + x + y)CO_2 + H_2O + 2e^- \rightarrow CO + 2(1 - x)OH^- + xCO_3^{2-} + yCO_2$$

$$SPC = \frac{1}{1 + x + y} \% \quad (2.9)$$

$$Reacted\ CO_2\ Fraction = \frac{1 + x}{1 + x + y} \%$$

Here, x and y represent the ratios of CO₂ involved in carbonation and CO₂ directly vented at cathode without participating in the reaction, respectively, relative to the CO₂ involved in eCO₂RR.

Considering the side product is H₂, the values of x and y can be determined using the volumetric concentration data (C in ppm) obtained from gas chromatography and the volumetric flow rate information (V in sccm) measured by the inlet and outlet mass flow meter (MFM), respectively.

$$x = \frac{V_{inlet} - (V_{outlet} - C_{H_2} * V_{outlet})}{C_{CO} * V_{outlet}} \quad (2.10)$$

$$y = \frac{V_{outlet} - C_{H_2} * V_{outlet} - C_{CO} * V_{outlet}}{C_{CO} * V_{outlet}}$$

Using calcium looping for carbon capture from air as an example, the energy required to sequester one ton of atmospheric CO₂ is 8.81 GJ of natural gas, or alternatively, 5.25 GJ of natural gas combined with 366 kWh of electricity [33]. When KOH is used as the anolyte to facilitate the use of earth-abundant materials, such as NiFe-based catalysts for the oxygen evolution reaction (OER), carbonation and carbonate crossover gradually lower its pH to a threshold that triggers nickel corrosion, making anolyte regeneration essential. In a bipolar membrane electrodialysis (BPMED) process, KOH can be electrochemically regenerated from K₂CO₃ accompanied by release of CO₂, with an energy consumption of 215 kJ per mole of CO₂ [34]. In addition, carbonation reduces the chemical potential of hydroxide ions at the anode, which increases the required thermodynamic potential for OER [35] and lower system conductivity [36].

Designing carbon-efficient carbon dioxide electrolyzers hinges on creating an acidic micro-environment at the cathode to facilitate the conversion of (bi)carbonate back to CO₂. This can be achieved using a cation exchange membrane (CEM) or a reverse-based bipolar membrane (r-BPM). However, acidic media enhance the hydrogen evolution reaction (HER), making it essential to balance carbonation and HER through engineering of the local cathodic environment. This topic will be elaborated upon in the subsequent section on the hydrogen evolution reaction.

2.2.3. Salt Precipitation in Low Temperature CO₂ Electrolyser

Salt precipitation at cathode poses a significant challenge in electrochemical CO₂ reduction electrolyzers, as it reduces the active area, leads to flooding, and impairs gas transport, ultimately compromising long-term durability and industrial viability [37]. This issue is particularly pronounced in MEA setups, where the zero-gap configuration results in a minimal electrolyte volume, making solute precipitation more likely. It represents another side effect of carbonation while also being an inevitable consequence of cation migration. Cation migration acts as a double-edged sword: on one hand, it enhances eCO₂RR through the cation effect, but on the other hand, it contributes to the formation of precipitates.

For the issue of precipitation, the solubility of (bi)carbonate species serves as a key piece of foundational information. Firstly, for the same type of cation, carbonate species exhibit significantly higher solubility than bicarbonate species. Secondly, the solubility of cesium ions is greater than that of potassium ions. At 20°C, the solubility values (in mol/L) are as follows: Cs_2CO_3 (8.01) > K_2CO_3 (7.93) > $CsHCO_3$ (3.49) > $KHCO_3$ (2.24) [37].

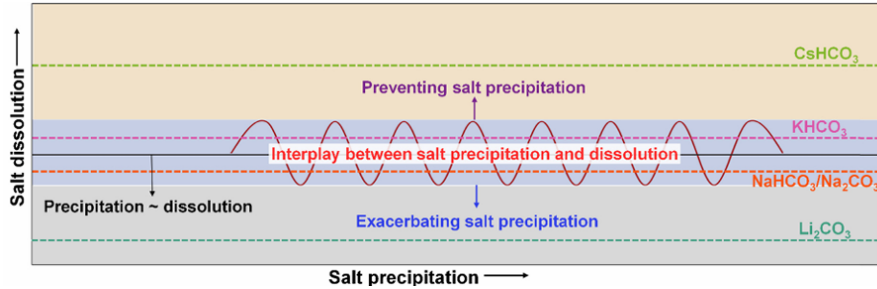


Figure 2.5: Qualitative display of interplay between salt precipitation and dissolution phenomenon with different alkali (bi)carbonate salts. The dashed lines represent the solubility limit of respective alkali cation (bi)carbonate salts [6]

In the discussion of precipitation, two issues deserve particular attention: cation back diffusion and salt re-dissolution. In MEA systems, the cation concentration near saturation is significantly higher than that in the anolyte, which may overcome migration resistance and diffuse back into the anolyte. Additionally, the presence of salt enhances capillary forces, driving water into the pores of the GDE, where the salt can be re-dissolved [6], as illustrated in Figure 2.5.

The mitigation of precipitation includes the following approaches: firstly, increasing the operating temperature, regularly flushing the cathode, and using a low-concentration anolyte to suppress diffusion are three effective methods. Secondly, one can choose the cation identity, such as cesium (Cs), which offers further potential to reduce the anolyte concentration due to its favorable contribution to Faradic efficiency. However, the drawback is its high cost. In addition, local pH and carbonation can be reduced by applying low current density pulses [38], which also promote cation back diffusion and (bi)carbonate transport. Using CEM and pure water anolyte, combined with a positive fixed charge ionomer to conduct cation effect requires the anode to use expensive and scarce Ir_2O , making it unfeasible.

2.3. Faraday Efficiency and Hydrogen Evolution Reaction

2.3.1. Faraday Law and Faraday Efficiency

Electrolysis adheres to the Faraday law. To complete the circuit, the anode undergoes a continuous oxidation reaction, losing electrons that are pumped by the external power source to the cathode, where they are consumed through a reduction reaction. The amount of reactants (and/or product) involved in the Redox reaction is directly proportional to the electric charge (in coulombs) passing through the external circuit. This relationship is described by Faraday's law, which can be expressed as follows:

$$i = \frac{dQ}{dt} \quad \& \quad j = \frac{i}{A}$$

$$N = \frac{Q}{zF} \quad \& \quad \boxed{J = \frac{j}{zF}} \quad (2.11)$$

Where i denotes current, A is area, thus j represents current density, Q represents quantity of electric charge, t is time, F is Faraday constant, z indicates the number of electron transferred, N represents the number of moles of involved reactant, J denotes the mole flux.

The boxed one in equation (2.11) is a fundamental and essential formula for this project, connecting mass transport with the electrolysis reaction (current density).

Faradic efficiency measures the selectivity of the cathodic reaction, specifically the actual yield of the

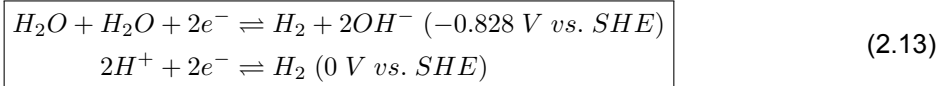
target product for a given quantity of electric charge, that can be described by the following formula:

$$FE = \frac{z * F * N}{Q} = \frac{z * F * \dot{N}}{i} \quad (2.12)$$

Where FE denotes Faradic efficiency, N represents the number of moles of target product, and $\dot{N}$ indicates the mole flow rate of target product.

2.3.2. Hydrogen Evolution Reaction

The hydrogen evolution reaction (HER) is the primary side reaction that reduces Faradic efficiency in the low temperature CO_2 electrolyzers, as represented by the following equations. In the AEM configuration, the first formula of (2.13) represents the HER, whereas in the CEM and r-BPM configuration, the second one plays a significant role.



To improve the Faradic efficiency, efforts typically focus on five aspects:

- ensuring smooth & sufficient CO_2 supply
- leveraging the cation ion effect
- regulating the local pH
- using acid-tolerant (molecular) catalyst such as Ni-N-C [39] and $[Ni(cyc)]^{2+}$ [40]
- optimizing water management to prevent flooding

The illustrations below highlight strategies to address a significant over-constraint challenge. On one hand, (bi)carbonate must be reverted to prevent carbonation and low SPC in an acidic environment, which can be created by CEM or BPM. However, at the same time, it is crucial to suppress HER while allowing cation transport to sustain eCO2RR.

Enhancing eCO2RR by using high concentrations of cations (e.g., potassium or cesium) to suppress HER at the catalyst surface is impractical in an r-BPM MEA configuration due to the limited catholyte volume. Solely relying on cation transport from the anolyte to overcome Donnan exclusion and reach the cathode risks salt precipitation. In addition, it is unfeasible to utilize a f-BPM systems due to delamination at the AEL-CEL interface by the reverted CO_2 gas. [41].

Sargent's group [41–45] primarily addressed this over-constraint issue by using ionomers to regulate the micro-environment of the cathode catalyst. Cationic ionomers aid in capturing OH^- at the catalyst surface, to effectively suppress HER, while cations from the electrolyte permeate through the ionomers to support eCO2RR. Alternatively, anionic ionomers can be used, which exclude both protons and cations. The cation effect is provided by the fixed charges of the anionic ionomer, while the release of (bi)carbonate is facilitated, enabling its reversion in the acidic environment.

2.4. Gas Diffusion Layer and Cathode Local Environment in Zero-Gap Gas Diffusion Electrode Reactors

2.4.1. Gas Diffusion Electrodes

To deploy CO_2 electrolyzers at scale as CO_2 utilization technologies, eCO2RR must be operated at practical conversion rates (e.g. 200 mA/cm^2) to minimize capital costs [46]. CO_2 solubility in water at atmospheric conditions at 25°C is only 33 $mMol/L$, thus electrolysis carried out in H-cells are prone to reach mass transfer limit and limit the current density to approximately 35 mA/cm^2 (C1 product, two electrons transfer) [7]. As current is increased the overpotential needed to further boost current density steadily increases due to pH gradients formed at the electrode and a decrease in the local concentration of CO_2 . This limit cannot be overcome via CO_2 electrokinetics at the electrode surface [47].

Porous hydrophobic electrode interfaces in gas diffusion electrodes (GDEs) were designed to address this issue above by delivering CO_2 gas directly to the electrode-electrolyte interface. This approach greatly enhances CO_2 mass transport to the catalyst by minimizing the diffusion distance. Supplying CO_2 in the gas phase leads to an approximate three-order-of-magnitude increase in the diffusion transport rate, thereby supporting high current densities [48]. GDEs indeed serve as an effective intensification strategy in low-temperature CO_2 electrolyzers.

Gas diffusion electrodes (GDEs) are generally composed of a gas diffusion layer (GDL) or carbon fiber layer (CFL) and a catalyst layer (Figure 2.6). This configuration enables the coexistence of liquid (electrolyte) and gas phases within the catalyst layer. The GDL is made up of a dense matrix of carbon-based fibers, such as carbon paper or a polytetrafluoroethylene (PTFE) membrane, providing a porous framework to support the catalyst layer. To enhance performance, GDLs are often coated with a microporous layer (MPL), which prevents flooding while increasing the surface area and improving interfacial electrical connectivity. The MPL is typically constructed from carbon black nanoparticles combined with a hydrophobic polymer like PTFE. The hydrophobic polymer restricts water intrusion, while the nanoporous structure of the MPL facilitates the transport of CO_2 gas to the catalyst layer and the removal of gaseous products to the flow field [48].

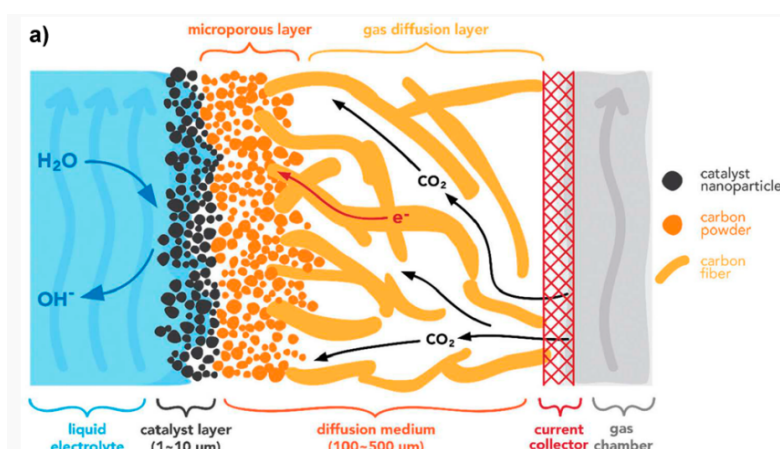


Figure 2.6: Diagram of gas diffusion electrode [7]

The typical parameters of GDLs include fabric structure (woven or non-woven), thickness (total and MPL, in μm), PTFE content (percentage, in both CFL and MPL), porosity (percentage), and applied compression ratio (percentage). The major suppliers of GDLs include Sigracet, Freudenberg, Toray, CeTech, Avcarb, Elat, and others [49].

2.4.2. Cathode Local Environments - Phase Boundary, pH Value and CO_2 Flow Rate

Burdyny et al. elucidated that the reactivity observed in e CO_2 RR on GDEs is primarily governed by the atomistic liquid-solid two-phase reaction interface, rather than the atomistic triple-phase boundary often assumed by many researchers. In this process, gas molecules reach the electrocatalyst surface via dissolution and diffusion through the electrolyte, not directly at the triple-phase boundary. It is anticipated that the e CO_2 RR current predominantly occurs at the catalyst surface within the liquid phase, with the reaction zone extending from the gas phase over a range of 10–1000 nm.[7]

Cathode local pH is a critical parameter for e CO_2 RR as it determines both the carbon efficiency and Faradic efficiency while also influencing the equilibrium electrode potential. The cathode local pH is significantly affected by current density. For example, in an anion exchange membrane (AEM) CO_2 electrolyser, the transfer of one electron to the cathode generates one OH^- at the cathode. This explains why Burdyny emphasizes that catalytic performance must be assessed under commercially relevant conditions [50].

In an AEM CO_2 electrolyser, the cathode local pH is approximately 10.5 at a current density of 200

mA/cm^2 [51]. Baumgartner et al. employed operando fluorescence lifetime imaging microscopy (FLIM) to visualize the pH distribution within a r-BPM flow CO_2 electrolyser. Using K_2SO_4 as the catholyte and operating at current densities of 50 or $100 \text{ mA}/\text{cm}^2$, they demonstrated that the catholyte pH remains below 6 [52]. Li et al. modified the local environment of the cathode catalyst layer using two different ionomers: Sustainion and Nafion. Based on this modification, they simulated the local pH profile, as shown in the Figure 2.7,

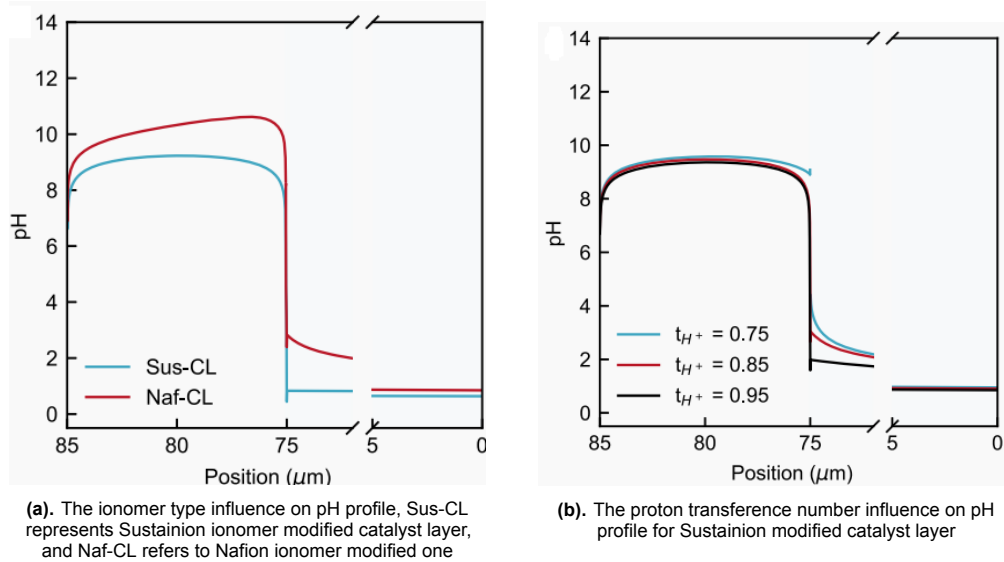


Figure 2.7: pH profile across ionomer modified cathode catalyst layer in r-BPM CO_2 electrolyser. Position $0 \mu\text{m}$ represents the inter layer, cation exchange layer thickness is $75 \mu\text{m}$, from 0 - 75 , catalyst layer thickness is $10 \mu\text{m}$, from 75 - 85 [8]

In Figure 2.7 a, Sustainion, an anion exchange ionomer, allows OH^- , HCO_3^- , and CO_3^{2-} to diffuse out of the catalyst layer and react with protons from the CEL, while repelling cations (e.g., potassium), resulting in a lower local pH (9). In contrast, Nafion, a cation exchange ionomer, retains more anions within the catalyst layer, leading to a higher pH. As shown in Figure 2.7 b, the proton transference number has little impact on the local pH.

The CO_2 flow rate plays a crucial role in balancing Faradic efficiency and carbon utilization. Subramanian et al. investigated this relationship using a membrane electrode assembly (MEA) setup. The system featured a sputtered silver catalyst on a gas diffusion electrode (GDE), 1 mol/L KOH as the anolyte, and an anion exchange membrane. By varying the CO_2 flow rate from 10 sccm to 50 sccm , they observed that increasing the flow rate enhanced Faradic efficiency from 35% to 75% , while reacted CO_2 fraction decreased significantly from over 90% to below 40% [53]. In addition, Subramanian et al. discovered that among the three flow field patterns—serpentine, parallel, and interdigitated—the serpentine flow field was the most effective in enhancing Faradic efficiency [18].

2.5. Mass Transport of Ion and Water

2.5.1. Ion Transport

The essence of the general ionic mass transfer equation lies in the relationship between the flux of species k (J_k) and its electrochemical potential ($\bar{\mu}_k$). In the absence of convection, where the solution is stagnant, the flux is directly proportional to the gradient of the electrochemical potential, with a proportionality constant of $-C_k D_k / RT$. Thus,

$$J_k = -\left(\frac{C_k D_k}{RT}\right) \nabla \bar{\mu}_x \quad (2.14)$$

Here, C_k denotes the concentration of species x , while D_k represents its diffusion coefficient, R is ideal gas constant and T is thermodynamics temperature. For linear mass transfer (one dimension), this is

$$J_k(x) = -\left(\frac{C_k D_k}{RT}\right) \frac{\partial \bar{\mu}_k}{\partial x} \quad (2.15)$$

Where x denotes the one-dimensional position coordinate. The electrochemical potential of species k in a given phase is defined as

$$\bar{\mu}_k = \mu_k + z_k F \phi \quad (2.16)$$

Here, the term μ_k is the chemical potential, ϕ represents the potential of the given phase.

Combining equation (2.15) with (2.16), the one dimensional Nernst-Planck equation (without convection) can be obtained as below,

$$J_k(x) = -D_k \left(\frac{\partial C_k(x)}{\partial x} \right) - \frac{z_k F}{RT} D_k C_k(x) \left(\frac{\partial \phi(x)}{\partial x} \right) \quad (2.17)$$

The Nernst-Planck equation (2.17) highlights two driving forces of ion transport: diffusion, driven by the concentration gradient (as described by Fick's Law), and migration, driven by the potential gradient.

Furthermore, the mobility of species k (u_k) requires clarification, as it is related to the diffusion coefficient through the Einstein-Smoluchowski equation,

$$u_k = \frac{|z_k| F D_k}{RT} \quad (2.18)$$

Here, D_k can further be expressed using Stokes-Einstein relations,

$$D_k = \frac{k_B T}{6\pi\eta a} \quad (2.19)$$

where k_B is the Boltzmann constant, a is the particle radius and η represents the viscosity of solvent.

Furthermore, the corresponding migration velocity ($v_{k,migration}$) is then given by

$$v_{k,migration} = -z_k u_k F \nabla \phi \quad (2.20)$$

2.5.2. Water Transport Cross Membrane

Water transport across a membrane is governed by the processes of osmosis and electro-osmosis. The phenomenon of osmosis is the spontaneous passage of a pure solvent into a solution separated from it by a semipermeable membrane, a membrane permeable to the solvent but not to the solute [54].

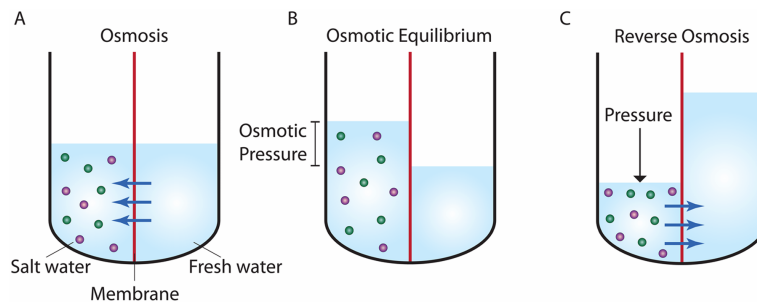


Figure 2.8: Schematic representation of (A) osmosis, (B) osmotic equilibrium, and (C) reverse osmosis. In osmosis (A), water moves from the freshwater side of the membrane into the salt water as a result of a difference in water concentration across the membrane. In osmotic equilibrium (B), the hydrostatic pressure reaches the pressure required to stop the net passage of water. This pressure is known as the osmotic pressure. An applied pressure higher than the osmotic pressure reverses the water passage and water starts to move from the salt water side of the membrane into the freshwater. This process is known as reverse osmosis (C). [9]

The chemical potential of water as solvent in the solution, μ_w , can be defined as

$$\mu_w = \mu_w^0 + RT \ln(\gamma_w x_w) + \bar{V}_w (P - P^0) \quad (2.21)$$

where μ_w^0 is the chemical potential at the standard state condition, x_w is the molar fraction of water, γ_w is its activity coefficient, $\bar{V}_w$ is the partial volume, P is pressure, and P^0 is the reference pressure of the standard state condition.

In Figure 2.8, the osmotic pressure (Π) required to maintain equilibrium in state B (osmosis equilibrium) is derived as:

$$\Pi = \frac{RT \ln(\gamma_w x_w)}{\bar{V}_w} \approx \frac{RT \ln(x_w)}{\bar{V}_w} \quad (2.22)$$

since $\ln(1-x) \approx -x$, then Van't Hoff equation can be derived as

$$RT x_B \approx RT \frac{n_B}{n_w} = \Pi \bar{V}_w \Rightarrow \Pi = c_B RT \quad (2.23)$$

where x_B is solute molar fraction, $x_B + x_w = \text{unity}$, n_B and n_w are the mole of solute and solvent (water), respectively.

For diffusion type membrane, the solvent (water) flux (J_w) can be expressed as

$$J_w = \frac{P_m}{L_m} (\Delta P - \Delta \Pi) = A_m (\Delta P - \Delta \Pi) \quad (2.24)$$

where P_m denotes the solvent membrane permeability, unit is mole solvent/s.m.atm, L_m is the membrane thickness, and A_m represents the solvent permeability constant, unit is mole solvent/s.m².atm. ΔP is the pressure difference across the membrane, at low applied pressure (when $\Delta P < \Delta \Pi$), water flows from dilute to concentrated, as illustrated in Figure 2.8 state B, when $\Delta P > \Delta \Pi$, it is called reverse osmosis, depicted in state C.

In an aqueous solution, ions are surrounded by a layer (shell) of hydrated water molecules. During ion transport via migration, the hydrated water molecules move along with the ions. This phenomenon is known as electro-osmosis (electro-osmotic drag/EOD). The EOD water flux (J_{EOD}) can be expressed as

$$J_{EOD} = n_d * J_{ion \text{ migration}} \quad (2.25)$$

where n_d is EOD coefficient, it can be seen that the electro-osmotic water flux depends on the number of water molecules coordinated by ion hydration, also referred to as hydration number.

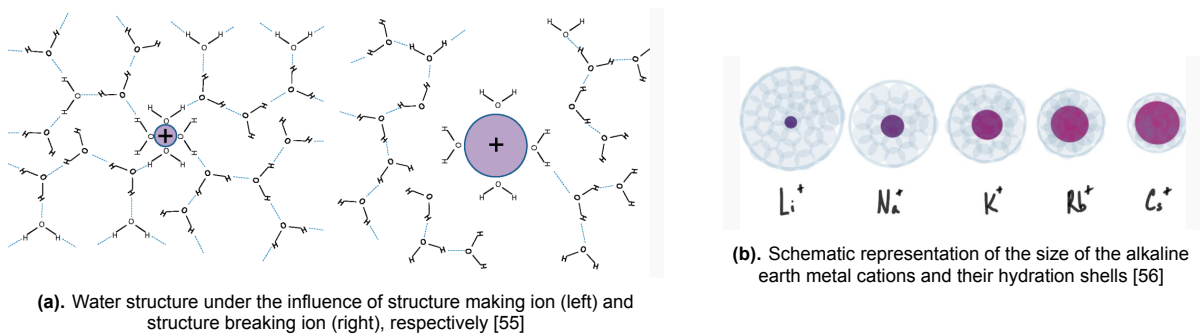


Figure 2.9: Alkaline Cation Hydration Shell Structure

The structure of the ion hydration shell is a complex topic, and there is no clear and quantitative theory to describe the hydration number of ions in aqueous solutions. Figure 2.9 (a) presents the structure making ion and structure breaking ion, respectively. The structure maker does remove water molecules from their network, but also has enough charge density to rebuild a new stronger structured network around itself. As this matrix is even more structured than bulk water. When the structure breaker

interacts with water, the latter molecule is removed from its network. Contrary to the structure maker, the structure breaking ion does not have enough charge density to rebuild a well structured new water network around itself [55]. Figure 2.9 (b) demonstrates that as the radius of alkali metal ions increases, the hydration mechanism transitions from structure-making to structure-breaking.

2.5.3. Water Transport in Zero-Gap CO₂ Electrolyser and Cathode Flooding

The role of water in CO₂ electrolyser is ambivalent, on one hand, it is the source of proton necessary for *eCO₂RR*, on the other hand, simultaneously a competing substrate for reduction in HER. Obviously, the flow-cell is more prone to flooding compared to the zero-gap MEA. Since MEA is the configuration adopted in industrial applications, this discussion will focus on the zero-gap scenario.

The water balance in the cathode of a zero-gap anion exchange membrane CO₂ electrolyser can be expressed as follows. The water flux driven by osmosis from the anode to the cathode is represented by J_{OSM} , while the net water flux due to electro-osmosis from the cathode to the anode is denoted as J_{EOD} (the cation-induced J_{EOD} from the anode to the cathode is significantly smaller). Additionally, the back-convective water flux from the cathode to the anode is referred to as J_{BC} , thus the net cathode water flux $J_{net-Cat}$ is given by

$$J_{net-Cat} = J_{OSM} - J_{EOD} - J_{BC} \quad (2.26)$$

Furthermore, the overall water flux balance for the cathode can be expressed as:

$$J_{H_2O-in} + J_{net-Cat} = J_{H_2O-out} + J_{reduction} \quad (2.27)$$

where J_{H_2O-in} represents the water supplying from humidifier, J_{H_2O-out} represents the emitted water from cathode, and $J_{reduction}$ denotes the water to be consumed by *eCO₂RR* and HER.

The key factors influencing cathode flooding are current density and salt precipitation [57], with the wettability of the GDL being the core determinant. Yang et al. found that a more negative applied potential tends to induce flooding by enhancing the wettability of the GDL [58]. Reyes et al.'s work also supported this viewpoint [59]. They found that a low-water-uptake AEM (with low conductivity) resulted in lower FE due to flooding and a higher overpotential compared to a high-water-uptake AWE. However, reducing the thickness of the low-water-uptake AWE (thereby improving conductivity) led to an increase in FE.

Similarly, addressing the flooding issue should also begin with wettability. A common approach is to introduce hydrophobic components into the GDE, such as PTFE [60] or graphene oxide [61]. Additionally, using carbon cloth offers better resistance to flooding compared to carbon paper, thanks to its bimodal pore structure [62].

2.6. Electrochemistry Fundamentals - Electrode Potential

2.6.1. Electrochemical Equilibrium and Electrode Potential

The electrode potential $\Delta\phi_{electrode}$ is defined as

$$\Delta\phi_{electrode} = \phi_M - \phi_S \quad (2.28)$$

where ϕ_M represents the electrode potential, and ϕ_S represents the electrolyte potential. This definition highlights that the electrode potential is a potential difference between the electrode and the electrolyte, rather than an absolute potential in isolation.

Following this, using the reduction of ferric ions to ferrous ions as an example, the electrode potential

at equilibrium is derived from the perspective of electrochemical potential.

$$\begin{aligned}
 Fe^{3+} + e^- &\rightleftharpoons Fe^{2+} \\
 \mu_{Fe^{3+}}^0 + 3F\phi_S^0 + \mu_{e^-}^0 - F\phi_M^0 &= \mu_{Fe^{2+}}^0 + 2F\phi_S^0 \\
 \mu_{Fe^{3+}}^0 + RT \ln a_{Fe^{3+}} + 3F\phi_S + \mu_{e^-}^0 - F\phi_M &= \mu_{Fe^{2+}}^0 + RT \ln a_{Fe^{2+}} + 2F\phi_S \\
 E^0 = \phi_M^0 - \phi_S^0 &= \frac{\mu_{Fe^{3+}}^0 + \mu_{e^-}^0 - \mu_{Fe^{2+}}^0}{F} \\
 E = \phi_M - \phi_S &= E^0 - \frac{RT}{F} \ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}
 \end{aligned}$$

where E is electrode potential, E^0 is electrode potential at standard state (activity = 1), and a represents ion activities. Based on this, the equilibrium electrode potential for a general redox half-reaction can be derived, which is expressed as the Nernst equation.

$$\begin{aligned}
 O + ze^- &\rightleftharpoons R \\
 E &= E^0 - \frac{RT}{zF} \ln \frac{a_R}{a_O}
 \end{aligned} \tag{2.29}$$

Although electrode potential represents a potential difference, its absolute value cannot be directly measured. To address this, a reference electrode is introduced. When paired with the working electrode to form a cell, the cell's electromotive force ($\mathcal{E}$) at equilibrium corresponds to the electrode potential of the working electrode, namely

$$\Delta\phi_{electrode} = \Delta\phi_{electrode} - \Delta\phi_{reference} = \phi_M^{electrode} - \phi_S - \phi_M^{reference} + \phi_S = \mathcal{E} \tag{2.30}$$

2.6.2. Polarity and Overpotential

Polarization refers to the phenomenon where the actual electrode potential deviates from the equilibrium electrode potential when current flows through the electrode. The extent of this deviation is called overpotential ($\eta > 0$). Overpotential always raises the anode potential and lowers the cathode potential.

$$\eta = E_{equilibrium}^{cathode} - E_{actual}^{cathode} \quad \text{or} \quad \eta = E_{actual}^{anode} - E_{equilibrium}^{anode} \tag{2.31}$$

Polarization can be classified into two main types: electrochemical polarization and concentration polarization. Electrochemical polarization is described by the Tafel empirical equation, which relates current to electrochemical overpotential (η^e). Fundamentally, polarization reflects the internal resistance of the electrochemical system. Here, the focus is not to delve into the Butler-Volmer model underlying the Tafel equation but rather highlights that electrochemical polarization essentially alters the reaction energy barrier via voltage changes, thereby affecting the reaction rate constant and, in turn, the relationship between reaction rate (current) and overpotential.

$$\eta^e = a + b * \log i \tag{2.32}$$

where a and b are constant, they are called Tafel intercept and Tafel slope, respectively.

The assumption of the uniformity near the electrode fails at high current densities because migration of ions towards the electrode from the bulk is slow and may become rate-determining [54]. Thus, the concentration over-potential (η^c) can be expressed as

$$\eta^c = E' - E = \frac{RT}{zF} \ln \frac{c'}{c} \tag{2.33}$$

where c represents bulk concentration, while c' is the reactant actual concentration at outer Helmholtz plane. E is equilibrium potential, refers to (2.29), and E' is actual potential.

According to Fick's law and Faraday law,

$$j = zFD \frac{c - c'}{\delta} \Rightarrow c' = c - \frac{j\delta}{zFD} \quad (2.34)$$

here δ denotes the Nernst diffusion layer thickness, thus

$$\eta^c = \frac{RT}{zF} \ln\left(1 - \frac{j\delta}{zcFD}\right) \quad (2.35)$$

2.7. Ion Exchange Membranes

2.7.1. Structure, Properties & Parameters and Water Uptake

Ion exchange membranes (IEMs) typically consist of a hydrophobic polymer matrix, fixed functional groups—either positively charged for anion exchange membranes (AEMs) or negatively charged for cation exchange membranes (CEMs)—and mobile counter-ions, as depicted in Figure 2.10. These membranes selectively permit the passage of oppositely charged ions (counter-ions) while blocking similarly charged ions (co-ions). Their hydrophilic nature also facilitates water transport alongside ions (although the framework of IEMs is hydrophobic, their polar groups are hydrophilic). Essentially, IEMs function as solid-state electrolytes and ion exchange resins in membrane form.

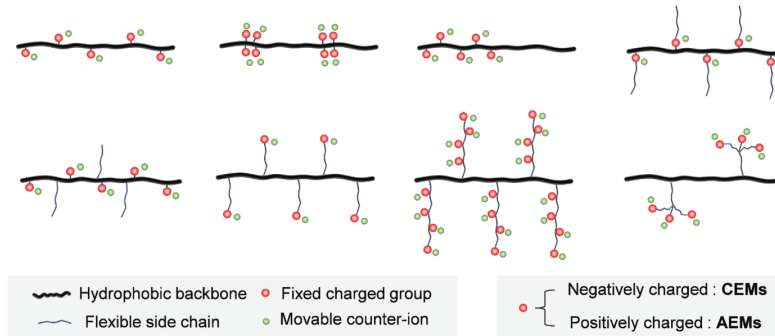


Figure 2.10: Schematic representation of the ion exchange membrane (IEM) polymer architectures [10]

The core properties of IEMs are perm-selectivity and ionic conductance. Perm-selectivity is typically quantified by the co-ion crossover rate, which is expressed as a percentage, while ionic conductance is measured in Siemens per square centimeter (S/cm²). Moreover, two critical parameters that influence the performance of ion exchange membranes (IEMs) are the fixed charge density (closely related to the fixed charge concentration and ion exchange capacity (IEC)) and the membrane thickness. The unit of fixed charge density ($C_{ion}^{M,L}$) is mol (fixed charge)/L(hydrated membrane), while the unit of fixed charge concentration is ($C_{ion}^{M,W}$) is mol (fixed charge)/L(water). The unit of IEC is mequiv (fixed charge)/g(dry membrane), where mequiv represents the number of exchangeable ions.

The ionic conductance (κ) can be expressed as

$$\kappa = \frac{F^2}{RT} \sum_k z_k^2 C_{ion}^{M,L} D_k^M \quad (2.36)$$

The relationship between fixed charge density and fixed charge concentration is

$$C_{ion}^{M,L} = C_{ion}^{M,W} * \xi_W \quad (2.37)$$

where ξ_W represents water volume fraction, the unit is L(water)/L(hydrated membrane).

The relationship between fixed charge concentration and IEC is

$$C_{ion}^{M,W} = \frac{IEC * \rho_w}{WU} \quad (2.38)$$

where ρ_w is the density of water in the membrane, which is generally assumed to be equal to that of bulk water. WU refers to water uptake, the unit is g(water)/g(dry membrane).

The relationship between water volume fraction and water uptake is

$$\xi_w = \frac{WU}{WU + \rho_w / \rho_p} \quad (2.39)$$

where the ρ_p represents the density of dry polymer.

Thus, the IEC, WU and ρ_p are the only parameters required to calculate fixed charge density (concentration). It is evident that water content is closely linked to ion exchange membranes. Compared to dry membranes, hydrated membranes receive more attention in research.

The conduction mechanisms of protons in CEM and hydroxide ions in AEM can be classified into two dominant categories: the vehicle mechanism and the Grotthuss (hopping) mechanism. Grotthuss hopping is the propagation of H^+ or OH^- through the hydrogen-bond network of water molecules by the formation and cleavage of covalent bonds with the neighboring molecules [63]. The vehicle mechanism refers to diffusion and migration but must rely on a moving carrier, namely water. Thus, the conduction mechanisms indicate that water content is crucial for ion transport within the membrane.

Perm-selectivity and ionic conductance often exhibit a trade-off in polymeric IEMs, and polymer water content can be used to rationalize the trade-off. As water sorption increases, the ionic resistance of the polymer decreases, but the effectiveness of Donnan exclusion is reduced resulting in lower perm-selectivity. Spatial variation of the electric potential within the polymer matrix may become more significant as water content increases than fixed charge concentration. Thus, swelling control may be more important for increasing perm-selectivity than fixed charge concentration alone.[64]

2.7.2. Donnan Potential and Ion Exchange Membrane Electro-neutrality

IEM perm-selectivity for counter-ions was first elucidated by Donnan; thus, the mechanism is referred to as the Donnan effect or Donnan exclusion (towards co-ions) [65]. The Donnan model says that only a few ions migrating out of a neutral phase are enough to create a high electric potential between the IEM and the solution. Donnan exclusion is the fundamental cause of the Donnan potential ($\Delta\phi_D$), which is defined as

$$\Delta\phi_D = \phi^M - \phi^S \quad (2.40)$$

where ϕ^M represents the potential of membrane, while ϕ^S represents the potential of solution.

At equilibrium, the electrochemical potential of species k in the two phases (membrane and solution) becomes equal, thus

$$\begin{aligned} \bar{\mu}_k^M &= \bar{\mu}_k^S \\ \mu_k^{0,M} + RT \ln(\gamma_k^M c_k^M) + z_k F \phi^M &= \mu_k^{0,S} + RT \ln(\gamma_k^S c_k^S) + z_k F \phi^S \end{aligned} \quad (2.41)$$

If the activity coefficient constant γ is approximately equal to unity, and the standard chemical potentials are assumed to be the same with each other, the Donnan potential can be expressed as

$$\frac{c_k^S}{c_k^M} = e^{\frac{z_k F}{RT} \Delta\phi_D} \Rightarrow \Delta\phi_D = \frac{RT}{z_k F} \ln \frac{c_k^S}{c_k^M} \quad (2.42)$$

By analyzing the osmotic pressure and Donnan potential, it can be concluded that, at equilibrium, external pressure or voltage is required to counteract the chemical potential difference caused by concentration gradients. Furthermore, a comparison between electrode potential and Donnan potential reveals that the essence of potential generation lies in charge distribution, with the concentration difference of charged particles being the fundamental cause, depicted in Figure 2.11.

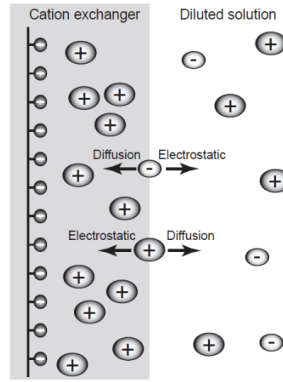


Figure 2.11: Donnan exclusion in CEM: The Donnan potential is illustrated when anions try to diffuse into the CEM. The electrical charge of each phase does not allow a considerable amount of anions into the CEM. [11]

The local electro-neutrality inside the membrane is an important constraint condition, can be expressed as

$$z_{ct}C_{ct}^M + z_{co}C_{co}^M + z_M X = 0 \quad (2.43)$$

where C_{ct}^M represents the concentration of counter-ion in the membrane, C_{co}^M represents the co-ion concentration and X refers to the fixed charge concentration, z stands for ions' valence.

In the case of symmetric electrolytes, such as KOH, the relationship between Donnan potential and fixed charge concentration can be expressed as based on equation (2.42) and (2.43)

$$\Delta\phi_D = \frac{RT}{F} \ln \left\{ \frac{X}{2c_{12}^w} + \left[\left(\frac{X}{2c_{12}^w} \right)^2 + 1 \right]^{1/2} \right\} \quad (2.44)$$

where c_{12}^w represents the bulk electrolyte concentration.

Based on equation (2.44), the concentration of co-ion (c_2^M) and counter-ion (c_1^M) in the IEM can be further expressed as

$$\begin{aligned} c_1^M &= (X/2) + [(X/2)^2 + (c_{12}^w)^2]^{1/2} \\ c_2^M &= [X^2 + (2c_{12}^w)^2]^{1/2} - c_1^M \end{aligned} \quad (2.45)$$

2.7.3. Ion Exchange Membrane for Low Temperature CO₂ Electrolyser

In a low-temperature CO₂ electrolyser, the ion exchange membrane primarily serves four roles, they are:

- to provide an electronic barrier between the cathode and anode to prevent short-circuiting
- to act as a physical barrier to facilitate the elimination of compartmental cross-contamination
- to maintain ionic connectivity of internal circuit
- to make the potentials of catholyte and anolyte different

The CEM in the low-temperature CO₂ electrolyser facilitates proton transfer, the typically commercial cation exchange polymer is PFSA (Nafion). The transported protons enable the conversion of bicarbonate to electrochemically active CO₂. In principle, a buffer electrolyte layer between the CEM and cathode is required to regulate the local environment pH for suppressing the HER.

Compared to CEM, AEM is more commonly used in low-temperature CO₂ electrolyses. It helps maintain an alkaline environment at the cathode, reducing parasitic HER (high Faraday efficiency) while promoting greater carbonation. The transported anion is not only OH⁻ but also includes carbonate and bicarbonate. The carbonation issue poses a major challenge to the use of KOH as an anolyte, leading to a pH drop and a significant rise in E_{cell} [66]. Moreover, it also hinders the adoption of PGM-free anode catalysts. Nowadays, KHCO₃ anolyte is widely used in CO₂ electrolyser with AEM,

with IrO_2 serving as the anode catalyst, and (bi)carbonate reverses back into CO_2 gas at the anode, which, in effect, appears similar to CO_2 membrane crossover. The typical anion exchange polymers are Piperlon, Sustainion, QAPPT and Aemion, their chemical structure is displayed in Figure 2.12.

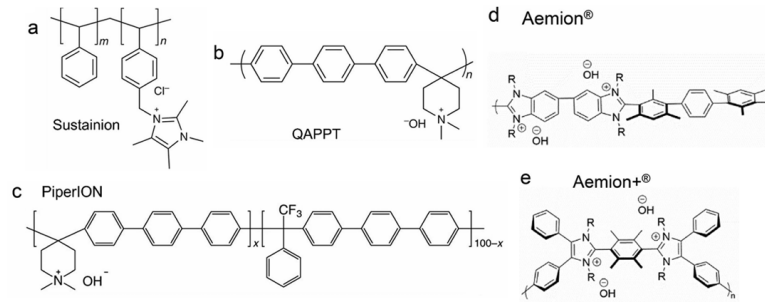


Figure 2.12: The chemical structure of some representative AEMs for MEA-based CO_2RR . (a) Sustainion, (b) QAPPT, (c) PiperION, (d) Aemion®, and (e) Aemion+®. [12]

2.8. Bipolar Membranes and Water Dissociation Reaction

2.8.1. Definition and Orientation of BPMs

Bipolar membranes (BPMs) are polymeric membranes composed of two layers, a negatively charged cation-exchange layer (CEL), and a positively charged anion-exchange layer (AEL) [13]. The interface between AEL and CEL is referred to as the inter layer (IL). There are two operating conditions for BPMs, reverse bias and forward bias, CEL facing the cathode is referred to as reverse bias condition.

The term bias originates from the PN junction. Both the PN junction and BPM have an built-in electric field. When the high-potential end of the built-in electric field is connected to the positive terminal of an external power supply, it is referred to as reverse bias. In a BPM, the fixed charge of the AEL is positive, making it the high-potential end of the built-in electric field.

The forward bias operating condition induces the water formation reaction, whereas the reverse bias facilitates the water dissociation reaction (WDR), as demonstrated in Figure 2.13.

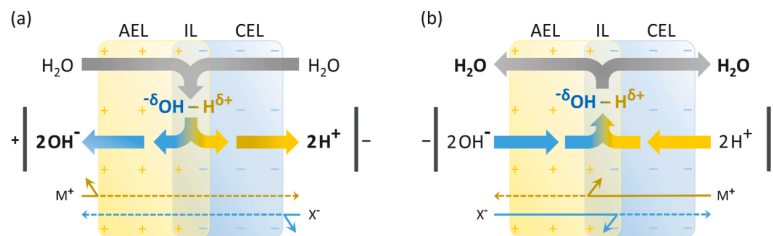
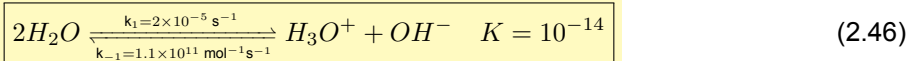


Figure 2.13: Schematic representation of the principle of a bipolar membrane; (a) BPM under reverse bias, where first the junction is depleted of ions and then water dissociates into proton and hydroxide ions; (b) BPM under forward bias, where ions are transported into the membrane and water is formed at the bipolar junction. [13]

WDR differs from water splitting; the latter typically refers to the reaction that produces hydrogen and oxygen, whereas WDR specifically results in protons and hydroxide ions, namely [14]



According to the Donnan exclusion principle, neither cations nor anions can traverse both layers of the BPM. In Figure 2.13, the solid-line rebound illustrates Donnan exclusion, while the dashed-line straight

arrow represents co-ion membrane crossover. Under reverse bias operation mode, since co-ion transport has limited conductivity capacity and cannot fulfill the ionic circuit's conductivity requirements, WDR to produce ionic carrier at the IL becomes indispensable.

Forward bias operation is not suitable for achieving a PGM-free anode catalyst. When the anolyte is neutral, such as $KHCO_3$, protons pass through the CEL, creating an acidic environment at the anode that causes catalyst corrosion. Additionally, protons react with (bi)carbonate, generating CO_2 gas in the inter layer, which leads to BPM delamination. In the case of an alkaline anolyte, such as KOH, potassium passes through the CEL and forms salt precipitates with (bi)carbonate at the interface. This salt accumulation and precipitation directly hinders CO_2 electroreduction at the cathode by disrupting cation effect [67].

2.8.2. Electrochemical Characteristics of BPMs

The thermodynamic potential of BPMs (V_{mem}) arises from three key elements: the Donnan potential at the CEL-catholyte interface, the Donnan potential at the AEL-anolyte interface, and the junction potential (V_j) difference across the inter layer.

$$V_{mem} = \phi^{anolyte} - \phi^{AEL} + \phi^{AEL} - \phi^{CEL} + \phi^{CEL} - \phi^{catholyte} = -\Delta\phi^{D anolyte} + V_j + \Delta\phi^{D catholyte} \quad (2.47)$$

according to equation (2.42)

$$\begin{aligned} -\Delta\phi^{D anolyte} &= -\frac{RT}{-F} \ln \frac{[OH^-]_{anolyte}}{[OH^-]_{AEL}} = \frac{RT}{F} \ln \frac{[H^+]_{AEL}}{[H^+]_{anolyte}} \\ \Delta\phi^{D catholyte} &= \frac{RT}{F} \ln \frac{[H^+]_{catholyte}}{[H^+]_{CEL}} \end{aligned} \quad (2.48)$$

next to obtain V_j based on electrochemical potential equilibrium, similar to equation (2.41),

$$\begin{aligned} \mu_{H^+}^{0,CEL} + RT \ln [H^+]_{CEL} + F\phi^{CEL} &= \mu_{H^+}^{0,AEL} + RT \ln [H^+]_{AEL} + F\phi^{AEL} \\ V_j = \phi^{AEL} - \phi^{CEL} &= \frac{RT}{F} \ln \frac{[H^+]_{CEL}}{[H^+]_{AEL}} \end{aligned} \quad (2.49)$$

to combine above three equations, thus,

$$V_{mem} = \phi_{anolyte} - \phi_{catholyte} = \frac{RT}{F} \ln \frac{[H^+]_{catholyte}}{[H^+]_{anolyte}} = \frac{2.303 * RT}{F} (pH_{anolyte} - pH_{catholyte}) \quad (2.50)$$

Here, "catholyte" and "anolyte" do not specifically refer to a flow cell but are equally applicable to a zero-gap membrane electrode assembly. At $T = 298 \text{ K}$, the dissociation of 1 mole of water produces 1 mole of protons and 1 mole of hydroxide ions, resulting in a pH difference of 14 between the two sides. Consequently, at equilibrium, the membrane potential difference (WDR voltage) of the BPM is $14 * 0.059 = 0.83 \text{ V}$. Hence, it is evident that the core characteristic of reverse-biased BPMs is their ability to independently regulate the pH of the cathode and anode through the WDR (maintain the steady state pH gradient). The essence of equation (2.50) lies in the fact that the high concentration of hydroxide in the anolyte and (or) the high concentration of protons in the catholyte hinder the outward diffusion flux of WDR, thereby increasing the voltage requirement for WDR.

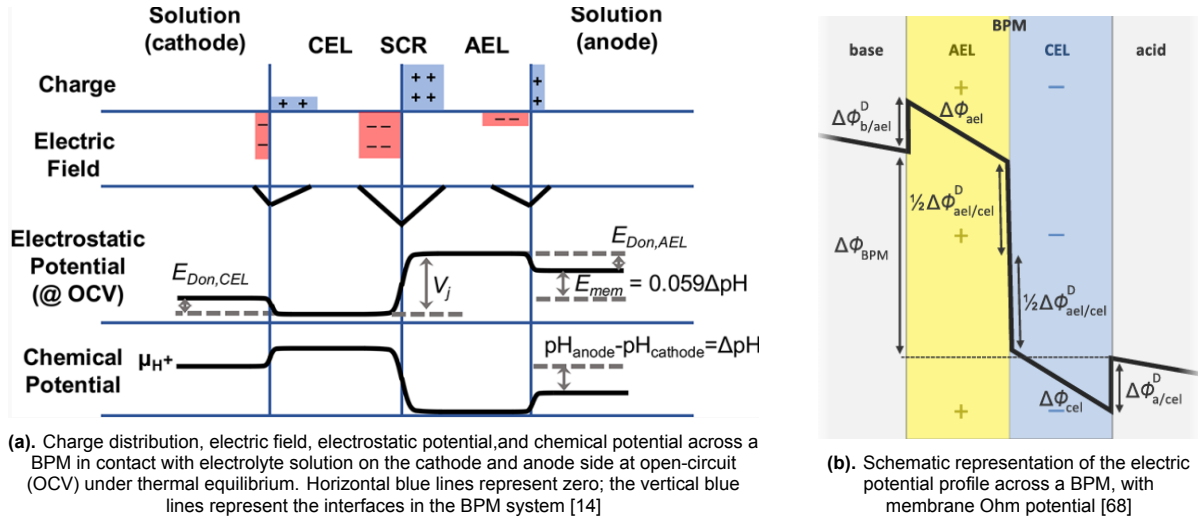


Figure 2.14: Reverse-bias bipolar membrane voltage profile

In Figure 2.14 a, the electric field is schematically depicted based on the charge distribution derived from Poisson's equation. Here, SCR refers to the space charge region, it specifically denotes the fixed charge of the CEL and AEL. Based on equation (2.48), the equilibrium voltage profile and pH profile of the BPM (as shown in Figure 2.14, expressed using the chemical formula of hydrogen ions) can also be determined. In Figure 2.14 b, the cross-membrane Ohm potential is depicted, too.

In a reverse-bias BPM electrochemical cell, the cell voltage can be decomposed into five key contributors: equilibrium electrode potential, equilibrium WDR potential, electrode reaction overpotential, WDR overpotential, and system ohmic potential (electrode, electrolyte and membrane). In a reverse-biased BPM system, additional energy is required to drive the water dissociation reaction (WDR). At the same time, a Nernstian pH shift voltage is gained due to the acidic environment at the cathode and the alkaline environment at the anode, as described by the Nernst equation. The cell voltage break-down is schematically demonstrated in Figure 2.15.

Moreover, the total cell voltage (V_{cell}) can be given by (ignore electrolyte ohmic losses):

$$\begin{aligned}
 V_{cell} &= \phi_{anode} - \phi_{cathode} \\
 &= \phi_{anode} - \phi_{anolyte} + \phi_{anolyte} - \phi_{catholyte} + \phi_{catholyte} - \phi_{cathode} \\
 &= \Delta\phi_{anode} + V_{mem} - \Delta\phi_{cathode}
 \end{aligned} \tag{2.51}$$

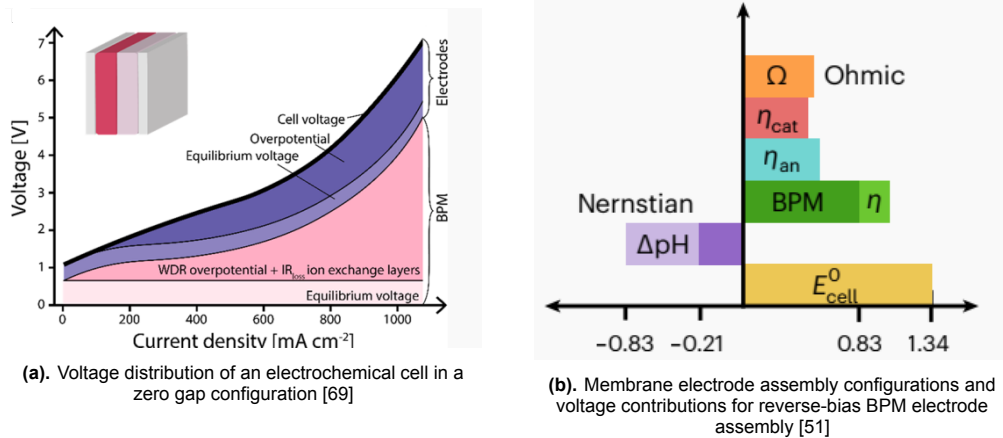


Figure 2.15: Voltage Breakdown of Reverse-Biased BPM MEA Cell in the low temperature CO₂ Electrolyser

The typical electrochemical characteristics of reverse bias BPMs are defined by two limiting currents, resulting from two ion conduction mechanisms: co-ion leakage and counter-ion conduction generated by the WDR. As shown in Figure 2.16, at low current densities, the membrane voltage remains low, insufficient to trigger WDR. As the current density increases, the curve reaches the first plateau, indicating the limit of co-ion leakage. At this stage, a slight increase in current density leads to a significant rise in voltage, until WDR onset voltage is reached. Subsequently, the membrane voltage increases with the current density, but at a very steep slope, representing the polarization overpotentials (kinetics and Ohm) of the BPM. As the current density continues to rise, the curve reaches the second plateau, indicating that the limit for water transport to the IL to supply WDR has been reached.

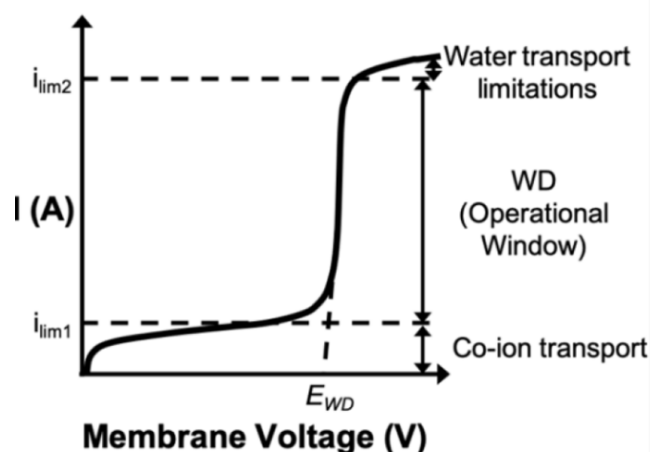


Figure 2.16: Polarization profile of a BPM operated under reverse bias conditions [14]

2.8.3. Ions Transport Cross Reverse-bias Bipolar Membrane

Bui et al. developed a comprehensive and sophisticated model to simulate the multi-ion transport mechanisms in bipolar membranes. The computational methods took into account:

- Kinetics of water splitting
- Homogeneous buffer reactions (electrolyte in the cathode and anode compartment, respectively)
- Membrane fixed charge spatial distribution profile
- Electrochemical potential of species ions
- Transport equation (Nernst-Planck equation)
- BPM water uptake (WU)
- Boundary conditions (electrolyte pH and concentration)

Simulations were performed for the four electrolyte environments experimentally studied by Vermaas et al., encompassing a total of four pH gradients: pH (7-7), pH (0-7), pH (7-14), and pH (0-14). In these notations, the first value in parentheses represents the catholyte pH, while the second corresponds to the anolyte pH. The electrolyte with pH = 0 consists of a 1 mol/L sulfuric acid solution, while the pH = 14 electrolyte is a 1 mol/L KOH solution. The pH = 7 electrolyte is a phosphate buffer composed of 0.45 mol/L K_2HPO_4 and 0.55 mol/L KH_2PO_4 , abbreviated as KP_i . As illustrated in Figure 2.17, the model exhibits a strong agreement with experimental results, reinforcing the credibility of the conclusions drawn from it.

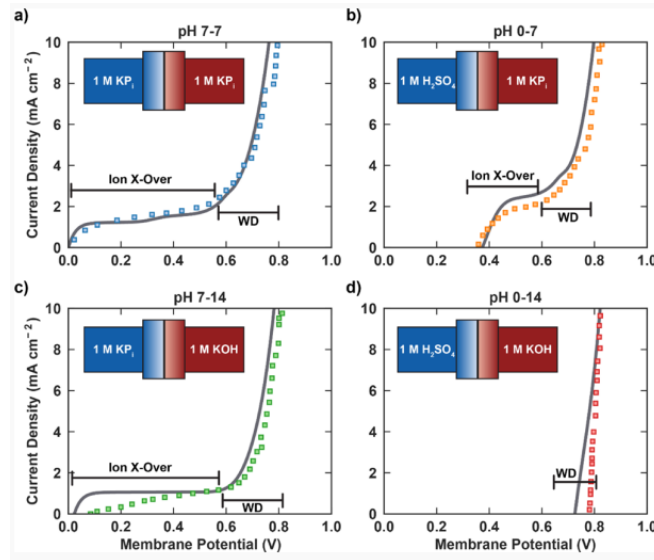


Figure 2.17: Calculated (solid lines) and measured (markers) polarization curves describing electrochemical behavior of bipolar membranes across various pH gradients. Brackets depict the regimes (salt-ion crossover and water dissociation) present in each polarization curve. Regimes are defined by the phenomenon dominating transport in each applied voltage window. Inset schematic displays the corresponding electrolyte combination for each modeled polarization curve [15]

Regarding the concentration polarization and transport mechanisms of hydronium and hydroxide ions, their concentrations reach a maximum at the AEL/CEL interface due to water dissociation. In contrast, at the ionomer/electrolyte interfaces, both species exhibit significantly lower concentrations, aligning with the Donnan equilibrium between the ionomer and the neutral electrolyte phases.

The driving forces for hydronium and hydroxide transport can be categorized into three components: diffusion ($-D_i \frac{dc_i}{dx}$), migration ($z_i D_i C_i \frac{FE}{RT}$), and the water concentration gradient ($D_i C_i \frac{d \ln(C_{H_2O})}{dx}$). Figure 2.18 shows in all cases, the fluxes of hydronium and hydroxide ions due to water concentration gradients within the BPM are small but contribute in a non-negligible manner to the measured ionic current. Nonetheless, for ion-exchange layers in contact with a neutral electrolyte, the majority (Ca.90%) of the hydronium or hydroxide current density is carried by diffusion. Conversely, for ionexchange layers in contact with an acidic or alkaline electrolyte, the hydronium or hydroxide current is dominated by migration.

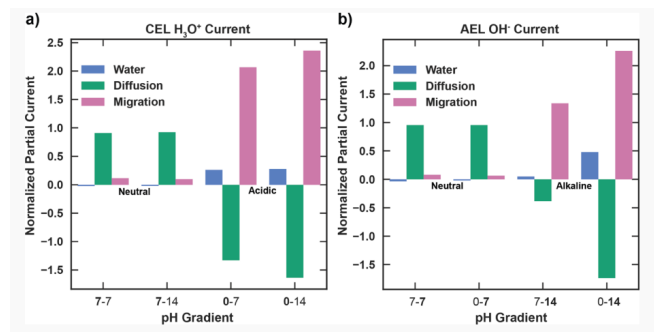


Figure 2.18: Breakdown of mechanistic contributions to (a) hydronium current in the CEL and (b) hydroxide current in the AEL at an applied potential of 0.8 V. All mechanistic partial currents are normalized by the total hydronium current or hydroxide current, respectively. Labels under bars display the neutrality, acidity, or alkalinity of the electrolyte adjacent to the given ion-exchange layer [15]

2.8.4. Field Enhanced WDR, BPMs' Junction Design and WDR Catalysts

Water dissociation in bipolar membranes was found to be accelerated by a factor of 5×10^7 . The first attempt to explain the enhanced water dissociation in bipolar membranes was based on the so-called

second Wien effect which describes the influence of a strong electric field on the water dissociation constant k_1 while the recombination rate constant k_{-1} is not effected by the electric field.[70] .

The current density of electric field enhanced (EFE) WDR i_d can be expressed as [71]

$$i_d \approx Fk_1(E)n\lambda = Fk_1^0 \exp(\alpha FE/RT)n\lambda \quad (2.52)$$

where $k_1(E)$ is the forward rate constant of the net reaction responsible for the EFE water dissociation, k_1^0 is the forward rate constant of the reaction when no external electric field is applied, E is electric field strength, n is the concentration of the active sites where the reaction is taking place, α is a characteristic parameter having the dimension of length that can be interpreted as the effective reaction distance for the dissociation reaction (typically $\alpha \sim 10^{-10}$ m) and λ is the thickness of space charge region.

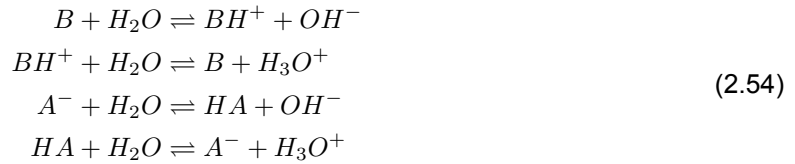
The influence of E on k_1 explains the origin of the kinetic overpotential in the WDR process. Apart from equation (2.52), the formally quantitative mathematical expression of the second Wien effect is given by [70]

$$\frac{k_1(E)}{k_1^0} = \left(\frac{2}{\pi}\right)^{1/2} (8b)^{-3/4} e^{\sqrt{8b}} \quad (2.53)$$

$$b = 0.09636 \frac{E}{\epsilon_r T^2}$$

where ϵ_r is relative permittivity.

At the microscopic level, EFE WDR originates from the protonation-deprotonation reactions induced by the fixed charges of the CEL and AEL in the BPM. The mechanism can be expressed as [72]



Here, B and HA represent a weak base and acid, respectively. Each membrane layer predominantly conducts one specific reaction. For example, the AEL, with its positive fixed charge, primarily facilitates the first two reactions in the formula (2.54).

The interface between membrane layers in a BPM is the most critical component for the optimal design of high-performance BPM [73]. In the past, BPMs were fabricated with a 2D (planar) interfacial junction (in Figure 2.19 a), where pre-formed anion-exchange and cation-exchange ionomer films were physically attached or sequentially cast to form the membrane. However, this 2D morphology is susceptible to dehydration under high current density. To address this limitation, Shen et al. were the first to introduce a novel BPM junction design featuring a 3D extended structure (in Figure 2.19 b), enabling more efficient water splitting via electrospinning. [16]

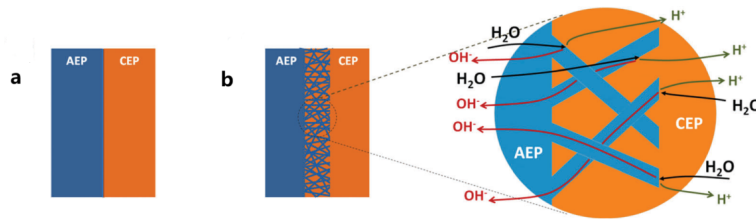


Figure 2.19: (a) conventional BPM, with 2D junction, and (b) the electrospun BPM with 3D dual-fiber junction, with a diagram showing transport pathways for water, hydroxide and proton species in the junction region [16]

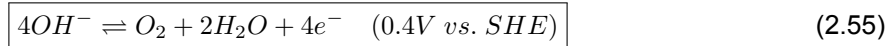
The extended junction area, with a randomly distributed network of AEL and CEL fibers, minimizes proton and hydroxide blockage caused by fibers aligned parallel to the membrane surface. This design creates tortuous yet continuous and unobstructed pathways, allowing ions to travel seamlessly from the water-splitting junction sites to the membrane's outer surfaces.

Common catalysts used in most commercial BPMs and those reported in literature are either weak acids or weak bases with a pKa between 4 and 10, such as tertiary amines, carboxylic acids, phosphoric acid metal hydroxides ($\text{Al}(\text{OH})_3$) and oxides (TiO_2 , SnO_2). Graphene oxide (GO_x) has been recognized as a more efficient catalyst for water dissociation in BPMs because of its large specific area and abundant oxygen containing hydroxyl, carboxyl, carbonyl, and epoxide functional groups. [74]

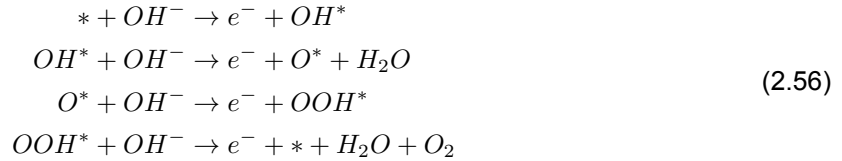
Yan et al. investigated the interplay between EFE and the catalyst on WDR [75]. BPMs with an interfacial catalyst layer were found to have smaller electric fields at the interface compared to samples without an added catalyst. Numerical simulations showed that the damping of the electric field in BPMs with a catalyst layer results from an increased flux of water dissociation products (H^+ , OH^-), which neutralize the net charge density of the CEL and AEL. In essence, the catalyst deployment mitigates the second Wien effect. This study underscores the importance of balancing the second Wien effect and the catalytic effect to achieve optimal WDR performance.

2.9. Alkaline Oxygen Evolution Reaction

The oxygen evolution reaction (OER) is a crucial electrochemical process, commonly occurring in electrochemical applications paired with cathodic reactions such as hydrogen evolution, carbon dioxide reduction, and ammonia synthesis.



The OER in alkaline solutions (equation (2.55)) involves four charge-transfer steps, where the * indicates surface-absorbed species (adsorbate evolution mechanism):



Transition metals oxides/hydroxides/oxyhydroxides (e.g. $\text{Ni}(\text{Fe})\text{OOH}$) have been studied as benchmarks for OER activity in alkaline water electrolysis. It is known that nickel based catalysts on their own have a low catalytic activity for the OER, while the incorporation of iron into the nickel lattice can substantially enhance the OER activity by facilitating the formation of high-surface-area structures. Fe atoms easily replace Ni atoms in the oxide/(oxy)hydroxide lattice. In the catalysts, the Fe is present as 3+ and the Ni is present as 2+, thus creating a change in the overall charge, which is compensated by the intercalation of anions such as carbonate and also water molecules, creating layered and high surface-area structures that can also facilitate ion transport. [17]

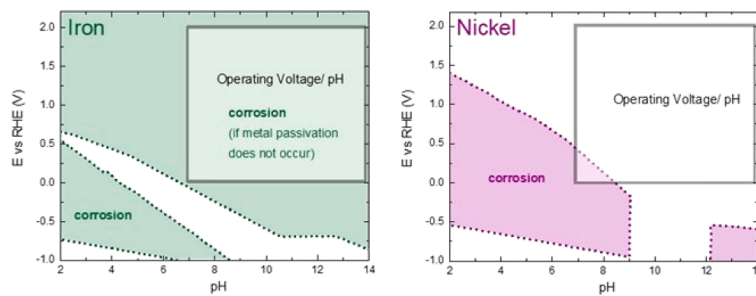


Figure 2.20: Pourbaix diagrams of iron and nickel in aqueous electrolytes at ambient pressure and 25 °C. The inset shows the voltage–pH range that an anode catalyst may experience in an alkaline water electrolyser [17]

Figure 2.20 presents the Pourbaix diagrams for Ni and Fe. It needs to be noted that Pourbaix diagrams are only guidelines based on thermodynamic information. They do not include reaction kinetics information, and experimental verification of the catalyst stability is needed. In addition, the stability of a

catalyst is influenced by its chemical and physical structure, including its physical size. Nevertheless, Pourbaix diagrams provide insights and initial material stability guidelines [17]. In reality, Ni-based anode catalysts undergo corrosion when pH value < 12 in a low-temperature zero-gap CO_2 electrolyser.

Experimental Method

3.1. Experimental Objectives, Method and Design (Control Variables)

The overall purpose of this experiment is to study the co-ions transport behavior cross r-BPM during the CO_2 electrolysis, which determines the anolyte pH directly, as governed by charge neutrality principle of equation (3.1).

$$[K^+] = 2 * [CO_3^{2-}] + [OH^-] \quad \text{ignore } [H^+] \quad (3.1)$$

The experiment is conducted under constant-current electrolysis conditions using chronopotentiometry (CP). After electrolysis, titration analysis is conducted on the electrolyte both before and after the process to measure the cation and bicarbonate ion concentrations, then calculate their transport flux. Additionally, voltage and Faradic efficiency data are collected.

Unless specifically investigating the effect of operation duration on co-ion transport behavior, all other experiments are conducted for a duration of 1 hour. A shorter duration results in minimal changes in ion concentration, leading to significant titration errors, while longer durations are time-consuming.

Supporting tasks include magnetron Ag sputtering for GDE preparation, electrolyte blending, weekly titrator calibration and regular baking and calibration of gas chromatography, as well as electrode cutting to size.

The experimental system's working package is divided based on the four control variables: two operational ones, current density (CD) and duration, and two anolyte-related ones, KOH concentration and cation identity (cesium vs. potassium).

Table 3.1: Experimental Working Packages Overview

Work Package	Content
1M KOH, CD	influence of current density (CD); set points: [25mA/cm ² , 50mA/cm ² , 100mA/cm ² , 150mA/cm ² , 200mA/cm ² , 250mA/cm ²] CD, 1mol/L KOH anolyte, 1 hour duration.
KOH Conc.	influence of KOH concentration; set points: [0.1mol/L, 0.5mol/L, 1mol/L, 2mol/L, 3mol/L] KOH anolyte, 100mA/cm ² CD, 1 hour duration
2M KOH, CD	combined influence of CD and concentration; set points: [50mA/cm ² , 100mA/cm ² , 150mA/cm ²] CD, 2mol/L KOH anolyte, 1 hour duration
1M CsOH, CD	influence of cation identity; set points: [25mA/cm ² , 50mA/cm ² , 100mA/cm ² , 150mA/cm ² , 200mA/cm ²] CD, 1mol/L CsOH anolyte, 1 hour duration
Duration	influence of duration; set points: [1 hour, 3 hour, 4 hour, 5 hour, 7 hour] duration, 1mol/L KOH anolyte, 100mA/cm ² CD

The design of the experimental working package is firmly centered on the two fundamental transport mechanisms-diffusion and migration, corresponding to the key variables of anolyte concentration and current density, respectively. Additionally, it takes into account the influence of cation identity. Given that most experiments are conducted over a one-hour duration, an extended-duration study is also incorporated to assess its long-term effects.

3.2. Experimental Setups and Measurable Data Processing

3.2.1. Experiment Setups

Table 3.2: Experimental Setups Overview - Codes, Device and Parameters

Setups	Elaboration
Code 1	Premise: the only negative co-ion species is bicarbonate, excluding carbonate.
Code 2	The electrolyte is the only object both analyzed and preserved after CP CO_2 electrolysis. Titration is the only characterization method used. while the analysis of $HCOO^-$ ions in the electrolyte by NMR or HPLC is not conducted.
Code 3	The GDE, IEM, and anode catalyst used in each experiment are each of the same model every time. Moreover, all three components are brand new for each experiment and are never reused.
Code 4	Each experiment was repeated three times in parallel, and the data in the plots are presented with error bars.
Code 5	Each electrolyte sample was titrated at least three times in parallel, and the standard deviation of the results was calculated.
Device 1	A single-cell electrolyzer system is used, with an area of $2.25 \times 2.25 \text{ cm}^2$, and the end plate flow field pattern is serpentine.
Device 2	A membrane-electrode assembly (MEA) configuration is used, the IEM is a fumasep BPM, and the cathode is 100 nm sputtered Ag on Sigracet 39 BB GDL.
Device 3	BPM orientation is reverse-bias, Recemat Ni-4753 nickel mesh (foam) as anode catalyst, and Sigma-Aldrich- 417661 KOH or Sigma-Aldrich-23204 CsOH as anolyte.
Device 4	A two-electrode system is used instead of four-electrodes, so the BPM voltage cannot be determined; only the cell voltage is measurable.
Device 5	When assembling the cell, the eight bolts are tightened with a torque of 2.5 Nm, following a diagonal tightening sequence.
Parameters 1-5	1) Electrolyte volume is 90 ml, 2) electrolyte flow rate by peristaltic pump is 20 ml/min, 3) CO_2 flow rate is 50 sccm, 4) room temperature, 5) cathode back pressure set point is 1250 mbar.

Liquid water can damage the mass flow meter (MFM) and gas chromatography (GC). Therefore, as shown in Figure 3.1, a water trap and a liquid water alarm (located between the liquid and MFM, not depicted in the figure) are required. Additionally, the zero-gap MEA setup requires a humidifier for CO_2 feed humidification.

As shown in Figure 3.2, the cell assembly follows this sequence: anode end plate, nickel mesh, silicone gasket, r-BPM, PTFE gasket, GDE, and cathode end plate. The gasket provides insulation and sealing, with insulating sleeves on the fastening bolts. The silicone gasket also protects the MEA from damage caused by compressive force.

The MFM integrates a back-pressure regulator (BPR) to maintain cathode pressure, counter osmotic pressure, and mitigate flooding propensity. The system has three control interfaces for the MFM (with BPR), GC, and potentiostat, with data collected separately from each.

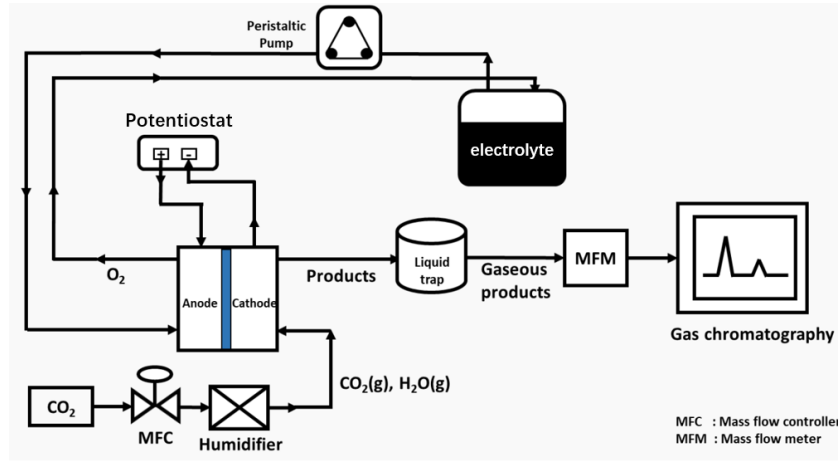


Figure 3.1: Flow diagram of the experimental setup used for CO₂ electroreduction in a MEA cell [18]

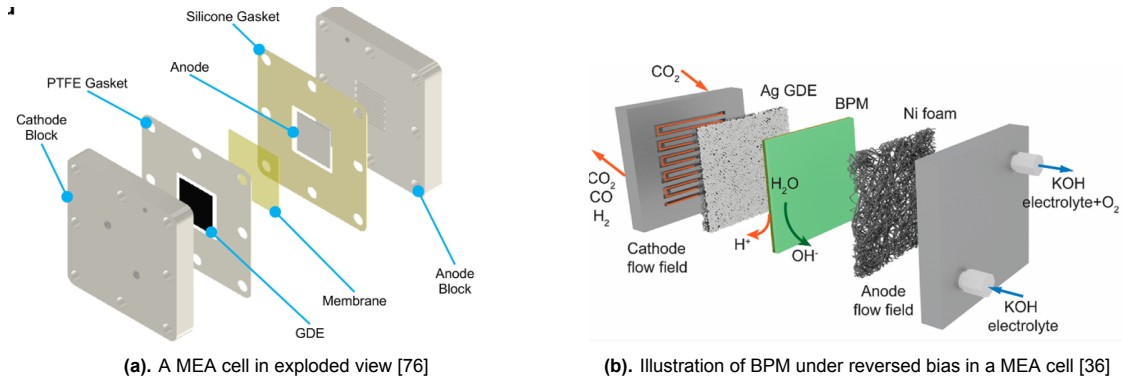


Figure 3.2: Schematic exploded MEA CO₂ electrolyser used in the experiments

3.2.2. Faradic Efficiency Calculation

The FE calculation is based on formula (2.12), assuming all products are gaseous (CO and H_2). It requires the cathodic outlet gas flow rate $\dot{V}$ (from the mass flow meter, MFM, in sccm - Standard Cubic Centimeters per Minute) and the product volume fraction x_{CO} and x_{H_2} (from gas chromatography, GC, in ppm). The key is to determine the molar flow rates of the products, $\dot{N}_{CO}$ and $\dot{N}_{H_2}$.

$$\begin{aligned} \dot{N}_{CO} &= \frac{P \dot{V}_{correct} * 10^{-6} * x_{CO} * 10^{-6}}{RT} = \frac{101325 * \dot{V}_{correct} * x_{CO} * 10^{-12}}{8.314 * 273.15} = Const * \dot{V}_{correct} * x_{CO} \\ \dot{N}_{H_2} &= \frac{P \dot{V}_{correct} * 10^{-6} * x_{H_2} * 10^{-6}}{RT} = \frac{101325 * \dot{V}_{correct} * x_{H_2} * 10^{-12}}{8.314 * 273.15} = Const * \dot{V}_{correct} * x_{H_2} \end{aligned} \quad (3.2)$$

The above formula is based on the ideal gas law, where P represents pressure and T represents temperature, both under standard conditions. The factor 10^{-6} is applied twice: the first accounts for converting the unit of $\dot{V}$ from cm^3 to m^3 , and the second converts x_{CO} or x_{H_2} from ppm to a dimensionless value. It is important to note that the calculation does not directly use $\dot{V}$ but instead uses $\dot{V}_{correct}$, which is related to $\dot{V}$ by the following equation.

According to the conversion method provided by the MFM manufacturer (formulas and constants):

$$\dot{V}_{correct} = \frac{\dot{V}}{0.74 * C_{mix}} \quad (3.3)$$

$$C_{mix} = x_{CO} * 10^{-6} + \frac{x_{H_2} * 10^{-6}}{1.01} + \frac{0.023}{0.79} + \frac{1 - 0.023 - x_{H_2} * 10^{-6} - x_{CO} * 10^{-6}}{0.74}$$

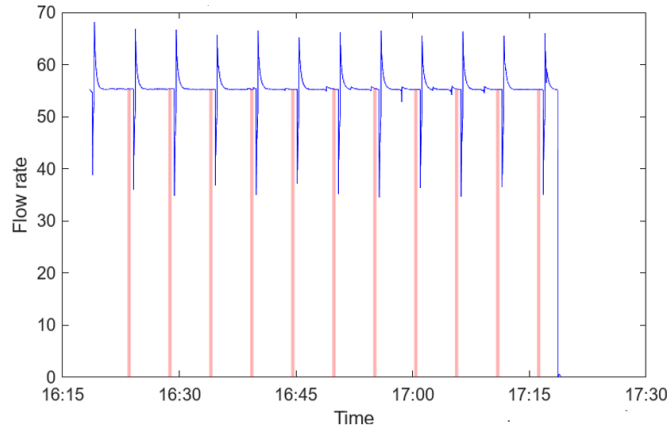


Figure 3.3: an example of 1-hour test gas flow plot with the $\dot{V}$ adoption range, before each injection time 45 ~ 20s

It should be noted that $\dot{V}$ represents the instantaneous value, and GC detection is intermittent, triggered after each injection moment. It analyzes the gas composition at the instantaneous state immediately before the injection. However, during the injection time, the gas flow fluctuates significantly. Therefore, the convention in this project is to take the average flow rate from 45 to 20 seconds before the injection time as $\dot{V}$, illustrated by the pink bar in Figure 3.3.

Thus, the FE_{CO} and FE_{H_2} can be obtained by the equation (2.12) (electron transfer number $z=2$) owe to the given mole flow. Because the cell area is $2.25 * 2.25 \text{ cm}^2$, the conversion relationship between current density and current is that a current density of 100 mA/cm^2 corresponds to a current of 0.5063 A . In addition, partial current (density) is defined as

$$\begin{aligned} i_{partial\ k} &= i * FE_k \\ j_{partial\ k} &= j * FE_k \end{aligned} \quad (3.4)$$

where k represents specific product species.

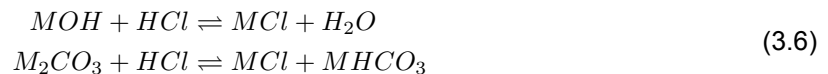
3.2.3. Titration Data Treatment

The titrant is a 0.1 mol/L HCl standard solution. If the sample is fresh anolyte before CP CO_2 electrolysis, the reaction can be expressed as

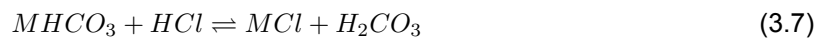


where M represents a cation, either potassium or cesium.

If the anolyte sample is taken after CP CO_2 electrolysis, it will contain $M_2\text{CO}_3$. In this case, the titration will undergo two equivalent points (EP1 and EP2). The reaction to reach EP1 ($\text{pH}=8.34$) is given by



The reaction to reach EP2 ($\text{pH}=4.68$) is given by



The purpose of titration is to determine the concentrations of M and bicarbonate, with the results expressed in terms of the volume of titrant consumed, thus

$$C_{HCl} * V_{titrant} = C_{TBD} * V_{sample\ delivery} \Rightarrow C_{TBD} = \frac{0.1 * V_{titrant}}{V_{sample\ delivery}} \quad (3.8)$$

The sample delivery volume varies with the electrolyte concentration, as a single titration can release a maximum of 20 ml of titrant. For 0.1 mol/L samples, 5 ml is delivered; for 0.5 mol/L, 1 ml or 2 ml; for 1 mol/L, **1 ml**; and for 2 mol/L, 0.5 ml. The titration endpoint is defined at pH 2.

Next, define $[M]_{before}$ as the cation concentration of the fresh electrolyte, and $[M]_{after}$ as the cation concentration of the electrolyte after undergoing CP CO_2 electrolysis. $[HCO_3^-]$ represents the concentration of carbonate ions in the electrolyte, but it is still referred to as bicarbonate. The titration results from formulas (3.5), (3.6), and (3.7) are denoted as V_0 , V_1 , and V_2 , respectively. Thus,

$$\begin{aligned} [M]_{before} &= \frac{0.1 * V_0}{V_{sample\ delivery}} \\ [HCO_3^-] &= \frac{0.1 * (V_2 - V_1)}{V_{sample\ delivery}} \\ [M]_{after} &= \frac{0.1 * [V_1 - (V_2 - V_1)]}{V_{sample\ delivery}} = \frac{0.1 * (2V_1 - V_2)}{V_{sample\ delivery}} \end{aligned} \quad (3.9)$$

Then the most important data in this project, co-ions flux (in the unit of $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) can be given by:

$$\begin{aligned} J_M &= \frac{([M]_{before} - [M]_{after}) * 0.09 * 10^6}{time(s) * 2.25 * 2.25 * 10^{-4}} \\ J_{HCO_3^-} &= \frac{[HCO_3^-] * 0.09 * 10^6}{time(s) * 2.25 * 2.25 * 10^{-4}} \end{aligned} \quad (3.10)$$

The above equation is based on the definition of flux. In the equation, 0.09 represents the volume of the electrolyte, which is 0.09 L. Multiplying by 10^6 converts the unit from mol to μmol , while $2.25*2.25$ represents the area of the cell (cm^2), and multiplying by 10^{-4} converts the unit from cm^2 to m^2 .

3.2.4. Other Quantities Derived from Co-ion Flux

Next, key data will be derived based on the co-ion flux results. Among these, the most critical is the water dissociation efficiency (WDE). Calculating WDE requires performing a flux balance, which also provides an opportunity to elaborate the assumption that bicarbonate is the only negative co-ion present.

Equation (2.11) defines the relationship between conductive ion flux and current density, thus

$$\begin{aligned} j * 10 &= [F * (J_{H^+} + J_{K^+} + J_{HCO_3^-}) + 2F * J_{CO_3^{2-}}] * 10^6 \\ &= [F * (J_{OH^-} + J_{K^+} + J_{HCO_3^-}) + 2F * J_{CO_3^{2-}}] * 10^6 \end{aligned} \quad (3.11)$$

The pH of the electrolyte used in the experiment is greater than or equal to 13. As a result, regardless of the species involved— H_2CO_3 , HCO_3^- , or CO_3^{2-} —all will ultimately convert to CO_3^{2-} upon entering the electrolyte. As shown in Figure 2.4, H_2CO_3 , HCO_3^- , and CO_3^{2-} cannot coexist simultaneously. If coexistence occurs, it can only involve two species, either H_2CO_3 and HCO_3^- or HCO_3^- and CO_3^{2-} .

Fundamentally, titration results only provide the total carbon content. Therefore, in cases where two species coexist, unless the exact local cathode pH value distribution is known, it is impossible to differentiate them. Due to the methodological limitations, an approximation must be made, and the species HCO_3^- chosen to act as the only carrier.

Taking into account that protons from the CEL layer of the r-BPM can significantly lower the local cathode pH, simulation results indicate that the cathode pH is approximately 9 [8]. According to Equation

(2.8), at pH = 8.1, HCO_3^- reaches its maximum proportion of 98%, and at pH = 9, CO_3^{2-} accounts for 4.458%. Therefore, this approximation is considered reasonable.

Based on equation (3.11), with $J_{CO_3^{2-}}$ omitted, WDE can be expressed as:

$$\textcircled{1} \quad WDE = \left(1 - \frac{(J_{K^+} + J_{HCO_3^-}) \cdot F \cdot 10^{-6}}{j \cdot 10} \right) \cdot 100\% \quad (3.12)$$

Here, multiplying 10 represents the conversion factor for j from units of mA/cm² to A/m².

Then the water dissociation flux (H^+ and OH^-) can be given by:

$$\textcircled{2} \quad J_{H^+} = J_{OH^-} = \frac{j \cdot 10}{F} * WDE * 10^6 \quad (3.13)$$

Furthermore, the ion transference number of each ion species (t_k) can be expressed as

$$\textcircled{3} \quad t_k = \frac{J_k}{\sum_k J_k} = \frac{J_k * F * 10^{-6}}{j * 10} \quad (3.14)$$

In addition, based on equation (3.1), the pH drop of the anolyte via electrolysis can be given by

$$\textcircled{4} \quad \Delta pH = \log_{10} \frac{[OH^-]_{before}}{[OH^-]_{after}} = \log_{10} \frac{[M]_{before}}{[M]_{after} - 2 * [HCO_3^-]} = \log_{10} \frac{1}{1 - WDE} \quad (3.15)$$

At last, the ratio of $J_{HCO_3^-}$ to J_{K^+} can be counted as the $\textcircled{5}$ derived parameter.

In addition, the partial current density (PCD) represents the conductive contribution of each ion species and is an important parameter. It breaks down the actual current density according to the ratio of the mass transfer flux of each ion species. In principle, it is not a derived parameter but merely has a conversion factor with the flux of co-ions. Referring to equation (2.11) or (3.12), take the partial current density (PCD) of bicarbonate as an example; it can be expressed as

$$\begin{aligned} \frac{PCD_{HCO_3^-} * 10}{F} &= J_{HCO_3^-} * 10^{-6} \\ \text{or} \\ PCD_{HCO_3^-} &= j * (1 - WDE) * \frac{J_{HCO_3^-}}{J_{K^+} + J_{HCO_3^-}} = 10^{-7} * F * J_{HCO_3^-} = 9.6485 * 10^{-3} * J_{HCO_3^-} \end{aligned} \quad (3.16)$$

Results and Discussion

4.1. The Influence of Anolyte Concentration on Co-ions Transport

4.1.1. Co-ions Transport Flux Under Different KOH Concentrations

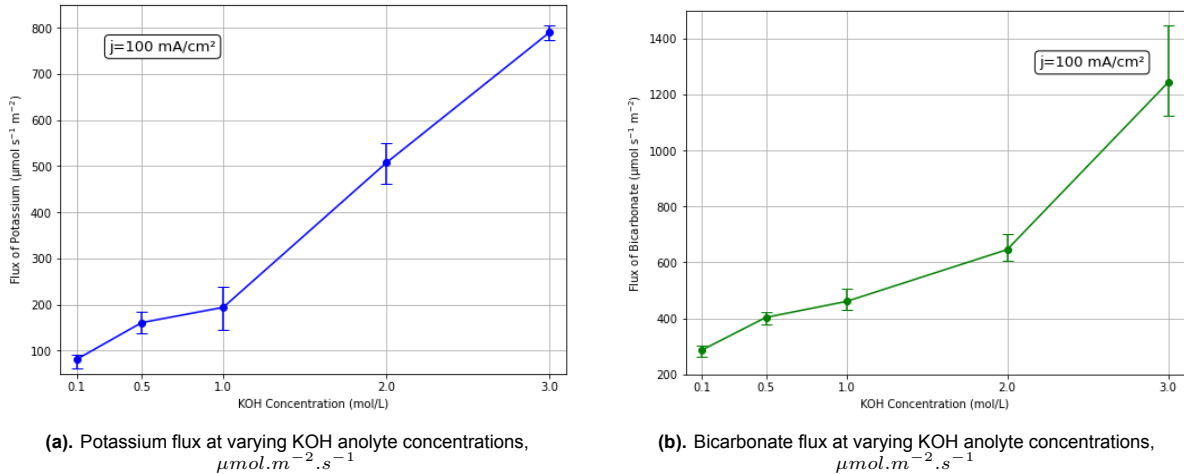


Figure 4.1: Co-ions flux at varying KOH anolyte concentrations over a 1-hour experiment duration, $j=100 \text{ mA/cm}^2$

Figure 4.1 conveys two key information:

- The anolyte concentration significantly enhances co-ions transport flux.
- The transport fluxes of potassium ions and bicarbonate ions exhibit a positive correlation.

The transport behavior of potassium ions is as expected—its mass transfer flux inevitably increases as the anolyte concentration rises due to diffusion control. However, the critical question lies in why the flux of bicarbonate also increases correspondingly. Since the current density remains constant, the cathode's local alkaline environment is maintained, which necessarily leads to a decrease in WDE and a weakening of the CO_2 reversion effect. However, this is merely a consequence and cannot serve as the fundamental explanation for the increase in bicarbonate flux with concentration.

To address this issue, we refer to a concept introduced by Parnamae in the article "Origin of Limiting and Overlimiting Currents in Bipolar Membranes (2023)" [68], namely, counter-ion adsorption. This concept is formulated based on the Langmuir adsorption isotherm, expressed as

$$X = \frac{X_{max}}{1 + [\text{Counter Ion}]/K}$$

where X represents the fixed charge density unoccupied by counter-ions, specifically, effective fixed charge density, X_{max} denotes the intrinsic fixed charge density of the ion-exchange membrane (IEM), and K refers to the adsorption constant.

For co-ions crossover in r-BPM, a "role-switching effect" occurs. Potassium ions, acting as co-ions in the anion exchange layer AEL, counteract Donnan exclusion. However, upon crossing the AEL and entering the CEL, they transition into counter-ions, where they adsorb onto the fixed charges of the CEL. This adsorption process weakens the perm-selectivity of the CEL to bicarbonates.

Therefore, the conclusion can be drawn as:

Higher anolyte concentration reduce rBPM permselectivity by both diffusion (AEL) and the hypothesis of role switching effect (CEL)

Furthermore, we have justification to believe that the counter-ion adsorption effect is more pronounced for potassium ions in the CEL than for hydronium, given that protons exhibit the fastest trans-membrane transport among all ions. This additional assumption is essential; without it, one might erroneously conclude that a higher WDE—implying an increased proton flux in the CEL—would lead to lower perm-selectivity of the CEL and consequently greater bicarbonate ion crossover.

Using 1 mol/L KOH as the threshold, when the concentration falls below this level, the potassium and bicarbonate ion fluxes increase slowly and non-linearly with the KOH concentration. This suggests that migration plays a dominant role in co-ion transport at low concentrations, where diffusion is less significant. In other words, as the electrolyte concentration increases from 0.1 M to 0.5 M and then to 1 M, the increase in co-ion flux becomes limited, indicating that migration is the primary contributor to the flux. The flux at 0.1 M most effectively reflects the intrinsic contribution of migration.

When the concentration exceeds this level, particularly at 2 mol/L, the co-ion flux experiences a sharp increase. The potassium flux rises from approximately $200 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ at 1 mol/L to around $500 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, and further reaches $800 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ at 3 mol/L. Based on this observation, it can be inferred that the fixed charge density of the AEL should be less than 2 M. When the electrolyte concentration increases from 2 M KOH to 3 M KOH, the rise in potassium flux (from $500 \mu\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$ to $800 \mu\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$) is directly proportional to the concentration change, reflecting the absolute dominance of diffusion after the Donnan exclusion limit breakthrough. As for the bicarbonate ion flux data, the fixed charge density is likely greater than 2 M but definitely less than 3 M.

4.1.2. Supplementary Information on Section 4.1

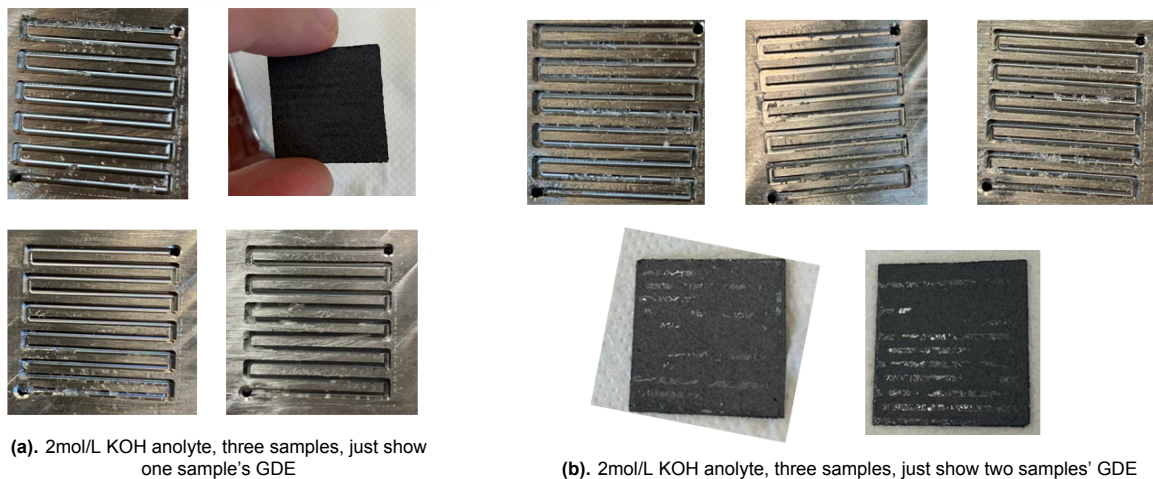


Figure 4.2: Salt precipitation on the flow field and GDE back surface after 1 hour of operation with high-concentration KOH anolyte at $j = 100 \text{ mA/cm}^2$

In Figure 4.2 a & b, salt precipitation is shown for 2 mol/L KOH and 3 mol/L KOH, respectively, after just 1 hour of operation at $j = 100 \text{ mA/cm}^2$. For the 2 mol/L sample, salt streaks are also present on the actual GDE back surface, though they are less obvious than those in the 3 mol/L sample and require closer inspection.

In the context of salt precipitation, potassium ions (salt precursor) act as a bicarbonate trap, preventing further migration of bicarbonate from the cathode side to the anolyte. As a result, salt precipitation reduces the bicarbonate flux.

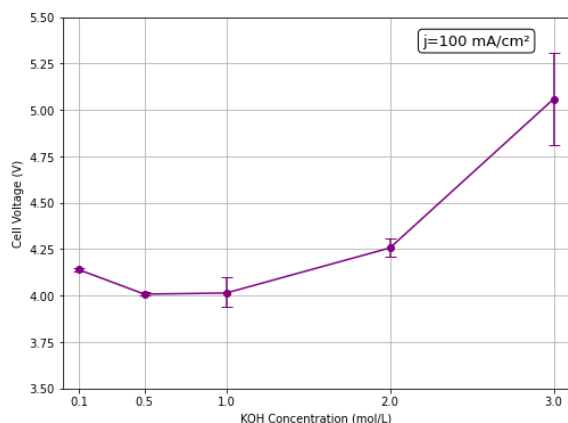


Figure 4.3: Cell voltage over different KOH anolyte concentration, $j=100 \text{ mA/cm}^2$, duration = 1 hour

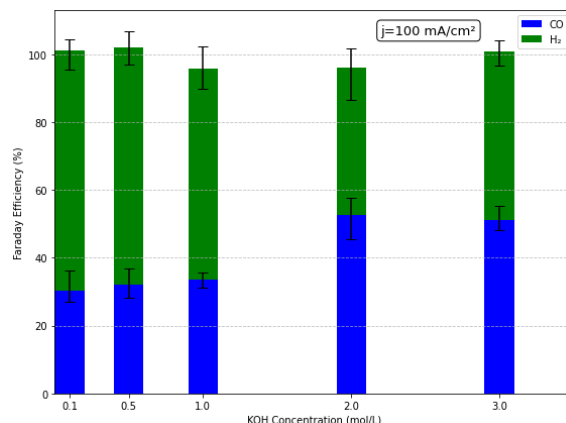


Figure 4.4: Faradic efficiency over different KOH anolyte concentration, $j=100 \text{ mA/cm}^2$, duration = 1 hour

Figure 4.3 shows that the cell voltage for the 0.1 mol/L electrolyte is higher than that of the 0.5 mol/L and 1 mol/L electrolytes. This is due to the lower OH^- concentration (i.e., lower chemical potential) in the 0.1 mol/L solution, which results in a higher anodic Nernstian electrode potential. However, for the 2 mol/L and 3 mol/L electrolytes, the cell voltage does not continue to decrease; instead, it increases significantly. This phenomenon cannot be explained solely from a thermodynamic perspective.

Starting from 2 mol/L, the cell voltage begins to rise, reaching approximately 4.25 V. At 3 mol/L, the voltage surges to 5.06 V. Kailun et al. [36] aimed to enhance the Faradic efficiency of the r-BPM MEA by using a high-concentration KOH anolyte, and in their work, they also observed that using a 3 M KOH anolyte significantly increased the cell voltage.

Bui et al. in their paper "Understanding Multi-ion Transport Mechanisms in Bipolar Membrane" [15] explain that for r-BPM immersed in high-concentration alkaline (acid) solutions, the outward transport of hydroxide (hydronium) within the membrane primarily relies on migration, while diffusion becomes a resistance (see Figure 2.18), which is a possible factor for the increase in cell voltage.

They also mentioned that as the fraction of co- or counter-ions in the membrane increases, the membrane retains less water. Moreover, the conductance of co-ions within the membrane is lower than that of hydronium and hydroxide. This is likely another contributing factor, as the 3M KOH solution results in excessive co-ions crossover.

At last, the increased viscosity (reduced diffusion coefficient) of the concentrated electrolyte leads to excessive concentration polarization at the anode based on equation (2.19) & (2.35). At 25°C, the viscosity of 1 mol/L, 2 mol/L, and 3 mol/L KOH aqueous solutions are 0.9980, 1.1200, and 1.2656 mPa·s, respectively [77].

Due to the significant variation in cell voltage at high concentrations, it remains unclear how/whether this elevated voltage influences the potential gradient ($\frac{\partial \phi}{\partial x}$) (migration-relevant) for co-ions transport across the r-BPM.

Finally, Figure 4.4 illustrates that under high-concentration anolyte conditions, Faradic efficiency is enhanced. This should be attributed to the pronounced cation effect on eCO₂RR, as well as the suppression of WDR.

4.2. The Influence of Operation Duration on Co-ions Transport

4.2.1. Co-Ions Transport Flux Across Varying Time Durations

In the previous section, the anolyte was adjusted primarily on the anode side to modify the diffusion driving force (concentration gradient). In contrast, this section alters the concentration gradient on the cathode side by extending the operating duration. The cathode side is a zero-gap, catholyte-free region, where the migration and gradual accumulation of potassium ions lead to a significant concentration change. Although carbonate ions also accumulate in the anolyte over time, their impact is evidently negligible.

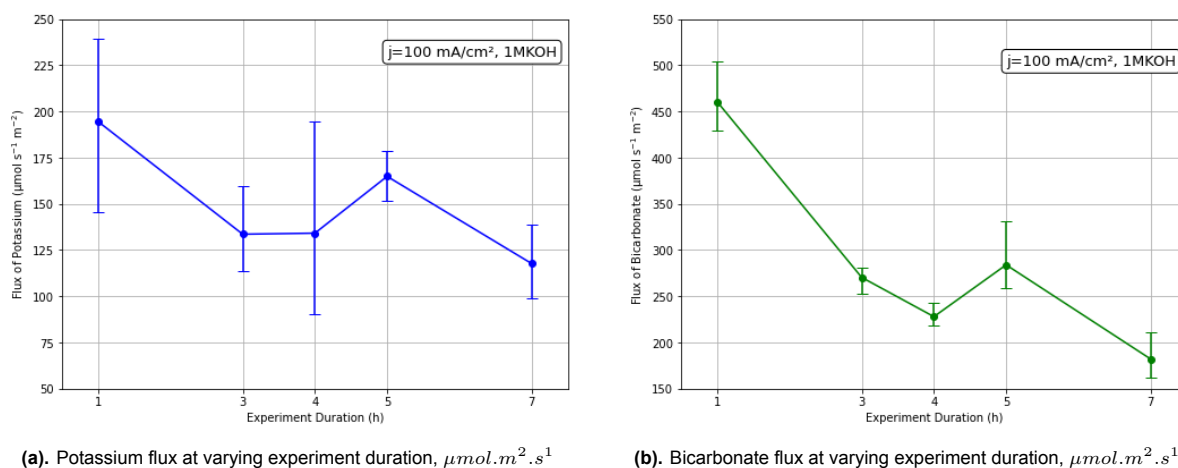


Figure 4.5: Co-ions flux at varying experiment duration, with 1 mol/L KOH anolyte, $j=100 \text{ mA/cm}^2$

Figure 4.5 a and b generally illustrate a trend where the flux of potassium and bicarbonate ions gradually decreases over time, approaching a quasi-steady plateau—though not achieving a true steady state. Notably, the co-ion flux here is derived from titration results at the end of the experiment, normalized by the total experiment duration, thus it is an average value, co-ions flux can vary hour by hour. The observed near-steady trend is closely linked to the salt dissolution-precipitation equilibrium on the cathode side. This expected outcome further reinforces the positive correlation between potassium and bicarbonate flux.

Figure 4.5a and b show a distinct rise in co-ions flux at fifth hour, indicating a significant increase in co-ions leakage between the fourth and fifth hour. A plausible explanation for this phenomenon lies in salt precipitation. As cations crystallize from the over-saturated solution phase, it ceases the trend of back diffusion trend of cation toward the anode and enhance cation transport from the anode to the cathode.

Nonetheless, at the seventh hour co-ions flux reduce notably decline, it is estimated the salt-precipitation re-dissolving occurred. Moreover, it is hypothesized that the re-dissolution of the precipitate could cause a divergence in the trends of potassium ion flux and bicarbonate flux at this point. Specifically, the potassium ion flux may decrease, while the bicarbonate ions previously captured in the crystal structure could be released, leading to an increase in their flux.

4.2.2. Supplementary Information of Section 2

In Figure 4.6, it is observed that after 5 hours, more salt crystals accumulate in the flow field compared to the 7-hour mark, suggesting subsequent re-dissolution of the precipitated salt. Moreover, a key insight emerges: the concentration required to trigger salt precipitation is significantly higher than that of the 1M anolyte, yet cation transport continues—demonstrating the critical role of migration in cation crossover.

In fact, in the one-hour experiment of Section 1, 2M and 3M KOH anolyte have already led to salt

precipitation. However, considering that the solubility of $KHCO_3$ is 2.24M, which is lower than or roughly comparable to the anolyte concentration, this alone is not sufficient to fully substantiate the contribution of migration. Additionally, the solubility of K_2CO_3 is 7.93M, which implies that although r-BPM can significantly suppress carbonate formation and potassium ion crossover compared to AEM, its ability to inhibit salt precipitation is still somewhat compromised, as the solubility of $KHCO_3$ is far lower than that of K_2CO_3 .

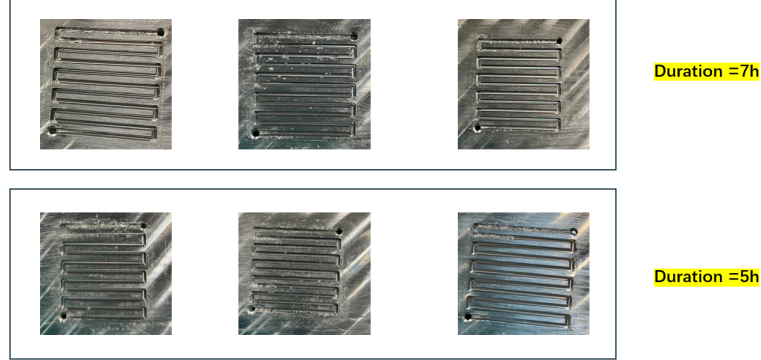


Figure 4.6: Salt precipitation on the flow field after 5 hour and 7 hour of operation with 1 mol/L concentration KOH anolyte at $j = 100 \text{ mA/cm}^2$

In the long-term test, the Faradic efficiency consistently increases with each GC injection, further reflecting the accumulation of cations at the cathode, while the cell voltage remains stable (as shown in Figure 4.7).

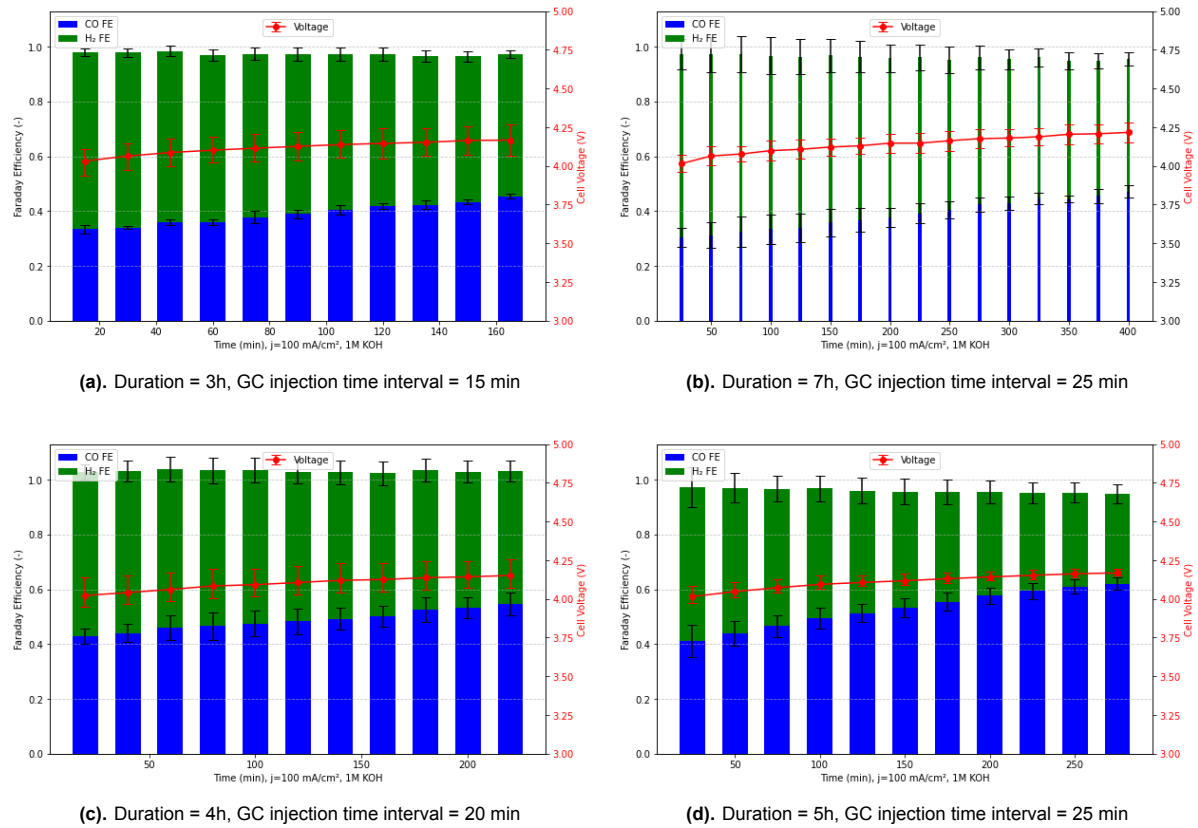


Figure 4.7: Long-term experiments Faradic efficiency and cell voltage at each injection time, $j=100 \text{ mA/cm}^2$, 1mol/L KOH anolyte

Figure 4.7 conveys an important insight. As the flux of co-ions gradually decreases over time, theoretically, WDE should increase accordingly. However, the fact that FE continues to rise throughout the long-term experiment suggests that the enhancement of FE due to the cation effect is more dominant than the suppression of WDR, which would otherwise contribute to FE enhancement. Moreover, in the final stages of the 5-hour and 7-hour experiments, FE remains essentially unchanged, indicating that the cation concentration is approaching saturation.

In this section, the conclusions can be drawn:

- With the accumulation of operation time, the cation concentration increases significantly at the cathode, and the impact of diffusion on co-ion transport becomes pronounced.
- The positive correlation between potassium ion flux and bicarbonate ion flux is further confirmed.
- Salt precipitation complicates co-ion transport but provides strong evidence for the contribution of migration to co-ion transport.
- The contribution of the cation effect to eCO₂RR becomes more pronounced over time.

4.3. The Influence of Current Density on Co-ions Transport

4.3.1. Co-ions Transport Flux at Different Current Density

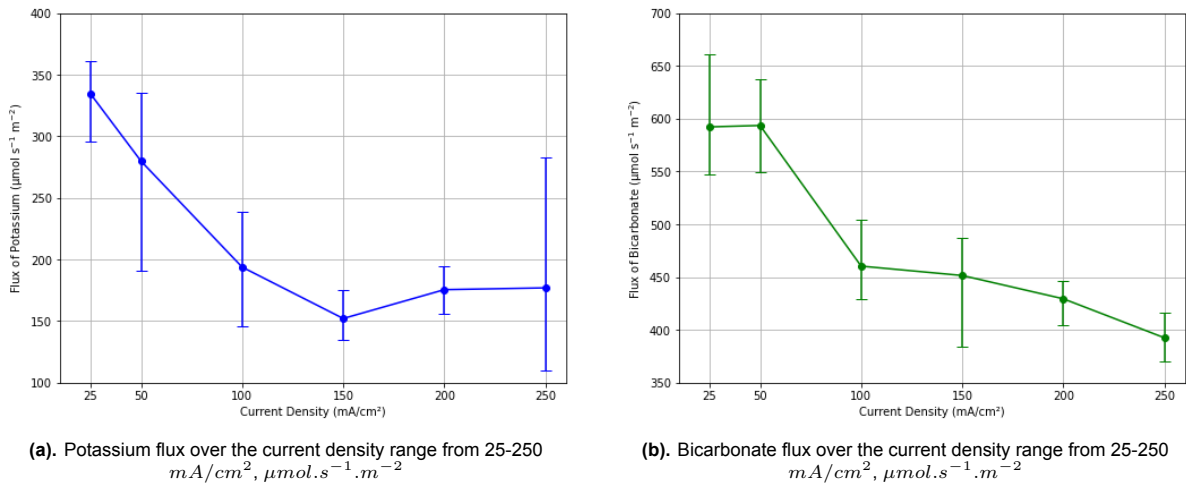


Figure 4.8: Co-ions flux over varying current densities, 1 mol/KOH, duration = 1 hour

Figure 4.8 illustrates the overall trend that the flux of co-ions decreases as current density increases. According to the characteristics of r-BPM, at low current densities (membrane voltage < 0.8V), co-ions transport dominates. Once WDR is triggered, hydronium-hydroxide transport becomes the primary mechanism. However, the critical question remains: why does the co-ions flux decrease? Our initial expectation was that the co-ions flux would either increase or at least remain stable, given that the rise in cell voltage could potentially enhance co-ions flux via the migration effect. A decrease in flux was not anticipated.

This critical question can be re-framed as: why does a higher current density enhance the permselectivity of r-BPM? Our approach is to examine this phenomenon through the lens of r-BPM electrochemical polarization. In their analysis of r-BPM CO_2 electrolyzer cell voltage decomposition, Vermaas et al. [51] explicitly mentioned the over-potential of r-BPM but were unable to fully decouple its electrochemical and ohmic polarization. While applying the Butler-Volmer equation (Tafel plot) to electrode reactions is a well-established approach, its application to WDR has rarely been reported.

Polarization invariably raises the anode potential while lowering the cathode potential. In the case of r-BPM, at higher current densities, the WDR kinetic rate becomes the limiting factor. Consequently, it is hypothesized that the fixed charges in both the AEL and CEL layers cannot be effectively occupied,

leaving more sites exposed. This aligns with that an elevated potential on the AEL (anode) side and a reduced potential on the CEL (cathode) side. Effective (exposed) fixed charge of IEM determines the IEM's perm-selectivity essentially, the more exposed fixed charge, the higher perm-selectivity (this point has been mentioned in section 1).

Furthermore, we hypothesize that at higher current densities, the enhancement of WDR leads to a greater outward flux of hydronium-hydroxide, which may increase congestion within the membrane's transport channels (channel congestion effect), thereby reducing the diffusion coefficient of co-ions within the membrane. For bicarbonate, the enhanced WDR implies increased CO_2 reversion; however, this cannot account for the reduction in bicarbonate flux, as the rate of bicarbonate formation also increases with the increasing current density.

Moreover, the co-ions flux at 200 & 250 mA/cm^2 most effectively reflects the intrinsic contribution of diffusion.

Therefore, the conclusion can be drawn as:

Higher current Density enhance rBPM permselectivity by the hypothesis of both polarity (membrane/solution inter face) and channel congestion effect (within membrane)

4.3.2. Supplementary Information of Section 3

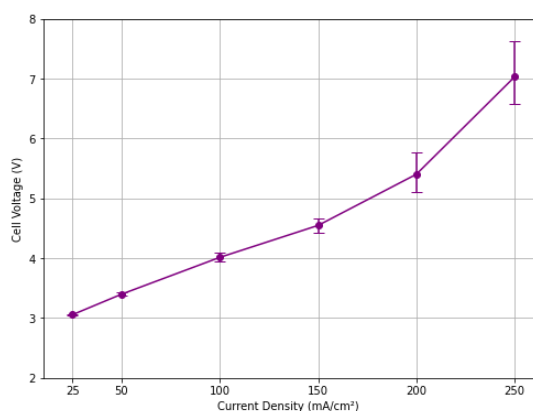


Figure 4.9: Cell Voltage Over Varying Current Density, 1 mol/L KOH, duration = 1h

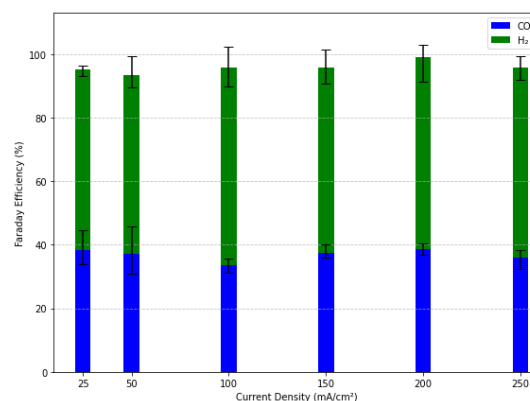


Figure 4.10: Faradic efficiency over varying current density, from 25 to 250 mA/cm^2 , 1 mol/KOH anolyte, duration = 1h

Figure 4.9 demonstrates the limiting behavior of the r-BPM at current densities of 200 and 250 mA/cm^2 . This limitation likely arises from both water penetration and water dissociation constraints. As shown in Figure 4.8 a, the potassium ion flux exhibits a rebound at 200 and 250 mA/cm^2 . This can be attributed to the electro-osmotic effect, as the system demands more water to enter the inter layer under these conditions, with potassium ions effectively acting as water carriers.

Figure 4.10 shows that the Faradic efficiency remains largely unchanged across varying current densities. This can be attributed to the r-BPM's ability to regulate the local pH. At high current densities, the H^+ concentration at the surface of the CEL increases. Simultaneously, the increasing of OH^- ions on the catalyst surface intensifies carbonation, which consumes H^+ ions and suppresses excessive HER.

4.4. The Combined Influence of Concentration and Current Density on Co-ions Transport

4.4.1. Co-ions Transport Flux under 2M KOH Anolyte at Current Density Range of 50-150 mA/cm²

The purpose of this working package primarily lies in verifying the drawn conclusions in section 1 and section 3.

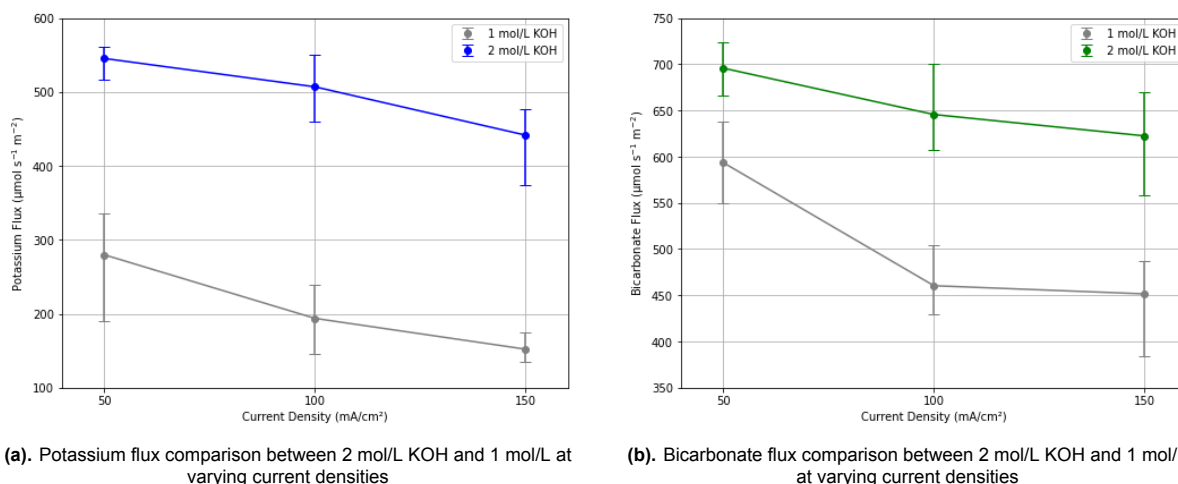


Figure 4.11: Comparison of co-ion flux between 2 mol/L and 1 mol/L KOH at current densities of 50, 100, and 150 mA/cm², respectively, duration = 1 hour

In Figure 4.11 a, diffusion has a significant impact on potassium ion transport. When the current density is extended to 50 mA/cm² and 150 mA/cm², a trend similar to that at 100 mA/cm² emerges—doubling the potassium ion concentration nearly doubles the flux. In Figure 4.11 b, at 50 mA/cm², the bicarbonate flux under 2 mol/L anolyte is relatively close to that of 1 mol/L anolyte, which is likely due to salt precipitation.

4.4.2. Supplementary Information of Section 4



Figure 4.12: GDE back surface of three parallel samples with 2 mol/L KOH anolyte, at $j=50 \text{ mA/cm}^2$, duration = 1h

Compared to Figure 4.2 a ($j = 100 \text{ mA/cm}^2$, 2 mol/L KOH), Figure 4.12 shows significantly more salt precipitation. This accounts for its relatively low bicarbonate flux ($j=50 \text{ mA/cm}^2$, 2mol/L KOH), as it is trapped by salt crystals. Additionally, at $j = 150 \text{ mA/cm}^2$, 2 mol/L KOH, with a duration of 1 hour, there is no observed salt precipitation behind the GDE, which further demonstrates that high current density impedes cation transport.

*Higher current density indeed inhibit cation transport , by
Visualized salt precipitaptn besides titration result*

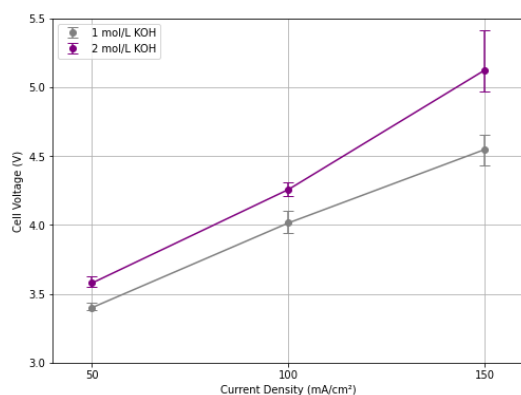


Figure 4.13: Cell voltage comparison between 2 mol/L KOH and 1 mol/L at varying current densities

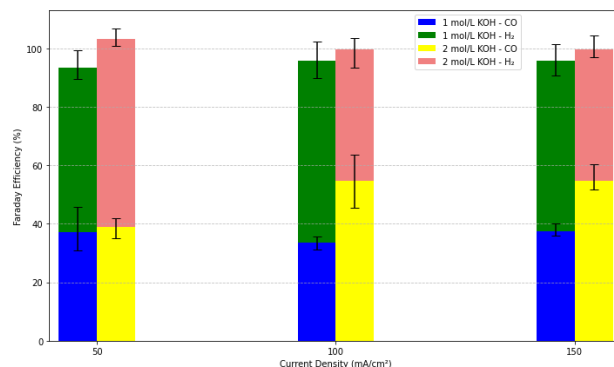
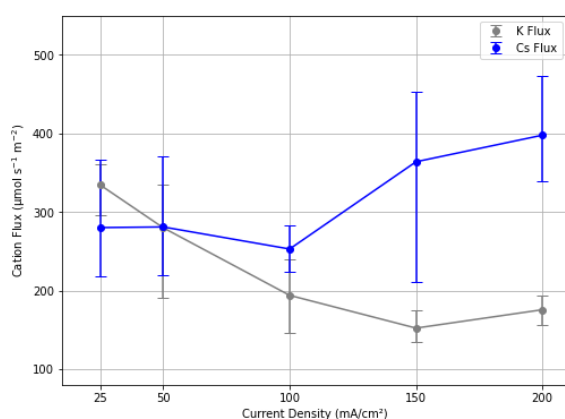


Figure 4.14: Faradic efficiency comparison between 2 mol/L KOH and 1 mol/L at varying current densities

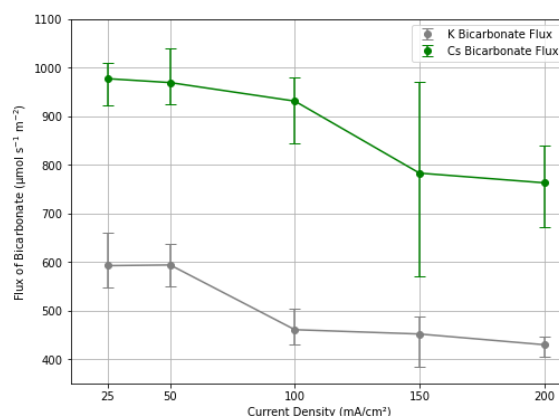
Figure 4.13 further confirms that a high-concentration anolyte leads to an elevated cell voltage, while Figure 4.14 once again demonstrates that the high cumulative potassium concentration at the cathode enhances the Faradic efficiency of eCO₂RR.

4.5. The Influence of Cesium Ions on Co-ions Transport Compared to Potassium Ions

4.5.1. Co-ions Flux at Different Current Densities under 1M CsOH Anolyte



(a). Cesium & potassium ion flux comparison at the current densities range from 25 to 200 mA/cm^2 , $\mu\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$



(b). Bicarbonate ion flux comparison at the current densities range from 25 to 200 mA/cm^2 between 1 mol CsOH and 1 mol/L KOH anolyte, $\mu\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$

Figure 4.15: Co-ions flux comparison at varying current densities, 1 mol/L CsOH vs. 1 mol/L KOH anolyte, duration = 1 hour

In experiments involving a 1 mol/L KOH anolyte, it was observed that a current density of $j = 250 \text{ mA}/\text{cm}^2$ imposed excessively harsh conditions on the r-BPM, even with an experimental duration of just 1 hour. Therefore, in this working package—using a 1 mol/L CsOH anolyte—this current density was excluded.

The ion flux comparison shown in Figure 4.15 highlights the significant impact of cation identity on ion transport behavior.

Figure 4.15 b reveals a clear trend: the CsOH analyte significantly boosts the bicarbonate flux at each corresponding current density compared to the KOH analyte. This observation raises the question of why cesium ions, compared to potassium ions, are more effective at reducing the perm-selectivity of the CEL. To address this, we refer to the concept introduced by Geise et al. in their paper "Specific Ion Effects on Membrane Potential and the Perm-Selectivity of Ion Exchange Membranes (2014)," [78] which discusses the binding affinity between counter-ions and fixed charges. This concept is similar to the counter-ion adsorption mentioned in Section 1, and even to the fixed charge exposure caused by IEM polarity discussed in Section 3. All these concepts aim to explain the impact of effective fixed charge on perm-selectivity. However, while counter-ion adsorption in Section 1 emphasizes the quantity, the counter-ion binding affinity here focuses more on the quality of the interaction.

The fundamental difference between potassium and cesium ions lies in their ionic radii, which in turn influences the structure of their hydration shells, as illustrated in Figure 2.9. In the context of the eCO₂RR reaction, cesium ions are more effective than potassium ions at enhancing Faradic efficiency, primarily because the hydration shell of cesium is thinner, leading to stronger electrostatic effects. This concept can be directly applied to counter-ion binding affinity. Specifically, cesium ions reduce the perm-selectivity of the CEL by virtue of their stronger binding affinity to the CEL fixed charge.

In Figure 4.15 a, at low current densities of 25 and 50 mA/cm², the fluxes of potassium and cesium ions are nearly identical (mainly controlled by diffusion). However, at higher current densities, the mass transfer flux of cesium ions is significantly higher than that of potassium ions. To explain this phenomenon, we once again apply the role shifting effect and complete the loop of co-ions transport mechanism across the r-BPM. Since cesium ions facilitate greater bicarbonate crossover at the CEL, and upon reaching the AEL, these bicarbonate ions transform into counter-ions, we propose that by the time they reach the AEL (or within the AEL), bicarbonate has converted into carbonate. The increased presence of divalent carbonate ions significantly weakens the polarization effect on which inhibit cesium ion crossover, thereby reducing AEL's perm-selectivity to cesium ions at higher current densities.

At high current densities, approaching the operational limit of the r-BPM, the flux of both potassium and cesium ions increases, with the rise being more pronounced for cesium. We attribute this to water feeding by cation electro-osmotic drag, as the system demands more water for dissociation. At this stage, cations reside on the anolyte side (the water reservoir), and their increased flux serves to supply IL with as much water as possible. Since cesium ions carry fewer water molecules than potassium, they require a greater electro-osmotic drag flux to meet the water demand of WDR. Alternatively, presumably at high current densities, the thinner hydration shell and lower permittivity of cesium ions may render them more sensitive to migration effects.

Therefore, the conclusion can be drawn as

Cesium ions reduce rBPM permselectivity by the hypothesis of dual role shifting effect

4.5.2. Supplementary Information of Section 5

Figure 4.16 shows that the cell voltage variation with current density for both 1 mol/L CsOH and 1 mol/L KOH analytes follows a similar trend, which further rules out the potential gradient as a factor influencing the two solutions. Figure 4.17 illustrates the cationic effect of cesium ions on eCO₂RR, with the Faradic efficiency for the 1 mol/L CsOH analyte being noticeably higher across all current densities compared to the 1 mol/L KOH analyte.

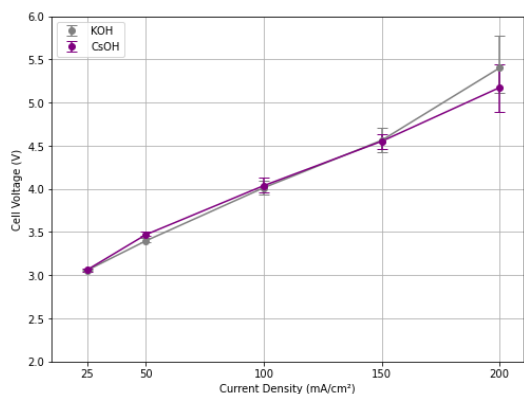


Figure 4.16: Cell voltage comparison at varying current densities, 1 mol/L CsOH vs. 1 mol/L KOH anolyte, duration = 1h

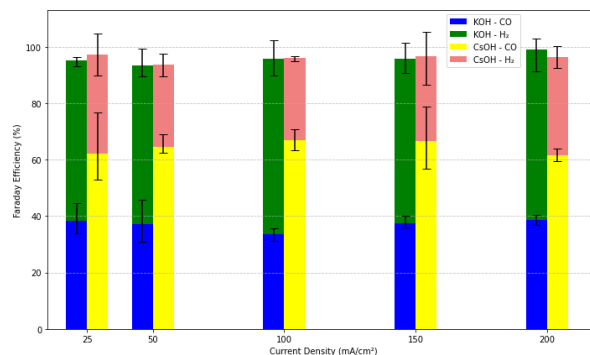
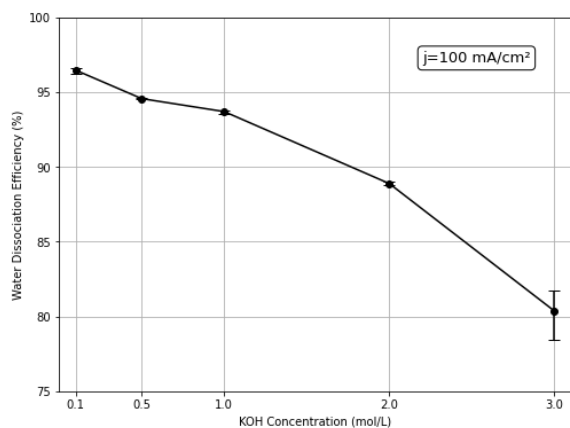


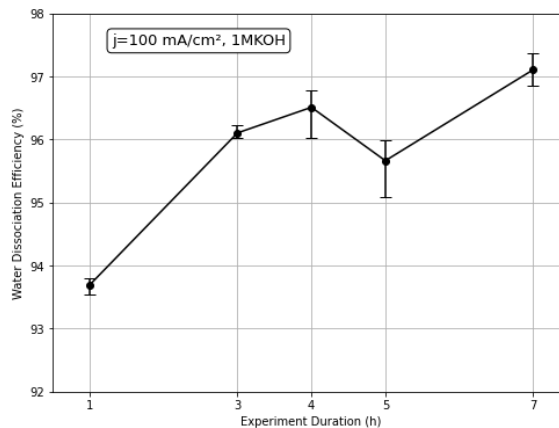
Figure 4.17: Faraday efficiency comparison at varying current densities, 1 mol/L CsOH vs. 1 mol/L KOH anolyte, duration = 1h

4.6. Two Key Parameters Derived from Co-ions Flux

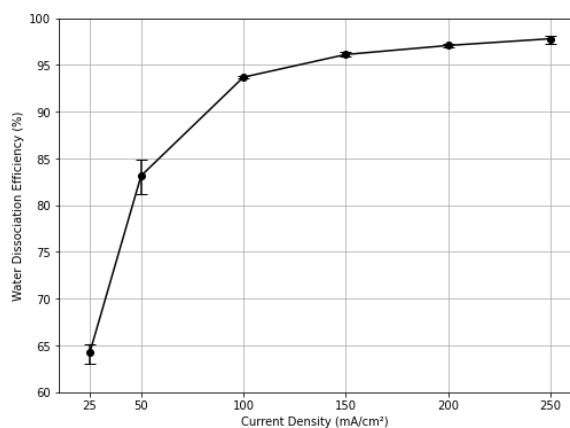
4.6.1. The Primary Derived Parameter - Water Dissociation Efficiency



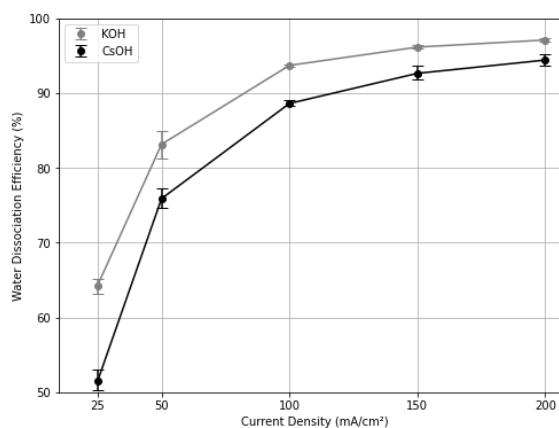
(a). WDE with varying concentration KOH anolyte, $j=100 \text{ mA/cm}^2$, duration = 1h



(b). WDE over varying experiment duration, 1 mol/L KOH, $j=100 \text{ mA/cm}^2$



(c). WDE at varying current densities, 1 mol/L KOH, duration = 1h



(d). WDE at varying current densities, 1 mol/L CsOH, duration = 1h

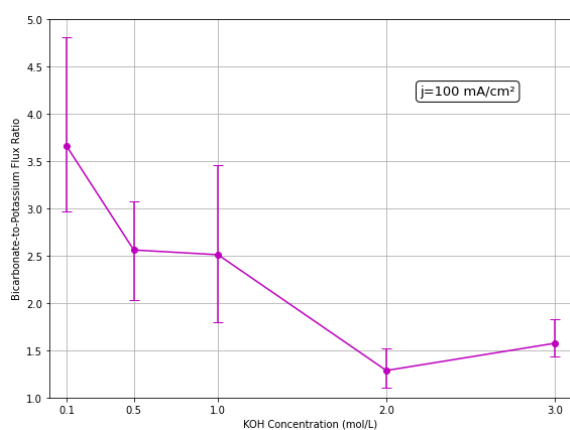
Figure 4.18: Water dissociation efficiency (WDE) overview throughout various working packages

Water dissociation efficiency (WDE) is a parameter highly relevant to industrial applications, as it directly affects the analyte's pH state and is closely linked to operating time, current density, and analyte volume. According to equation (3.12), compared to co-ions flux, WDE is a relative value determined by both co-ions flux and current density. The higher the current density and (or) the lower the co-ions flux, leading to a higher WDE.

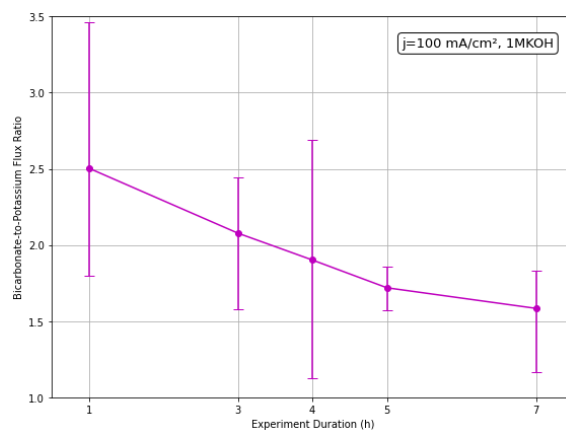
Figure 4.18 a shows that, for a constant current density, WDE decreases as concentration increases, which is inevitable due to the positive correlation between cation crossover and bicarbonate crossover. While higher concentration electrolytes bring about higher Faradic efficiency, they significantly reduce energy efficiency and WDE, thus not advisable to adopt high concentration analyte scheme. As shown in Figure 4.18 b, in principle, WDE can continue to improve with increasing operation time. However, salt precipitation is a major limiting factor.

Figure 4.18 c demonstrates that, under a 1 mol/L KOH analyte, WDE increases with rising current density. This effect is twofold: not only boost WDR, but also reduce co-ions flux. Increasing current density to enhance WDE is a sound strategy, but it is limited by the r-BPM's limiting current and energy efficiency. Figure 4.18 d shows that the WDE of a 1 mol/L CsOH analyte is lower than that of a 1 mol/L KOH analyte at all current densities. This is due to its higher co-ions flux at each current density. While CsOH provides high Faradic efficiency, it results in a loss of WDE. Given its high cost, CsOH analyte is therefore not recommended.

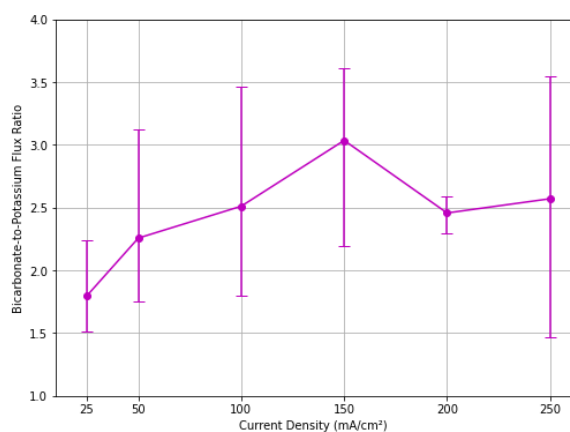
4.6.2. The Secondary Derived Parameter - Bicarbonate to Cation Flux Ratio



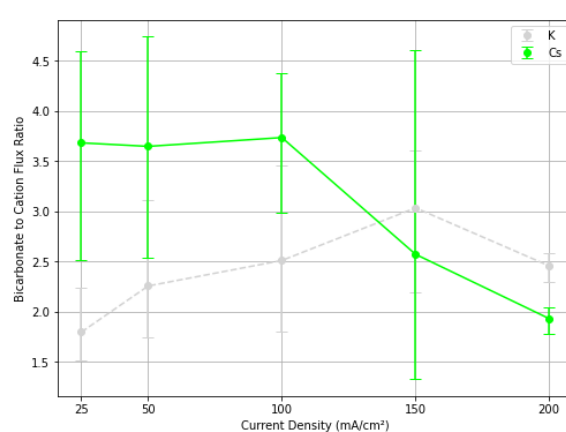
(a). Co-ions flux ratio varying concentration KOH analyte, $j=100\text{ mA/cm}^2$, duration = 1h



(b). Co-ions flux ratio over varying experiment duration, 1 mol/L KOH, $j=100\text{ mA/cm}^2$



(c). Co-ions flux ratio at varying current densities, 1 mol/L KOH, duration = 1h



(d). Co-ions flux ratio at varying current densities, 1 mol/L CsOH, duration = 1h

Figure 4.19: Bicarbonate to cation flux ratio throughout various working packages

The co-ions flux ratio provides additional information compared to the individual cation flux and bicarbonate flux. As shown in Figure 4.19, the bicarbonate to cation flux ratio is greater than 1. One factor contributing to this is the diffusion of bicarbonate from the zero-gap side to the anolyte side. The concentration gradient driving this diffusion is greater than that of the cation diffusion. Unlike cations, which have a higher concentration at the cathode, bicarbonate does not experience back diffusion. If H_2CO_3 crosses the membrane in its molecular form, it is also mistakenly considered as part of the bicarbonate flux. In addition, (bi)carbonate is recurrently produced as electrons are continuously injected into the cathode, whereas the number of cations is limited to those present in the anolyte.

Figure 4.19 a & b can support that salt precipitation can capture the bicarbonate and hinder its transport to anode. Furthermore, Figure 4.19 c show that the bicarbonate to potassium flux ratio is on average stabilized to 2 (stable positive correlation between two co-ion flux), while Figure 4.19 d embodies pretty different behavior of co-ions transport with CsOH anolyte compared to KOH anolyte, ascribed to their different hydration structure shell with each other.

4.7. Zero-gap CO₂ Electrolyser Operation Limit with Reverse-bias Bipolar Membrane

4.7.1. Corrosion Limit

In this section, the anodic electrolyte samples after electrolysis are neither subjected to titration analysis nor required to follow the quantitative principle of conducting three parallel experiments under identical conditions.

As shown in the previous results, the WDE of the 0.1 mol/L KOH anolyte is high, however, due to its low intrinsic OH^- reserve, it is necessary to investigate its corrosion onset time. Consistent with all experiments, the anolyte volume is maintained at 90 mL.

A preliminary 9-hour experiment was conducted, after which the nickel mesh remained silvery-white with no visible signs of corrosion. Subsequently, a 14-hour experiment was performed, during which the nickel mesh underwent complete corrosion. The voltage evolution over time for both experiments is illustrated in the Figure 4.20.

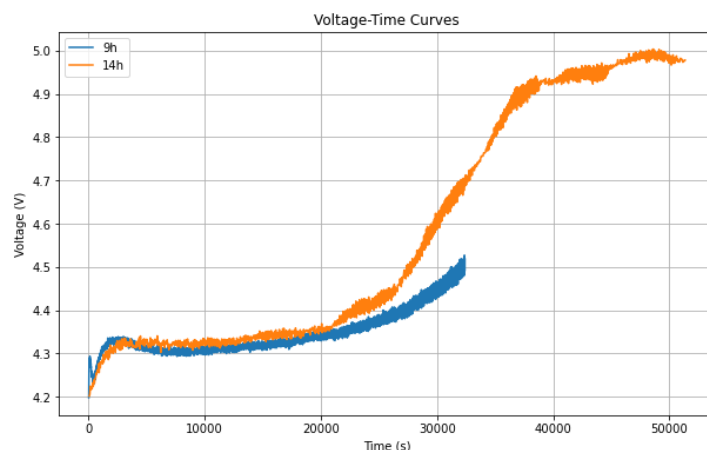


Figure 4.20: Chronopotentiometry voltage-time plot, 0.1 mol/L KOH anolyte, $j=100 \text{ mA/cm}^2$, duration =9h & 14h

The initial voltage rise is likely attributed to the gradual depletion of the anolyte's OH^- reserve. However, the sharp, linear increase in voltage observed around 27,000 seconds in the 14-hour experiment can be definitively linked to the corrosion of the nickel mesh, with the affected area progressively expanding. When the voltage increase eventually stabilizes into another plateau at approximately 40,000 seconds, it indicates that the nickel mesh has been nearly completely corroded.

The voltage profiles of the 9-hour and 14-hour experiments exhibit some divergence beyond 27,000

seconds, which is likely due to differences in co-ion flux crossover between the two experiments. To better capture the system's corrosion onset time, an additional 11-hour experiment was conducted. After 11 hours, the nickel mesh showed edge corrosion, while corrosion spots appeared in the central region. The post-experiment corrosion states of the 14-hour and 11-hour tests are illustrated in the Figure 4.21.

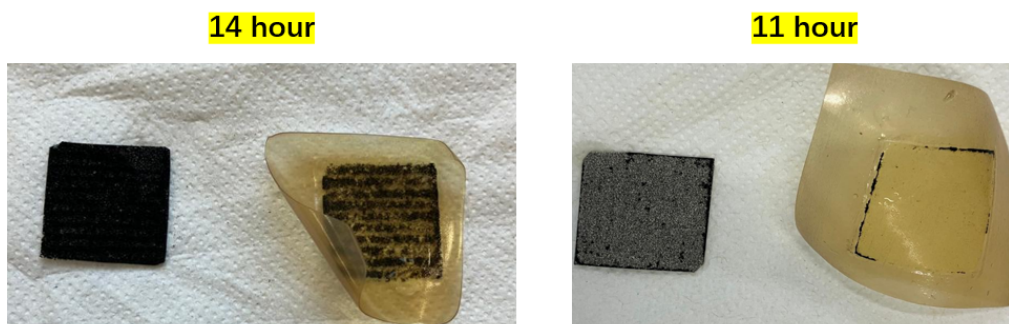


Figure 4.21: Nickel mesh corrosion image (fully back after 14h), with the BPM image after experiment, 0.1 mol/L KOH anolyte, duration = 11h & 14h, anolyte volume =90 ml, $j=100 \text{ mA/cm}^2$

In addition, within the experimental duration range, anode catalyst corrosion doesn't influence on cathode reaction (Faradic efficiency). And there is almost precipitation-free for three long-term experiments with 0.1 mol/L KOH. At last, the conclusion is that based on this setup (90 ml anolyte, 0.1 mol/L KOH, $j=100 \text{ mA/cm}^2$), the nickel corrosion-free operation duration is approximately 9 to 10 hours

4.7.2. Blocking Limit

r-BPM can suppress carbonation, enhance carbon efficiency, and mitigate salt precipitation. The 1 mol/L KOH anolyte is the most commonly used electrolyte in this project, with a sufficient reserve of OH^- . Therefore, the impact of salt precipitation on system reliability under long-term operation with this anolyte was investigated.

First, an 8-hour experiment was conducted, at end the gas channel was fully blocked. This also served as the basis for setting the maximum duration to 7 hours in the co-ions transport over longer duration working package.

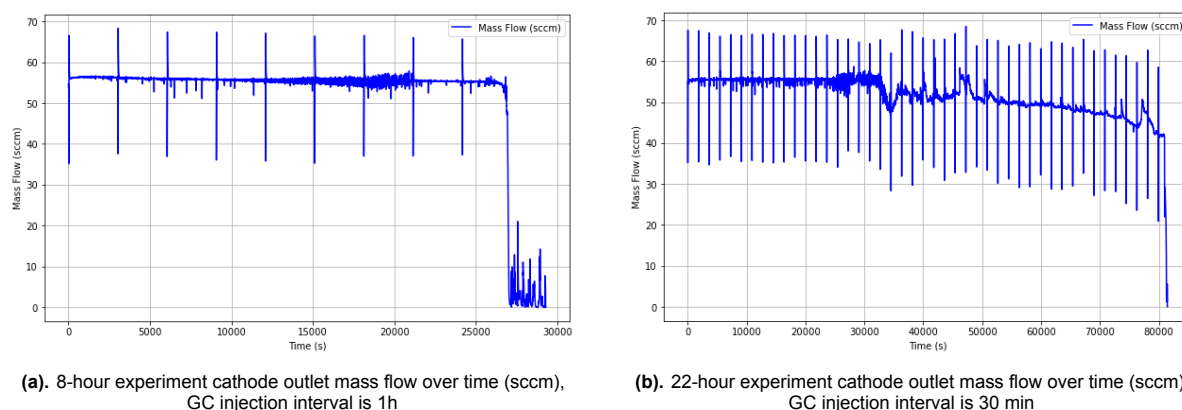


Figure 4.22: Long-term experiment for witnessing gas flow field blocking, cathode inlet CO₂ mass flow setting is 50 sccm, $j=100 \text{ mA/cm}^2$, 1 mol/L KOH anolyte

To verify the repeatability of the experiment and confirm blocking onset time, it was conducted once again. However, this time, it took an 22 hours for the gas channel to become completely blocked. The significant difference between 8 hours and 22 hours warrants a analysis of the underlying reasons.

Figure 4.22 illustrates the evolution of cathode outlet gas flow over time for both experiments. In the 8-hour experiment (subfigure a), the outlet flow rate experienced a sharp drop near the end, forcing the experiment to be terminated. In contrast, in the 22-hour experiment (subfigure b), the outlet flow began to exhibit significant fluctuations around the 8-hour mark and had already dropped below 50 sccm by the 9.5 hour. Although the flow showed some recovery afterward, it never exceeded 50 sccm beyond the 14th hour and eventually became completely blocked at the 22-hour mark.

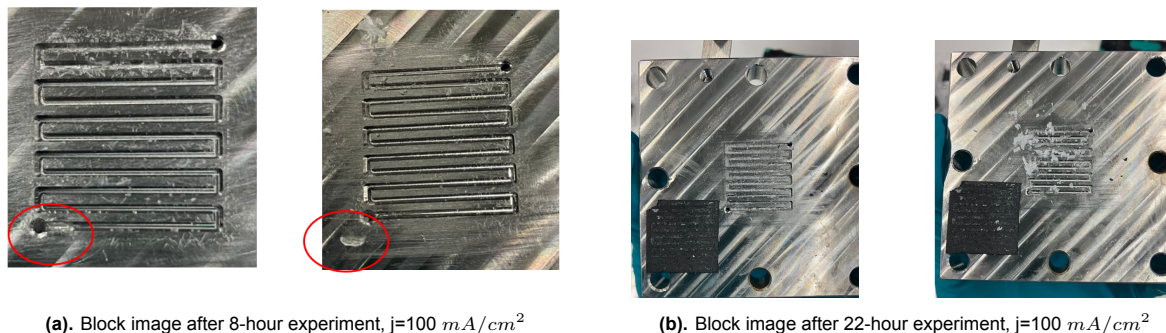


Figure 4.23: Picture of salt precipitation to fully block gas flow field, 1 mol/KOH anolyte

By examining the salt precipitation in the cathode gas flow channel after the experiment, as shown in Figure 4.23, it was observed that the amount of salt accumulation in the 8-hour experiment was relatively modest. The right image in sub-figure (a) shows the salt collected by scraping with a blade. Most notably, a single rice-grain-shaped crystal (indicated by red circle) was found precisely blocking the gas channel outlet, which was the decisive factor leading to the complete blockage at the 8-hour mark.

In contrast, for the 22-hour experiment (subfigure b), the gas channel was densely packed with salt, forming a solid blockage that required considerable effort to scrape off with a blade. Additionally, a significant amount of salt residue had permeated through to the back of the GDE.

Both experiments share a common pattern: in one case, complete blockage occurred at the 8-hour mark, while in the other, severe fluctuations in outlet gas flow began around the 8th hour, followed by a progressive system decline. This suggests that the effective operational duration in both cases was limited to approximately 8 to 9 hours. Moreover, it was observed that salt crystal formation exhibits greater randomness compared to nickel mesh corrosion. Once a crystal lodges itself in a critical position, even a relatively small amount of salt can be sufficient to trigger a system shutdown.

At last, in the longest experiment in this project, salt re-dissolving was observed in directly. As shown in Figure 4.24, the spike of hydrogen Faradic efficiency indicates the salt-induced flooding occurring.

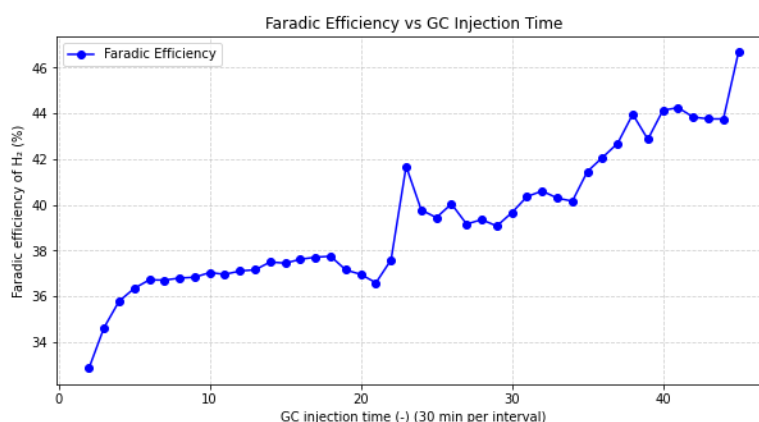


Figure 4.24: Hydrogen Faradic efficiency of 22-hour experiment, $j=100 \text{ mA/cm}^2$, 1M KOH

5

Conclusion

This project found: A high-concentration anolyte enhances diffusion control over co-ions transport and reduces the perm-selectivity of r-BPM. While migration contributes to co-ion transport, its correlation with current density is not explicitly evident and high current density improves the perm-selectivity of r-BPM. Long-term operation exhibits pronounced diffusion control characteristics and induces precipitation, further complicating co-ion transport. Due to the significant differences in the hydration shell structure between cesium and potassium ions, cesium ions reduce the perm-selectivity of r-BPM (especially CEL) significantly, compared to potassium ion.

The study focus of co-ions transport cross r-BPM lies in how the membrane's effective fixed charge density are influenced, thereby altering its perm-selectivity toward co-ions. Furthermore, the role shift of co-ions to counter-ions after crossing corresponding mono-layer membrane is an intrinsic characteristic of ion transport through r-BPM. Moreover, it is supposed to emphasize the dominant role of cations compared to bicarbonate ions. This fundamental feature determines the positive correlation between cation flux and bicarbonate co-ion transport.

The reliability of the current zero-gap r-BPM CO_2 electrolyser system is low, constrained by three major limitations: current density, blockage, and corrosion. The maximum stable operating current density is approximately 100–150 mA/cm². Under 1M KOH at $j = 100$ mA/cm², stable operation lasts for only about 8 hours, after which salt precipitation deteriorates the operating environment. Similarly, under 0.1M KOH at $j = 100$ mA/cm², stable operation is limited to 10 hours, beyond which nickel mesh corrosion occurs.

In addition, we briefly recap five previously published conclusions that have been reproduced in this study: 1. A high-concentration anolyte (cation) enhances Faradic efficiency. 2. Cesium ions improve Faradic efficiency more significantly than potassium ions. 3. A high-concentration anolyte leads to a higher cell voltage. 4. A higher current density increases water dissociation efficiency. 5. Salt induces water flooding and precipitation can be re-dissolved.

6

Recommendations

The recommendations provided in this chapter are based on three aspects from the experiments: the directions indicated by the research findings; areas of curiosity that remain unclear; and exposed pain points that highlight the bottlenecks hindering industrialization.

In a zero-gap r-BPM CO_2 electrolyser, water primarily penetrates from the AEL side, and reducing the AEL thickness can facilitate this process. Additionally, increasing the AEL's fixed charge density enhances the Donnan exclusion effect, effectively blocking cation crossover. Since cation crossover can lead to increased bicarbonate crossover, controlling it becomes even more crucial. Furthermore, the AEL should exhibit extremely low carbonate conductance, meaning that Piperlon and Sustainion are unsuitable for this role. On the CEL side, increasing thickness can further suppress bicarbonate crossover, but a higher fixed charge density is not recommended, as the negatively charged fixed anions in the CEL could negatively impact eCO₂RR performance.

In this study, only one type of Fumasep r-BPM was used as the research subject. No design of experiments (DOE) was conducted to explore the relationship between the membrane's specific property/performance parameters between co-ions transport behavior, as well as water dissociation efficiency, Faradic efficiency, and energy efficiency. This area warrants further investigation.

The voltage profile of r-BPM is complex, and solely relying on the cell voltage measured by a two-electrode system is inadequate. This limitation prevents a deeper understanding of the co-ions migration transport mechanism and hampers the development of effective strategies to reduce voltage of r-BPM CO_2 electrolyser. While a four-electrode system using an H-cell or flow-cell configuration offers an alternative, these setups can introduce biases due to enhanced water penetration from the cathode side, which significantly deviates from the MEA architecture. Therefore, developing advanced experimental techniques to apply a four-electrode system within an MEA configuration is necessary.

In the experiments conducted for this project, it was found that r-BPM still cannot effectively prevent salt precipitation and the resulting blockage of the cathode gas field. Increasing the operating temperature is necessary to enhance carbonate salt solubility. Additionally, since water penetration—alongside water dissociation—can also be a rate-limiting step, moderately increasing the operating pressure on the anode side can promote water penetration into the inter layer. This approach works synergistically with the r-BPM's inherent resistance to flooding.

Research on water dissociation kinetics, the Tafel slope of WDR, r-BPM electrochemical polarity, and WDR catalysts remains insufficient and requires further in-depth exploration. Additionally, in r-BPM, after carbonate reversion at the boundary layer of the CEL, it remains unclear whether H_2CO_3 can permeate the CEL in molecular form. Moreover, the spatial distribution of r-BPM cathode carbonation species fractions warrants comprehensive investigation to achieve a clearer understanding.

Co-ion crossover in r-BPM cannot be completely eliminated, and some co-ion leakage is inevitable. As a result, the anolyte pH will gradually decrease over time. It is recommended to assess the energy consumption of anolyte regeneration ($K_2CO_3 \rightarrow KOH$) using a techno-economic approach to determine

the WDE target for the BPM, as well as the optimal electrolyte volume and concentration.

Based on current research, integrating carbon capture into CO_2 electrolyzers (bicarbonate electrolyzers) is not recommended. It is advised to explore higher-value alternatives, such as organic oxidation reactions (OORs), to replace OER and help reduce cell voltage at the anode.

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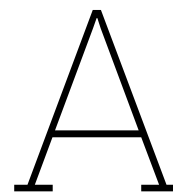
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Experimental Appendix

A.1. Reagents and MEA Materials

The reagents used in this project include three categories: experimental reagents, titration and calibration reagents, and deionized water. The experimental reagents consist of KOH (Sigma-Aldrich-417661), where 85.5 mL of concentrated KOH solution is required to prepare 1 liter of 1 mol/L KOH aqueous solution, CsOH (Sigma-Aldrich-232041), where 174 mL of concentrated CsOH solution is required to prepare 1 liter of 1 mol/L CsOH aqueous solution and CO_2 gas.

0.1 mol/L HCl standard solution is used as the titrant. The pH calibration standard buffer solutions for the titrator include pH 7 (A518.1), pH 4 (A517.1), pH 1 (T180.1), pH 10 (8086.4), and pH 13 (0762.2). Additionally, the pH meter requires a 3 mol/L saturated KCl electrolyte solution (Mettler Toledo, 51350072). All reagents are sourced from Carl Roth.

The MEA materials comprise r-BPM (Fumasep), GDL (Sigracet 39BB), and nickel foam (Recemat 4753). The dry thickness of Fumasep r-BPM ranges from 110 to 160 μm , with a rated current density of 100 mA/cm^2 and a maximum operating temperature of 40°C. The Sigracet 39BB GDL has a thickness of 315 μm , a Gurley number of 1.5 seconds, a water contact angle exceeding 130°, and an in-plane (IP) electrical resistance of 0.56 $\Omega\cdot\text{mm}$. The Recemat 4753 nickel foam features a porosity of 95.2% and consists of Ni (99.5%), Fe (0.2%), Cu (0.1%), and Zn (0.1%).

A.2. Magnetron Sputtering of Silver

The GDE is fabricated via Ag magnetron sputtering deposition onto the GDL. To ensure uniformity and structural consistency, a continuous rotation system is employed under a controlled environment of 20 sccm Ar at 3 μbar , with a deposition rate kept constant. The sputtering process operates at a DC power of 50 W. The thickness of the deposited layer is directly dependent on the sputtering duration, with a 100 nm Ag layer requiring a deposition time of 5 minutes and 28 seconds.

In principle, vacuum magnetron sputtering is a physical vapor deposition (PVD) technique used to deposit thin films onto substrates. The process involves the following steps:

Plasma Generation: In a high-vacuum chamber, an electric field is applied between the Ag target (cathode) and the carbon paper substrate (anode). This electric field accelerates electrons, which collide with Ar gas atoms. These collisions ionize the Ar atoms, creating a plasma composed of Ar^+ ions and free electrons. The plasma is essential for the sputtering process.

Magnetic Confinement of Electrons: A magnetic field is applied to the target surface to trap and confine the electrons near the cathode. This creates a high electron density, increasing the probability of Ar^+ ion formation and reducing the pressure required for plasma ignition. This magnetic confinement enhances sputtering efficiency and ensures a more stable plasma.

Sputtering of Ag Atoms: The generated Ar^+ ions are attracted to the negatively charged Ag target and gain energy from the electric field. When these ions collide with the Ag target, they dislodge Ag atoms from the target surface in a process known as sputtering. These ejected Ag atoms are propelled towards the substrate.

Deposition on the Substrate: The sputtered Ag atoms travel through the vacuum towards the carbon paper substrate, where they adsorb onto the surface. Over time, the Ag atoms diffuse across the substrate and nucleate, forming a continuous thin Ag film.

Film Growth and Nucleation: As more Ag atoms deposit, they interact and connect to form a uniform, high-quality thin film. The substrate temperature and sputtering time control the final properties of the deposited Ag film.

The Magnetron Sputtering device is shown in Figure A.1, AJA is the name of instrument manufacture.

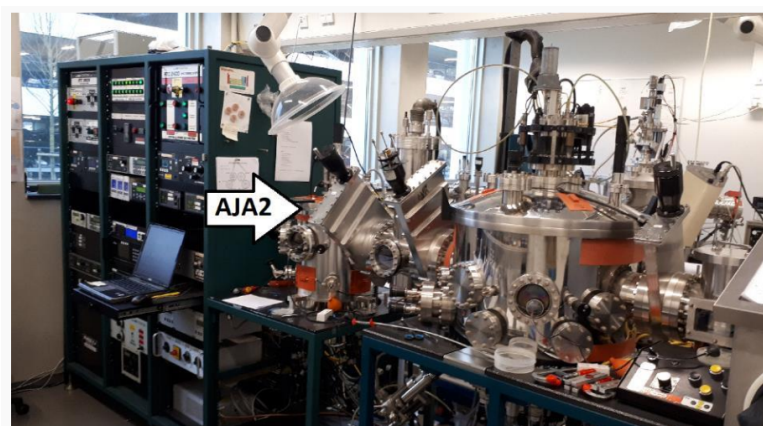


Figure A.1: Image of the magnetron sputtering device. For Ag material deposition, the leftmost chamber (AJA2) is utilized

A.3. Acid-Base Titrations

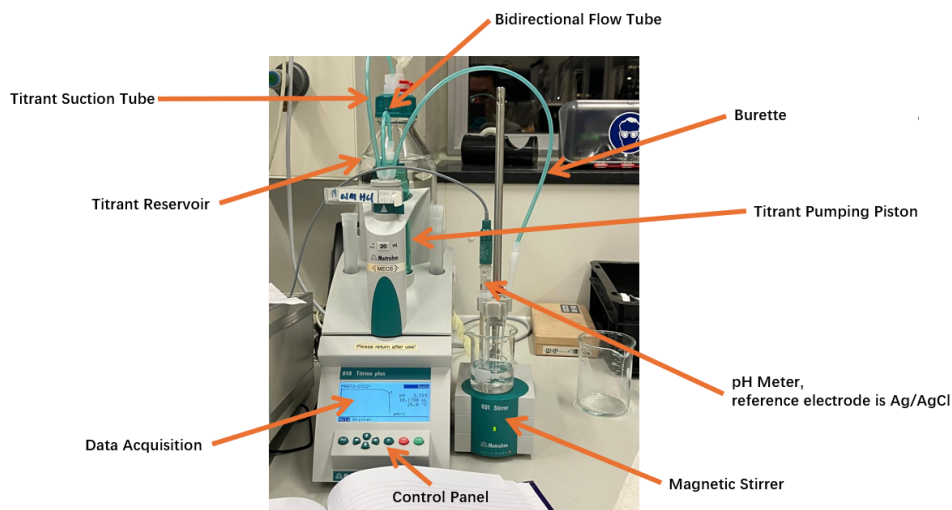


Figure A.2: Image of Titrator Rig

This experiment involves titrating two types of samples. The first is the pre-electrolysis sample, which falls under the titration of a strong base with a strong acid, exhibiting a single equivalence point (EP). The second sample contains carbonate ions mixed into a strong base electrolyte, classifying it as titration in a diprotic system, where two equivalence points are present.

The determination of equivalence points is based on pH electrode measurements, utilizing the Equivalence Point by Rate of Change (ERC) method. Specifically, the first and second derivatives of the pH-V curve are calculated, where equivalence points are identified as the maxima in the first derivative curve and the zero crossings of the second derivative, expressed as below formula,

$$\left(\frac{\Delta pH}{\Delta V}\right)_{V_{result}} = Extremum$$

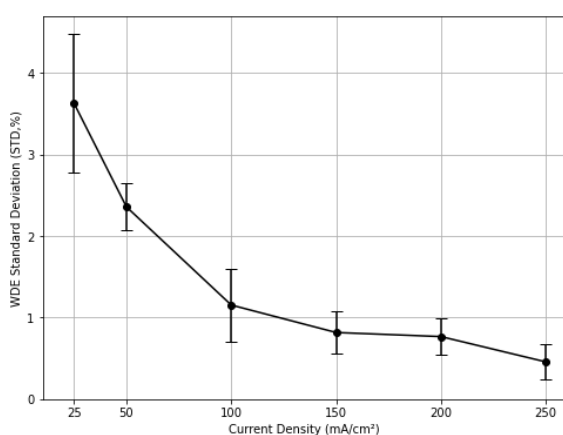
$$\left(\frac{\Delta\left(\frac{\Delta pH}{\Delta V}\right)}{\Delta V}\right)_{V_{result}} = 0$$

To enhance the accuracy of experimental measurements, the following steps should be taken:

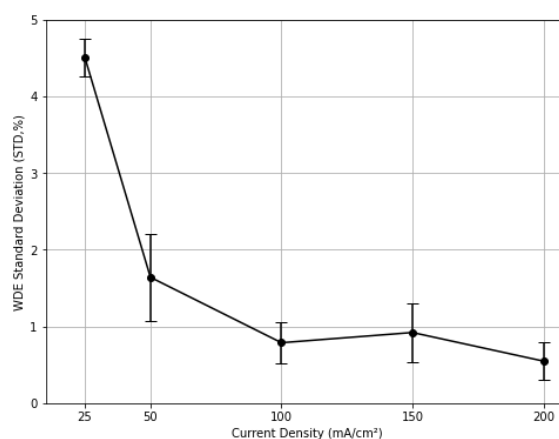
1. Perform weekly calibration of the titrator to ensure consistent and reliable performance.
2. Prepare the electrolyte solution using a volumetric flask instead of a graduated cylinder to achieve the highest possible concentration accuracy. This also allows the electrolyte to serve as an internal reference during the experiment.
3. Ensure thorough cleaning of the pH meter, burette, and beaker before each test to prevent contamination and measurement errors.
4. Accurately control the sample volume in the anolyte, ensuring the absence of air bubbles. When diluting, take precautions to avoid splashing.
5. Maintain an air-free titrant pumping system, as the accuracy of the titrator heavily depends on it. As shown in Figure A.2, the bidirectional flow tube and burette must be free of air bubbles. This requires frequent execution of the preparation procedure to flush out bubbles using the titrant.
6. The bicarbonate flux can be determined solely from the titration of the after-electrolysis sample, whereas the cation flux requires results from both the before-electrolysis and after-electrolysis samples. Consequently, cation flux measurements are subject to greater uncertainty. To minimize errors, before-electrolysis and after-electrolysis samples should be measured sequentially, ensuring that the titrator remains in a consistent state between tests.
7. For higher accuracy, the titrator can be allowed to rest for a period after completing the sample measurements—for instance, by conducting a repeat test the following day.

B

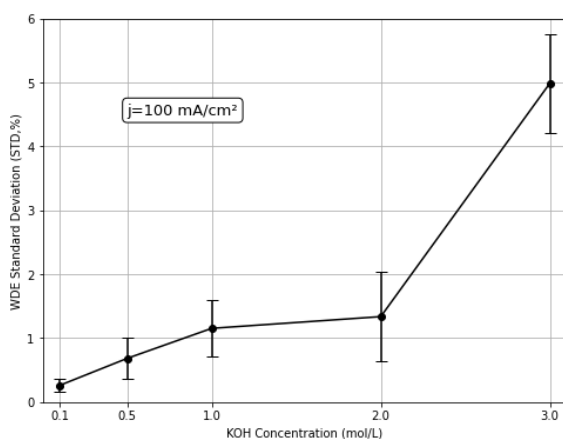
Complementary Data on Standard Deviation of WDE



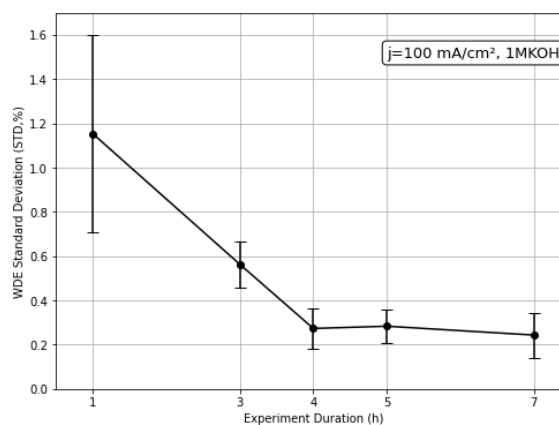
(a). 1 mol/L KOH at varying current density, duration = 1h



(b). 1 mol/L KOH at varying current density, duration = 1h

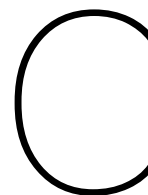


(c). $j=100 \text{ mA/cm}^2$, duration = 1h, with varying KOH analyte concentration



(d). $j=100 \text{ mA/cm}^2$, 1 mol/L KOH analyte, over varying operation duration

Figure B.1: WDE standard deviation (STD) calculated via cross-checking titration data. For each experiment, both the $\text{analyte}_{\text{before}}$ and $\text{analyte}_{\text{after}}$ samples were titrated at least three times, ensuring consistency in STD calculation



Source Code on Data Treatment

C.1. Faradic Efficiency Calculator Matlab Code

```
filename_MFM = 'D:/0. Thesis Data Management/datapool/MFM_data';
filename_GC = 'D:/0. Thesis Data Management/datapool/GC_data';
current = 0.5063 * 1; % Current value used for Faradic efficiency calculation

% Step 1: Import data from Mass Flow Meter (MFM) and Gas Chromatography (GC) files

% Automatically detect import options for MFM and GC files
opts = detectImportOptions(filename_MFM);
opts_GC = detectImportOptions(filename_GC);

% Select only the first column (time data) for import
opts.SelectedVariableNames = opts.VariableNames(1); % Select the first column
opts_GC.SelectedVariableNames = opts_GC.VariableNames(1); % Select the first column

% Read data from the Excel files
T = readtable(filename_MFM, opts); % Read MFM data into table T
T_GC = readtable(filename_GC, opts_GC); % Read GC data into table T_GC

% Extract the first column data (time information)
timeDataNumeric = T.(1); % Extract numeric time data from MFM file
timeDataNumeric_GC = T_GC.(1); % Extract numeric time data from GC file

% Convert Excel serial numbers to datetime format
% Format: Hours:Minutes:Seconds
% This allows for proper time-based calculations and comparisons
timeData = datetime(timeDataNumeric, 'ConvertFrom', 'excel', 'Format', 'HH:mm:ss');
timeData_GC = datetime(timeDataNumeric_GC, 'ConvertFrom', 'excel', 'Format', 'HH:mm:ss');

% Step 2: Import the second column (flow data) from the MFM file
opts.SelectedVariableNames = opts.VariableNames(2); % Select the second column
T_MFM = readtable(filename_MFM, opts); % Read flow data into table T_MFM
flow = T_MFM.(1); % Extract flow data

% Step 3: Find the corresponding mass flow data for each GC injection time
averagedValues = []; % Initialize array to store average flow values
for i = 1:length(timeData_GC)
    % Get the current GC injection time
    currentTime_GC = timeData_GC(i);
```

```

% Define the time window (45 seconds before to 20 seconds before injection)
startTime = currentTime_GC - seconds(45);
endTime = currentTime_GC - seconds(20);

% Find indices in MFM time data that fall within this window
validIndices = find(timeData >= startTime & timeData <= endTime);

if ~isempty(validIndices)
    % Extract corresponding flow values within the time window
    valuesInRange = flow(validIndices);

    % Compute the average flow value for this time range
    avgValue = mean(valuesInRange);

    % Store the averaged value
    averagedValues = [averagedValues; avgValue];
else
    % If no matching data is found, store NaN (missing data representation)
    averagedValues = [averagedValues; NaN];
end
end

% Step 4: Import gas concentration data from the GC file
opts_GC.SelectedVariableNames = opts_GC.VariableNames(2); % Select the second column
T_GC_CO = readtable(filename_GC, opts_GC);
CO_concentration = T_GC_CO.(1); % Extract CO concentration

opts_GC.SelectedVariableNames = opts_GC.VariableNames(3); % Select the third column
T_GC_H2 = readtable(filename_GC, opts_GC);
H2_concentration = T_GC_H2.(1); % Extract H2 concentration

% Convert concentrations to molar fractions
x_CO = CO_concentration * 1e-6;
x_H2 = H2_concentration * 1e-6;
x_H2O = 0.023; % Assumed water vapor content
x_CO2 = 1 - x_CO - x_H2 - x_H2O; % Compute CO2 fraction based on balance

% Compute inverse of the gas mixture correction factor
C_mix_inverse = x_CO + x_H2 / 1.01 + x_H2O / 0.79 + x_CO2 / 0.74;
C_mix = 1 ./ C_mix_inverse; % Compute correction factor

% Corrected flow rate accounting for gas composition
flow_corr = averagedValues .* C_mix / 0.74;

% Step 5: Compute molar flow rates (n_CO and n_H2)
n_CO = (101325 * (flow_corr .* x_CO) / (8.3145 * 273.15)) * 1e-6; % CO molar flow rate
n_H2 = (101325 * (flow_corr .* x_H2) / (8.3145 * 273.15)) * 1e-6; % H2 molar flow rate

% Step 6: Compute Faradic Efficiency (FE) for CO and H2
FE_CO = (2 * n_CO * 96485.3321 / 60) / current; % Faradic Efficiency for CO
FE_H2 = (2 * n_H2 * 96458.3321 / 60) / current; % Faradic Efficiency for H2

% Step 7: Compute the total Faradic efficiency sum (should be close to 1)
unity = FE_CO + FE_H2;

% Compute average Faradic efficiencies for summary
A_CO = mean(FE_CO); % Average Faradic Efficiency for CO
B_H2 = mean(FE_H2); % Average Faradic Efficiency for H2
C_unity = mean(unity); % Average total Faradic efficiency (should be near 1)

```

C.2. Ions Flux and WDE Calculator Matlab Code

```

%% Section 1: Input Data
% Define titration volumes in milliliters (ml)
V_0 = [10.0070 10.0020 10.0086 10.0220]; % OH- titration volume before sample
V_1 = [9.8461 9.8689 9.8711 9.8709]; % CO32- titration volume (EP1) after sample
V_2 = [9.9403 9.9540 9.9927 9.9680]; % CO32- titration volume (EP2) after sample

% Experimental parameters
CD = 150; % Current density in mA/cm2
time_s = 3600*1; % Experiment duration in seconds
V_electrolyte = 0.09; % Anolyte volume in liters
C_HCL = 0.1; % HCl concentration in mol/L
V_sample = 1; % Sample volume for titration in ml
Dilution_Ratio = 1; % Sample dilution factor

%% Section 2: Water Dissociation Efficiency (WDE) Calculation

% Preallocate matrices for results
WDR = zeros(length(V_0), length(V_1)); % Water dissociation efficiency results
n1_matrix_K = zeros(length(V_0), length(V_1)); % Cation transport (K+)
n2_matrix_bicarbonate = zeros(length(V_0), length(V_1)); % Anion transport (HCO3-)

% Loop through each V_0 data point and V_1/V_2 data pair
for i = 1:length(V_0)
    for j = 1:length(V_1)

        %% Section 2.3: Calculate Ion Concentrations
        % K_B: Initial K+ concentration before sample (mol/L)
        % CO3: Carbonate concentration after sample (mol/L)
        % OH: Hydroxide concentration after sample (mol/L)
        % K_A: Final K+ concentration after sample (mol/L)
        K_B = C_HCL * V_0(i) / V_sample * Dilution_Ratio;
        CO3 = C_HCL * (V_2(j) - V_1(j)) / V_sample * Dilution_Ratio;
        OH = C_HCL * (2 * V_1(j) - V_2(j)) / V_sample * Dilution_Ratio;
        K_A = OH + 2 * CO3;

        %% Section 2.4: Calculate Ion Crossover Moles
        % n1: Moles of cation (K+) transported
        % n2: Moles of anion (HCO3-) transported
        n1 = K_B * V_electrolyte - K_A * V_electrolyte;
        n2 = CO3 * V_electrolyte;

        % Store values in matrices
        n1_matrix_K(i, j) = n1;
        n2_matrix_bicarbonate(i, j) = n2;

        %% Section 2.5: Calculate WDE
        % WDR formula: WDE = 1 - (n1 + n2) * Faraday constant / (experiment conditions)
        WDR(i, j) = 1 - (n1 + n2) * 96485.33212 / (time_s * 2.25^2 * 10^-4 * CD * 10);
    end
end

%% Section 2.6: Output the Results
% Display computed matrices
disp('WDR Matrix:');
disp(WDR);
disp('n1_matrix_K:');
disp(n1_matrix_K);
disp('n2_matrix_bicarbonate:');
disp(n2_matrix_bicarbonate);

```

```
disp(n2_matrix_bicarbonate);

%% Section 3: Compute Mean and Standard Deviation of WDE
mean_WDR = mean(WDR(:)); % Mean value of WDE
std_WDR = std(WDR(:)); % Standard deviation of WDE

% Display mean and standard deviation
disp(['Mean of WDR: ', num2str(mean_WDR)]);
disp(['Standard deviation of WDR: ', num2str(std_WDR)]);

%% Section 4: Compute Average Ion Crossover Flux
% Convert moles to micromoles (mol) and cm² to m² for flux calculation
mean_J_matrix_K = mean(n1_matrix_K(:)) * 10^6 / (time_s * 2.25^2 * 10^-4);

mean_J_matrix_bicarbonate = mean(n2_matrix_bicarbonate(:)) * 10^6 / (time_s * 2.25^2 * 10^-4);

% Display ion crossover flux values
disp(['Mean of J_matrix_K [mol.s^-1.m^2]: ', num2str(mean_J_matrix_K)]);
disp(['Mean of J_matrix_bicarbonate [mol.s^-1.m^2]: ', num2str(mean_J_matrix_bicarbonate)]);

%% Section 5: Output Original Titration Data for Archival
% Display titration volumes
disp('V_0:');
disp(V_0);
disp('V_1:');
disp(V_1);
disp('V_2:');
disp(V_2);
```