

Development and Performance Characterization of Bipolar Electrodialysis Flow Batteries

By

Keith Cleland

A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Applied Science

in

Chemical Engineering

Waterloo, Ontario, Canada, 2022

© Keith Cleland 2022

Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Energy storage is becoming increasingly important to have a consistent renewable power supply. Limitations on the cost of current energy storage technologies have prevented the mass adoption of renewable energy. This research focusses on the development of a flow battery using low-cost electrolyte materials based on bipolar electrodialysis technology. The battery operates by splitting salt water via electricity in conjunction with a bipolar membrane and ion exchange membranes to make acidic and basic solutions. The acid and base can then be neutralized at the bipolar membrane, generating voltage and current that can be used as electricity. A bipolar electrodialysis flow battery was designed, constructed, and improved to provide reliable and repeatable operation. Bipolar membranes with different membrane chemistries and supporting materials were tested at different temperatures to understand the losses associated with bipolar electrodialysis flow batteries. A protocol was developed with an analytical framework to compare the results of the polarization curves in a simple way, without the need for fit parameters. Through the measurement of the membrane resistance and a polarization curve, ohmic and overpotential related losses could be distinguished. Links between these losses and the physical phenomena that take place within the bipolar membrane were made. This analysis has shown that the overpotential during the charging process made the largest contribution to the voltage losses, especially at lower current densities. Minimizing these overpotential losses associated with salt leakage through the bipolar membrane will be important in reducing voltage losses for efficient operation. This research provides insight on how to tailor improvements to the bipolar membranes for more efficient flow batteries using cost effective, sustainable electrolytes.

Acknowledgements

I would like to thank Jeff Gostick and Anne Benneker for their excellent guidance and insights provided throughout my degree, and for their patience and continued support while I explored future opportunities. I'm especially grateful for their willingness to apply their expertise to support a new project and idea – without it this work wouldn't have been possible.

I would like to thank John Barber for all the insightful discussions around ion exchange membranes and cell design.

I'm grateful for the support of family friends and loved ones and all their encouragement along the way.

Table of Contents

Author's Declaration	ii
Abstract.....	iii
Acknowledgements	iv
List of Figures	vii
List of Tables	x
1 Introduction	1
2 Background.....	3
2.1 Overview	3
2.2 Electrodialysis and Reverse Electrodialysis.....	4
2.2.1 Uses and Applications	4
2.3 Ion exchange membrane fundamentals	7
2.3.1 Anion exchange membranes and cation exchange membranes	7
2.3.2 Bipolar Membrane Fundamentals.....	9
2.4 BPED Flow Batteries.....	16
3 Experimental Techniques	21
3.1 Equipment.....	21
3.1.1 Cell Description.....	21
3.1.2 Flow Battery Components.....	22
3.1.3 Electrical Equipment.....	23
3.2 Development of Flow Battery Design	24
3.2.1 Electrode Endplate design.....	24
3.2.2 Gasket and membrane design.....	25
3.2.3 Electrode Streams.....	27
3.2.4 Pumping considerations.....	28
3.2.5 Power supply and voltage / current measurement	28

3.3	Testing and Calculation Methods.....	31
3.3.1	Current Efficiency	31
3.3.2	Voltage Efficiency	31
3.3.3	Membrane Resistance.....	32
3.3.4	Open Circuit Voltage.....	35
3.3.5	Polarization Curve Measurement.....	35
3.3.6	Polarization Curve Parameters.....	36
4	Impact of Membrane Type on Performance.....	40
4.1	Introduction	40
4.1.1	Ion Exchange Membrane Structure	41
4.2	Results and Discussion	43
4.2.1	Ion Exchange Polymer Variation.....	43
4.2.2	Cloth Variation.....	50
4.2.3	Compression Test.....	53
4.2.4	Temperature effects.....	54
5	Conclusions and Recommendations.....	59
	References	63

List of Figures

Figure 1: (a) Electrodialysis cell schematic. Upon application of an electric field over the membrane stack ions are selectively removed from the middle channel, while they are enriched in the outer two channels (b) Reverse electrodialysis cell schematic, where the energy of mixing streams of different concentration is harvested through the same membrane stack. The inlet concentration gradients drive the movement of ions through the IEMs, and the current generated through this is harvested.....	5
Figure 2: Schematic of Donnan potential in an ion exchange membrane, adapted from [7], with permission.....	6
Figure 3: Anion exchange membrane, and cation exchange membrane with detailed structure	7
Figure 4: Bipolar membrane schematic used in (a) reverse bipolar electrodialysis and (b) forward bipolar electrodialysis, with (c) the water splitting mechanism	9
Figure 5: (a) Concentration and (b) potential profiles in a bipolar membrane	11
Figure 6: Form and junction potential of bipolar membrane at zero current	13
Figure 7: (a) Water dissociation in bipolar membrane generating H^+ and OH^- to convert fixed charge groups and (b) Form and junction potential of bipolar membrane under charging current	14
Figure 8: (a) Discharge process for bipolar membrane and salt leakage converting fixed charge groups to Na^+ and Cl^- form (b) Form and junction potential of bipolar membrane under discharging current.....	16
Figure 9: BPED Flow battery cell triplet, (a): Forward bipolar electrodialysis (b): Reverse bipolar electrodialysis.....	17
Figure 10: BPED Flow battery triplet with electrode streams	18
Typically a sodium sulfate solution is used in conjunction with platinized titanium electrode to catalyze the hydrogen evolution and oxygen evolution reactions [1]. When the battery is discharging, the hydrogen evolution reaction occurs at the positive electrode, and the oxygen evolution reaction occurs at the negative electrode, as depicted in Figure 11. The electrodes are identical and can catalyze both reactions, so when the battery charges the opposite reactions occur at each electrode. The voltage needed to drive these reactions becomes an irreversible loss. While this can be significant for a lab scale system, in practice hundreds of cell triplets are stacked in between the electrodes, and the electrode loss becomes minimal [14].	18
Figure 12: BPED Flow battery recirculation schematic.....	19

Figure 13: BPED Flow Battery. (a) Sealed BPED flow battery showing outlet streams with a medium (empty) coffee cup for size reference. (b) Disassembled cell showing the flow channel made up of a rubber gasket with holes cut for the manifolds, and the mesh flow field in the gasket space. The Pt wire pseudo reference electrode is in the lower right.	22
Figure 14: BPED flow battery arrangement and auxiliary equipment from left to right showing: the pumps, the battery, storage tank, and the temperature baths	22
Figure 15: Electrode end plate final design.....	24
Figure 16: Rubber spacer gaskets for flow channels in between membranes in the BPED flow battery. The configurations shown are for the (a) acid channel, (b) base channel, (c) electrode channel and (d) salt channel	26
Figure 17: Schematic diagram showing electrode stream reaction and circulation	27
Figure 18: Schematic diagram showing power supply and measurement devices for the BPED system.....	29
Figure 19: Pt wire pseudo reference electrode schematic.....	30
Figure 20: 2-electrode resistance clamp used for measurements	33
Figure 21: Charging polarization curve parameters	37
Figure 22: Discharging polarization curve parameters.....	39
Figure 23: Chemical structure of the (a) CR61 and (b) AR103 chemistries [12]	42
Figure 24: Current efficiency and open circuit voltages for different cation exchange layer chemistries in a bipolar membrane	43
Figure 25: Charging (a) and discharging (b) polarization curves for varied cation exchange layer chemistry in a bipolar membrane at concentrations of 0.5mol/L for the acid (HCl), base (NaOH), and salt (NaCl) streams	45
Figure 26: Areal specific resistance of (a) BPM cell triplet components (b) BPM components and dissociation resistance.....	47
Figure 27: Voltage losses for charging (above x-axis) and discharging (below x-axis) for varied CELs in a bipolar membrane for (a) +3A charging current and -0.6A discharging current, and (b) +0.4A charging current and -0.3A discharging current	48
Figure 28: Voltage efficiency for different cation exchange layers in a bipolar membrane for charging current of (a) +3A charging current and -0.6A discharging current, and (b) +0.4A charging current and -0.3A discharging current.....	49
Figure 29: Open circuit voltages plotted against charge and discharge overpotentials for different CEL in bipolar membranes.....	50

Figure 30: Charging (a) and discharging (b) polarization curves for varied bipolar membrane support cloth / thickness at concentrations of 0.5mol/L for the acid (HCl), base (NaOH), and salt (NaCl) streams.....	51
Figure 31: Effect of cell compression on the BPED cell triplet with CR61P/AR103P bipolar membrane for (a) charging and (b) discharging at concentrations of 0.5mol/L for the acid (HCl), base (NaOH), and salt (NaCl) streams.....	54
Figure 32: (a) Charging polarization curves (b) and discharging (b) polarization curves for CR61P/AR103P bipolar membrane at 10°C, 20°C and 30°C at concentrations of 0.5mol/L for the acid (HCl), base (NaOH), and salt (NaCl) streams.....	55
Figure 33: Charging resistances <i>R_{cell}</i> , <i>R_{comp}</i> , and <i>R_{diss}</i> plotted as a function of temperature	57
Figure 34: Voltage losses for charging (above x-axis) and discharging (below x-axis) 10°C, 20°C and 30°C for (a) +3A charging current and -0.6A discharging current, and (b) +0.4A charging current and -0.3A discharging current	58
Figure 35: Voltage efficiency for 10°C, 20°C and 30°C of BPED flow battery for charging current of (a) +3A charging current and -0.6A discharging current, and (b) +0.4A charging current and -0.3A discharging current	58

List of Tables

Table 1: Ion Exchange Membrane Codes.....	41
Table 2: Measured parameters from the charging polarization curves for varied cation exchange layers in a bipolar membrane	46
Table 3: Measured parameters from the discharging polarization curves for varied cation exchange layers in a bipolar membrane	46
Table 4: Measured parameters from the charging polarization curves for varied supporting cloth in a bipolar membrane	52
Table 5: Measured parameters from the discharging polarization curves for varied supporting cloth in a bipolar membrane.....	52
Table 6: Measured parameters from the charging polarization curves at various temperatures in a bipolar membrane.....	55
Table 7: Measured parameters from the discharging polarization curves at various temperatures in a bipolar membrane	56
Table 8: Temperature coefficient of variation in conductivity for pure water, and acidic and basic solutions [26]	57

1 Introduction

As greenhouse gas emissions increase and stronger climate goals are set, pressure is growing to shift to renewable energy. As the world begins to widely adopt more renewable energy sources, it is clear that more effective energy storage is needed. Energy stored from solar and wind resources can be used to manage intermittencies when the sun is not shining, and the wind is not blowing. In this way, a reliable, fully renewable electricity system could be employed.

A major problem with energy storage technologies today is their high cost. Lithium batteries, which are currently the main option for stationary energy storage in the US [1], are still too costly for widescale adoption. While solar panels paired with energy storage can reduce user electricity bills, the payback period of the system is much too long, at approximately 9 years for lithium-ion batteries [2], whereas most businesses opt for much shorter payback periods on their investments. Despite the environmental benefits of renewable energy paired with energy storage, the main drivers for implementation of new technologies are often economic reasons. Thus, low-cost energy storage technologies are crucial to become cost competitive with not only the lithium batteries on the market today, but with conventional forms of electricity generation such as fossil fuels.

Flow batteries are an emerging technology that can be used for large scale energy storage [3]. Flow batteries are unique in that their power and energy specifications can be decoupled for a battery system. This means that the power output of a battery can be sized and scaled independently of its energy capacity. Vanadium redox flow batteries were among the first type of flow batteries to be used at the commercial scale [4]. This battery type, like lithium-ion batteries uses a limited resource, in this case vanadium, which has both cost and sustainability implications. Due to the high cost of vanadium metal, it is very expensive to scale the energy storage duration [5]. Having low-cost electrolytes for flow batteries could allow for affordable and scalable long duration energy storage, which is important for energy security of an electricity grid that will be more and more dependent on renewable sources.

Salt water is an appealing and economically attractive option for electrolyte in flow batteries due to its abundance and low cost [6]. Energy can be transferred to and from salt water using electrodialysis processes. Conventional electrodialysis is used as a water treatment technology that utilizes electricity and ion exchange membranes to desalinate salt water [7], concentrating salt ions in one stream and diluting them in another. The electrodialysis process can be reversed to harness

the energy of mixing the two streams with different concentration through the same stack of ion exchange membranes [7]. In practice however, the (reverse) electrodialysis technology is too inefficient and has too low of a power density to be practically used to store energy in most applications [8]. However, modifications to the electrodialysis process have allowed for new, more efficient ways to store energy [6],[9].

When electrodialysis is used in conjunction with bipolar membranes, the salt water undergoes an additional process where water molecules are split to make acidic and basic solutions [10]. This process, called bipolar electrodialysis is used industrially to generate acids and bases by splitting water molecules. Like electrodialysis, this process can be reversed – recombining the acid and base and harvesting the energy stored in this process [6]. The chemical energy stored in the acidic and basic solutions can be converted to electricity with a higher power density and efficiency than conventional (reverse) electrodialysis [6]. This is primarily due to a high concentration gradient at the bipolar membrane, leading to a higher junction potential, thereby increasing the power at similar ohmic losses to (reverse) electrodialysis. This promising new technology, bipolar electrodialysis flow batteries, has potential to be used as a low cost, environmentally sustainable alternative to store renewable energy [6].

Storing energy using bipolar electrodialysis flow batteries has gained attention in recent years, with several research studies devoted to evaluating and improving their performance [6],[9],[11],[12]. Due to recent improvements in ion exchange membrane technology, the cost and performance of these flow batteries are becoming increasingly competitive with alternative energy storage technologies [11]. Since it is a rapidly emerging field, several opportunities exist for both improving the performance of bipolar electrodialysis flow batteries, and in gaining a fundamental understanding of the bipolar electrodialysis process when used for energy storage.

In this thesis, a prototype bipolar electrodialysis flow battery was designed, built, and tested. The design of the battery and auxiliary equipment was iterated to obtain a system with repeatable, reliable energy storage operation. The battery was used to evaluate the performance of different commercial bipolar membrane types, and the performance at different temperatures. A theoretical framework was proposed, using polarization curve features to quickly analyze and characterize the performance bipolar electrodialysis flow batteries. Insights learned from applying this framework to varied bipolar membranes and temperatures provided clarification on physical phenomena occurring in the bipolar membrane.

2 Background

2.1 Overview

Bipolar electrodialysis (BPED) flow batteries can be used to store energy harvested from renewable resources. Currently, BPED is used for commercial production of acids and bases. Electricity is applied to a stack of ion exchange membranes, and an electrochemical process occurs at a catalyst layer in the membranes where saline water undergoes a dissociation reaction to produce acid and base simultaneously. This process can be reversed to convert stored chemical energy in the acidic and basic solutions to electricity. Both the forward and reverse BPED processes can be performed in a single system to operate as an energy storage device [6], [9].

While the forward operation of generating acids and bases (charging the BPED flow battery) is a commercially developed technology, the reverse process (discharging the BPED flow battery and harvesting the energy) is far less studied. Forward bipolar electrodialysis (FBPED) has been commercially available for the last 30-40 years. Reverse bipolar electrodialysis (RBPED) however, has not been a feasible technology until recently, with the first recent proof of concept experiment proposed in 2016 [9]. While the idea for RBPED was evaluated in the 1990's [13], the main component, ion exchange membranes (IEMs), were not sufficiently advanced to be effective enough for RBPED. Specifically, the ion selectivity was too low to achieve feasible efficiencies in the recovery of stored energy [13]. Poor membrane selectivity could be compensated in FBPED by increasing current density [14], but higher current density operation becomes inefficient for flow battery applications due to resistive losses. However, IEM technology has evolved through innovations in the field of (reverse) electrodialysis (ED), and bipolar membranes, to the point where BPED flow battery technology is becoming technologically feasible to store energy efficiently [6], [9].

To fully understand the challenges associated with BPED flow batteries, the basic principles of IEMs, bipolar membranes, ED and BPED should be understood. Background on these topics is elaborated upon in the sections below.

2.2 Electrodialysis and Reverse Electrodialysis

2.2.1 Uses and Applications

One of the main uses of forward electrodialysis (ED) is to desalinate brackish water by applying an electric field to move ions across a stack of ion selective membranes [7]. A standard ED system involves a stack of alternating cation exchange membranes (CEMs) and anion exchange membranes (AEMs), with flow channels between the membranes for saline solutions to flow, as shown in Figure 1. The circuit is completed by electrolysis cells on each end of the stack (not shown in the figure). Any redox couple can be used for the electrode reactions. Typically, water electrolysis cells are used, which generates H^+ and OH^- ions. Saline water is fed through the dilute stream. Upon application of an electric field, ions migrate through the ED cell, as seen in Figure 1a. Cations migrate towards the negative electrode and anions migrate towards the positive electrode. The IEM's only allow one type of ion to pass through it, i.e. an anion or a cation [7]. The CEM allows the cations to pass through the membrane into the concentrate stream, while the AEM allows the anions to pass through it to the concentrate stream on the other side. Within the concentrate stream, the cation is blocked by the AEM on the other side of the concentrate stream from further migrating to the negative electrode, and vice versa for the anion migration. Thus, through operation of ED, the concentration of ions in the dilute stream decreases, and the concentrate streams become more concentrated.

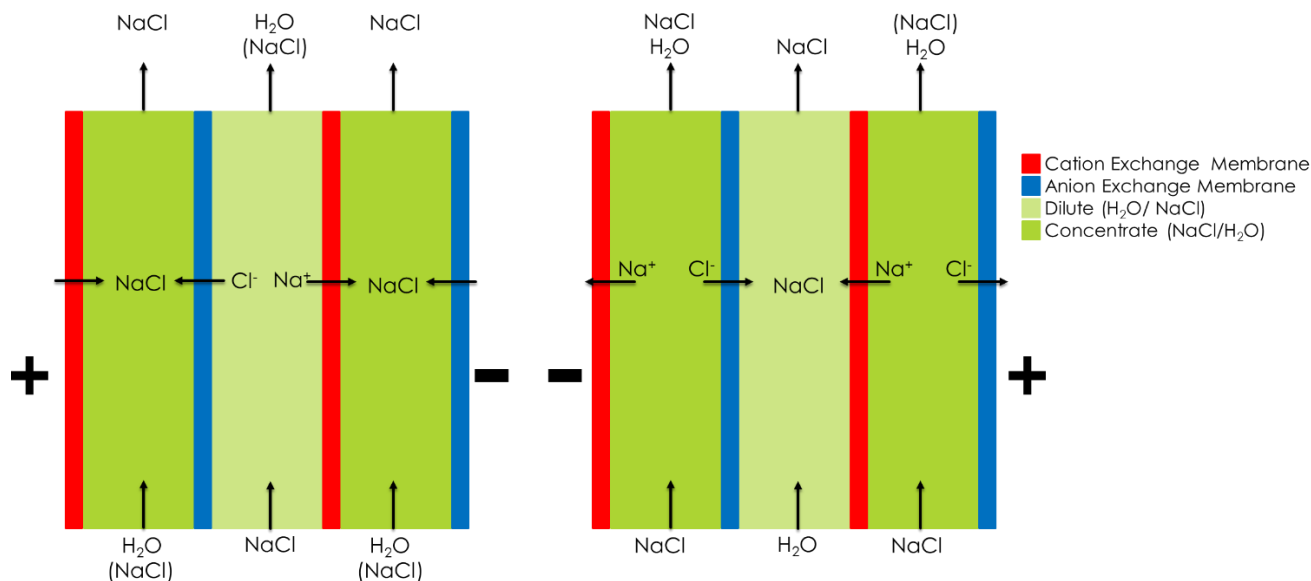


Figure 1: (a) Electrodialysis cell schematic. Upon application of an electric field over the membrane stack ions are selectively removed from the middle channel, while they are enriched in the outer two channels (b) Reverse electrodialysis cell schematic, where the energy of mixing streams of different concentration is harvested through the same membrane stack. The inlet concentration gradients drive the movement of ions through the IEMs, and the current generated through this is harvested.

Although ED is typically used as a water treatment technology to desalinate brackish water, it can also be used to store energy in concentration/salinity gradients [8]. The forward ED process consumes electricity, moving ions from a diluted stream into a more concentrated stream. This process can be run in reverse to harvest some of the energy stored in the concentration gradient in a process called reverse electrodialysis (RED), as shown in Figure 1b. In the RED cell, the concentration gradient between these streams is a driving force for ions to flow in the opposite direction in which they flow for the ED process – from the concentrate stream to the dilute stream, as seen in Figure 1b. This driving force generates an electrical potential and ionic current, allowing for the energy stored in the concentration gradients to be harnessed in RED. The current and voltage are converted to electricity through electrodes placed at the end of the stack, where typically a simple redox couple such as $\text{Fe}^{2+}/\text{Fe}^{3+}$ is used for the electrode reaction. Useful electrical potential, termed the Donnan potential, generated between the IEM and the adjacent solution enables electrical energy to be harvested. A schematic of the Donnan potential in IEM's can be seen in Figure 2. Due to a fixed charge present in the IEM, the concentration of ions in the membrane is higher than that in the solution. This creates a junction potential which can be calculated by the following equation:

$$\Delta\varphi = \frac{RT}{nF} \ln \frac{[A^{+/-}]_m}{[A^{+/-}]_s} \quad (1)$$

where $\Delta\varphi$ is the junction potential (V), R is the ideal gas constant (J/mol K), T is temperature (K), n is the valence state (-), F is Faraday's constant (C/mol e⁻), and $[A^{+/-}]$ is the concentration of ions (mol/L), with the m and s subscripts referring to membrane and solution, respectively.

The concentration difference between the IEM and concentrate stream on the left of Figure 2 generates a junction potential of $E_{Don,1}$, while a concentration difference between the dilute stream and the IEM generates a junction potential of $E_{Don,2}$. A potential difference E_{diff} also exists across the membrane due to ions diffusing through the membrane [15]. The overall membrane potential, E_m can be calculated as the sum of these potentials.

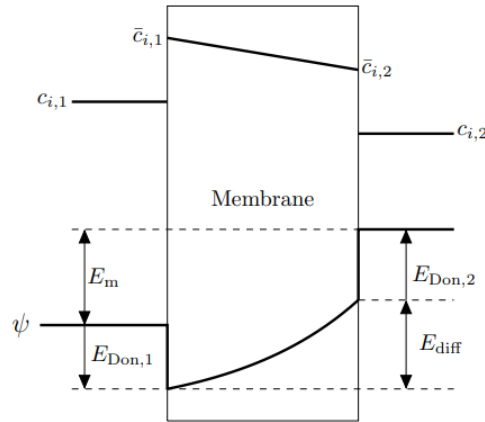


Figure 2: Schematic of Donnan potential in an ion exchange membrane, adapted from [15], with permission

While using ED/RED to store energy using salt water sounds a promising concept, the concentration of salt water is limited due to IEM selectivity, which in turn limits the energy density and efficiency that can be achieved through an ED/RED system [7]. Most applications for RED are used for harvesting energy in salinity gradients between river water and seawater [16]. The few studies on the use of ED/RED as a flow battery, reported their energy efficiency and energy density to be low at 34% and 0.1 Wh/L, respectively [8]. Given the high cost of IEMs, the cost of a RED system is too high for practical use in a flow battery, without significant improvements to IEM technology [8]. Principles from RED however have inspired research into BPED flow batteries, where higher efficiencies are attainable through higher cell potentials.

2.3 Ion exchange membrane fundamentals

2.3.1 Anion exchange membranes and cation exchange membranes

IEMs are used to separate the species in flow streams by selectively allowing anions or cations to be transported through the membrane in an electric field [17]. An ideal IEM only allows one type of ion through the membrane (only anions through an AEM and cations through a CEM), i.e., a perfect selectivity (different than the selectivity between types of anions/cations in an AEM/CEM). In reality, membrane properties are not perfect – unwanted ion transport occurs (cations through an AEM and vice versa) [17]. Ohmic losses due to the resistance to transport of ions also occur. These membrane properties are intertwined with the structure of the IEM, such as the IEM chemistry, amount of fixed charge and pore volume, etc., and changes in the structure of the IEM due to process conditions such as solution type/concentration, temperature, etc. [7].

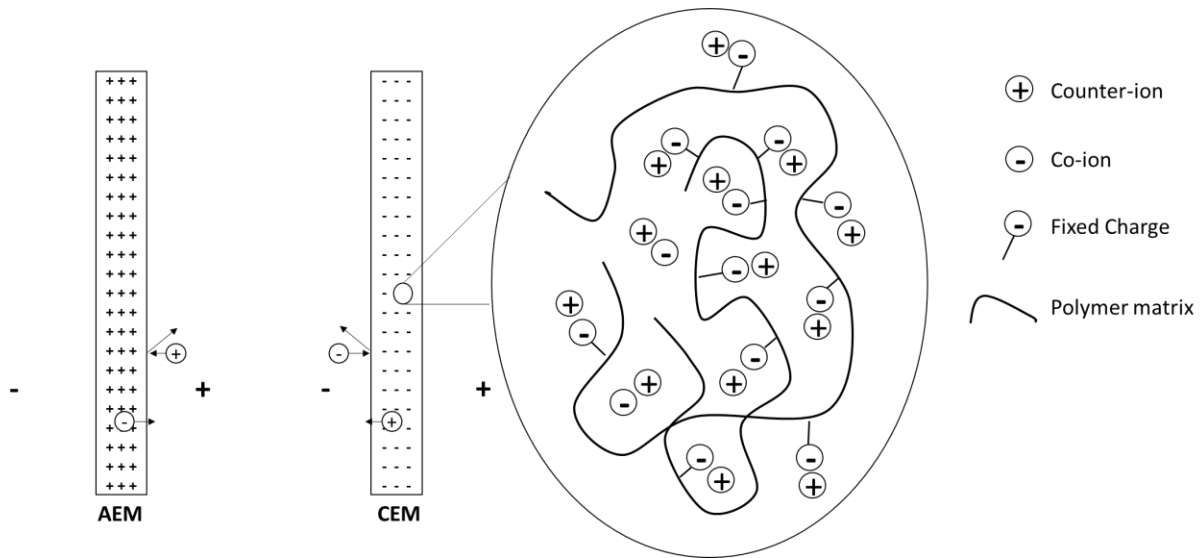


Figure 3: Anion exchange membrane, and cation exchange membrane with detailed structure

An ion exchange membrane (IEM) is typically made of a polymer matrix that is conductive to ions, as shown in Figure 3. The membrane has a porous structure in which the pores, typically on the order of 4 nm [18] are filled with electrolyte solution. The polymer has charged functional groups in its polymer structure [7]. In an anion exchange membrane (AEM) mobile ‘counter-ions’ are attracted to positively charged functional groups, termed the fixed charges, in the polymer

structure to maintain electroneutrality. Similarly, a cation exchange membrane (CEM) contains negatively charged functional groups (fixed charge), to which mobile positive ‘counter-ions’ are attracted to maintain electroneutrality. These counter-ions are free to move through the membrane structure via the water-filled pores in the membrane, unlike the fixed charges. Under the influence of an electric field the counter-ions migrate through the membrane, entering from one side of the membrane and leaving through the other side, as schematically depicted in Figure 3. ‘Co-ions’ are ions of the same charge as the fixed charge groups within the membrane, and also are present in the pores of the IEM, albeit at much lower concentrations than the counter-ions [7]. Co-ions must have accompanying counter-ions to satisfy electroneutrality, as shown in Figure 3.

The IEM properties and structure can be affected by the type of counter-ion that is bound to the fixed charges in the polymer matrix [7]. The form of IEMs is particularly important in BPED flow batteries, as it is closely linked to the cell voltage, as elaborated upon in the bipolar membrane section. If an IEM has a certain counter-ion predominantly adsorbed to its fixed charge groups, the IEM is in the ‘form’ of that ion. For example, a CEM with mainly H^+ ions in its structure is in the H^+ form, and an AEM with mainly OH^- ions in its structure is in the OH^- form. It is possible for a membrane to have more than one type of counter-ions adsorbed to the fixed charges if it is in contact with a solution with multiple types of ions. The type of ion adsorbed to the structure of the membrane can influence the IEM in several ways, such as affecting the ohmic resistance of the membrane due to the mobility of different ions, or the size of the membrane. This can be due to ionic attraction between the counter-ion and the fixed charge that can change the shape of the membrane structure, and correspondingly its properties [7].

The IEM resistance and selectivity are intertwined and linked to the membrane structure [7]. While it is desirable to have a membrane that is extremely selective, a trade-off with the overall resistance should be considered. The fixed charges present in the membrane polymer structure block co-ions from passing through the membrane. At the same time, these charges occupy more of the pore volume in the membrane, causing ionic attractions in the polymer chain, making for a tighter membrane. This means less space exists for ions to diffuse through the membrane. The diffusivity is related to the ionic resistance through the Nernst-Einstein equation:

$$\sigma_i = \frac{n_i^2 C_i D_i}{k_b T} \quad (2)$$

where σ_i is the ionic conductivity of species i (S/m), C_i is the concentration (mol/L), D_i is the diffusion coefficient (m^2/s), n_i is the charge (-), T is the temperature (K), and k_b is the Boltzmann

constant (J/K). Due to the reduction of the effective diffusivity of ions in the membrane, the resistance of the membrane will increase as the selectivity of the membrane increases.

Membrane properties such as resistivity and selectivity can also change as a function of external process conditions, as the porous polymer structure of the IEM can change shape. The concentration of ions in contact with the IEM for example can cause the IEM to change size; as the concentration is increased, the membrane structure will shrink due to the increase in ionic attraction [7]. With a higher concentration the resistivity of the membrane decreases, but so does the selectivity [7].

2.3.2 Bipolar Membrane Fundamentals

A bipolar membrane (BPM) is a special type of IEM, which combines an anion exchange layer (AEL) and a cation exchange layer (CEL) joined together into a dual-layer membrane as shown in Figure 4. BPMs are most commonly used to dissociate H_2O into H^+ and OH^- , upon application of an electric field [10]. When applying an electric field, ions will leave the membrane, and high voltage gradients at the junction between the AEL and CEL within the membrane will cause the water at the centre of the BPM to dissociate into H^+ and OH^- . While this water splitting phenomena can occur with just an AEL and a CEL in contact with each other, a catalyst is typically present at the BPM interface (between the AEL and CEL) to enhance the water splitting process, lowering the voltage required to split H_2O [19]. The H^+ and OH^- then respectively migrate through the CEL and AEL to the acid and base streams, which typically contain HCl and NaOH (on the left and right side of Figure 4a/b respectively).

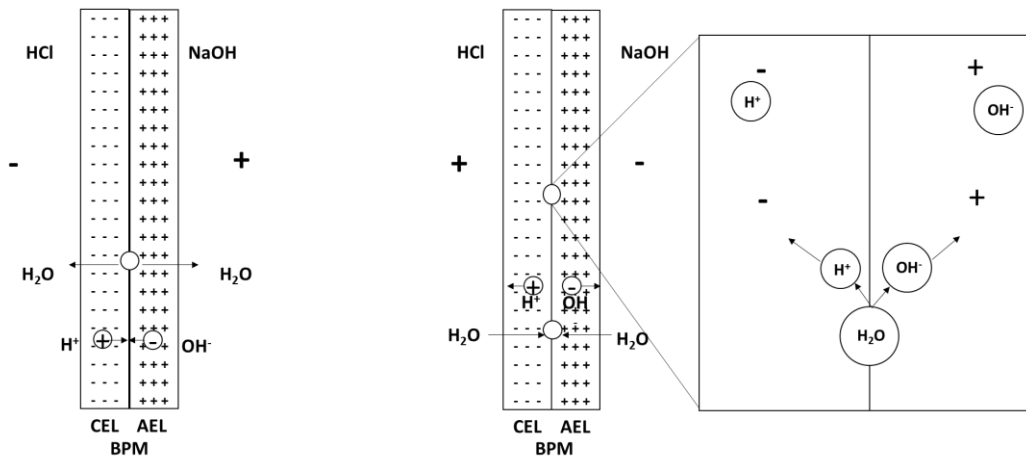


Figure 4: Bipolar membrane schematic used in (a) reverse bipolar electro dialysis and (b) forward bipolar electro dialysis, with (c) the water splitting mechanism

Water is split at the interface of the AEL and cation exchange layer CEL, (i.e., the BPM interface), by a strong electric field which exists at the interface of the BPM, depicted in Figure 5. This electric field arises when electroneutrality is no longer present at the BPM interface. The main electric field generated by the electrodes causes anions to move through the AEL and cations to move through the CEL, in opposite directions from each other. As these counter-ions leave the fixed charge groups, where the AEL and CEL meet, an ion-depleted region forms [10], (depicted at the centre of Figure 5a) causing local non-electroneutrality. This generates a local voltage gradient (depicted in Figure 5b) according to Poisson's equation:

$$\nabla^2 \Phi = \frac{F}{\varepsilon} \sum z_j C_j \quad (3)$$

where Φ is the electric potential (V), F is Faraday's constant (C/mol e⁻), ε is the permittivity (F/m), z_j and C_j are the charge and concentration (mol/L) of species j . This sharp voltage gradient, localized in a nanometer scale region at the membrane interface is strong enough to split water at the bipolar membrane interface, into a proton, H⁺, and a hydroxyl ion, OH⁻ [18], generating ions to fill the gap in electroneutrality. This voltage gradient also attracts co-ions in the membrane AEL and CEL (e.g. Na⁺ and Cl⁻) to the BPM interface in a 'salt leakage' effect [6] as elaborated upon below. Concentration profiles of these ions in the BPM are shown schematically in Figure 5a. These ions then migrate out of the BPM, from the BPM interface to the solution it is in contact with, driven by the electric field.

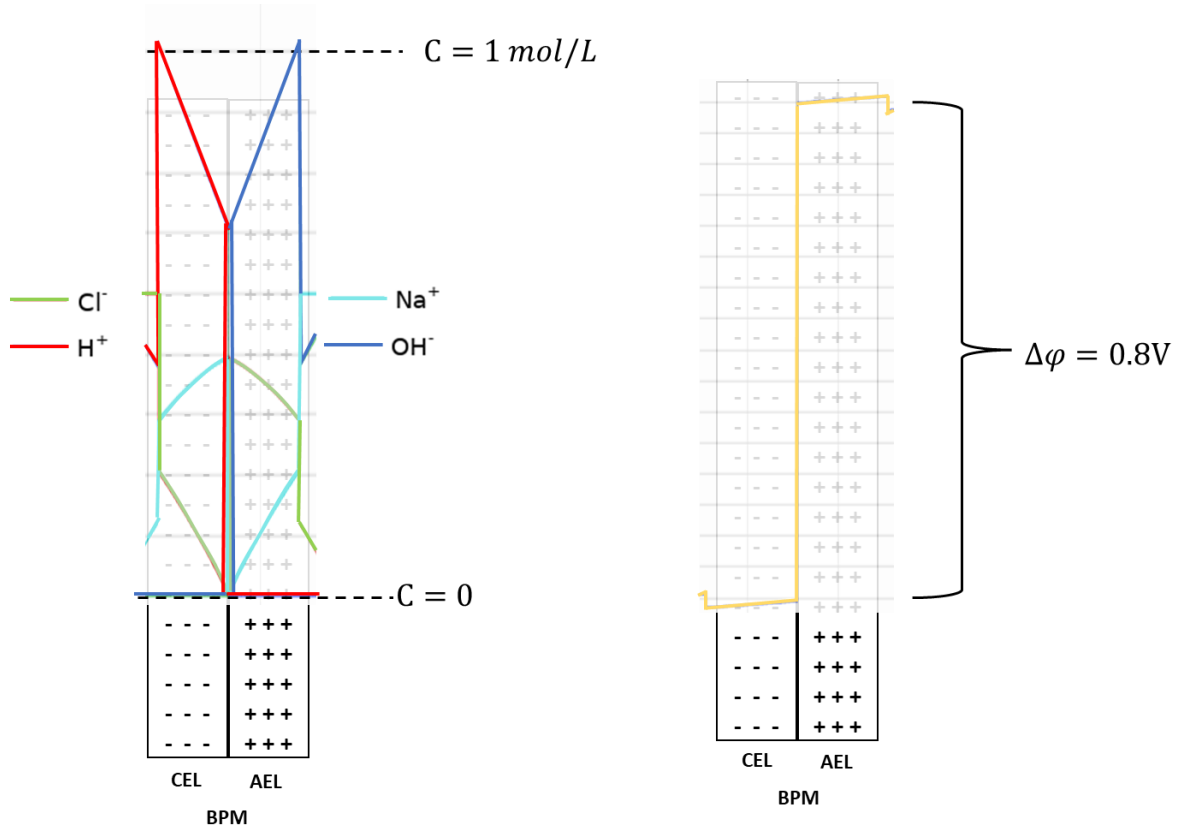


Figure 5: (a) Concentration and (b) potential profiles in a bipolar membrane

BPMs have garnered attention for their application in RED because of the high potential gradient across the membrane, which enhances the RED energy harvesting efficiency and power. When compared to RED, incorporating a BPM into RED generates a higher junction potential due to high concentration gradients when the acid and base are neutralized in the BPM. During reverse bipolar electrodialysis (RBPED), H^+ and OH^- are neutralized at the centre of the BPM, the BPM interface, where water is produced. As shown in Figure 4a, H^+ migrates through the CEL, OH^- migrates through the AEL, and H_2O is formed at the BPM interface. As a result, the BPM interface has a concentration of approximately 10^{-7} M H^+ and OH^- (governed by H_2O dissociation equilibrium), while the concentration of H^+ and OH^- throughout the CEL and AEL are approximately equal to the fixed charge density of the IEM polymers [20]. This steep concentration gradient results in a high junction potential across the BPM. This potential can be calculated using the following equation:

$$\Delta\phi = \frac{RT}{nF} \ln \frac{[\text{H}^+]_{\text{CEL}}}{[\text{H}^+]_{\text{interface}}} + \frac{RT}{nF} \ln \frac{[\text{OH}^-]_{\text{interface}}}{[\text{OH}^-]_{\text{AEL}}} \quad (4)$$

where $[H^+]$ and $[OH^-]$ are the concentrations of H^+ and OH^- , (mol/L) and the subscripts *interface* refers to the concentration at the BPM interface, and *AEL* and *CEL* refer to the concentration of the ions adjacent to the interface. The theoretical open circuit voltage (OCV) of BPMs has been reported in various studies to be 0.8V-0.9V, depending on the amount of fixed charge present in the BPM, and the external concentration of the acid and base solutions in contact with the BPM [9].

The actual OCV is typically measured to be lower than that of the theoretical OCV [6], [9] due to imperfect selectivity to co-ions in the AEL and CEL of the BPM. This imperfect selectivity allows unwanted ion transport to occur, with the Na^+ ions and Cl^- ions from the NaOH and HCl being transported into the BPM through the AEL and CEL, respectively. These Na^+ and Cl^- ions occupy fixed charge sites within the BPM, reducing the concentration of H^+ and OH^- within the CEL and AEL, as seen in Figure 6 to have a 'mixed form' of two counter-ions present in each layer (e.g. H^+ and Na^+ in the CEL). Since the junction potential is mainly a function of the H^+ and OH^- concentration gradients (as the junction arises from the difference in concentration of H^+/OH^- in the membrane and the near zero concentration of H^+/OH^- ions in the middle), any reduction in their concentrations will reduce the OCV. Concentration gradients of an imperfectly selective BPM are presented in Figure 5, and a schematic of voltage gradient and the mixed form of the BPM is presented in both Figure 5 and Figure 6. For example, Na^+ co-ions from the base solution adjacent to the AEL can be transported through the AEL, due its imperfect selectivity to cations, to the CEL. From the CEL, the Na^+ (now a counter-ion) will ultimately migrate to the acid solution adjacent to the CEL. As Na^+ is migrating through the CEL, it occupies fixed charge sites in the CEL that H^+ would have otherwise occupied, and therefore reduces the concentration of H^+ within the CEL, reducing the junction potential according to Equation (4). The only source of these undesired Na^+ counter-ions present in the CEL is due to co-ion leakage (due to its imperfect selectivity) from the AEL, as the CEL is only in fluid contact with HCl solution, and the AEL (which is in contact with NaOH). A similar scenario is true for Cl^- ions occupying sites in the AEL. This phenomenon shows how the selectivity and the OCV of the BPMs are related.

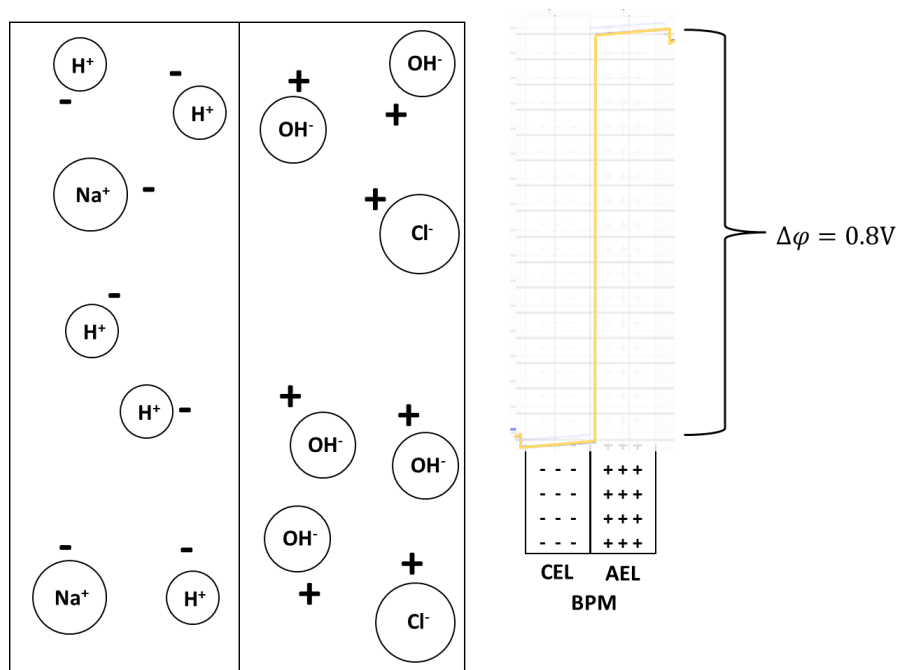


Figure 6: Form and junction potential of bipolar membrane at zero current

When electric current is applied to a BPM, various types of voltage losses occur, depending on whether the BPM is dissociating water (charging) or forming water (discharging). While there are voltage losses specific to external electrode reactions and various resistive losses, three main types of voltage loss occur within the BPM: the resistance of the AEL and the CEL, the overpotential required to split water in FBPED, and the added resistance due to water formation in the BPM during RBPED. These are elaborated upon below.

When charging the battery, two physical phenomena that facilitate water splitting in the BPM can be linked to the potential required to split water when current is applied. As charging current is applied, cations and anions in the CEL and AEL migrate away from the BPM interface, creating a strong electric field due to a loss of electroneutrality. Under that strong electric field, the water molecule dipoles will align in such a way that enhances the dissociation reaction, which is known as the “second Wien effect” [18]. The other contributing factor is the catalyst effect, where water molecules interact with the catalyst, enhancing the water dissociation [19]. A recent study has shown that as the catalyst activity in the BPM is increased, the second Wien effect becomes negligible, and the potential required to split water under electric current is reduced [19].

Voltage losses under electric current for the charging process for the BPM can be expressed in terms of ohmic resistance, and a change in the junction potential as the current is increased (referred to in this study as an overpotential). As seen in Figure 7, as a charging current is applied the amount of salt present in the BPM changes based on the relative ion fluxes of salt ions and H^+/OH^- , which affects both the ohmic resistance and the overpotential [21]. This changing of membrane form to a full H^+/OH^- form due to water splitting is shown in Figure 7.

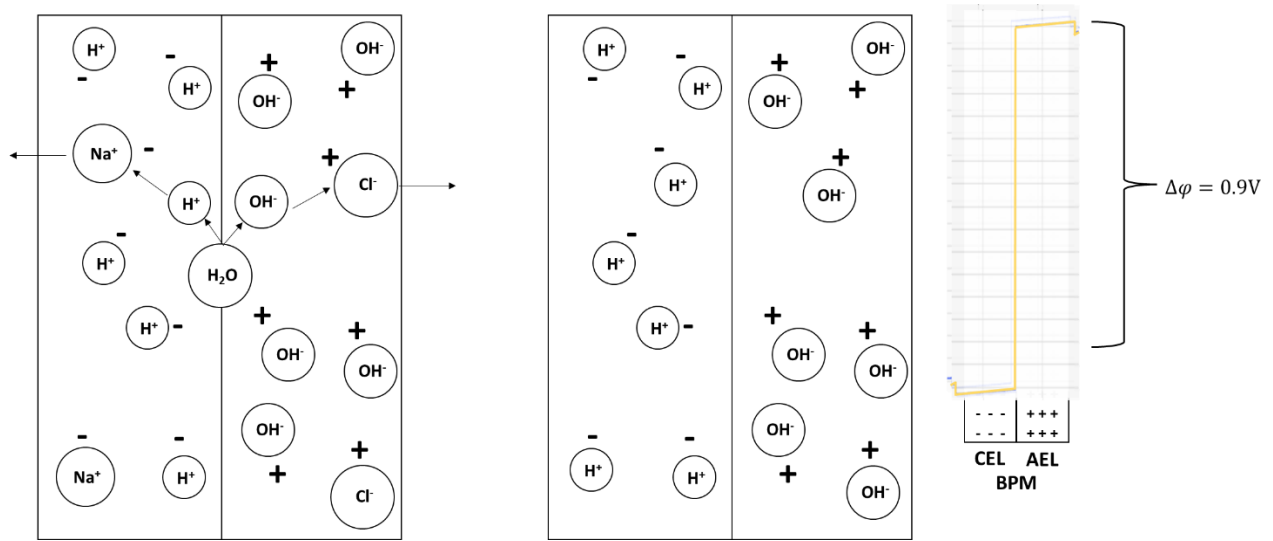


Figure 7: (a) Water dissociation in bipolar membrane generating H^+ and OH^- to convert fixed charge groups and (b) Form and junction potential of bipolar membrane under charging current

It was shown by [21] through chronopotentiometry experiments that the junction potential depends on the form of the fixed charges in the BPM, and increases as a function of current density. The overpotential in the BPM can be attributed to the conversion of residual fixed charges with Na^+/Cl^- (a partial salt form) to the full H^+/OH^- form. At low current densities, there is salt leakage through the BPM, so some of the fixed charge sites will be occupied by Na^+ and Cl^- ions. At higher current densities the transport rate of H^+ and OH^- from the water splitting reaction is high, compared to Na^+ or Cl^- transport. The form of the membrane reflects the relative amounts of transport of each counter-ion (i.e., Na^+ vs. H^+). When water splitting occurs, H^+ and OH^- transport far exceeds any transport of Na^+ and Cl^- at the interface, converting the fixed charges here more fully to the H^+ and OH^- form [21], as seen in Figure 7b. Based on Equation (4), the membrane voltage increases with higher concentrations of H^+ and OH^- present in the BPM. At a high enough current

density, when the majority of the fixed charge sites are changed to the H^+ and OH^- form, the contribution from junction potential is small and the ohmic resistance is the predominant cause of voltage loss [21].

The ohmic resistance for the charging process has two components – the bulk resistance of the AEL and CEL, and the resistance near the interface of the BPM where water splitting occurs, in the so-called ‘ion depletion zone’. This interfacial resistance has two contributing effects which depend on the concentration of ions and type of ions present in the ion depletion zone. At low current densities, co-ions in the AEL and CEL are depleted, leading to an increase in the resistance of the membrane near the BPM interface, due to lower solution concentration. Based on modelling work [18], the local resistance in a nanometer scale region at the interface can increase by about 8 orders of magnitude. As the current density increases, the ion depletion shrinks due H^+ and OH^- formation [21]. The second way that the ohmic resistance of this zone changes is dependent on the forms of the BPM. The Na^+ and Cl^- forms of the CEL and AEL have higher resistance than the H^+ and OH^- form [21]. When going from low to higher current densities, the amount of H^+ and OH^- produced is sufficient enough to change the form of the membrane to almost entirely H^+ for the CEL and OH^- for the AEL, which then reduces the membrane resistance [21].

For the discharge process, the junction potential will be lower than that of the OCV, for the following reasons. In addition to the salt leakage effect that occurs at zero-current, more salt ion leakage occurs through the BPM for the discharge process [6]. Because of this, salt ions will be present in the BPM as counter-ions, as seen in Figure 8a. Since H^+/OH^- are consumed at the BPM interface, the relative amount of salt ion flux increases at the interface, opposite to what happens during the charging process. This results in more salt ions accumulating in the BPM interface, occupying more of the fixed charge groups that H^+/OH^- could otherwise occupy, resulting in a lower junction potential at zero current. This is an important distinction because in addition to ohmic losses, the overpotential due to salt leakage during discharge (which has not been widely reported in the literature) is significant.

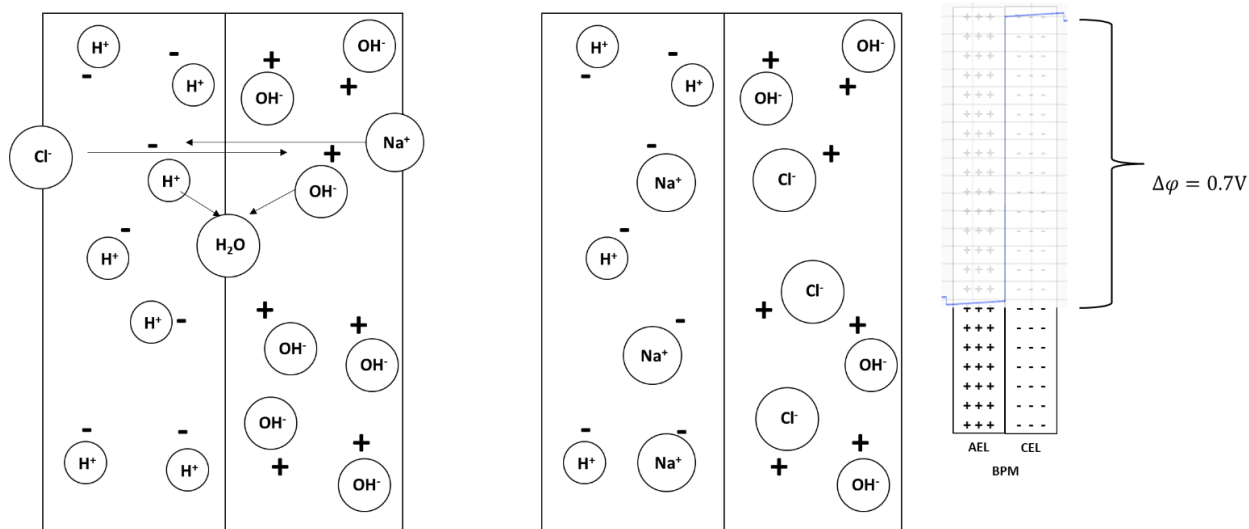


Figure 8: (a) Discharge process for bipolar membrane and salt leakage converting fixed charge groups to Na^+ and Cl^- form (b) Form and junction potential of bipolar membrane under discharging current

When discharging the battery, water that is formed from H^+ and OH^- reacting at the BPM interface needs to be transported to the flow channels. This leads to complications regarding the voltage losses. At low current densities, the rate of water formation is low enough that the water formed can escape via pressure driven flow through the BPM. At moderate current densities, the accumulation of water in the BPM interface is enough for a layer of water to form at the BPM interface, which adds to the overall resistance of the BPM [19]. At high current densities, so much water forms and accumulates that the resistance of the water layer becomes increasingly high, causing the voltage of the BPM to drop to 0V [6]. In this study, this phenomenon is referred to as the water transport limiting current for the RBPED / discharge process, which is different from the traditionally defined limiting current for ED processes. In extreme cases, the production of water at the interface can cause the BPM to delaminate [6]. The water accumulation effect is important to understand as it affects voltage losses at high current densities (which should be avoided), and in extreme cases may damage BPMs.

2.4 BPED Flow Batteries

BPMs are used in FBPED and RBPED in conjunction with AEMs and CEMs to first produce acid and base streams and subsequently convert chemical energy stored in those acids and bases back to

electricity. A unit cell for BPED combines an ED cell with a BPM, called the cell triplet, as seen in Figure 9. During FBPED, H^+ migrates through the CEL to the acid stream, and OH^- migrates through the AEL to the base stream. At the same time, ions such as sodium and chloride migrate across the CEM and AEM adjacent to the base and acid streams to combine with the H^+ and OH^- , forming hydrochloric acid and sodium hydroxide, respectively. Ions flow in the opposite direction for RBPED (a more detailed description of ion flow for FBPED and RBPED is given below). In practice, cell triplets are repeated in a stack in series to achieve sufficiently high voltages for energy storage applications.

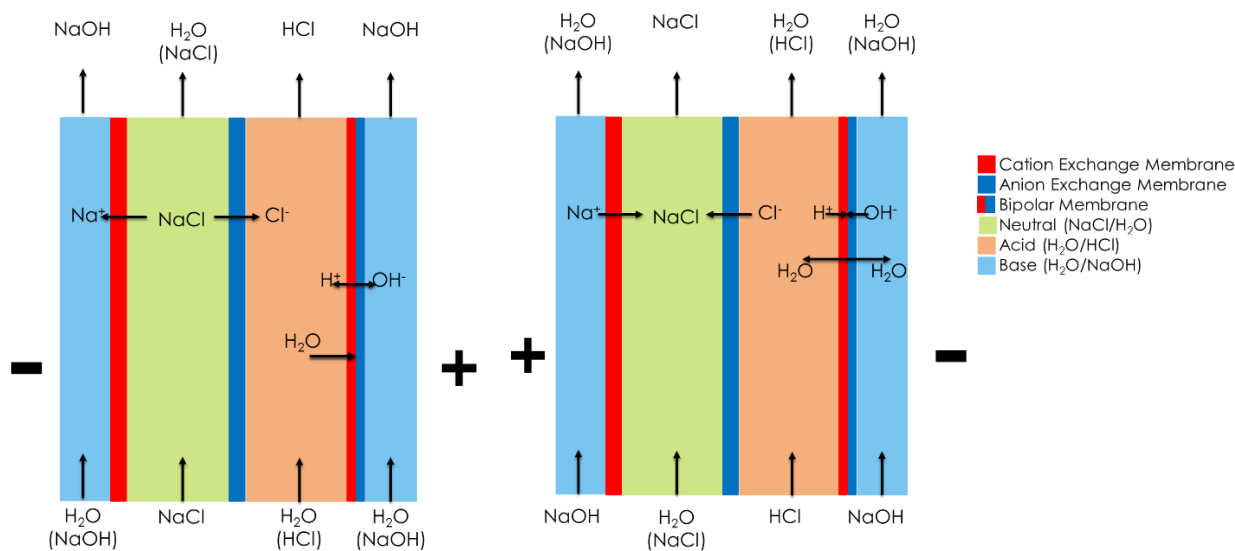


Figure 9: BPED Flow battery cell triplet, (a): Forward bipolar electro dialysis (b): Reverse bipolar electro dialysis

At the ends of the stack of cell triplets an electrode channel is present where an electrochemical reaction takes place to convert the ionic current generated in the cell triplets to an electric current, as shown schematically in Figure 10. The redox couple at the electrodes or electrochemical reactions used is arbitrary (though they should be chosen to have sufficiently fast kinetics), as the main mechanism for energy storage in BPED is via water splitting at the membranes. For example, if a CEM separates the electrode stream and the cell triplets, a cation will leave/enter the electrode stream and an electrochemical reaction will take place that results in either an oxidation or reduction of a component in the electrode stream, causing electrons to flow through the external circuit.

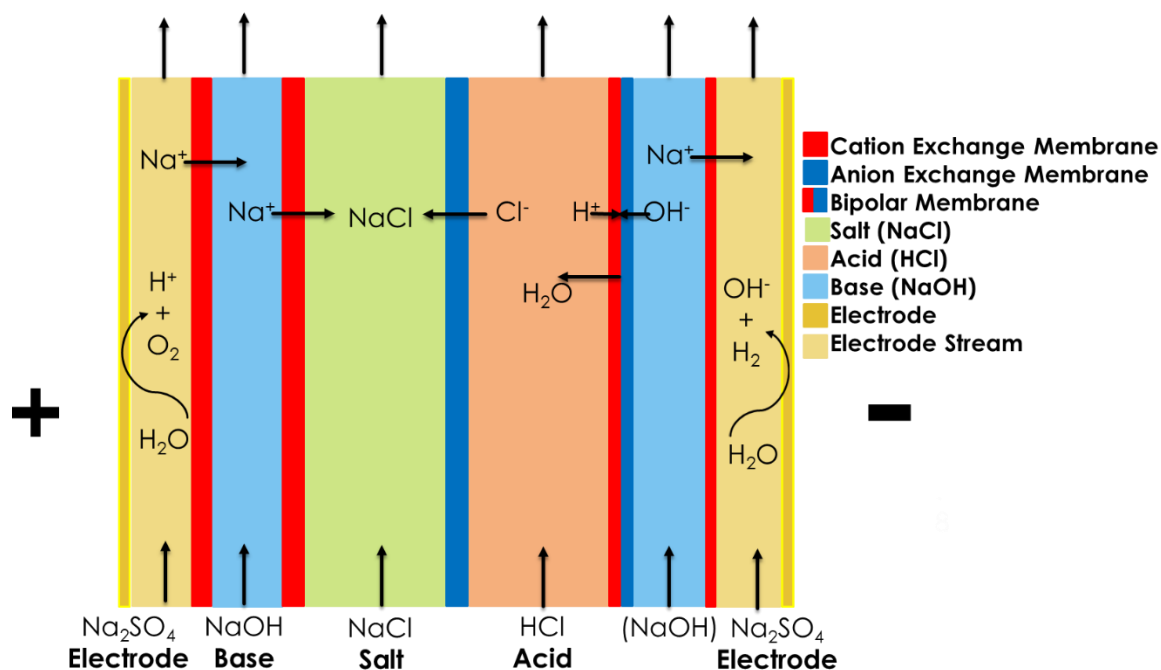


Figure 10: BPED Flow battery triplet with electrode streams

Typically a sodium sulfate solution is used in conjunction with platinized titanium electrode to catalyze the hydrogen evolution and oxygen evolution reactions [6]. When the battery is discharging, the hydrogen evolution reaction occurs at the positive electrode, and the oxygen evolution reaction occurs at the negative electrode, as depicted in Figure 10. The electrodes are identical and can catalyze both reactions, so when the battery charges the opposite reactions occur at each electrode. The voltage needed to drive these reactions becomes an irreversible loss. While this can be significant for a lab scale system, in practice hundreds of cell triplets are stacked in between the electrodes, and the electrode loss becomes minimal [12].

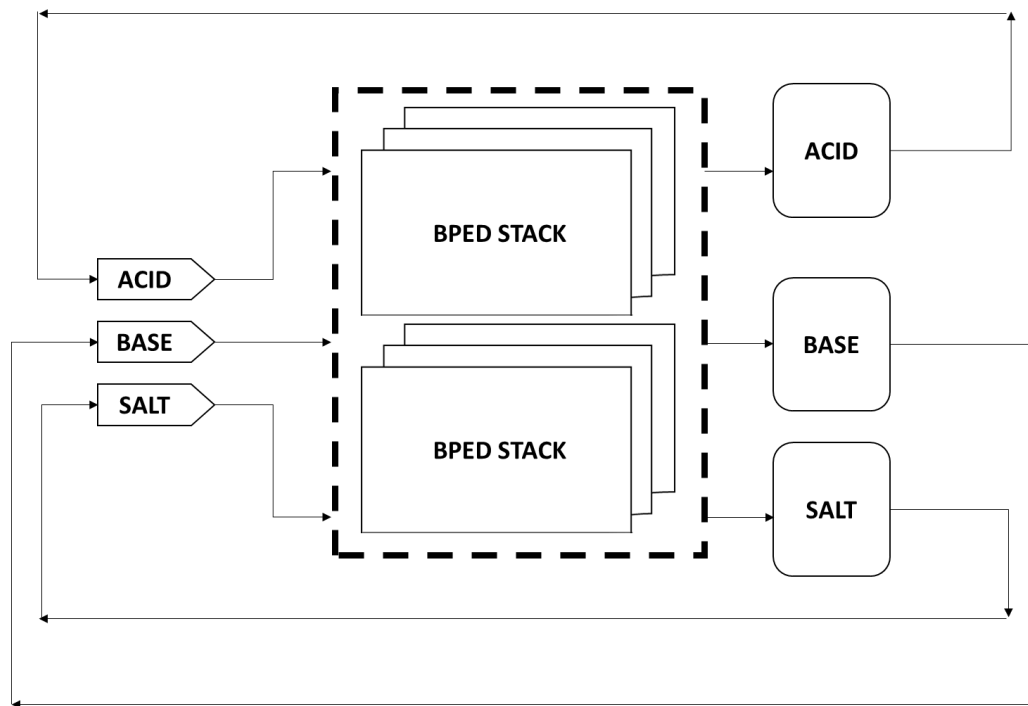


Figure 11: BPED Flow battery recirculation schematic. Acid, base and salt solutions are circulated from the tanks on the right through the BPED stack in the centre, typically via pumps (not shown in the figure)

In practice, to operate as a flow battery, BPED stack(s) are connected to tanks to store the acid, base and salt solutions, as shown in Figure 11. Pumps (not shown in the figure), recirculate the streams from the storage tanks to the stack and back to the tanks. As shown in Figure 9a, the acid and base streams become more concentrated during the charging FBPED process, and the salt stream becomes more diluted. The opposite is true for the discharging RBPED process as seen in Figure 9b. While the streams could in theory be concentrated up to their solubility limits, the IEMs are only sufficiently selective to concentrations of approximately 1M [6].

Even with advanced highly selective IEMs, the trade-off between resistance and selectivity is still important for BPED flow batteries, showing up in the battery as a compromise between current efficiency and voltage efficiency. Low resistance membranes are ideal to achieve a high voltage efficiency, resulting in low ohmic losses. However, membranes with low resistance usually also have a low selectivity, resulting in a low current efficiency (CE) of the battery. Operating a battery with low CE leads to an imbalance in ions in the BPED flow battery streams over time. Over prolonged cycling, the battery will not have sufficient concentrations of acid/base to maintain the battery voltage. This causes voltage during discharge to drop significantly over the lifetime of the

battery as more salt accumulates in the acid/base streams which also become more depleted in H^+ and OH^- [9].

The FBPED and RBPED processes can be operated at a lower current density to reduce resistive losses, but several complications arise. In general, for energy storage devices, it is preferred to operate at high currents, which lead to higher power output. At low current density, less ions migrate across the membranes due to a smaller overall electric field. With a smaller ion flux, back diffusion processes become significant – this is amplified by the high diffusion rates of H^+ and OH^- , the major current carriers in BPED. The trade-off between diffusion and migration processes can be seen in the Nernst-Planck equation:

$$J_i = -D_i \left[\frac{dC_i}{dx} + \frac{n_i F C_i}{RT} \frac{d\Phi}{dx} \right] \quad (5)$$

where J_i is the flux of species i ($\text{mol}/\text{m}^2 \text{ s}$), and Φ is the electric potential (V). H^+ for example can diffuse across the anion exchange membrane (governed by the first term on the right-hand side) to which it is adjacent and cause contamination of the salt stream of the cell, making the salt stream more acidic. The salt leakage effect also can contaminate the acid and base streams with sodium chloride. A published study demonstrated low current efficiency of 13%-27% for BPED flow batteries while operating at low current densities [22] whereas it has been shown the efficiency can be much higher at a higher current density [11].

The research presented in this thesis aims to evaluate the performance of BPED flow batteries as the structure and chemistry of IEM used in the BPM is modified, as well as changing process conditions such as the temperature. A simple framework was proposed and developed to analyze and characterize bipolar membrane performance based on only polarization curves and membrane resistance measurements. Links between important BPED flow battery parameters such as the CE and VE are linked to features of the membrane structure that change as both the internal and external properties of the membrane change. Insights learned were used to select membrane properties and a set of process conditions to improve the overall performance of BPED flow batteries. It is especially important to have strong performance so that BPED flow battery technology can be competitive with other energy storage types as it is scaled up for commercial applications.

3 Experimental Techniques

3.1 Equipment

3.1.1 Cell Description

BPED flow battery experiments have been conducted using a custom-built BPED stack. The active area of the cell is $15.5 \times 6.5 \text{ cm}^2$. The three feed streams are in a co-flow arrangement, with the direction of flow down the length of the cell. Two cell triplets were assembled in the stack using commercially available AEMs, CEMs and BPM. The membranes are separated by flow channels consisting of rubber gaskets and polypropylene woven mesh with strand thickness of 0.3 mm to form a flow channel distance of 0.6 mm. The rubber gasket is slightly thinner at 0.58 mm than the flow channel to ensure proper sealing under compression. The rubber gaskets and flow channels have been cut using a water-jet cutter. The membrane manifolds have been cut using a punch and template manufactured in-house. The endplates have been manufactured from 4 cm thick acrylic blocks. A vertical mill was used to machine rectangular cavities to set the electrode and the electrode spacer in place, with connection tabs sticking out the side of the cell. Manifold holes for the feed and outlet solutions to flow to the channels/spacers have been drilled into the end plates. The end plates are reinforced with 1.5 cm thick aluminum plates, on the outside of the of the acrylic end plates, to reduce deformation under compression. The cell is compressed with bolts through the endplates along the perimeter, adjacent to the membrane / flow spacer stack.

Figure 12b shows the flow channel design, with the rubber gasket and the mesh flow spacer. The electrolyte fluid enters this flow channel through the bottom left manifold hole cut into the rubber gasket, and out through the hole at the top of the image. The electrode can be faintly seen through the membrane (darker area), which is the active area of the cell. The triangular shaped inlet and outlet regions allow for effective flow distribution through the cell. A rectangular flow channel has been chosen to ensure a good flow distribution through the cell, compared to cells reported in the literature which typically have a square design that may not allow for well developed flow.

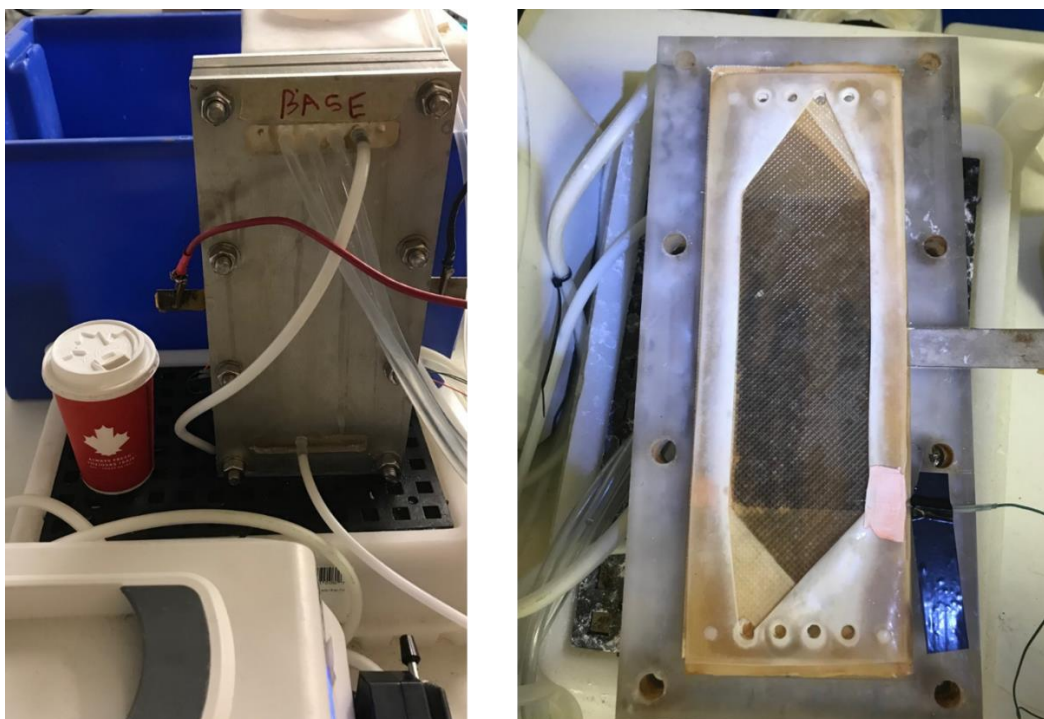


Figure 12: BPED Flow Battery. (a) Sealed BPED flow battery showing outlet streams with a medium (empty) coffee cup for size reference. (b) Disassembled cell showing the flow channel made up of a rubber gasket with holes cut for the manifolds, and the mesh flow field in the gasket space. The Pt wire pseudo reference electrode is in the lower right.

3.1.2 Flow Battery Components

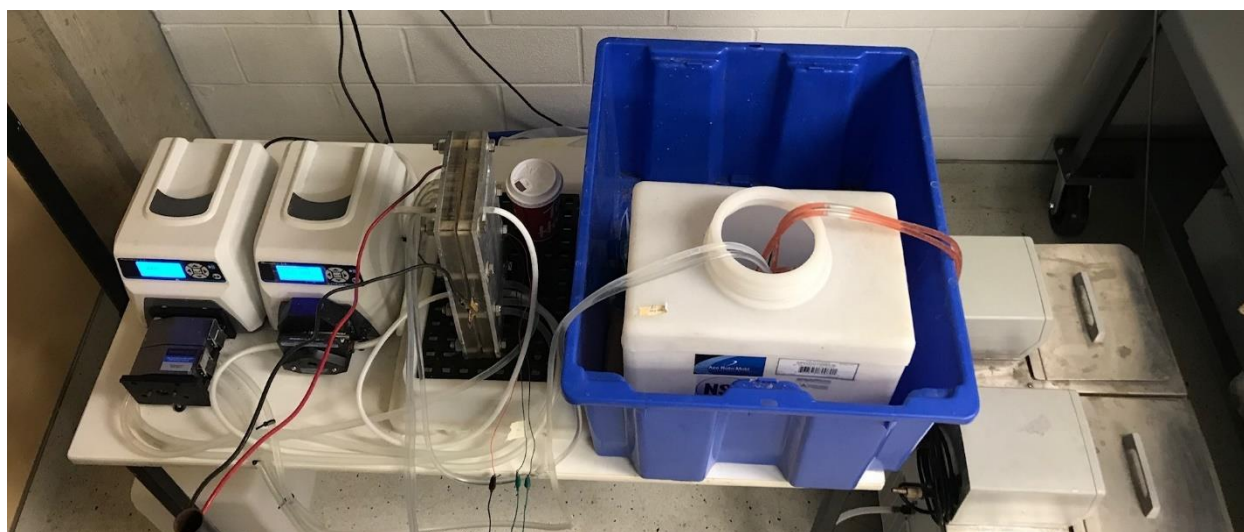


Figure 13: BPED flow battery arrangement and auxiliary equipment from left to right showing: the pumps, the battery, storage tank, and the temperature baths

Figure 13 shows the BPED flow battery components. The two peristaltic pumps on the left circulate the electrolyte solutions through the battery stack. One peristaltic pump (Cole-Parmer) has a 4-channel pump head – 3 of which are used to pump the acid, base, and salt streams through the battery stack. The other peristaltic pump is used to pump the electrode rinse solution through the outer electrode compartments of the cell. Water is split for the hydrogen and oxygen evolution reactions at the electrodes. The electrodes are fed in series, i.e., the outlet of one electrode stream flows to the inlet of the other electrode stream.

The electrode solution used is a 0.25 M Na_2SO_4 solution, which is used in most studies [6], [19]. With an aqueous Na_2SO_4 solution, the electrode reactions that occur at the platinized titanium electrodes are the hydrogen evolution and oxygen evolution reactions. A downside of these electrode reactions is that the gas generation causes them to be irreversible, with a net Nernst cell potential between the charge and the discharge. In addition, high overpotentials are required to drive the irreversible hydrogen and oxygen evolution reactions. A reversible redox couple like $\text{Fe}^{2+}/\text{Fe}^{3+}$ could be used so that the electrodes have a net Nernst potential of zero between the charge and the discharge (excluding the overpotential). However, it was shown that iron ions in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple can leak across the membrane adjacent to the electrode stream to the base stream and precipitate as iron hydroxide [9]. In practice the voltage losses from the hydrogen and oxygen evolution electrode reactions are typically negligible on full scale systems with 100+ cells in between the electrodes, but on a laboratory system the voltage losses can be significant.

The right side of Figure 13 shows the temperature baths (Neslab RTE 6) to control the electrolyte temperature. A coil of plastic tubing carries heat exchange fluid pumped by the temperature baths into the acid, base and/or salt tanks. The tanks can also be placed directly in the temperature bath, as the lid is removable.

3.1.3 Electrical Equipment

Voltage is applied to the cell using a Kepco BOP 20-20M power supply / load box. The voltage is applied through Pt-coated titanium electrodes. Current was measured using a digital multimeter (Tektronix), connected in series with the cell stack. The voltage is measured using a potentiostat (Biologic SP-150). The potential across a full cell triplet is measured via pseudo reference electrodes made from thin Pt wire. Direct measurement of the cell triplet voltage is preferred to measuring the potential at the electrodes, as no correction needs to be made to remove the electrochemical behaviour of the electrode reactions (which don't contribute to the energy storage

process in the cell triplet). The Pt wire is inserted in the acid compartment of the cell against the CEL of the BPM. On the outer edge of the membrane where the rubber spacer gasket seals against the membrane, the Pt wire is electrically insulated from the membrane using Teflon tape from the edge of the membrane to the start of the flow channel, as seen in Figure 12b. Two cell triplets are used in the stack in order to measure the potential across a full cell triplet.

3.2 Development of Flow Battery Design

Over the course of this work, several design decisions were made to arrive at the ultimate battery design described in the above section to achieve a working system. Each component of flow battery cell used in this thesis was custom-built for the system. Modifications were made to the system based on learnings shared below.

3.2.1 Electrode Endplate design

A top view of the final design for the end blocks is shown in Figure 14. It contains two rectangular pockets milled into the end plate. The 6.5 cm x 15.5 cm rectangular pocket provides a seat (100 cm² active area) for the electrode, while the 10 cm x 30 cm pocket holds the spacer gaskets. The outer holes drilled are for the bolts used to compress the stack. The holes on the inside provide fluid inlets and outlets, leading to the manifold holes on the spacer gasket.

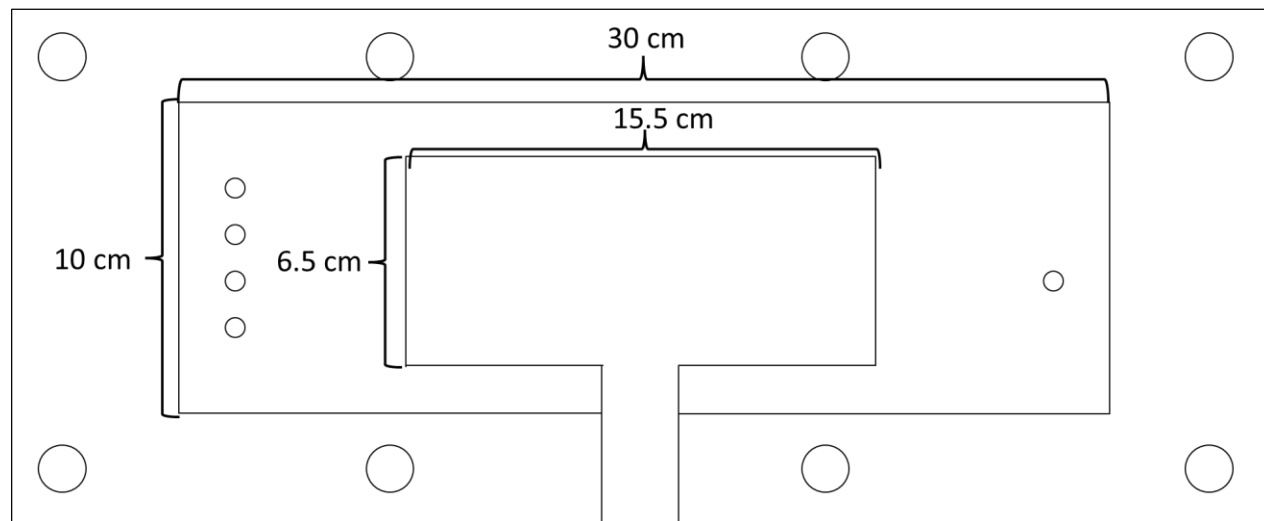


Figure 14: Electrode end plate final design

The electrode pocket in Figure 14 has a tab sticking out the side so that alligator clips to provide electrical connection. In a previous design, the electrode connection was connected through a titanium screw welded on the back of the plate, without the rectangular tab insert milled. However, welding the screw to the plate caused the plate to deform. This was problematic as the electrode plate should be flat to prevent external leakage. The electrode tab design was then adopted so that the electrode could be in contact with external wiring. This however caused a leak path in the corners where the electrode tab did not perfectly fit. This leak was prevented through the use of a combination of a rubber gasket behind the electrode and silicone rubber along the crack where the electrode did not perfectly fit. In future designs it is recommended that the electrode be cut with a water jet cutter (as opposed to a corner punch) to ensure precise dimensions when fitting into the electrode pocket.

The 10 cm x 30 cm pocket for the spacer gasket originally was not included in the design. It was later included to help align the spacer gaskets and membranes when assembling the stack. It was milled at approximately 1 mm deep to hold one spacer gasket and one membrane.

3.2.2 Gasket and membrane design

Figure 15 shows the design of the rubber gaskets used in conjunction with spacer mesh to create flow channels between the membranes. The spacer mesh sits in the gap of the rubber gasket, as shown earlier in Figure 12b. Each of the configurations shown in Figure 15 are different orientations of the same gasket, flipped and rotated to have the four options for types of flow channels. Natural rubber was chosen as the material due to its chemical inertness when in contact with acidic, basic and saline solutions.

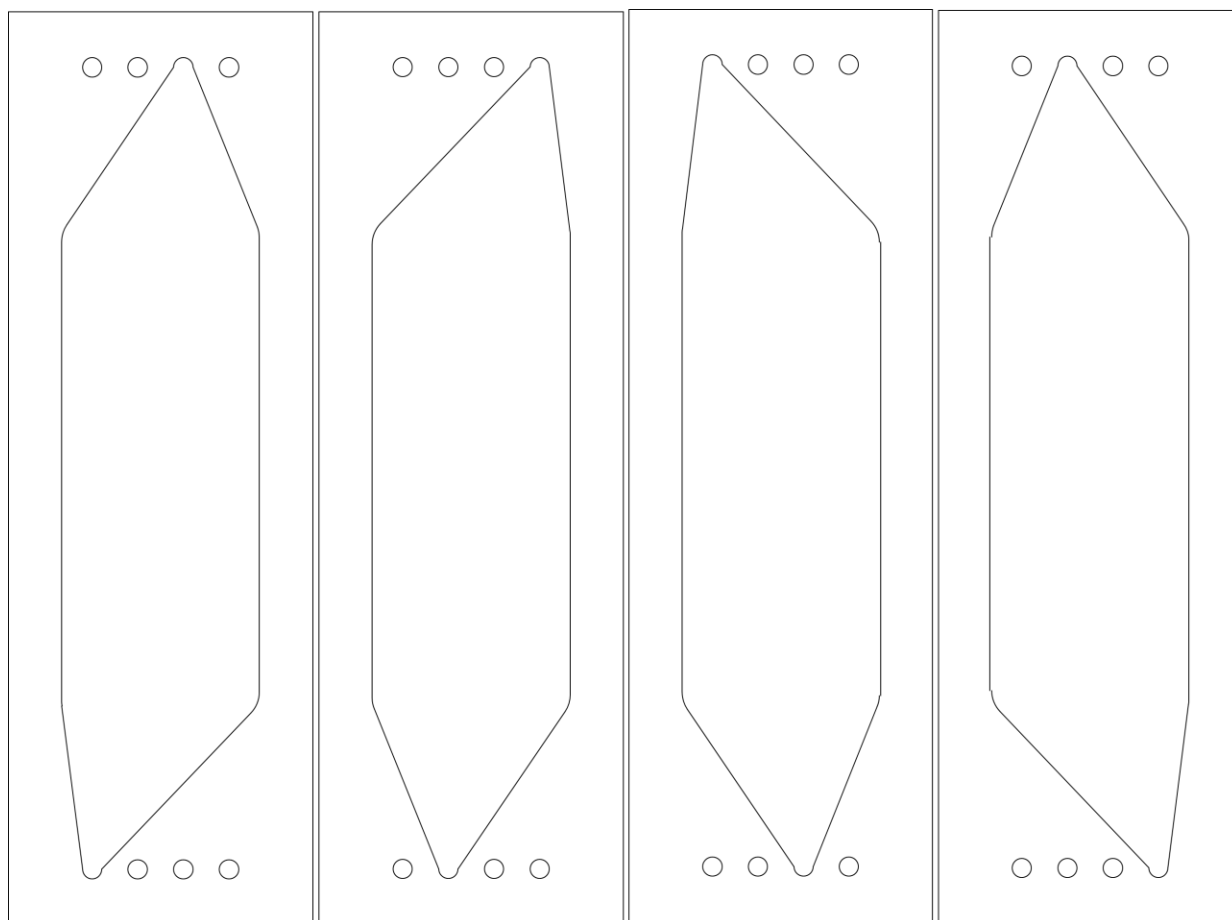


Figure 15: Rubber spacer gaskets for flow channels in between membranes in the BPED flow battery. The configurations shown are for the (a) acid channel, (b) base channel, (c) electrode channel and (d) salt channel

Initially these rubber gaskets were hand cut. This method was feasible for cutting the square edges but could not reproduce identical gaskets in case of the middle pocket. A water jet cutter was subsequently used as a way to rapidly obtain consistent gaskets. This was possible by sandwiching a stack of rubber sheets between two sacrificial rigid plastic sheets. Eventually a precision cutting machine (Cricut Maker) was used to perform the cuts. The outer rectangle and middle pocket were cut, and a punch was used for the manifold holes, as the Cricut was less accurate at cutting the small circles. The rubber gaskets had to be cut while wet, as it was found the dry rubber swelled 5-10% in size when wet, though this could be avoided by using a different material. Dry cut rubber gaskets caused leakages in the flow battery due to swelling after exposure to liquid in the battery.

3.2.3 Electrode Streams

Figure 16 shows a schematic diagram of the electrode system design. Electrode rinse solution is pumped from a tank containing Na_2SO_4 to one electrode, circulated to the other electrode and back to the tank. The net reaction is the generation of H_2 and O_2 gas at the electrodes. During the charging process, the H_2 evolution happens at the negative electrode and O_2 evolution happens at the positive electrode, and vice versa for the discharge process. The sodium and sulfate ions do not react over the potential range applied.

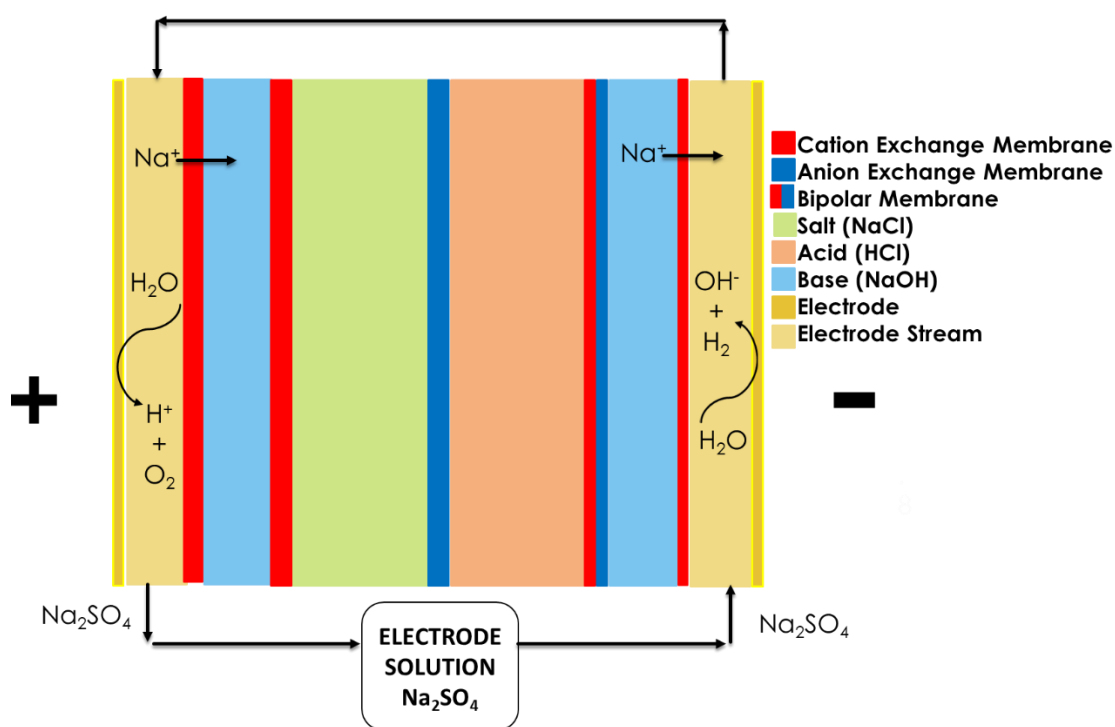


Figure 16: Schematic diagram showing electrode stream reaction and circulation

Other redox couples were considered, such as an $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple. This can be beneficial as there is no net cell potential from converting Fe^{2+} to Fe^{3+} at the anode and Fe^{3+} back to Fe^{2+} at the cathode (excluding overpotentials), as compared to the H_2 and O_2 evolution reactions where the Nernst cell potential is 2.06V. However the use of a $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple can lead to precipitation of $\text{Fe}(\text{OH})_2$ / $\text{Fe}(\text{OH})_3$ in the base stream if the iron ions cross the CEM separating the electrode stream [9]. While the H_2 and O_2 generation is miniscule at the lab scale, this irreversible loss should be considered in scaled up systems.

3.2.4 Pumping considerations

Two separate peristaltic pumps were used to pump the acid, base, salt and electrode streams through the BPED flow battery. These pumps are shown on the left side of Figure 13. The pump on the left has a four channel pump head, and controls the flow rate of the acid, base and salt streams. The pump on the right has a single channel pump head and controls the electrode stream. Different pumps are used because of the high flow rate required by the electrode stream, which can differ from that of the other streams. A high flow rate is required to sparge the gas generated from the electrode reactions, at around 150 mL/min. This high flow rate is also applied to the other streams each time the battery is built to purge any air in the spacers.

It is also important for the tubes to have exactly the same length, so that the flow rate through each tube is the same. The pumps had to be calibrated if the tubing length changed to ensure accurate flow rate delivery. This was especially important for the current efficiency tests, where the flow rate was used in the calculation.

3.2.5 Power supply and voltage / current measurement

Figure 17 shows a schematic diagram of the devices used to supply and measure the current and voltage to the BPED flow cell. The final design shows a bipolar power supply, where a voltage is supplied to the electrodes of the BPED flow battery. In series with the power supply is a digital multimeter to measure the electric current. A potentiostat is used to measure the voltage of the BPED cell triplet through the Pt wire pseudo-reference electrodes.

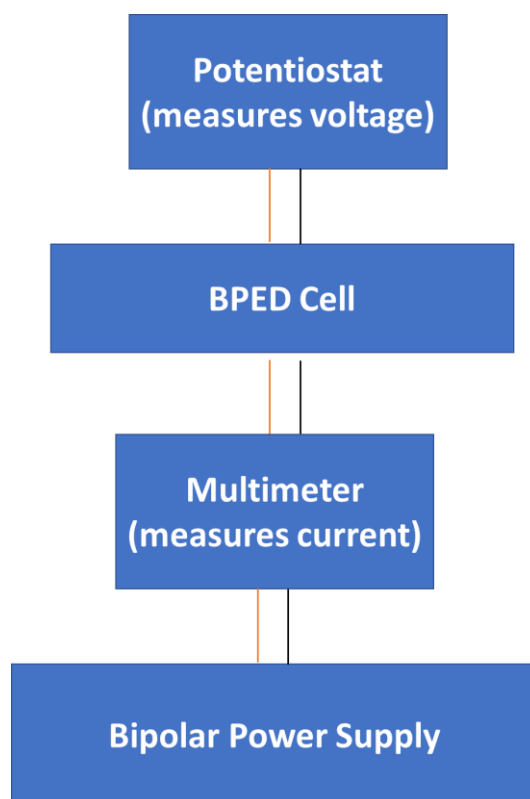


Figure 17: Schematic diagram showing power supply and measurement devices for the BPED system

This system has evolved in complexity over time. For initial testing, only a potentiostat was used for all measurements on a single BPED cell triplet. The potentiostat used however had a current limit of $0.8A$, which corresponds to $80A/m^2$. The currents reached in this study however were up to $600A/m^2$. To achieve higher currents, an external power supply was used as a current booster. The potentiostat was then used to measure the electrode voltage and control the external power supply through a 0-1V auxiliary signal. However, since the same potentiostat was both sending a voltage signal to the power supply, and recording the voltage of the cell, either signal interference between these processes, or an electrical short-circuit occurred. It was observed through an external multimeter that the voltage being recorded by the potentiostat and the multimeter were different. Thus, in the final design the power supply was controlled manually and the potentiostat just measured the voltage.

The voltage measurement method also went through iterations. Initially the voltage was measured at the electrodes. To know the voltage of the BPED cell triplet, the electrode reaction voltage would have to be subtracted. This proved to be less trivial than expected. While the Nernst potential of the

electrode reactions could be easily known, the overpotentials would depend on the catalyst on the electrode. Initially, polarization curves were measured and Tafel slopes were fit to try to distinguish and separate out the electrode overpotential. However, as elaborated upon in this work, an overpotential related to the BPED cell triplet was present and could not be easily separated from the electrode overpotential through data analysis.

To accurately measure the BPED cell triplet voltage, platinum wire pseudo-reference electrodes were used, as schematically shown in Figure 18. The system had to be redesigned to have two cells in which each Pt wire could be in an acid stream under identical process conditions to have the same reference voltage. As seen in Figure 18 the Pt reference wire was placed against the CEL of the BPM in the acid compartment each of the two adjacent cells. Due to pH effects on the Pt wire reference voltage, the reference electrodes could only be used in locations with the same pH – i.e., in the same stream. This means that only the voltage of the full BPED cell triplet could be known, but not the voltage across the BPM. Cells with more conventional reference electrodes paired with Haber-Luggin capillaries have been used in other studies [6], but this was not desirable due to the potential for leaks and the need for a modified cell design to have wider chambers. Other studies have successfully used Pt wires as pseudo reference electrodes to study BPED flow batteries [12].

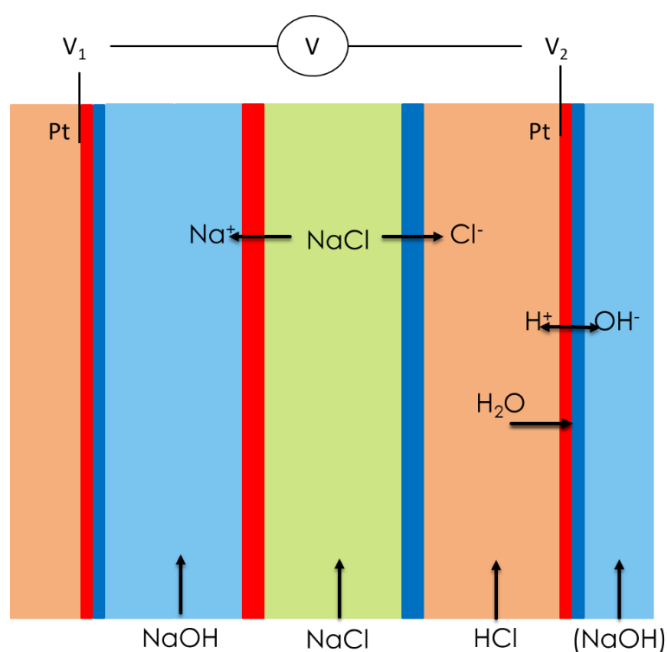


Figure 18: Pt wire pseudo reference electrode schematic

3.3 Testing and Calculation Methods

3.3.1 Current Efficiency

The current efficiency of a BPED flow battery can be calculated by comparing the overall electric current that is measured to the effective transport of the ions of interest to the system i.e., the transfer of H^+ and OH^- through the BPM to charge/discharge the flow battery. Sources of inefficiency can be due to salt leakage through the BPM, or unwanted diffusion of ions such as H^+ or OH^- into other streams. The current efficiency (based on H^+) is calculated using Equation (6)

$$CE = \frac{(C_{out}Q - C_{in}Q)F}{nI} = \frac{\Delta C Q F}{nI} \quad (6)$$

where ΔC is the change in concentration of the acid stream from the inlet (C_{in}) to the outlet (C_{out}) of the battery, Q is the total flow rate of the acid stream, F is Faraday's constant, I is the electrical current and n is the number of cells in the stack.

The current efficiency is obtained by measuring the concentration of H^+ of a feed sample in the acid stream before and after applying a current to the BPED stack, and then measuring the outlet H^+ concentration. This required collecting a sample from the acid tank (C_{in}) for analysis. A constant current was applied to the stack and samples were collected at the outlet of the acid stream (C_{out}). For current efficiency experiments, a flow rate of 20mL/min/cell was used.

Titration were then conducted to determine the concentration of H^+ in the samples. Approximately 15mL of each sample was diluted to 500mL. A standard solution of 0.02M NaOH was prepared and used as the titrant. The indicator for the titration was a 0.5% phenolphthalein solution in 50:50 ethanol : water. 4-5 drops of phenolphthalein indicator were added to the sample volume of 100mL. The titrant was added until the colour changed from clear to a faint pink colour. The average of 3 samples was taken to determine the concentration of each sample.

3.3.2 Voltage Efficiency

An approximation was used for the voltage efficiency so that it could be directly and quickly obtained from the polarization curve data. The definition for voltage efficiency is:

$$VE = \frac{1/t_d \int V_d dt}{1/t_c \int V_c dt} \quad (7)$$

where t_d and t_c are the discharging and charging times, and V_d and V_c are the discharging and charging voltages. Assuming no significant fluctuation in the voltage occurs over time when transferring between different states of charge, Equation (7) can be simplified to:

$$VE = \frac{V_d}{V_c} \quad (8)$$

Using Equation (8), the data from the charging and discharging polarization curves at a 50% state of charge (0.5M acid/base/salt) can be used to obtain a representative voltage efficiency over the state of charge range. While not as accurate as measuring the change in voltage over time, this offers a fast method to obtain the voltage efficiency. To double check the accuracy of this method, the charging and discharging voltages were measured at a 25%, 50% and 100% state of charge (corresponding to 0.25M/0.25M/0.75M, 0.5M/0.5M/0.5M, and 1M/1M/0.1M acid/base/salt solutions respectively), and no major deviations in the charging/ discharging voltages were observed, with a maximum difference of 6% when a 40A/m² current was applied.

3.3.3 Membrane Resistance

Electrochemical impedance spectroscopy (EIS) was used to measure the resistance of the IEMs. A 2-electrode setup was used, as shown in Figure 19. Either side of the membrane was in contact with the solution when the clamp and the membrane was immersed in the solution where the membrane was equilibrated. The working/counter electrodes on the ends of the cell were platinum-coated titanium to catalyse hydrogen/oxygen evolution reactions. An AC signal was applied to the system with a voltage of 0.02 V, at a low frequency of 1000 Hz. On an impedance spectrum, the impedance value at low frequency is interpreted as the resistance, as described by Bard and Falkner [23].

In EIS, any capacitive effects arising from double layer capacitance, etc. at high frequency are negligible, leaving only the cell ohmic resistance as the contributor to impedance. In this case, the ohmic resistance consists of the solution resistance in addition to the membrane resistance. To isolate the membrane resistance, the solution resistance was measured separately using the same cell, without the membrane present. The solution resistance was again taken as the high frequency intercept on the Nyquist plot (only a high frequency impedance was measured). This value is then subtracted from the measured resistance from the membrane cell, to obtain the true membrane resistance.



Figure 19: 2-electrode resistance clamp used for measurements

The resistance of the membranes adjacent to the salt channel is affected by the fact that the membrane is in contact with different solutions on either side of the membrane. As it is only possible to measure the membrane resistance in one solution using the resistance measuring apparatus, the resistances of the CEM and AEM were approximated. The resistance of the CEM was measured in a 0.5M NaCl solution and a 0.5M NaOH solution, and similarly the resistance of the AEM was measured in a 0.5M NaCl solution and a 0.5M HCl solution. The resistance of the membrane should have a value between the membrane resistance in the pure solutions. Since the counter-ion is the same on either side of the membrane, the IEM will be in the same form for each case (i.e., Cl^- form for the AEM and Na^+ form for the CEM). The resistance value therefore depends on the resistance of the co-ions. Since only minimal migration of co-ions occurs during measurement the transport through the membrane should depend only on the diffusion of the co-ions. Hence, when calculating the membrane resistance, the ratio of the diffusion coefficients of the co-ions on either side of the membrane was used to estimate the proportion of co-ions within the

membrane, and subsequently the resistance of the membrane. The calculations for the resistance of the monopolar membranes are shown below in Equations (9) and (10),

$$R_{AEM} = R_{AEM}^{NaCl} + (R_{AEM}^{HCl} - R_{AEM}^{NaCl}) * \frac{D_{H^+}}{D_{H^+} + D_{Na^+}} \quad (9)$$

$$R_{CEM} = R_{CEM}^{NaCl} + (R_{CEM}^{NaOH} - R_{CEM}^{NaCl}) * \frac{D_{OH^-}}{D_{OH^-} + D_{Cl^-}} \quad (10)$$

where R is the resistance (Ω) and the subscript and superscripts refer to the membrane and the solution it is in contact with

The resistances of the solutions are found by considering the conductivity of the solutions, and the impact of the spacer mesh on the resistance of the solution. The resistance is calculated using Equation (11),

$$R_{sol} = f_s \frac{\Delta x}{A \sigma_{sol}} \quad (11)$$

where Δx is the thickness of the flow channel (m), A is the cell triplet active area (m^2), σ_{sol} is the conductivity of the solution (S/m) (obtained from [24]), and f_s is the shadow factor of the spacer (—), which can be approximated as the inverse of the porosity of the spacer flow channel [25].

Once the membrane and solution resistances are measured, the resistance of the cell triplet is taken as the sum of the resistances of the ion exchange membranes, and the resistance of the flow channels. The resistance can be found with the following equation:

$$R_{cell} = R_{AEM} + R_{CEM} + R_{AEL} + R_{CEL} + R_{sol}^{acid} + R_{sol}^{base} + R_{sol}^{salt} \quad (12)$$

where the subscripts and superscripts refer to the resistance of each component / flow stream.

When calculating the resistance as a function of temperature, the following formula was used to calculate the change in conductivity of the solutions:

$$\kappa_1 = \frac{\kappa_2}{1 + (\alpha * (T_2 - T_1))} \quad (13)$$

where κ is the solution conductivity (S/cm), α is the temperature coefficient of variation ($\%/^{\circ}C$), the subscripts 1 and 2 refer to different temperatures. α was assumed to be 2%, based on recommendations in the literature [26]. This formula was used to calculate the difference in solution conductivity and membrane conductivity.

3.3.4 Open Circuit Voltage

The open circuit voltage was measured while flowing solutions of 0.5M HCl through the acid channel, 0.5M NaOH through the base channel and 0.5M NaCl through the salt channel. The test was run for 1-2 hours until a stable voltage reading was recorded. It is worth noting that the open circuit voltages for the charging and discharging polarization curves were typically measured to be lower than the OCV measured in this technique. This is because for a more accurate OCV measurement, a much longer period of time should elapse before measuring the voltage, as it takes longer to reach the steady state junction potential in the absence of current [21].

3.3.5 Polarization Curve Measurement

Polarization curves were measured by changing the current of the system and measuring the cell voltage through the platinum wire reference electrodes. Prior to each cell assembly, the reference electrodes were treated to remove any potential contaminants by heating the Pt wire with a butane torch for approximately 10 seconds [27].

The flow rate through the system when measuring the polarization curves was 70mL/min/cell. This flow rate was chosen to be sufficiently high that no major change in concentration exists between the inlet and the outlet. Obviously, the concentration of the streams would change as current is applied, and at higher flow rates this change is negligible. 2L of electrolyte solution was used for polarization curves. This size was chosen to have a sufficiently large reservoir so that the concentrations do not significantly change over the course of the test, as calculated with Faraday's law:

$$\Delta CV = \frac{NIt}{Fn} \quad (14)$$

where ΔC is the concentration difference from the passage of current (mol/L), V is the volume in the tank (L), N is the number of cells (two) and t is time (s). Based on a charging profile from $10A/m^2 \rightarrow 600A/m^2$ with average times of 45 seconds at each current density, the change in concentration over a polarization curve test was found to be approximately 0.01mol/L.

Current was applied manually, and the voltage response was allowed to stabilize at a constant value before moving to the next current density. Depending on the current density, between 30 seconds to 2 minutes was needed for a stable voltage to be attained.

3.3.6 Polarization Curve Parameters

Several important properties can be inferred from the polarization curves. For the charging curve, the open circuit potential, the ohmic resistance, the water splitting or dissociation resistance and the overpotential are inferred from the curves. For the discharging curve, the open circuit voltage potential, the ohmic resistance, the overpotential, the onset of the water transport limiting current and the resistance of the water transport limiting current region are obtained from the curves. Each curve is split into characteristic regions as depicted below.

Charge

Figure 20 shows a schematic diagram of the characterization of a charging polarization curve. The counter-ion transition region occurs at low current densities where the slope of the curve changes. In the counter-ion transition region, the fixed charge groups in the BPM are changing from the Na^+/Cl^- form to the full H^+/OH^- form, causing the overpotential η_c (caused by growing junction potential) to grow. η_c becomes constant at the end of the counter-ion transition region and at the beginning of the ohmic region, at higher current densities. In the ohmic region, the form of the membrane is no longer changing, and a constant resistance is observed, indicated by a constant slope of the curve. The measurement of the different parameters is discussed below.

Four representative voltages are shown in Figure 20: E_{OCV} , iR_{comp} , iR_{diss} , and η_c . E_{OCV} represents the reversible cell potential, measured as the open circuit voltage (OCV). iR_{cell} represents the total resistive loss. R_{cell} is measured as the slope of the polarization curve at high current densities. R_{cell} includes the resistance of the solutions in the flow channels, the AEM and CEM, and the BPM. When these resistances are measured independently (R_{comp}), the resistance value differs from R_{cell} . This difference in resistance values can be interpreted as a water dissociation resistance (discussed below), R_{diss} . η_c , which is constant in the ohmic region, can then be calculated by subtracting E_{OCV} , iR_{comp} and iR_{diss} from the total voltage at high current densities.

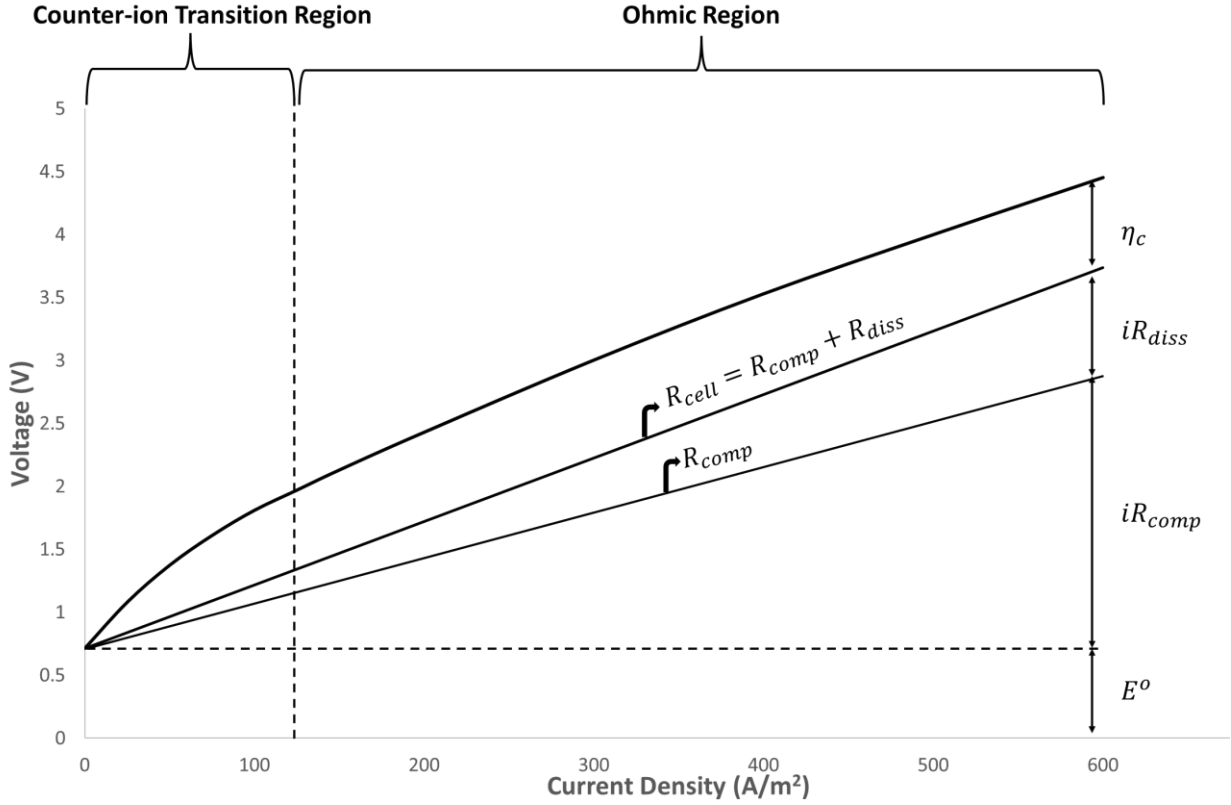


Figure 20: Charging polarization curve parameters

BPMs in other studies have been characterized in terms of the resistance of the membrane, and the water dissociation resistance. The resistance of the membranes can be found by measuring the resistance of the AEL and the CEL independently. This resistance however does not match the resistance when the slope of the polarization curve in the second region is determined. This indicates another resistance attributed to the dissociation reaction that must exist. This ‘water splitting resistance’ can be expressed in multiple ways, as a resistance [28], or it has also been reported as an overpotential [19].

The effect of water dissociation in this study is reported as a combination of an overpotential and a dissociation resistance. The overall resistance is found by taking the slope of the second region of the polarization curve. The dissociation resistance is then found by taking the resistance of the overall resistance and subtracting it from the resistance of the solution and membranes, which are measured independently:

$$R_{diss} = R_{cell} - R_{comp} \quad (15)$$

where R_{cell} is the slope of the ohmic region (Ωm^2), and R_{comp} is the resistance of the cell triplet measured independently (Ωm^2), as described in Section 3.3.3.

Once the current density is high enough, the membrane is almost exclusively transferring H^+ and OH^- . Wilhelm et al [21] observed that the reversible contribution levels off at high current densities when all of the ion exchange sites have been converted to the acid and base form. In the ohmic region of the polarization curve, the overpotential value is relatively constant. This overpotential value is used as a simple way to compare and evaluate between varying membrane and solution properties.

Discharge

Figure 21 shows the schematic plot for characterizing a discharge polarization curve. The discharge polarization curve can be broken into 3 regions which consume the useful junction potential E_{OCV} in different ways. Similar to the charging curve, it contains a counter-ion transition region at low current density, where the BPM is changing form due to salt leakage, as elaborated upon in Section 2.3.2, and below. Any further increase to the current density and the voltage/current relationship is linear, based on the ohmic resistance of the BPM cell triplet, R_{cell} . This corresponds to the ohmic region, where the resistance of the cell triplet should match the resistance of the components R_{comp} when measured individually. In the water transport region, water accumulation in the BPM contributes to a higher resistance. Water transport out of the bipolar membrane becomes a limiting factor above the ‘water transport limiting current density’ i_{wt} . The regions are described in more detail below.

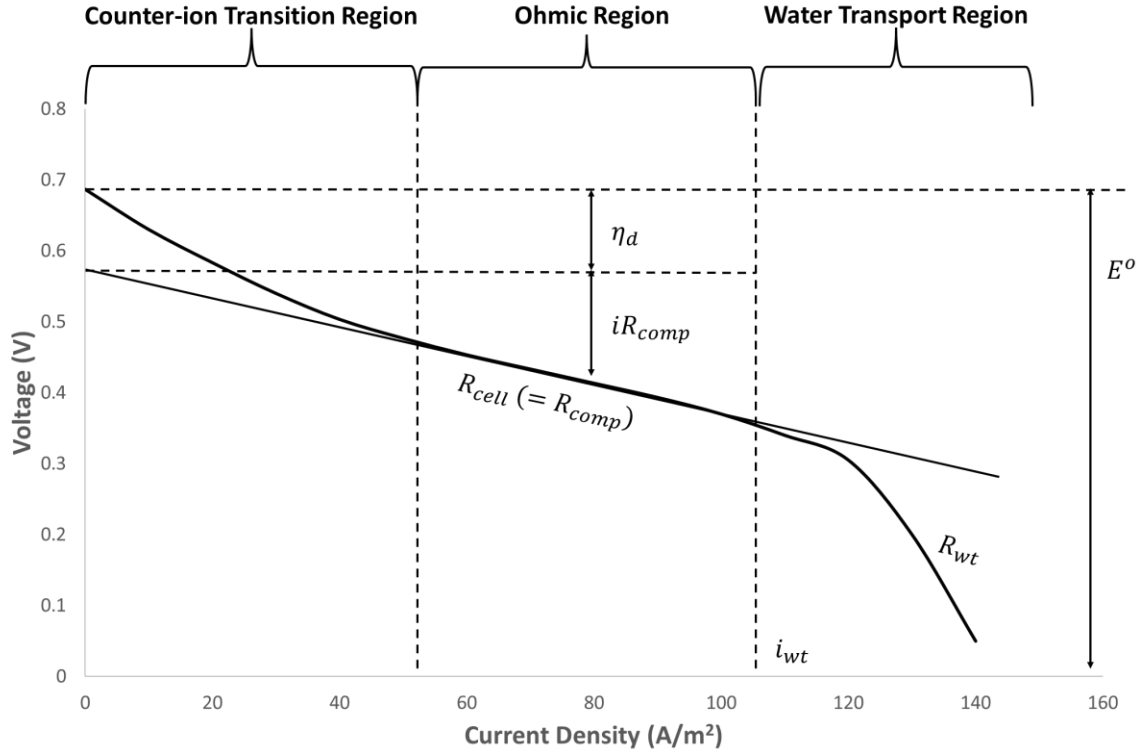


Figure 21: Discharging polarization curve parameters

The low current density counter-ion transition region was observed in some BPM discharging polarization curves in previous studies [11]. Due to the salt ion leakage effect through the BPM for the discharge process (as discussed in Section 2.3.2), more salt ions will occupy fixed charge sites in the BPM resulting in a lower junction potential for the discharge process. This is expressed as an overpotential η_d . At higher current densities, migration of H^+ and OH^- becomes dominant, and a ‘steady state’ develops between the Na^+/Cl^- flux from salt leakage and H^+/OH^- transport, causing the same concentration of fixed charges in the BPM interface. In the ohmic region, the voltage losses become linear with the current density, dependent on the resistance of the cell. In the water transport region, the current density drops off further due to water accumulation in the BPM interface [19], adding a resistive layer of accumulated water. As the current density increases and water accumulates the voltage drops off steeply.

4 Impact of Membrane Type on Performance

4.1 Introduction

As mentioned above, the membrane characteristics, including selectivity and resistance has a significant effect on the performance of the BPED battery. Since these characteristics are dependent on the physical structure and chemistry of the membranes, it is expected that the efficiency of the battery is altered by changing these properties. In this work, various ion exchange membranes (IEMs) were tested, and substantial differences were observed in the performance of the BPED flow batteries based on the nature of the membranes used. Both the cloth type used as the support onto which the membrane was applied, and the chemical formulation of the ion exchange polymer varied significantly for the IEMs assessed. The anion exchange layer (AEL) and the cation exchange layer (CEL) of the bipolar membrane (BPM) were independently changed. Performance indicators such as current efficiency, water transport limiting current and junction potentials were related to membrane properties such as resistance.

In most studies on BPED flow batteries, a single type of BPM has been used, most commonly the Fumasep FBM [6], [12]. Only one study was found in the literature which focussed on the performance of multiple (five) different commercial BPMs for BPED flow batteries [11]. These researchers assessed BPMs from several manufacturers, using polarization curves, battery efficiency, among others, to evaluate the performance [11]. While it is useful to have a comparison of different commercial BPMs, these membranes have many differences, such as the membrane type (homogeneous vs. heterogeneous), catalyst type, membrane chemistry, etc., making difficult to completely understand the phenomena that take place in the BPM, and the important design parameters to improve. Most of the membranes tested showed high voltage losses, causing efficiencies to be too low to be feasible for flow batteries. In this work we tested a series of membranes commercially used for forward BPED, but have not been evaluated for use in BPED flow battery applications. The advantage of using these membranes is that they are commercially available, and have a reliable track record for durability due to their deployment in other applications. The tests were helpful to understand the nature of the voltage losses, and gain insight on the critically important membrane characteristics.

This study aims to provide a systematic comparison of BPM characteristics for use in BPED flow batteries. Various aspects of BPM design are altered, while others are left fixed. The effects of the following two aspects of membrane design are investigated: a change in the cloth support structure

of the BPM while leaving the membrane chemistry fixed, and a change in the CEL membrane chemistry using a given cloth support structure. In all studies, the type of catalyst and the AEL chemistry remain the same. This allows for performance parameters such as voltage losses, and efficiencies to be isolated and linked to specific changes in the BPM design. It has been shown that the performance of the BPM is more dependent on the CEL, where more water and co-ions are usually present and can influence salt leakage [29].

4.1.1 Ion Exchange Membrane Structure

IEMs have various structures depending on the type. In general, IEMs are typically made up of a polymeric material with fixed charge groups that selectively block anions or cations. IEMs can be categorized into two types: homogeneous and heterogeneous. Homogeneous membranes typically consist of the ion exchange polymer containing functional groups, in a continuously crosslinked polymer structure. Depending on the mechanical integrity of the polymer, they may or may not require a support material. The function of the supporting material is to provide mechanical strength to the membrane and allow for the membrane polymer to adhere to it. Heterogeneous ion exchange membranes consist of ion exchange polymer particles, such as ion exchange resins, held together with a binder material. The focus of this study is on homogeneous membranes and the effect of membrane chemistry and supporting material on its performance.

The supporting material for the IEMs can be made of various materials, including acrylic, polyester polypropylene, among others. [30]. The support material influences properties such as the swelling, diffusivity and the mechanical strength of the membranes, among others. It can also dictate the thickness of the membrane, which directly affects the resistance and transport properties of the membranes [29]. Two types of polypropylene cloths were used as support material in this research: a woven cloth and a non-woven cloth.

Table 1: Ion Exchange Membrane Codes

Cloth Type ->	Woven	Non-Woven
Chemistry Type		
103 (anion)	AR103P	AR103N
61 (cation)	CR61P	CR61N
62 (cation)	-	CR62N
63 (cation)	-	CR63N

Table 1 shows the various IEMs used in this study, with the codes explained as follows. In the cloth variation study, the supporting cloth is varied for both the CEL and the AEL. The membranes used for the CEL are CR61P and CR61N (referred to as 61P and 61N in short form). In these codes, 'CR61' indicates the type of ion exchange polymer chemistry, and the 'P' or the 'N' indicate the cloth type for the membrane. The 'P' cloth is a polypropylene woven cloth, while the 'N' cloth is a non-woven polyethylene cloth. The membranes used for the AEL are AR103P and AR103N (referred to as 103P and 103N in short form). Again, in the coding 'AR103' indicates the ion exchange polymer chemistry, while the 'P' or the 'N' indicate the cloth type for the membrane. The 'P' cloth is a polypropylene woven cloth, while the 'N' cloth is a non-woven polypropylene cloth. In the chemistry variation study, the chemistry of the ion exchange polymer is varied for only the CEL. For this chemistry variation, the membranes used for the CEL are CR61N, CR62N and CR63N (referred to as 61N, 62N and 63N in short form). The AEL is fixed as AR103N. All of the variations conducted in the study are done on the BPM. In all studies, the AEM and CEM separating the salt channel (not the BPM) were fixed as the AR103P and the CR61P.

Figure 22 shows the polymer structure of CR61 and AR103 chemistries [20]. These are available in the literature, although the polymer structures of CR62 and CR63 chemistries are not publicly available to the author's knowledge.

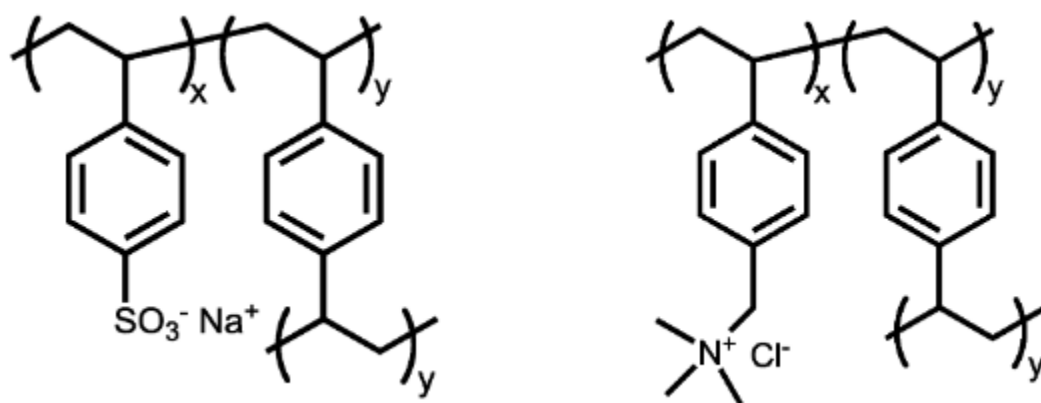


Figure 22: Chemical structure of the (a) CR61 and (b) AR103 chemistries [20]

4.2 Results and Discussion

4.2.1 Ion Exchange Polymer Variation

Figure 23 compares the charging current efficiency (CE) obtained at 300 A/m^2 , and the open circuit voltage (OCV) for the various CEL chemistries in the BPM. A current density of 300 A/m^2 was initially chosen as a current density since it is within the operating typical range for FBPED [10]. A clear trend between the CE and the OCV is observed and both of these can be related to the BPM selectivity. A more selective BPM allows less salt ions (Na^+ or Cl^-) to leak through the membrane layers. This relates to the OCV, as with less salt ions present in the membrane, the fixed charge groups are more fully occupied by H^+ and OH^- in the BPM, increasing their concentration and therefore increasing the OCV, or E^o , as inferred from Equation (4). The selectivity is related to the CE, as a more selective membrane will be more efficient at transporting current, with perfectly selective membranes exhibiting a current efficiency of 100%. More specifically, the current efficiency of protons which is measured and reported in Figure 23 can be related to the salt leakage. For electroneutrality to be maintained, the flux of Na^+ and Cl^- through the BPM must be compensated by an equal flux of H^+ and OH^- into the BPM, which then react to form water at the BPM interface [6]. In terms of the H^+ efficiency, this compensating flux is opposite to the direction of desired H^+ transport (from BPM into the acid stream for charging). Thus, for a higher selectivity of the BPM, both the CE and the OCV should be higher.

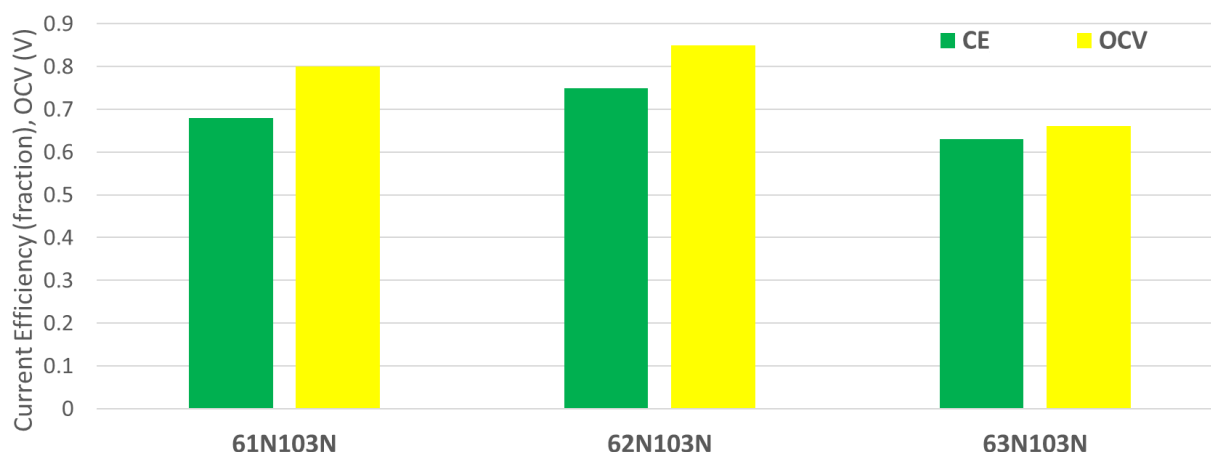


Figure 23: Current efficiency and open circuit voltages for different cation exchange layer chemistries in a bipolar membrane

Figure 24a shows the charging polarization curves for the CELs, CR61N, CR62N and CR63N with the same AEL, AR103N, in a BPM. The slopes of the curves in the ohmic region for CR61N and CR63N are similar. This indicates that the resistance for the CR61N and CR63N are similar. The CR63N has a lower voltage in the counter-ion transition region when compared to the CR61N and CR62N, despite having slightly higher ohmic resistance (reported in Table 3). This could indicate that the CR63N is less selective than the other membranes, with lower junction potentials due to salt leakage (as described above). When comparing the CR61N and the CR62N, they start from a similar potential, and the slope is similar in the counter-ion transition region, before deviating at higher current densities. This could indicate that the CR61N and CR62N have a similar selectivity (due to a similar open circuit voltage), and a differing resistance. These trends are elaborated upon with more in-depth analysis below.

Figure 24b shows the discharging polarization curves for the CELs, CR61N, CR62N and CR63N with the same AEL, AR103N in a BPM. Similar to the charging curves, the CR61N and CR62N exhibit similar potentials in the counter-ion transition region at low current densities, whereas the potential was lower using the CR63N. Again, this indicates the CR63N could be less selective with more salt leakage. The slopes for the CR61N and the CR62N are similar at moderate current densities in the ohmic region, indicating the ohmic resistance of these two membranes are similar. At higher current densities, in the water transport region, the slopes of the curve for the CR61N and CR62N deviate from each other. The slope increases for both, but the transition between the ohmic region and the water transport region occurs at a lower current density for the CR62N, and the slope is higher. This could indicate the CR62N is more prone to water accumulation, or perhaps accumulates more water than the CR61N. For all three membranes the slope of the curves increases at high current densities in the water transport region, likely due to water accumulation in the BPM. Additionally for all three membranes, the deviation in measurements is higher at high current densities. This could be due to the water accumulation in the membranes which also occurs at high current densities. It is not clear why, but it is possible that the amount or mode of water accumulation is not fully consistent during operation.

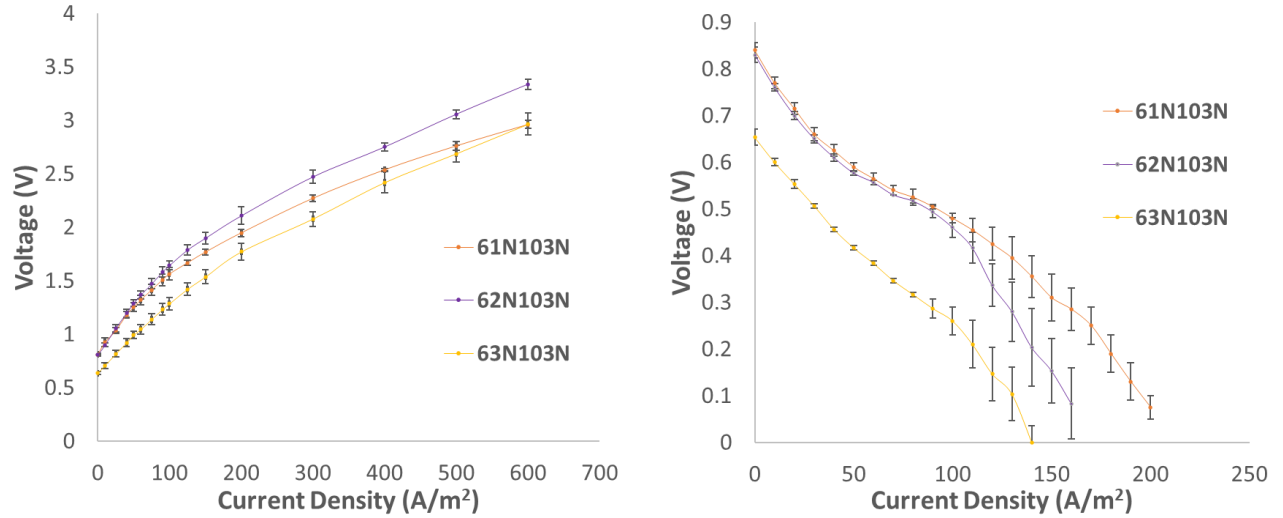


Figure 24: Charging (a) and discharging (b) polarization curves for varied cation exchange layer chemistry in a bipolar membrane at concentrations of 0.5mol/L for the acid (HCl), base (NaOH), and salt (NaCl) streams

Table 2 and Table 3 show the voltage loss parameters for the charging and discharging polarization curves. The resistances and overpotentials are derived from analysis of the polarization curves in Figure 24, as described in Section 3.3.6. These parameters attempt to distinguish different types of voltage losses, separating out the effect of the overpotential from the resistance and breaking the overall resistance R_{cell} into the individually measured resistance of the components R_{comp} and the so-called dissociation resistance R_{diss} . These parameters are linked to physical phenomena such as salt leakage (through η), increased resistance when dissociating water (R_{diss}), and water accumulation (i_{wt} and R_{wt}). Understanding the differences between these voltage losses and the relationship to the physical phenomena is important, as it allows for BPM selection with high efficiency and can provide insight to membrane manufacturers on the parameters to change when designing new membranes.

As shown in Table 3, the R_{cell} and the R_{comp} values matched well for the CR61N and CR62N, within 1%. This is expected from the discharge polarization curve in the ohmic region where the only voltage losses present should be from the resistances of the solutions and the membranes. However, for the CR63N, a large deviation is observed between these resistances at 76%. No clear transition between the counter-ion transition region and the ohmic region is observed, so it may not be accurate to characterize this membrane in this way. It is possible that effects of overpotential

losses extend to higher current densities, causing the counter-ion transition region and the ohmic region to overlap.

Table 2: Measured parameters from the charging polarization curves for varied cation exchange layers in a bipolar membrane

	E^o (V)	R_{cell} (Ωm^2)	R_{comp} (Ωm^2)	R_{dis} (Ωm^2)	η_c (V)
CR61N	0.81	0.00229	0.00208	0.000212	0.790
CR62N	0.81	0.00291	0.00209	0.000823	0.789
CR63N	0.635	0.00293	0.00211	0.000822	0.585

Table 3: Measured parameters from the discharging polarization curves for varied cation exchange layers in a bipolar membrane

	E^o (V)	R_{cell} (Ωm^2)	R_{comp} (Ωm^2)	R_{cell} vs. R_{comp} (% difference)	η_d (V)	i_{wt} (A/m ²)	R_{wt} (Ωm^2)
CR61N	0.84	0.00210	0.00208	1%	0.148	100	0.0045
CR62N	0.83	0.00207	0.00209	1%	0.151	110	0.0063
CR63N	0.65	0.00372	0.00211	76%	0.0747	110	0.0067

Figure 25a shows the resistance of each of the components within the BPM cell triplet. In all cases, the AEL and CEL resistance contributes a comparatively small resistance to the cell triplet when measured independent, as the AEL and the CEL are in the OH⁻ and H⁺ form, respectively. These ions have very high diffusion coefficients, which contributes a low ohmic resistance, as seen in Equation (2). However, in actual operation, the dissociation resistance is present in the BPM, contributing to a much higher resistance in the cell triplet.

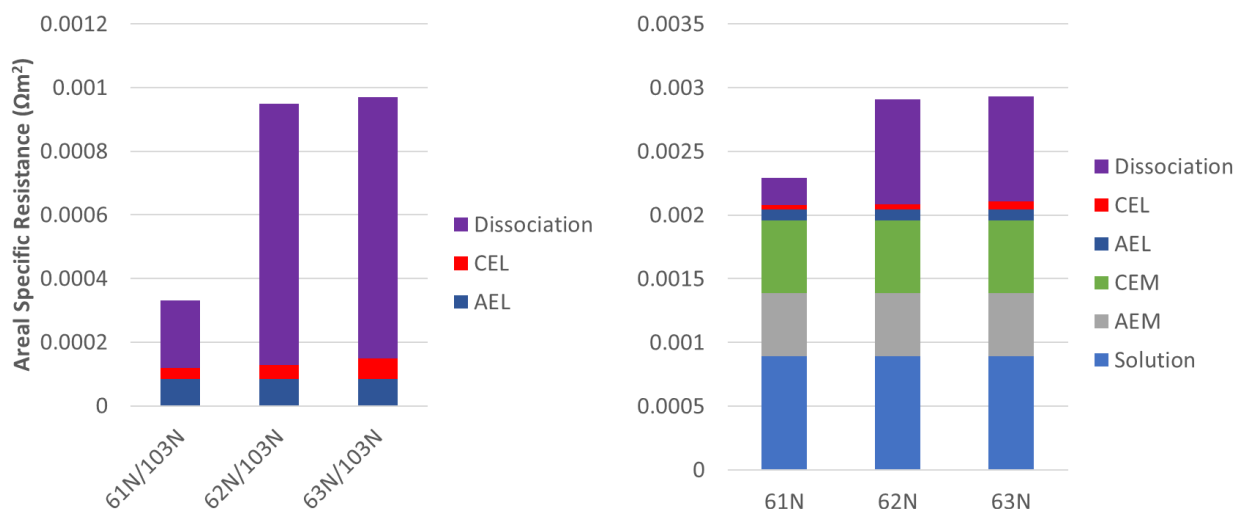


Figure 25: Areal specific resistance of (a) BPM components and dissociation resistance (b) BPM cell triplet components

Figure 25b shows the resistance of the BPM and the calculated water dissociation resistance. A notable difference that distinguishes the CR61N from the CR62N and CR63N is the lower dissociation resistance. This could be due to differences in the chemistry of the CELs. The CR61 chemistry and AR103 chemistry both have a similar styrene based ion exchange polymer chemistry [20], as seen in Figure 22. It is possible that the very similar polymer structures interact at the molecular level to yield a smaller ion depletion region. Since the chemical structures of the CR62N and CR63N are not known, it is difficult to draw conclusions on their differing resistance. Assuming they are not styrene-based as are the CR61 and AR103, this could be a reason why the dissociation resistance is different.

Another notable result is observed when comparing the resistance of the CR61N with the CR63N in Figure 25. Even though resistance of the CR63N is nearly doubled compared to that of the CR61N, this is negligible when compared to the high dissociation resistance. This may be an important note for BPM manufacturers when trying to reduce the voltage losses. It seems intuitive to design a bipolar membrane with lower ohmic resistance to reduce the voltage loss, but as shown, reducing the effect of the dissociation resistance will have a much higher impact. It is apparent that the cation membrane chemistry can play a role in reducing the dissociation resistance, perhaps through its chemical interaction with the AEL or the catalyst.

Figure 26a shows a breakdown of the voltage losses for charge and discharge currents of $+300 \text{ A/m}^2$ and -60 A/m^2 . These currents were chosen based on data in [11] stating that operating at a charging : discharging current ratio of about 5:1 would improve the efficiency. This trend is not observed in this study, as a high voltage loss is associated with operating at high charging currents. Upon further inspection it seems that an error has been made in the voltage efficiency formula reported in [11]; a missing $1/t$ term, could explain the trend they observed of higher VE at higher charging currents. Figure 26b shows the voltage losses for lower charge and discharge currents of $+40 \text{ A/m}^2$, and -30 A/m^2 .

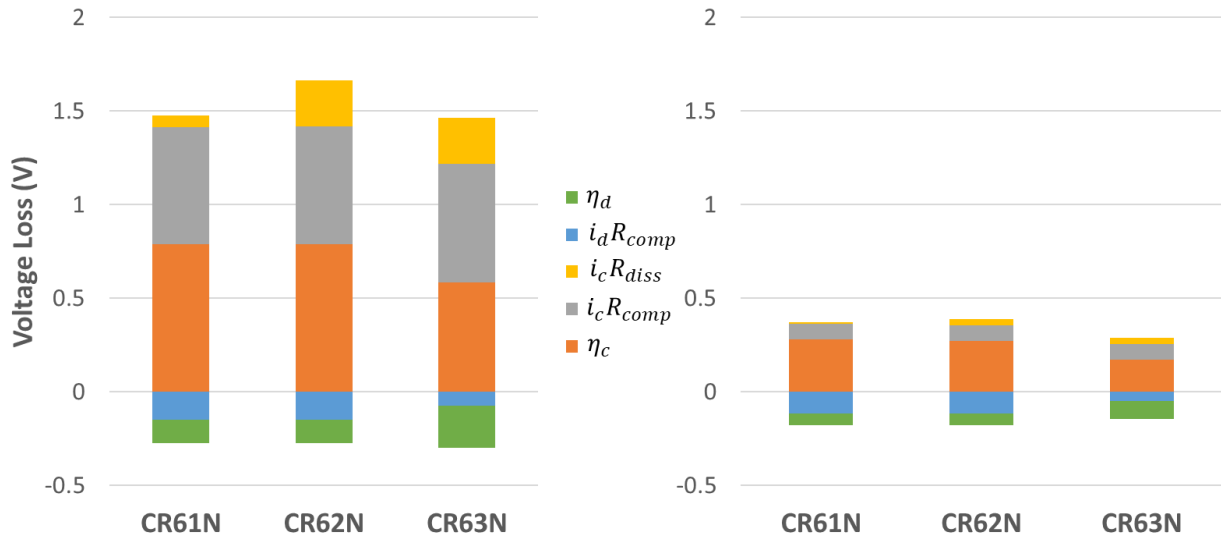


Figure 26: Voltage losses for charging (above x-axis) and discharging (below x-axis) for varied CELs in a bipolar membrane for (a) $+300 \text{ A/m}^2$ charging current and -60 A/m^2 discharging current, and (b) $+40 \text{ A/m}^2$ charging current and -30 A/m^2 discharging current

At both high and low current densities, large contributions to the voltage losses come from η_c and $i_c R_{comp}$. At low current densities, the largest contributor to the voltage losses is the charging overpotential η_c . Most of the voltage losses are reduced by operation at low currents, with a high reduction in $i_c R_{comp}$. This results in better voltage efficiencies at lower currents, as shown in Figure 27. The voltage efficiencies at high currents are all lower than 25%. By operating at lower current densities, the VE more than doubled.

It is worth noting that commercial FBPED systems are typically designed for operation at high current densities ($>400 \text{ A/m}^2$) [31], but clearly for BPED flow batteries lower current operation is

desirable. This could have implications on a BPED stack design that may have been optimized to perform well under these high current densities. For example a high pump flow rate might be employed on a commercial FBPED system to reduce mass transport losses associated with concentration polarization [7].

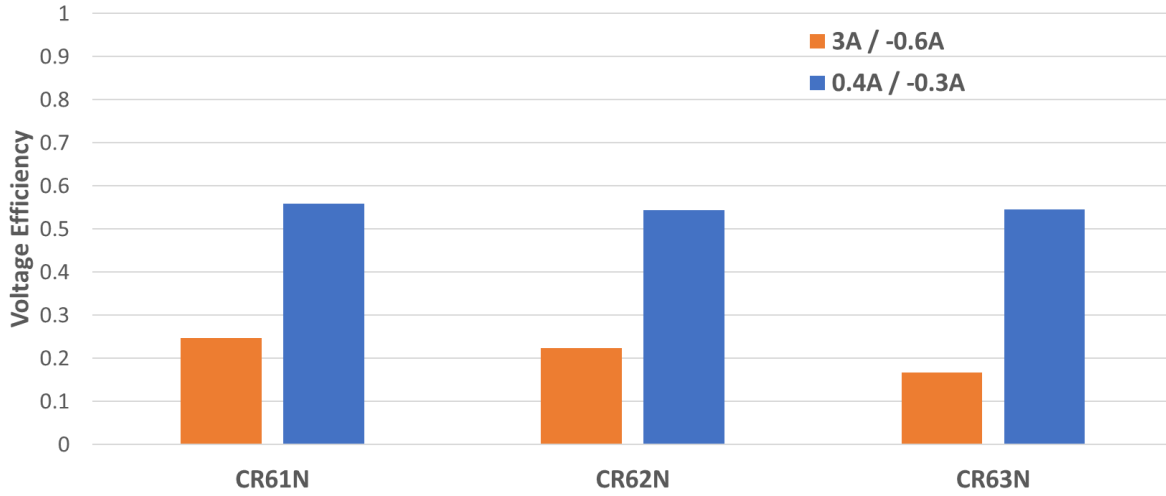


Figure 27: Voltage efficiency for different cation exchange layers in a bipolar membrane for charging current of (a) +300 A/m² charging current and -60 A/m² discharging current, and (b) +40 A/m² charging current and -30 A/m² discharging current

Figure 28 shows a plot relating the junction potential E^o to the overpotentials from the charge and discharge polarization curves. The values of η_c , η_d , and E^o are all correlated between the different CEL types in the BPM. It is interesting to note that the data for the η_d and η_c nearly mirror each other, albeit at different magnitudes. This correlation implies that the nature of the charging and discharging overpotentials are similar, supporting the theory that the overpotential is dependent on selectivity and salt ion transport through the BPM, similar to the OCV [6]. It is also worth noting the magnitude of the discharging overpotentials is much lower than that of the charging overpotential. Given that the charging overpotential η_c is the largest contributor to the voltage losses (from Figure 26), and at the same time it is related to the junction potential E^o , this provides an interesting challenge to designing BPMs for BPED flow batteries. It is desirable to both raise E^o to have a high available voltage, and to lower η_c to reduce the voltage losses. They are clearly related when changing the CEL chemistry, but perhaps the trend does not occur when changing other design parameters. For example Ortega et al. [19] carried out multiphysics modelling of

BPMs, and found that an increasing catalyst activity reduces voltage losses related to the overpotential.

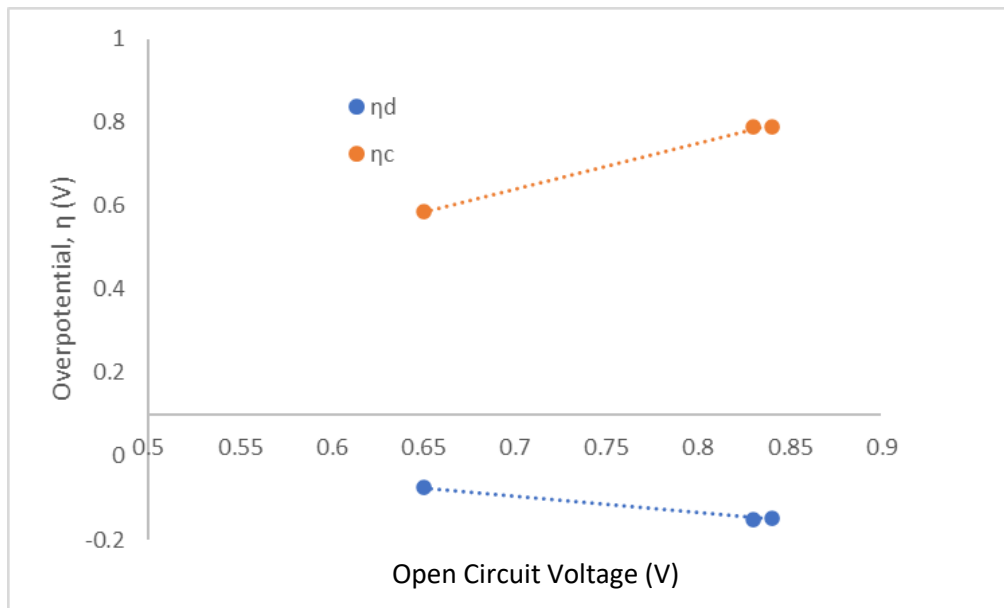


Figure 28: Open circuit voltages plotted against charge and discharge overpotentials for different CEL in bipolar membranes

4.2.2 Cloth Variation

The main difference between the different supporting cloths for the IEMs is their thickness. Membranes with the P cloth have a thickness of approximately 0.6 mm, while membranes with the N cloth have a thickness of approximately 0.3 mm.

When observing the charging polarization curves in Figure 29a, a clear difference between both support types is observed. The OCV of the membranes made with the P cloth are higher than those with the N cloth. This result is in alignment with a previous study investigating the thickness of BPM layers, where they observed that higher potentials are required to split water using thicker membranes [29]. They attributed the higher potential to a reduced amount of salt leakage through thicker BPMs [29] (and therefore more material to block salt from leaking through the BPM). The slopes of the polarization curves for the P cloth membranes are also higher than those for the N cloth membranes. This general trend is expected, as thicker membranes would increase the ohmic

resistance of the membrane. However, as elaborated upon below, the overall resistance measured from the polarization curve is higher than the sum of the resistance of the cell components when measured independently.

When observing the discharging polarization curves in Figure 29b, the difference is more subtle. Similar to the charging curves, the open circuit junction potential is higher for the thicker P cloth membranes. The slope of the curve at moderate current densities in the ohmic region is higher than that of the N cloth membranes which again is expected as a thicker membrane would be more resistive. The P cloth membranes do not exhibit a clear transition between the counter-ion transition region and the ohmic region. The N cloth membranes do not exhibit a clear transition between the ohmic region and the water transport region. At high current densities in the water transport region, the thick P cloth membranes exhibit a steep drop in voltage, whereas the N cloth membranes show a more gradual transition.

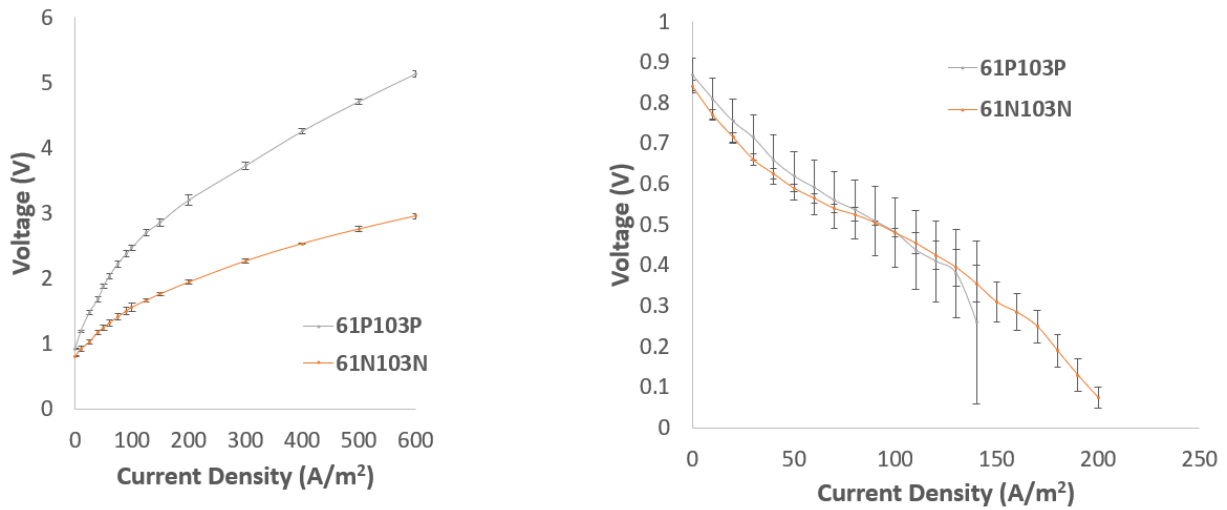


Figure 29: Charging (a) and discharging (b) polarization curves for varied bipolar membrane support cloth / thickness at concentrations of 0.5 mol/L for the acid (HCl), base (NaOH), and salt (NaCl) streams

Table 4 and Table 5 present the calculated parameters from the polarization curves. Similar to the previous section it is worth highlighting in Table 3 that the CR61N discharge curve has clear transition regions (refer to Figure 21), and a close match between R_{cell} and R_{comp} . The CR61P on the other hand does not exhibit a clear transition between the counter-ion transition region and the

ohmic region. Therefore, it is hard to determine an accurate value for R_{cell} from the curve, explaining the high deviation from R_{comp} .

Table 4: Measured parameters from the charging polarization curves for varied supporting cloth in a bipolar membrane

	E^o (V)	R_{cell} (Ωm^2)	R_{comp} (Ωm^2)	R_{dis} (Ωm^2)	η_c (V)
CR61P	0.92	0.00469	0.00221	0.00248	1.428
CR61N	0.81	0.00229	0.002078	0.000212	0.79

Table 5: Measured parameters from the discharging polarization curves for varied supporting cloth in a bipolar membrane

	E^o (V)	R_{cell} (Ωm^2)	R_{comp} (Ωm^2)	R_{cell} vs. R_{comp} (% difference)	η_d (V)	i_{wt} (A/m ²)	R_{wt} (Ωm^2)
CR61P	0.87	0.00272	0.00221	-23%	0.117	140	-
CR61N	0.84	0.0021	0.002078	1%	0.148	100	0.0045

A key difference in the discharge behaviour between the P cloth and the N cloth membranes is the onset of the water transport limiting current. For the P cloth BPM, the water transport limiting current is observed at approximately 140 A/m², where a steep decline in the voltage was observed. This decline in voltage is consistent with findings in other studies [6]. For the N cloth BPM, no steep drop-off in the voltage is observed, with a less clear transition to a water transport limiting current regime compared to the P cloth. Instead, the resistance of the cell triplet increases gradually at current densities higher than 90 A/m². This increase in resistance is likely due to the build up of water in the BPM interface, adding a resistive layer, which has been observed in other studies [19]. The transport of water is likely the main difference between the two membrane cloths. Transport of water molecules can be driven by diffusion or pressure, the latter being more likely. Given the accumulation of water due to the H⁺/OH⁻ neutralization reaction in a confined space, this will build up pressure. In either case, the water flux depends on the thickness of the membrane through which it is transported. Pressure-driven flow through a porous material (in this case the AEL or CEL) is governed by Darcy's law:

$$Q = \frac{-kA \Delta P}{\mu L} \quad (16)$$

where Q is the water flow rate (mL/s), k is the pressure-driven permeability (m²), A is the area of the membrane (m²), μ is the viscosity of the fluid (Pa. s), ΔP is the pressure difference between the centre of the BPM and the flow channel (Pa), and L is the thickness of the AEL or CEL. In terms of Darcy's Law, the only differences between the P cloth and N cloth are the membrane thickness L , and potentially the permeability k . The thickness of the N and P cloths are 0.3 mm and 0.58 mm, respectively. Assuming all other parameters to be similar, the flow rate of water would be 1.9x higher at a given current density for the thinner N cloth membrane. This increase is approximate as differences in the cloth structure would likely change the permeability k , and ΔP would be a function of how much water is present at the BPM interface. It is likely that the thinner N cloth membrane permits a higher rate of water transport out of the membrane than the P cloth. This is consistent with the discharge polarization curve, where the effects of voltage losses due to water accumulation are lower for the N cloth membrane than the P cloth membrane.

4.2.3 Compression Test

Figure 30 shows the effect of the cell compression on the charging (a) and discharging (b) polarization curves for N cloth and P cloth membranes, respectively. In all curves, the junction potential is higher for the compressed cell, as elaborated upon below. In a membrane under higher compression, the amount of water present in the membrane could be reduced and the fixed charge groups could be compressed closer together, increasing the effective concentration of H⁺ and OH⁻ which would increase the junction potential. Since IEMs can swell [7], it seems plausible that under higher compression, the shape of the polymer structure can change, reducing the pore volume and thereby increasing the effective concentration of ions.

When the cell containing the P cloth membranes is discharged, (Figure 30b) the water transport limiting current is reached at higher current densities. This is likely due to less space in the BPM interface for water to accumulate under compression, and a higher pressure within the membrane to drive generated water out of the BPM.

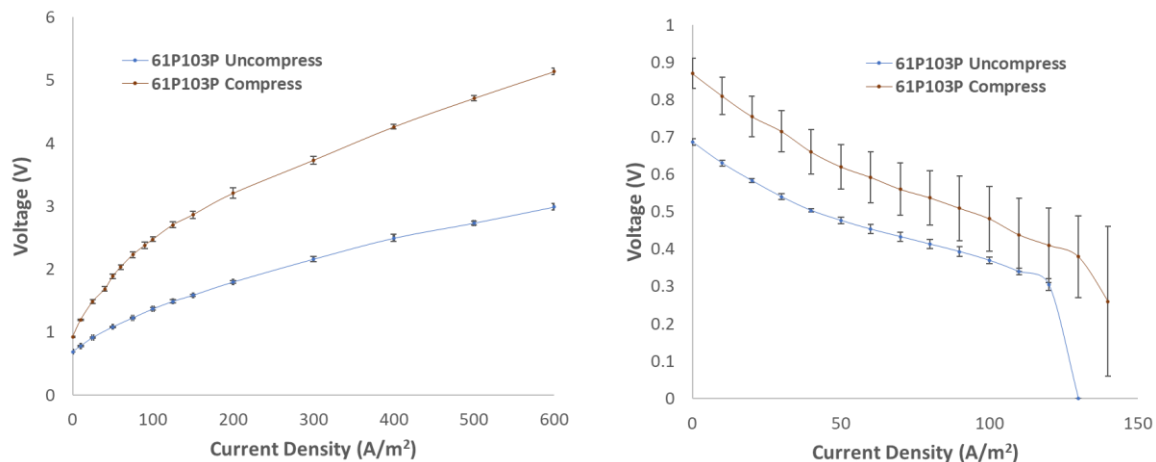


Figure 30: Effect of cell compression on the BPED cell triplet with CR61P/AR103P bipolar membrane for (a) charging and (b) discharging at concentrations of 0.5 mol/L for the acid (HCl), base (NaOH), and salt (NaCl) streams

4.2.4 Temperature effects

When observing the charging polarization curves in Figure 31a, the curves follow a clear trend with changing temperatures. At lower temperatures, the slope of the curves is higher than at high temperatures. This is likely due to the change in resistance of the solutions as a function of temperature. In general, the resistance increases as the temperature decreases, as expected.

When observing the discharging polarization curves in Figure 31b, the curves also follow a clear trend with the temperature. Overall, the total voltage losses are less at higher temperatures than at lower temperatures. The slope of the curve at 10°C is higher than the slope of the curves at 20°C and 30°C. This is expected as at lower temperatures the resistance would increase. The slopes of the curves at 20°C and 30°C are similar. At 30°C, no clear distinction between the counter-ion transition region and the ohmic region is present. It is possible that these 2 regions overlap, which could explain why the resistance appears similar between data at 20°C and at 30°C is observed. At 10°C, no clear distinction between any of the regions of the curve appears. A clear water transport limiting current region with a steep voltage drop is observed at both 20°C and 30°C.

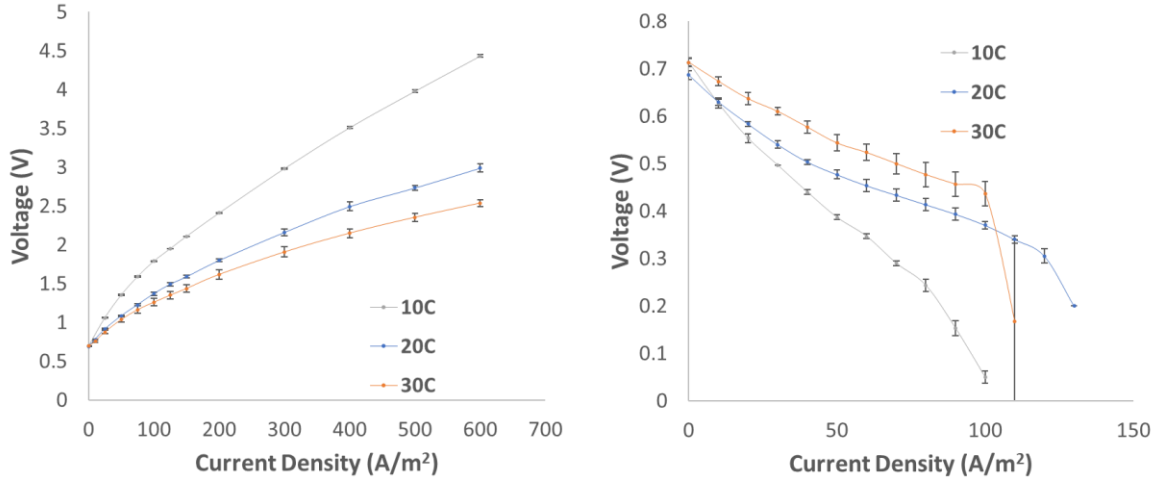


Figure 31: (a) Charging polarization curves (b) and discharging (b) polarization curves for CR61P/AR103P bipolar membrane at 10°C, 20°C and 30°C at concentrations of 0.5 mol/L for the acid (HCl), base (NaOH), and salt (NaCl) streams

Table 6 and Table 7 show the calculated parameters from the polarization curves. Similar to curves above, whenever a clear distinction/separation between the counter-ion transition region, the ohmic region and the water transport region exists, R_{cell} and R_{comp} closely match. Here, the data at 20°C show the closest match, with only a 0.4% difference between the resistances. A larger deviation of 9%, no clear distinction (or possibly overlap) between the counter-ion transition region and the ohmic region is observed at 30°C. The largest deviation between R_{cell} and R_{comp} of 69% is observed at 10°C, with no clear distinction on the polarization curve between any of the regions. This may imply that all 3 regions overlap, with effects of overpotential losses extending to higher current densities, and/or water accumulation related losses occurring at lower current densities.

Table 6: Measured parameters from the charging polarization curves at various temperatures in a bipolar membrane

	E^o (V)	R_{cell} (Ωm^2)	R_{comp} (Ωm^2)	R_{dis} (Ωm^2)	η_c (V)
10°C	0.69	0.00504	0.002908	0.002132	0.75
20°C	0.69	0.00296	0.00221	0.00075	0.56
30°C	0.69	0.00229	0.001905	0.000385	0.5

Table 7: Measured parameters from the discharging polarization curves at various temperatures in a bipolar membrane

	E^o (V)	R_{cell} (Ωm^2)	R_{comp} (Ωm^2)	R_{cell} vs. R_{comp} (% difference)	η_d (V)	i_{wt} (A/m ²)
10°C	0.71	0.0049	0.002908	-69%	0.078	130
20°C	0.69	0.0021	0.00221	-0.4%	0.059	100
30°C	0.71	0.0022	0.001905	-9%	0.108	-

Figure 32 shows the effect of temperature on total resistance R_{cell} , the independently measured resistance R_{cell} and the calculated dissociation resistance R_{diss} from the charging polarization curve data. R_{cell} varies more strongly with temperature variation than R_{comp} , which accounts for the variation in resistance due to changes in solution properties as a function of temperature (i.e., viscosity, ionic mobility). As a result, R_{diss} (the difference between R_{cell} and R_{comp}), contributes a higher variation with respect to temperature. Wilhelm et. al [10] linked the dissociation resistance to a region at the BPM interface where ions are depleted; this resistance is reduced when more ions are present. The observed temperature variation of R_{diss} could be explained in a few ways. The conductivity of pure water (which would be present in the ion depletion zone) has a higher dependence on temperature than acidic and basic solutions as seen in Table 8. It is also possible that the width of the ion depletion region is smaller at higher temperatures. As the temperature increases, the diffusion coefficient of the ions increases. With a larger diffusion rate, the ions near the boundary of the ion depletion region will have a larger mean free path, as described in the Einstein-Smoluchowski equation:

$$D = \frac{\lambda^2}{\tau} \quad (17)$$

where λ is the mean free path (m) and τ is the time between particle collisions (s). Since the ion depletion region is approximately 40 nm in size [18] and the mean free path of ions is also on the nanometer scale, an increased mean free path of ions near the depletion region enables them to diffuse closer to the centre of the BPM. Therefore, an increase in diffusion coefficient due to an increase in temperature could shorten the ion depletion region, reducing the dissociation resistance. This, or the higher dependence of temperature for the conductivity of pure water could explain the stronger dependence of temperature on R_{diss} .

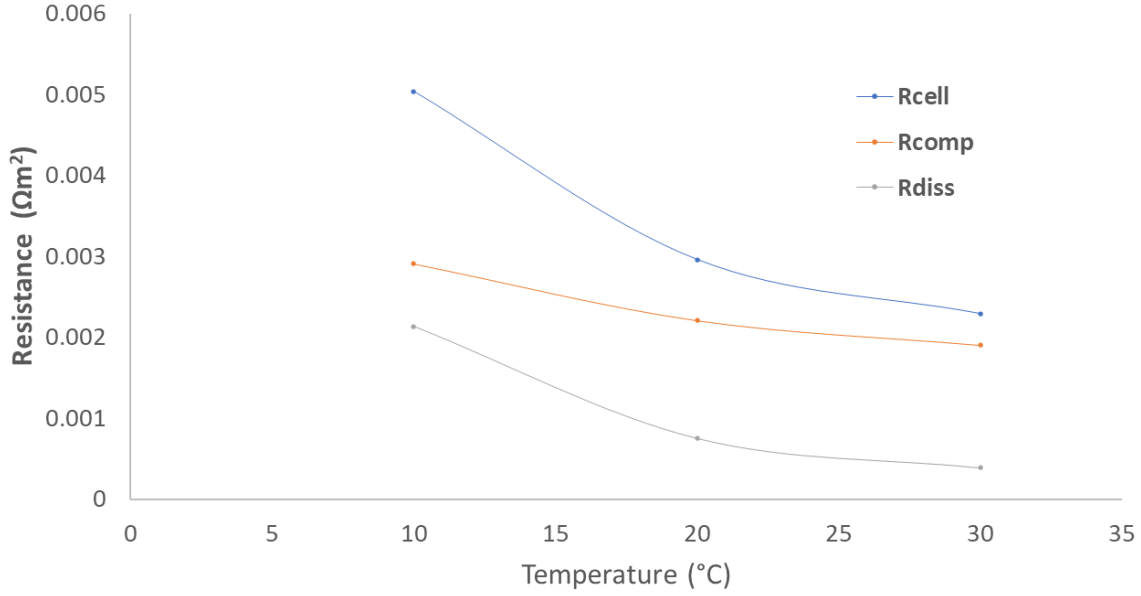


Figure 32: Charging resistances R_{cell} , R_{comp} , and R_{diss} plotted as a function of temperature

Table 8: Temperature coefficient of variation in conductivity for pure water, and acidic and basic solutions [26]

Solution	Temperature Coefficient of Variation in Conductivity at 25°C (%/°C)
Ultrapure Water	5.5
HCl (5%)	1.6
NaOH (5%)	2.01

Figure 33 shows the voltage losses as a function of temperature at high and low current densities. As discussed above, the dissociation resistance varies strongly with temperature. Similar to the various CEL's, operation at lower current should significantly reduce the ohmic losses. A slight reduction in the overpotentials η_c and η_d with temperature is observed. This is reasonable as the overpotentials are related to selectivity which has been shown previously to be a function of temperature [32].

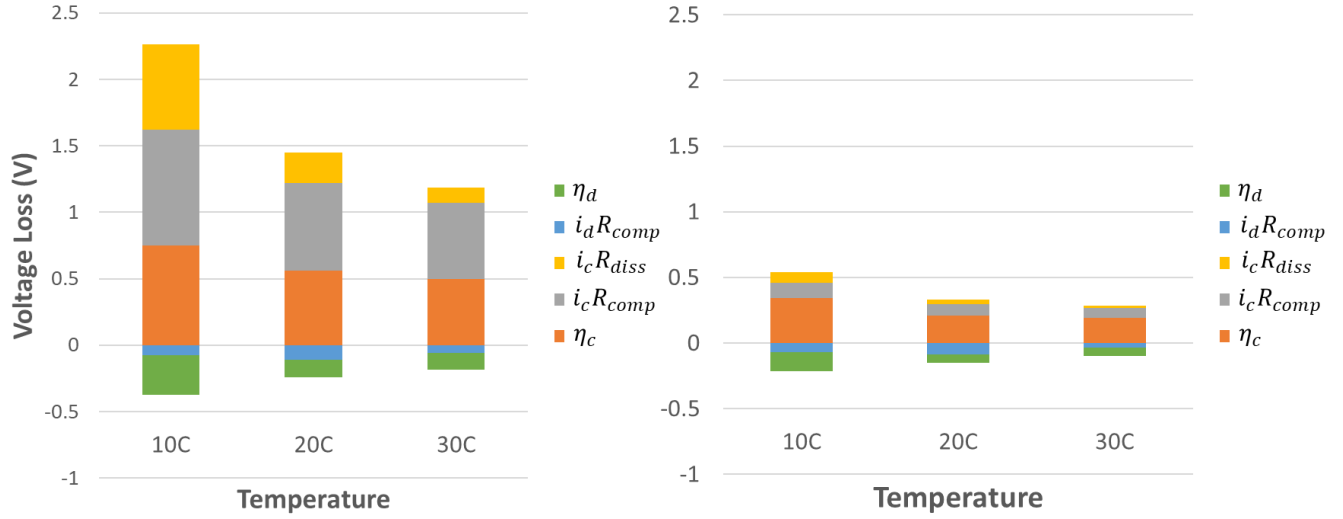


Figure 33: Voltage losses for charging (above x-axis) and discharging (below x-axis) 10°C, 20°C and 30°C for (a) +300 A/m² charging current and -60 A/m² discharging current, and (b) +40 A/m² charging current and -30 A/m² discharging current

Figure 34 shows the voltage efficiency as a function of temperature. As expected, the voltage efficiency increases as temperature rises. Given this trend, it is beneficial for BPED flow batteries to operate at high temperatures. If the trend holds for higher temperatures at 40°C or higher, this could give BPED flow batteries a competitive edge over lithium batteries as the performance of Li-ion batteries degrades at high temperatures, with major safety risks at elevated temperatures.

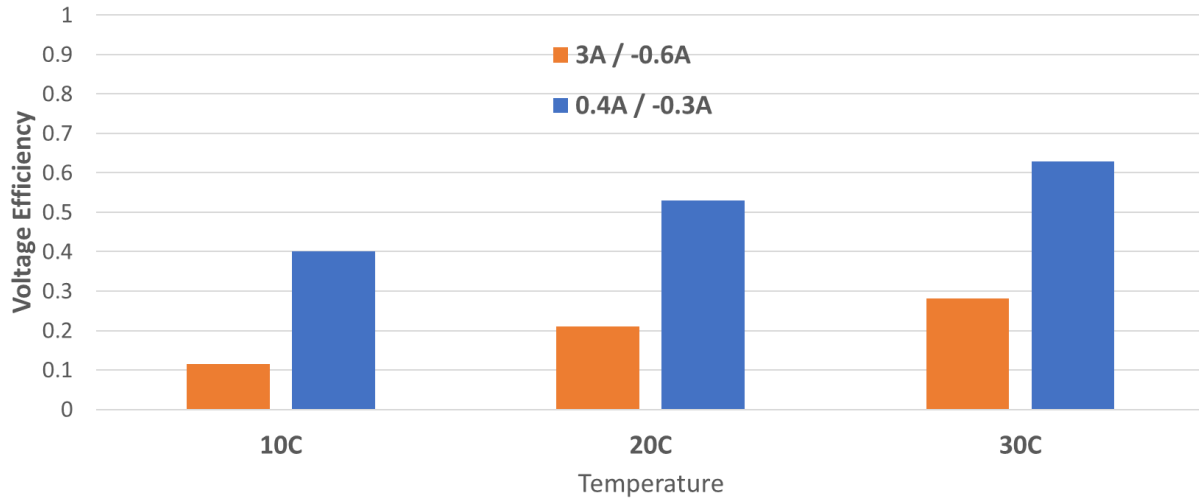


Figure 34: Voltage efficiency for 10°C, 20°C and 30°C of BPED flow battery for charging current of (a) +300 A/m² charging current and -60 A/m² discharging current, and (b) +40 A/m² charging current and -30 A/m² discharging current

5 Conclusions and Recommendations

The work presented in this thesis has focussed on the development of a bipolar electro dialysis flow battery system and testing the battery to understand and optimize its performance. The battery stack was constructed and manufactured from scratch using commercially available ion exchange membranes and electrodes. The battery design went through several iterations to improve operation. Similarly, the testing protocol was improved over the course of the study in order to reliably and repeatably characterize battery performance. Several commercially available ion exchange membrane layers for a bipolar membrane were tested in the battery. The goals of these experiments included finding the best performing membrane for scaled up bipolar electro dialysis flow batteries, as well as observing differences in the polarization curves to gain a more fundamental understanding of the effect of membrane parameters on voltage losses in the battery. Tests were also performed at varied temperatures to understand how bipolar electro dialysis flow batteries will perform in real life environments at different temperature, and to gain insights into physical phenomena that affect battery performance as temperature is varied. The following are the main conclusions of this work:

- The use of an AEL and CEL with similar chemical structure and operating at higher temperature were found to reduce the dissociation resistance.
- The overpotentials were found to be lower with a less selective membrane, which reduces the current efficiency.
- The use of thinner membranes helped reduce the voltage losses in the BPM at high discharging current densities, likely due to lower water accumulation in the BPM. The use of a thinner membrane could result in a lower resistance to pressure driven flow out of the membrane, allowing more water to escape at higher currents when more water is generated.
- Higher compression in the BPM increased the junction potential. It also increased the water transport limiting current density of the discharge process. This could be due to higher compression that reduced the amount of space at the BPM interface where water could accumulate and/or, higher pressure within the membrane pores which forced the water through the membrane. This also indicates that the effectiveness of the battery depends

strongly on the assembly characteristics and that care should be taken to make the assembly fully reproducible. For instance, a torque measurement on the bolts when assembling would ensure the same force is used for the compression of the cell in all experiments.

- The use of polarization curve analysis tools separating the charging curves into low and high current density regimes based on overpotential and ohmic losses was shown to be an effective tool to distinguish between the various voltage losses during charging in all cases. Voltage losses can be attributed to the membrane/solution resistances, the overpotentials (related to the form of the fixed charges in the BPM) and the dissociation resistance (related to the ion depletion region where water splits). This analysis has shown that the overpotential during the charging process made the largest contribution to the voltage losses, especially at lower current densities.
- The use of polarization curve analysis tools separating the discharging curves into low, moderate and high current density regimes based on overpotential losses, ohmic losses, and water accumulation regimes was an effective tool in some cases but not all. In some cases it was not possible to distinguish the various regions due to the overlap of the regions. This tool can be used on a case by case basis, or more work should be done to better distinguish these regions when they overlap. In cases where a clear distinction between the 3 regions existed, the independently measured resistance of the membranes and solutions matched well with the resistance in the ohmic region. This both gives confidence in the theoretical framework for the polarization analysis method and confirms that a purely ohmic region exists in the discharge curves for some membranes. Minimizing overpotential losses in the counter-ion transition region will be important in reducing voltage losses for efficient operation.
- Operation of bipolar electrodialysis flow batteries at low current densities around 30-40 A/m² improved the voltage efficiency by reducing resistive losses and overpotentials.
- The effect of temperature on the dissociation resistance was more similar to how the ohmic resistance of pure water changes as a function of temperature, as opposed to that of ionic solutions. This may confirm that the dissociation resistance is related to a region of pure

water caused by ion depletion at the centre of the BPM during charging of BPED flow batteries.

- Selectivity of the bipolar membrane was found to increase as the temperature decreased, which is in line with the expectations and previous findings [32]. This led to a higher current efficiency at low temperatures but a higher overpotential loss (in addition to the higher resistive loss). This can be explained by the reduced ionic mobility at lower temperatures and the increased viscosity of the solution. For the design and use of these batteries under varying conditions encountered in practice (temperature can range from -40°C - 50°C), this means that the efficiency and power output of the battery can change significantly.
- The junction potential and overpotentials were correlated to the current efficiency and the selectivity of the membranes, creating an interesting trade-off. The use of a more selective membrane will both increase the useful junction potential but will also increase the overpotential losses.
- Operation at higher temperatures reduced the voltage losses in both the ohmic losses and the overpotentials. Consequently, the voltage efficiency was higher at higher temperatures.

The following are the main recommendations based on this work:

- Investigate approaches to reduce the charging overpotential without reducing the junction potential. This could include the modification of other design features such as the type of anion exchange membrane used, or the type / amount of catalyst present in the BPM, leading to insight on how and if the trend between charging overpotential and junction potential could be broken.
- Further tests should be conducted to fully understand the nature of the dissociation resistance and the overpotentials. The evaluation of BPMs with different catalysts could give insight on their effect on voltage losses.

- BPM manufacturers should focus on improving the selectivity of the BPMs to reach a higher OCV, improving the available usable voltage. The nature of the dependence of overpotential on the concentration of H^+/OH^- in the membrane suggests that more fixed charge sites are available to be occupied at OCV; if more of these sites could be occupied by H^+/OH^- at low/zero current (with a lower salt leakage), more of this overpotential could be harnessed as a usable, junction potential for energy storage.
- Efforts should be made to reduce the dissociation resistance and the overpotentials in addition to the bulk membrane resistance. The bulk membrane resistance had a significant effect on the performance of the anion exchange membrane and cation exchange membrane in the cell triplet, but for the bipolar membrane the dissociation resistance and overpotential contributed much more to the voltage losses than the resistance of the membrane layers themselves.
- If possible, BPED flow batteries should be operated at higher temperatures to attain a higher voltage efficiency

References

- [1] "Battery Storage in the United States: An Update on Market Trends".
- [2] N. DiOrio, A. Dobos, and S. Janzou, "Economic Analysis Case Studies of Battery Energy Storage with SAM," NREL/TP--6A20-64987, 1226239, Nov. 2015. doi: 10.2172/1226239.
- [3] A. Z. Weber, M. M. Mench, J. P. Meyers, P. N. Ross, J. T. Gostick, and Q. Liu, "Redox flow batteries: a review," *J Appl Electrochem*, vol. 41, no. 10, pp. 1137–1164, Oct. 2011, doi: 10.1007/s10800-011-0348-2.
- [4] "Cunha, Martins, J., Rodrigues, N., & Brito, F. P. (2015). Vanadium redox flow batteries: a technology review. *International Journal of Energy Research*, 39(7), 889–918. <https://doi.org/10.1002/er.3260>".
- [5] C. Thompson-Clarke, "Ebb and Flow: High Vanadium Prices Hinder the Spread of Redox Flow Batteries," *The Assay*, 2018. [Online]. Available: <https://www.theassay.com/technology-metals-edition-insight/ebb-and-flow-high-vanadium-prices-hinder-the-spread-of-redox-flow-batteries/>
- [6] J. Xia, G. Eigenberger, H. Strathmann, and U. Niekem, "Flow battery based on reverse electrodialysis with bipolar membranes: Single cell experiments," *Journal of Membrane Science*, vol. 565, pp. 157–168, Nov. 2018, doi: 10.1016/j.memsci.2018.07.073.
- [7] H. Strathmann, "Electrodialysis, a mature technology with a multitude of new applications," *Desalination*, vol. 264, no. 3, pp. 268–288, Dec. 2010, doi: 10.1016/j.desal.2010.04.069.
- [8] R. S. Kingsbury, K. Chu, and O. Coronell, "Energy storage by reversible electrodialysis: The concentration battery," *Journal of Membrane Science*, vol. 495, pp. 502–516, Dec. 2015, doi: 10.1016/j.memsci.2015.06.050.
- [9] J.-H. Kim *et al.*, "Proof-of-concept experiments of an acid-base junction flow battery by reverse bipolar electrodialysis for an energy conversion system," *Electrochemistry Communications*, vol. 72, pp. 157–161, Nov. 2016, doi: 10.1016/j.elecom.2016.09.025.
- [10] F. G. Wilhelm, *Bipolar membrane electrodialysis: membrane development and transport characteristics*. Enschede: Twente University Press, 2001.

- [11] E. Al-Dhubhani, R. Pärnamäe, J. W. Post, M. Saakes, and M. Tedesco, "Performance of five commercial bipolar membranes under forward and reverse bias conditions for acid-base flow battery applications," *Journal of Membrane Science*, vol. 640, p. 119748, Dec. 2021, doi: 10.1016/j.memsci.2021.119748.
- [12] J. Xia, G. Eigenberger, H. Strathmann, and U. Nieken, "Acid-Base Flow Battery, Based on Reverse Electrodialysis with Bi-Polar Membranes: Stack Experiments," *Processes*, vol. 8, no. 1, p. 99, Jan. 2020, doi: 10.3390/pr8010099.
- [13] E. K. Zholkovskij, M. C. Müller, and E. Staude, "The storage battery with bipolar membranes," *Journal of Membrane Science*, vol. 141, no. 2, pp. 231–243, Apr. 1998, doi: 10.1016/S0376-7388(97)00306-2.
- [14] J. J. Krol, M. Jansink, M. Wessling, and H. Strathmann, "Behaviour of bipolar membranes at high current density Water diffusion limitation," *Separation and Purification Technology*, vol. 14, no. 1–3, pp. 41–52, Aug. 1998, doi: 10.1016/S1383-5866(98)00058-6.
- [15] A. M. Benneker, "From small to big : ion transport at interfaces," PhD, University of Twente, Enschede, The Netherlands, 2018. doi: 10.3990/1.9789036544924.
- [16] J. W. Post, H. V. M. Hamelers, and C. J. N. Buisman, "Energy Recovery from Controlled Mixing Salt and Fresh Water with a Reverse Electrodialysis System," *Environ. Sci. Technol.*, vol. 42, no. 15, pp. 5785–5790, Aug. 2008, doi: 10.1021/es8004317.
- [17] Y. Tanaka, *Ion exchange membranes : fundamentals and applications*. Amsterdam, Netherlands: Elsevier, 2015.
- [18] R. Kodým, D. Šnita, and K. Bouzek, "Mathematical Modeling of Electromembrane Processes," in *Current Trends and Future Developments on (Bio-) Membranes*, Elsevier, 2019, pp. 285–326. doi: 10.1016/B978-0-12-813551-8.00012-7.
- [19] A. Ortega *et al.*, "Modelling water dissociation, acid-base neutralization and ion transport in bipolar membranes for acid-base flow batteries," *Journal of Membrane Science*, vol. 641, p. 119899, Jan. 2022, doi: 10.1016/j.memsci.2021.119899.
- [20] J. Kamcev, D. R. Paul, G. S. Manning, and B. D. Freeman, "Ion Diffusion Coefficients in Ion Exchange Membranes: Significance of Counterion Condensation," *Macromolecules*, vol. 51, no. 15, pp. 5519–5529, Aug. 2018, doi: 10.1021/acs.macromol.8b00645.

- [21] F. G. Wilhelm, "Current-voltage behaviour of bipolar membranes in concentrated salt solutions investigated with chronopotentiometry," p. 11.
- [22] W. J. van Egmond, M. Saakes, I. Noor, S. Porada, C. J. N. Buisman, and H. V. M. Hamelers, "Performance of an environmentally benign acid base flow battery at high energy density," *Int J Energy Res*, vol. 42, no. 4, pp. 1524–1535, Mar. 2018, doi: 10.1002/er.3941.
- [23] A. J. Bard and L. R. Faulkner, *Electrochemical methods: fundamentals and applications*, 2nd ed. New York: Wiley, 2001.
- [24] Rosemount Analytical and Emerson Process Management, "Conductance Data For Commonly Used Chemicals." Dec. 2010.
- [25] A. Culcasi, L. Gurreri, A. Zaffora, A. Cosenza, A. Tamburini, and G. Micale, "On the modelling of an Acid/Base Flow Battery: An innovative electrical energy storage device based on pH and salinity gradients," *Applied Energy*, vol. 277, p. 115576, Nov. 2020, doi: 10.1016/j.apenergy.2020.115576.
- [26] J. J. Barron and C. Ashton, "The Effect of Temperature on Conductivity Measurement," no. 3, p. 6.
- [27] W. Alnoush, R. Black, and D. Higgins, "Judicious selection, validation, and use of reference electrodes for in situ and operando electrocatalysis studies - ScienceDirect," 2021.
<https://www.sciencedirect.com/science/article/abs/pii/S2667109321001044?via%3Dihub> (accessed Aug. 29, 2022).
- [28] J. Balster, D. F. Stamatialis, and M. Wessling, "Membrane with integrated spacer," *Journal of Membrane Science*, vol. 360, no. 1–2, pp. 185–189, Sep. 2010, doi: 10.1016/j.memsci.2010.05.011.
- [29] J. Balster *et al.*, "Asymmetric bipolar membrane: A tool to improve product purity," *Journal of Membrane Science*, vol. 287, no. 2, pp. 246–256, Jan. 2007, doi: 10.1016/j.memsci.2006.10.042.
- [30] "Ionics Ion Exchange Membranes," p. 2.
- [31] M. Herrero-Gonzalez, P. Diaz-Guridi, A. Dominguez-Ramos, A. Irabien, and R. Ibañez, "Highly concentrated HCl and NaOH from brines using electrodialysis with bipolar membranes," *Separation and Purification Technology*, vol. 242, p. 116785, Jul. 2020, doi: 10.1016/j.seppur.2020.116785.

[32] A. M. Benneker, J. Klomp, R. G. H. Lammertink, and J. A. Wood, "Influence of temperature gradients on mono- and divalent ion transport in electrodialysis at limiting currents," *Desalination*, vol. 443, pp. 62–69, Oct. 2018, doi: 10.1016/j.desal.2018.05.005.